Radionuclide Retention in Geologic Media

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(SKB)

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ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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FOREWORD

GEOTRAP, the OECD/NEA Project on Radionuclide Migration in Geologic, Heterogeneous Media, is devoted to the exchange of information and in-depth discussions on present approaches to acquiring field data and testing and modelling flow and transport of radionuclides in actual (and therefore heterogeneous) geologic formations for the purpose of site characterisation and evaluation and safety assessment of deep repository systems of long-lived radioactive waste. The project comprises a series of structured, forum-style workshops on the following themes:

(i) Field tracer transport experiments: design, modelling, interpretation and role in the prediction of radionuclide migration.

(ii) The basis for modelling the effects of spatial variability on radionuclide migration.

(iii) The characterisation of water-conducting features and their representation in models of radionuclide migration.

(iv) Confidence in models of radionuclide transport for site-specific performance assessment.

(v) Geological evidence and theoretical bases for radionuclide-retention processes in heterogeneous media.

The workshops, which comprise technical presentations, discussion periods, poster sessions, and *ad hoc* working group discussions, are designed to enable national waste management agencies, regulatory authorities, and scientists to interact and contribute to the advancement of the state of the art in these areas.

The fifth workshop in the series was held in Oskarshamn, Sweden, on 7-9 May 2001, and hosted by the Swedish Nuclear Fuel and Waste Management Company (SKB). The workshop focused on radionuclide-retention processes that may operate in the geologic environment of a nuclear waste repository. The workshop examined retention processes from the standpoints of fundamental understanding, geological and field evidence, methods of representing them in models, and their consideration and representation in performance assessments. Sixty-three delegates from thirteen NEA Member countries attended the workshop. They represented waste management organisations (implementing agencies and regulatory authorities), nuclear research institutes, the academic community, and scientific consulting companies. The workshop provided an overview of the state of the art in this technical field, both in national waste management programmes and the scientific community, as well as a forum for discussing more general aspects of radionuclide-retention processes.

This publication is a compilation of the materials that were presented (oral and poster presentations), the discussions that took place, and the conclusions and recommendations drawn, notably during the working group sessions. A written synthesis also puts these conclusions and recommendations into perspective within the scope of the GEOTRAP project. The opinions, conclusions and recommendations expressed are those of the authors only, and do not necessarily reflect the view of any OECD Member country or international organisation.

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SYNTHESIS OF THE WORKSHOP

Synthesis

1. Introduction

1.1 Background to and aims of the Fifth GEOTRAP Workshop

Deep geologic repositories are sited and designed such that most or all radionuclides remain within the repository and the surrounding geosphere for prolonged periods. Thus, for most radionuclides, substantial radioactive decay is expected to occur before migration processes can convey them to the biosphere. Processes that prevent or delay the migration of radionuclides are termed retention processes. Retention processes that operate in the geosphere were the focus of the Fifth GEOTRAP Workshop.

As discussed at the preceding GEOTRAP workshop, performance assessment supports decision-making in the step-wise process of repository planning and development. In particular, it provides a tool to evaluate the suitability of a site and design from the point of view of long-term safety, based on current scientific understanding of relevant features, events and processes. The consideration of retention processes in the geosphere forms a part of most performance assessments. At early stages of repository planning (where decisions, in general, involve a lower commitment of resources), a less refined treatment of retention (and other) processes in performance assessments is likely to be acceptable, compared to later stages, including stages of repository licensing. Adequate justification of the selected treatment is, however, always required. The first aim of the Fifth GEOTRAP Workshop was thus:

> (1) To review the theoretical bases and supporting evidence for the operation and modelling of retention processes, with emphasis on field evidence, and the treatment of retention processes in performance assessments.

The justification of the selected treatment may include the identification of work that will, if necessary, be undertaken in the course of future stages to refine the treatment of features, events and processes and address unresolved issues. Further aims of the workshop were thus:

> (2) To identify issues related to retention processes that have been sufficiently resolved for current and future performance assessment purposes.

> (3) To identify future trends that can be foreseen and, in particular, unresolved issues that should be (or are being) addressed.

1.2 Scope of the workshop and definitions

The migration of radionuclides in solution through the geosphere may occur by advection and by diffusion; off-diagonal Onsager processes are, in general, negligible. Radionuclides may also be sorbed or incorporated into the structure of colloids, which themselves may migrate by advection and diffusion. The scope of the workshop encompassed a number of processes that may prevent or delay radionuclide migration by advection and diffusion of solutes and/or radionuclide-bearing colloids and thus fall under the category of retention processes.

For the purposes of the workshop, retention processes were broadly divided into those that result in *retardation* and those that result in *immobilisation*. These terms were defined as follows:

– Retardation is the slowing of the passage of radionuclides through a geologic medium. Retardation may be caused, for example, by the reversible attachment of radionuclides to mineral surfaces by a range of mechanisms, including adsorption, collectively referred to as *sorption* processes. It may also be caused by the diffusion of radionuclides from regions of flowing water, such as fractures, to connected regions of stagnant water, such as connected pore spaces in the fracture wallrock (*matrix diffusion*).[1]

– Immobilisation[2] is the halting of the passage of (at least some) radionuclides through a geologic medium. Immobilisation may be caused, for example, by the long-term attachment of radionuclides to (or incorporation of radionuclides in) fixed solid surfaces, e.g., by precipitation or co-precipitation. It may also be caused by the filtration of radionuclide-bearing colloids.

These retention processes are affected both by the properties of the radionuclides themselves and by the properties of the geologic medium, and are favoured by:

– The presence of stagnant, or very slowly moving groundwater in the host rock around the repository, including zones of stagnant water adjacent to zones containing flowing water (e.g., fractures) into which matrix diffusion can occur.

– Groundwater and mineralogical compositions that favour geochemical interactions of radionuclides at mineral surfaces.

– The accessibility of sorbing surfaces (e.g., by diffusion from fractures).

– A porous structure that favours the filtration of radionuclide-bearing colloids.

The broad categories of retention processes, namely the retardation processes of sorption and matrix diffusion, as well as immobilisation, were addressed at the workshop. Colloid-related retention processes were treated as a separate category.

Although the processes that lead to the association of radionuclides with colloids are the same as those that lead to the sorption or immobilisation of radionuclides on (or in) solids, colloids are generally characterised by a much larger specific surface area. The rate of migration of radionuclide-bearing colloids may differ considerably from that of radionuclides in solution, due, for example, to colloids being filtered or excluded from the pore spaces of fracture wallrock. It should also be noted that the migration of radionuclide-bearing colloids was explicitly excluded from the scope of the first four GEOTRAP workshops. This is a very broad topic, which is covered in other international for a,[3]

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1. Some lists of retardation processes exclude matrix diffusion, because the effect of this process on the rate of radionulide transport cannot, in general, be simply described using a retardation coefficient.

2. For the purposes of the workshop, immobilisation processes were defined as those with the potential to render radionuclides immobile over the time scales of relevance to performance assessment (10^5 to 10^6 years, say). As discussed in the course of the workshop, however, re-mobilisation may also occur, e.g., if geochemical conditions change, by dissolution of solids incorporating immobilised radionuclides (see Section 3.5.1).

3. The work of the "CoCo (Colloid and Complexation) Group" was summarised in a final report of the MIRAGE project [1]. Since then, several EC-supported projects have been initiated dealing with related topics, although the emphasis is now more on radionuclide complexation with natural organic materials, including humic substances, than on colloid-facilitated radionuclide transport. There is, however, the CARESS project (the role of colloids in the transport of radionuclides from a radioactive waste repository), co-ordinated by AEA Technology, UK [2]

and its exclusion was felt to be necessary in order to keep discussions focused on a manageable range of issues. Colloid-related issues were, however, discussed in this Fifth Workshop, due to their direct contribution to retention processes and their corresponding potential to alter the rates of radionuclide migration significantly.

Sorption, matrix diffusion, colloid-facilitated radionuclide transport and immobilisation were addressed in a series of invited presentations. They were also discussed by the participants, both in general discussion sessions involving all participants, and in four *ad hoc* working groups, with participants divided between the groups. In addition, a special working group was set up to discuss the lessons learnt from the entire GEOTRAP workshop series, and the follow-up actions that might usefully be taken.

As in previous workshops, the scope of the Fifth GEOTRAP Workshop explicitly excluded repository-induced effects on retention processes in the geosphere (e.g., effects related to excavation-disturbed zones, high-pH or organic plumes, thermal impact of the emplaced wastes). Long-term natural changes in the retention-relevant characteristics of the geosphere were, however, included within the scope.

1.3   *Structure of the synthesis*

An assessment of the achievements of the workshop, and a number of observations arising from the workshop presentations and discussions, are given in Section 2. Section 3 discusses individual findings relating to specific retention processes in more detail. Recommendations arising from the workshop are given in Section 4 and some concluding remarks are made in Section 5.

Annex 1 details the workshop structure and lists the key questions that were established for each session and for the *ad hoc* working groups. Annexes 2 to 6 present the main points made during the working group discussions. These annexes consist of reports prepared by the working group chairmen.

2.   **Workshop achievements and general observations**

2.1   *Workshop achievements and observations on workshop organisation*

As in previous GEOTRAP workshops, the wide range of experience and backgrounds of the workshop participants, and the attendance of scientists from the broader academic community, played a major role in developing, discussing, and challenging the findings that were drawn. Also as in previous GEOTRAP workshops, the establishment, in advance, of a series of key questions to be addressed in each session and by the working groups proved to be a very effective way of focussing the discussions and reaching practical conclusions and recommendations. The workshop achieved lively interaction among the participants and many points of consensus emerged, leading to the observations below and the recommendations given in Section 4.

In the course of the workshop, it became clear that the segregation of working group discussions according to categories of retention processes (retardation processes of sorption and matrix diffusion, colloid-related retention processes, and immobilisation) was not entirely possible. Firstly, the distinction between the different retention processes is to some extent arbitrary. For example, immobilisation may begin with sorption onto surfaces (a "retardation" process), followed by incorporation into the bulk solid. This incorporation may, furthermore, be reversible under certain conditions (see Section 3.5.1). Secondly, the effectiveness of one retention process is often closely related to the occurrence and effectiveness of another. The importance of colloid-facilitated radionuclide transport depends, in part, on whether the radionuclides are sorbed reversibly onto colloids or immobilised within (or form part of) the solid structure of colloidal particles. The effectiveness of sorption as a retention process is greatly enhanced if matrix diffusion provides access

to additional sorbing surfaces. Presentations and discussions thus often encompassed more than one category of retention process, even if their focus was primarily on one particular category.

2.2   The importance of an iterative approach

The need for an iterative approach to the development of understanding and the building of conceptual and quantitative models, with close interaction between performance assessors and technical specialists in the various scientific disciplines, has been a recurring theme of the GEOTRAP workshop series. In the Fifth GEOTRAP Workshop, interaction was discussed, for example, in the context of colloid-facilitated radionuclide transport, where significant uncertainties exist in several potentially relevant underlying phenomena. Feedback from performance assessment may usefully indicate for which, if any, of these phenomena improved understanding is required, and also help in establishing the "data quality objectives" that are required in order to assess the safety of a proposed repository adequately. In particular:

– How well does a phenomenon need to be understood?

– What are the consequences of omitting a phenomenon from a performance assessment model?

– How are site-characterisation specialists to judge when they have sufficient data for performance assessment purposes?

In the context of natural analogues, it was noted that the active participation of performance assessment personnel at all stages of planning, execution, and interpretation of data has linked analogue studies more directly to performance assessment requirements. Efforts have also been made to integrate analogue studies with laboratory and *in situ* field experiments [3].

2.3   The importance of retention processes

The existence and importance of retention processes is recognised not only in the field of radioactive waste disposal, but also in other areas such as mining and the management of non-radioactive hazardous wastes. There are differences in the factors that affect the operation of retention processes at different types of sites. The concentration of organic materials, which will be far higher within and around landfill sites than many deep disposal sites for radioactive wastes, is, for example, an important factor affecting many retention processes. The fact, however, that the same processes are recognised to operate in systems or applications unconnected to radioactive waste disposal means that a large body of expertise exists that radioactive waste disposal projects might benefit from, in terms of either the further development of understanding and analysis tools, or review.

In the context of deep geologic repositories, the importance of retention processes in general, and the relative importance of different retention processes, is, to some extent, site-specific. For example, for many rocks considered as host formations for deep geologic repositories, it is thought that colloid-related retention processes are of limited importance, based, for example, on the low observed concentrations of groundwater colloids or arguments for the low mobility of colloids in some dense clays. Both retardation and immobilisation processes are recognised as important by all programmes discussed at the workshop, although only the retardation processes of sorption and (for fractured media) matrix diffusion are widely incorporated in performance assessment models. Table 1 lists the various processes that were discussed at the workshop and summarises the current level of understanding, the process-level models that have been developed, and the extent to which the processes are included in geosphere transport models for performance assessment.

Table 1. **Summary of processes discussed at the workshop,**
the current level of understanding, the process-level models that have been developed,
and the extent to which processes are included in geosphere transport models for performance assessment.

	Retardation processes (see Sections 3.2 and 3.3)		
Processes/definitions	**Current level of understanding**	**Process-level modelling**	**Performance-assessment modelling**
Sorption: A radionuclide that is sorbed is reversibly attached to a solid surface by one of a range of mechanisms, including **adsorption** (an accumulation of matter at the interface between a solution and a solid adsorbent) and **ion exchange** (a special type of adsorption, in which counter-ions accumulate at the interface of a solid adsorbent with permanent structural change).	Processes widely observed in laboratory and field experiments, as well as in natural systems. Nature of surface species and stoichiometry of surface reactions in complex geologic environments becoming better constrained by high-resolution surface analytical techniques.	Mechanistic models well developed for simple (clean) mineral/water interfaces and improving for more complex geological situations. Models are subject to uncertainties associated e.g., with mineral/organic coatings and electric double-layer properties. Models used mainly to develop understanding of the effects of varying groundwater conditions. Semi-empirical site-binding models are not widely used to date, but may represent a good compromise in terms of data collection needs and the need to predict radionuclide distributions over a range of chemical conditions.	Use of conservatively selected K_ds is widespread and likely to continue. Some performance assessments use non-linear sorption isotherms. Others use semi-empirical functions to represent dependence of K_ds on geochemical conditions (pH, Eh). Mechanistic models are regarded as too complex/subject to uncertainty for direct inclusion in performance assessment models, but valuable for justifying the selection of K_d values.
Matrix diffusion: The diffusion of radionuclides (i.e., movement under the influence of their kinetic activity in the direction of a concentration gradient) between regions of flowing water, such as fractures, and connected regions of stagnant water, such as pore spaces in the fracture wallrock; matrix diffusion may be increased by **surface diffusion**, or restricted by **anion exclusion**.	Numerous field observations give mainly generic evidence that matrix diffusion occurs in fractured rock systems. Several methods exist (or have been suggested) to characterise matrix diffusion and accessibility of pore spaces. Interpretation may be complicated by matrix heterogeneity. Evidence provided by field tracer transport experiments may relate to only a part of the total pore space that is of interest to performance assessment.	The key issue to be addressed in modelling matrix diffusion in geologic media is matrix heterogeneity. Approaches include (i) the use of probability distributions of "matrix residence times" and (ii) the explicit modelling of different rock matrix zones, assigning different characteristics to each. Further development of process-level models is likely to require better understanding of the geometry and connectivity of matrix pores. The degree to which matrix diffusion retards radionuclide transport also depends on flow conditions (as described, e.g., by the "flow-wetted surface"), and as such may be strongly influenced by heterogeneous groundwater flow.	Performance assessment models are based on Fick's Laws. Matrix heterogeneity is often treated in a simplified manner in performance assessment models due to uncertainties in the characterisation of the matrix – e.g., the matrix may be represented as a homogeneous zone of limited extent (e.g., considering only altered wallrock adjacent to fractures). Some programmes have developed and applied performance assessment models that allow explicit modelling of different rock matrix zones. Surface diffusion is generally omitted from models. Anion exclusion is sometimes included via parameter selection (diffusion coefficients/porosities).

Table 1 *(continued)*

Colloid-facilitated radionuclide transport (see Section 3.4)			
Processes/definitions	**Current level of understanding**	**Process-level modelling**	**Performance-assessment modelling**
Colloid-facilitated radionuclide transport: The association (e.g., by **sorption, precipitation,** or **co-precipitation)** of radionuclides with either natural groundwater colloids or colloids arising from the presence of a repository, and the subsequent transport of radionuclide-bearing colloids through the geosphere. The distances over which transport occurs depend, in part, on colloid stability and the rate of **filtration.**	Colloid-facilitated radionuclide transport is generally of concern in performance assessment only for more radiotoxic nuclides. Also, colloids must be able to compete against immobile-phase solids in the sorption of radionuclides and must be transported over considerable distances to be of concern. Radionuclide-bearing colloids arising from processes associated with a repository may be of most concern n performance assessments, since natural colloid concentrations are often low. Colloid generation, deposition, radionuclide uptake, and transport are understood in general terms, but subject to numerous uncertainties. With respect to transport, it has not, in general, been possible to demonstrate that radionuclide-bearing colloids will be immobile in natural systems, other than some dense clays. The role of natural organic matter (NOM) colloids in radionuclide transport has been relatively little studied but may, in some instances, enhance the transport of radionuclides through subsurface systems.	Many systems are dominated by a specific class of colloids, and process-level models thus have to be tailored for application to specific systems. Many process-level models have been developed, but are subject to numerous uncertainties. Recent advances in understanding of the role of geochemical heterogeneity in colloid transport and release suggest promising avenues for understanding and modelling colloid transport in real systems. There is a need for more high-quality datasets from relevant systems in order to test and further refine colloid-facilitated radionuclide transport models and a need to develop better methods to upscale process models developed for laboratory systems to the field scale.	Some performance assessments have explicitly included colloid-facilitated radionuclide transport in geosphere transport models, although such models are generally highly simplified due to the absence of relevant site-specific data and the complexity and consequent uncertainties associated with the relevant processes. Other assessments have used a variety of lines of reasoning to argue that the process is unimportant for the particular system under consideration.

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Table 1 (*continued*)

Immobilisation processes (see Section 3.5)			
Processes/definitions[4]	**Current level of understanding**	**Process-level modelling**	**Performance-assessment modelling**
"Irreversible sorption": The situation where the timescale of desorption from a mineral surface is very slow. **Surface precipitation:** The growth of a solid phase exhibiting a primitive molecular structure that repeats itself in three dimensions on the surface of a different contiguous solid phase. A radionuclide that is **precipitated** sits in a regular position for ions of that element in a single solid phase. A radionuclide that is **co-precipitated** exists either in one solid phase that is mixed with another, or in the form of a solid solution, where it sits in an atomic site that would normally be occupied by an ion of a different element. **Surface substitution/re-precipitation/ surface mixing (formation of solid solution):** The formation of a solid solution in the superficial layers of a contiguous solid phase by exchange of elements between solution and the solid phase structure. **Adsorption** followed by **solid-state diffusion:** The diffusion of adsorbed radionuclides into the bulk of a mineral by ion-by-ion replacement, especially along defects running into a surface at high angle, driven by a concentration gradient.	Immobilisation of radionuclides in the bulk of a solid may (depending on the nature and rates of any remobilisation processes) be a more effective retention mechanism than sorption at surfaces. Highly effective immobilisation of ions in mineral phases in diverse environmental settings is widely observed in nature, although conditions under which immobilisation occurred often differ significantly from those of interest to performance assessment. Laboratory and modelling studies, often integrated with analogue research, also support development of basic understanding of immobilisation processes. Immobilisation by precipitation and by co-precipitation in carbonates and Fe-and Mn-oxyhydroxides are of particular importance in many natural analogues and are also likely to be important in many repository systems. Short-term laboratory measurements on bulk systems often do not allow slow immobilisation processes to be resolved and fundamental understanding is, in many cases, poor. High-resolution techniques offer the prospect of improved understanding in this area. The incorporation of radio-nuclides in a solid can, under some circumstances and over long timescales, be reversible. The dissolution or erosion of solids incorporating immobilised radionuclides may occur as physicochemical conditions change over the long times of interest in performance assessment.	The difficulties encountered in the mechanistic modelling of sorption also apply to the application of these models to immobilisation processes. In particular, until recently, the lack of high-resolution techniques has been an obstacle to process-model development. Nevertheless, current knowledge is adequate to perform simplified calculations of the likely magnitude of immobilisation processes in some systems, enabling such processes to be compared in terms of their possible effectiveness with (reversible) retardation processes.	Immobilisation processes have not so far been taken into account in performance assessments in a quantitative manner. This omission is generally the result of the absence of relevant site-specific data and uncertainties associated with the slowness and complexity of the processes and is usually justified on the grounds of conservatism. Uncertainties are such that the prospects of including immobilisation processes in performance assessment models used to demonstrate compliance with regulatory guidelines in the near future appear low at present. Nevertheless, there are good prospects for some improvement in the understanding of these processes, which will at least improve qualitative arguments for the long-term retention of many safety-relevant radionuclides in the geosphere.

4.   These processes all have the potential to immobilise radionuclides over prolonged periods. Whether or not the period of immobilisation approaches (or exceeds) the timescales relevant to performance assessment (e.g., 105 to 106 a) depends on the nature and rates of remobilisation processes, and will thus be system- and site-specific.

2.4   Development of understanding of retention processes

There is substantial geological and other evidence that provides information relevant to retention processes. Evidence comes from a range of observations of natural systems, including some that are perturbed by human activities such as the geologic environment within and around mines. The opening technical presentation of the workshop gave several examples of such evidence [4]. In general, the challenge facing organisations seeking to implement a radioactive waste repository is to demonstrate that retention processes will occur at specific sites and to develop the understanding to quantify the processes, so that credit can be taken for them in performance assessments.

The isotopic fractionation that is observed in some natural systems can be used to develop at least a qualitative understanding of some retention processes, as well as of the long-term movement of groundwater [5]. The Peña Blanca natural analogue in Mexico and the Lac du Bonnet Batholith in Canada were examples cited at the workshop where isotopic fractionation indicates, respectively, open-system and closed-system behaviour. In particular, the secular equilibrium of radionuclides in the uranium and thorium decay chains indicated, in the case of Peña Blanca, a system that is closed on a timescale that is long relative to the half-lives of the daughter radionuclides in these chains. In some cases, information can be obtained on retention processes that operated in the past under different geochemical conditions from those prevailing today (and may occur again in the future, for example due to glacial cycling). Examples from the Finnish natural-analogue study site at Palmottu were given at the workshop, where selective extraction processes, using different chemical reagents, have been applied to study the isotopic ratios of different sorbed phases and provide information on the past immobilisation and mobilisation of radionuclides [6].

Obtaining more quantitative understanding of retention processes from isotopic fractionation, i.e., the subject of *in situ* K_ds, is widely recognised as being complex and challenging in practice. Processes that have been neglected or incompletely represented in various interpretations of data include non-linear sorption and sorption site saturation, as well as the various immobilisation processes discussed in Section 3.5. Nevertheless, evaluation of *in situ* K_ds has the potential to provide an alternative line of evidence that may be used to evaluate laboratory-based data [5].

Evidence relevant to retention processes also comes from field experiments and their associated laboratory studies. Those conducted at the SKB Äspö Hard Rock Laboratory in Sweden and at the Waste Isolation Pilot Plant (WIPP) in the USA were cited several times at the workshop. Field tracer transport experiments play a particularly important role in developing generic understanding of retention processes, testing methodologies for up-scaling measurements obtained in the laboratory to field conditions, and in characterising actual sites. Working Group 5 noted that there has been a move away from simply adjusting model parameters, in an unconstrained manner, in order to "fit" models to the breakthrough curves from such experiments. There is now more of an emphasis on constraining free parameters using independent information (e.g., direct geological observations, results of laboratory experiments) and, where possible, making blind predictions of experimental outcomes. This was illustrated at the workshop in, for example, the presentations of modelling work carried out by different teams as part of the TRUE (Tracer Retention Understanding Experiments) programme at the Äspö Hard Rock Laboratory.

Blind predictions have not always been successful and, in the context of TRUE-1, which focused on a single fracture, models have been repeatedly refined and new predictions made for different experimental configurations. At each stage of refinement, model developers consult with, for example, geological specialists in order to constrain the possibilities for the representation of geological structure, mineralogy, matrix volumes accessible to diffusion, etc. [7,8]. This is an example of an iterative approach to the development of understanding and the building of conceptual and quantitative models. Such approaches are used not only in the interpretation of experiments, but also performance assessment, which, as mentioned above, has been a recurring theme of the GEOTRAP workshop series.

2.5   *Representation of retention processes in performance assessments*

Ideally, the scientific understanding of retention processes would be sufficient to include all retention processes in realistic performance assessment models. In practice, uncertainties are such that conservative assumptions often have to be made and, in some cases, processes are omitted from quantitative models.

The retardation process of sorption is considered important by all repository programmes discussed at the workshop. It is widely incorporated in performance assessment models (although often via the simple approach of assigning a conservatively chosen sorption coefficient, K_d, to each radioelement). Matrix diffusion is also considered important by repository programmes that consider fractured geologic media. Together with the very slow movement of groundwater, these retardation processes determine the overall effectiveness of the geosphere as a barrier in most geosphere transport models for performance assessment. It is widely recognised that immobilisation processes are also likely to be an important factor contributing to the actual effectiveness of the geosphere as a barrier to transport. Models and data for these processes are not, however, currently considered to be sufficiently reliable to allow the processes to be incorporated quantitatively in performance assessments. As mentioned above, colloid-related retention processes can, for many geologic settings of interest to radioactive waste disposal, be shown to be of limited importance. Models for colloid-facilitated radionuclide transport have, however, been developed and, in a highly simplified form, included in some geosphere transport models for performance assessment.

Spatial and temporal variability can considerably complicate the representation of retention processes in performance assessment models, and are often a significant source of site-specific uncertainties, as mentioned in several of the workshop presentations. Regulators are likely to require the effects of variability to be investigated by implementers, and implementers to justify the models as well as the parameter values used [9]. Disposal systems avoid uncertainties associated with temporal variability, to some extent, by selecting sites that are expected to remain stable over very long periods. Over a 10^5 to 10^6 year period, however, it may be difficult to exclude the possibility of some changes in relevant factors such as groundwater chemical composition, porosity, and permeability. Uncertainties regarding the long-term effects of the repository on the geologic environment are also relevant to some disposal systems, although these were beyond the scope of the workshop.

The way in which it is appropriate to represent heterogeneity and temporal variability in performance assessment models is site- (and system-) specific. A general observation is, however, that they must be represented at appropriate scales and caution must be exercised if spatial or temporal averaging is used. The sorption coefficient of a given radionuclide may, for example, vary over several orders of magnitude at different (sometimes closely spaced) locations and at different times (see Section 3.2.3 for a discussion of the treatment of spatial variability in the context of sorption).

In performance assessment models, the differences in chemical properties and transport behaviour of isotopes of the same element are generally neglected [5]. Isotopic fractionation is, however, observed in nature (and may help to develop system understanding; see Section 2.4). Processes that lead to isotopic fractionation, such as enhanced release rates of alpha-decay products from solid matrices by alpha recoil, are in principle relevant to performance assessment, but are generally thought to be negligible in the context of the large uncertainties that usually are encountered in modelling retardation and immobilisation. There are, however, a few cases where chemical properties and transport behaviour may be significantly affected by isotopic ratios. An example cited at the workshop is colloid-facilitated radionuclide transport, where the stability of plutonium colloids depends on their isotopic composition because of radiological effects on colloid formation and degradation. Furthermore, although not directly relevant to geosphere transport, it was also noted at the workshop that preferential ejection of ^{234}U from the matrix of spent nuclear fuel by alpha-recoil is a potentially important near-field phenomenon.

2.6   The regulatory view of the representation of retention processes

A role of regulators is to evaluate potential vulnerabilities in the safety case presented by implementing organisations. Regulators are, therefore, likely to question all assumptions regarding retention processes, including those that are incorporated into assessment models (and other incorporated phenomena, especially those that favour good performance of the multi-barrier system) and those that are omitted. The intensity of regulatory scrutiny of the treatment of retention processes in performance assessment will depend on the importance of these processes to the safety case of an implementer [9].

Regulators require "reasonable assurance", or "sufficient confidence", that the representation of retention processes in assessment models can be relied upon, at least not to underestimate radiological consequences. While it is preferable to have as realistic a description of retention processes as possible, a wholly realistic description is not absolutely necessary to support regulatory decisions. Thus, for example, the omission of immobilisation processes or colloid-facilitated radionuclide transport may be acceptable so long as it can be shown with reasonable assurance that radiological consequences are not significantly underestimated under any conditions. The workshop raised (but did not resolve) the question as to what can be said to constitute reasonable assurance. It must, however, be seen as dependent on the decision that the performance assessment supports, and, in particular, the commitment that the decision entails.[5] In this context, greater regulatory emphasis on quality assurance of data and models and transparency of documentation is expected as programmes approach the licensing phase [9].

Regulators often encourage or require the use of "multiple lines of evidence" for demonstrating safety. Multiple lines of evidence can refer to the different types of evidence that support the treatment of retention processes within models, including studies of natural analogues. In addition, retention processes that are not included in performance assessment models, such as immobilisation processes, can sometimes be cited as qualitative evidence that safety margins will be higher in reality than those indicated by performance assessment calculations.

3.   Observations on specific retention processes

3.1   Introductory comments

The manner in which retention processes are incorporated in performance assessments depends on the level of fundamental understanding, and on the availability of models to simulate the processes, as well as on the existence of appropriate site- and/or concept-specific data. Fundamental understanding is, ideally, based on a wide range of laboratory and field experiments and on observations from nature, and on the development and testing of process-level models that aim at consistency with available experimental results and field observations, as well as the ability to predict future results and observations. The following sections are structured accordingly. For each retention process, there is a summary of:

– The level of fundamental understanding attributed to the process.

– The degree to which the process can be represented in detailed process-level models that aim at realism.

– The representation of the process in performance assessments.

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5.   The relationship of performance assessment and decision-making is discussed at length in [10].

3.2 Sorption

3.2.1 Fundamental understanding of sorption processes and the evidence on which it is based

The sorption processes of adsorption and ion exchange are widely observed both in laboratory and field experiments, as well as in natural systems. Advances in the fundamental understanding of these processes were recognised at the workshop and discussed in Working Group 1. The group noted an overall impression that the scientific community has a good "feeling" for the major processes responsible for the sorption of radionuclides over a wide range of conditions that might exist in relevant geologic systems. Furthermore, the Group concluded that the capacity to make "expert judgements" concerning sorption processes reflects a broadly good understanding of the underlying mechanisms.

Although the density of sorbed ions can be measured by a variety of macroscopic techniques (e.g., batch sorption experiments), the molecular structure of sorbed species (bond distances, co-ordination numbers, and stoichiometries of surface reactions) can only be determined by surface analytical techniques [11]. Macroscopic observations alone may not resolve all relevant processes. Recently developed high-resolution surface analytical techniques, borrowed from physics and materials science, make it possible to collect nanometre-scale information and are leading to a better understanding of the molecular structure of adsorbed species in complex geologic environments (until recently, resolution limits were commonly considered to be about one micrometre). Examples of specific high-resolution techniques were given at the workshop, including scanning probe microscopy (SPM), atomic force microscopy (AFM), X-ray photoelectric microscopy (XPS), X-ray absorption spectroscopy (XAS), and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Such techniques, which are also relevant to the discussion of immobilisation (Section 3.5), offer direct observation at the nanometre scale, allowing molecular-level processes to be described and offering the potential for more realistic process-level models.

These techniques have revealed, for example, that [12]:

– A radionuclide can adsorb to a surface that is actively dissolving.

– Radionuclides can "hide" in colloidal-size particles or in thin coatings that are impossible to detect with classical methods.

The combination of data from macroscopic methods with that from high-resolution techniques offer the prospect for further improvements in fundamental understanding, as well as improved process models of both sorption and immobilisation.

3.2.2 Process-level modelling of sorption

At least three types of models have been developed for describing radionuclide sorption at mineral surfaces at which equilibrium exists between aqueous and sorbed phases [11]:

– Empirical partitioning relationships, which are widely used in performance assessment, the most simple of which use the concept of a distribution coefficient, K_d.

– Mechanistic models that describe the details of chemical species formation at mineral surfaces using thermodynamic formalisms and the surface complexation concept to describe absorption.

– Semi-empirical site-binding models that utilise concepts from the first two model types.

Models of sorption kinetics, on the other hand, are less well developed and take the form of empirical relationships.

Advances in mechanistic models of sorption were recognised at the workshop and discussed in Working Group 1. Ideally, the surface species postulated in mechanistic models are supported by evidence from high-resolution techniques (discussed above in Section 3.2.1). In any case, they require the collection of considerable data. Thus, mechanistic models are well developed for simple (clean) mineral/water interfaces, but are improving for more complex geological situations, due, in part, to the increasing amount of information available using high-resolution techniques. They are, nevertheless, still subject to uncertainties associated, for example, with mineral or natural organic coatings (fulvic and humic acids) and electrical double-layer parameters, to which they are highly sensitive. These uncertainties make application of mechanistic models difficult at present, even at the microscopic scale; they are thus widely regarded as being currently unsuitable for inclusion in geosphere transport models for performance assessment. Their usefulness lies rather in the development of understanding of the effects of varying groundwater composition on sorption. They may be applied, for example, to supporting the selection of K_ds for performance assessment scenarios where groundwater composition is affected by climate change, or to extrapolate K_ds measured in the laboratory (often in the presence of air) to field conditions.[6]

Semi-empirical site-binding models represent a less rigorous "engineering" approach to sorption modelling than fully mechanistic models. They have not been widely used to date, but may represent a good compromise in terms of data collection needs and the need to predict radionuclide distributions over a range of chemical conditions. Their application in performance assessment will, however, require a greater emphasis to be placed on the site-specific characterisation of the mineral assemblages and variable groundwater composition along radionuclide transport paths [11].

3.2.3 *Representation of sorption in performance assessment models*

The use of empirical partitioning relationships to represent sorption continues to be widespread in performance assessments and there seems little desire among performance assessors or regulators to discontinue their use. Some performance assessments have employed non-linear sorption isotherms [13]. Most, however, employ the K_d approach, which implicitly assumes rapid, reversible, and linear sorption.

The K_d approach can, in some cases, give unsatisfactory predictions of tracer breakthrough in tracer transport experiments in the laboratory and field, due, for example, to desorption being slower in reality than the instantaneous reversibility that is implicitly assumed in the K_d approach. Slow desorption kinetics are, however, unlikely to be of concern over the very long timescales of interest in performance assessments. A greater concern is how to apply the K_d approach in performance assessments addressing systems that are subject to spatial and temporal variability of mineral and groundwater composition.

Working Group 1 addressed this issue. It is also discussed, for example, in [14]. The Group considered that spatial variability poses greater challenges to site characterisation and performance assessments in the case of fractured formations than in the case of unconsolidated rocks. Furthermore, the Group considered that the capacity to represent spatially variable sorption in performance assessment is likely to be limited largely by the density of data available.

Many performance assessments use single K_d values to represent radionuclide sorption across a range of possible geochemical conditions. Values are selected that err towards the low end of the range that is expected [e.g., 15]. There may, however, be cases where such bias is non-conservative.

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6. Modelling of the TRUE-1 tracer transport experiments indicates higher retention of tracers in the field than is suggested on the basis of laboratory studies. Several factors may contribute to this discrepancy.

Examples were cited from the Drigg case in the United Kingdom and the case of the SFR repository for low-level and intermediate-level waste in Sweden. In the latter example (though not directly related to geosphere transport), preliminary calculations suggest that sorption on engineered materials is the key contributor to safety [9]. The consequences of near-field releases are strongly dependent on the time at which the releases occur, being affected by the changes in the level of the Baltic Sea and the consequent changes to the hydrological regime and biosphere. A seemingly conservative assumption of zero sorption will lead to earlier releases, leading to potentially non-conservative dose calculations. Thus sorption (and other retention processes) should be considered in the context of the complexity of the total system. Bias in the selection of K_ds (and other parameters) needs to be clearly explained, and supported by logical arguments and possibly sensitivity analysis in order to demonstrate conservatism.

Another approach is to employ semi-empirical functions to represent the dependence of K_ds on (space- and time-dependent) geochemical conditions and, in particular, on pH and Eh, which may be derived from the results of mechanistic models [9, 11]. This approach can be used to represent the effects of spatial and temporal variability of geochemical conditions on radionuclide transport more realistically than fixed value K_ds (or K_ds sampled randomly from probability density functions). In particular, to represent spatial variability, probability density functions can be assigned to parameters representing the geochemical conditions (pH, Eh, etc.), and K_ds calculated for randomly sampled conditions. The U.S. Nuclear Regulatory Commission, for example, intends to implement such an approach in its total system performance assessment code [9]. It was pointed out, however, that care must be taken not to use such empirical relationships to describe radionuclide partitioning beyond the range of conditions to which they have been shown to be applicable.

3.3 *Matrix diffusion*

3.3.1 *Fundamental understanding of matrix diffusion and the evidence on which it is based*

The workshop provided numerous examples of field observations that give convincing, though mainly generic, evidence that matrix diffusion occurs in fractured rock systems. Working Group 2 cited, for example, the Poços de Caldas uranium mine in Brazil, where there is direct evidence of diffusion on a decimetre to metre scale over a timescale of tens of millions of years. If an implementer wishes to invoke matrix diffusion in site-specific performance assessments, however, the regulator is likely to require convincing evidence that it can be relied upon as a retention mechanism at the site in question. In particular, evidence must be sought that diffusion-accessible pore spaces exist, for example, in fracture-infill material and in the wallrock adjacent to fractures, and an understanding of the characteristics of these pore spaces must be developed that provides a sound basis for performance assessment models. Rock matrices within and around fractures are spatially variable over a range of scales. The degree of heterogeneity and the most appropriate way to characterise it are site-specific.

Matrix heterogeneity can be associated with the presence of a range of matrix block sizes between fractures and, within the blocks, ranges of pore shapes and sizes, degrees of sorption, and other characteristics. Hydrogeochemical processes often result in the alteration of wallrock adjacent to fractures. It was, for example, pointed out at the workshop that almost all of the fractures studied at the Äspö Hard Rock Laboratory show alteration of the wallrock [8]. Altered zones with higher porosities and sometimes more favourable sorption properties than unaltered wallrock may extend over distances as large as a few centimetres, depending on the rock type and its history. Working Group 2 concluded that, while it may, in some cases, be difficult to demonstrate matrix diffusion in unaltered rock, there is little doubt that matrix diffusion will take place in altered zones.

Several methods that exist, or have been suggested, to characterise matrix pores, and particularly those of fracture wallrock, were discussed in Working Group 2. The Group observed that

there is a wealth of observations from laboratory measurements [e.g., 16]. Due to the slowness of the diffusion process, however, most give information on distances of less than 5-10 cm normal to fracture surfaces. The methods can also be subject to artefacts, e.g., changes in porosity associated with de-stressing when samples are taken or underground drifts constructed. There are also *in situ* methods, including the measurement of electric conductivity in deep boreholes [17]. These too may be subject to artefacts, including the effects of conductive minerals that may connect otherwise dead-end pores. Methods to characterise wallrock matrix pores are an area of ongoing research in some programmes, and Working Group 2 considered some techniques that might be applied in the future, including *in situ* electromigration, where a DC current would drive a charged tracer through the matrix. In spite of the uncertainties, there are clear indications of decreasing connectivity of wallrock pores with depth in many fractured rocks (e.g., [18]).

Field tracer transport experiments can also provide site-specific evidence of matrix diffusion and can be used to test conceptual models for the distribution and accessibility to diffusion of matrix pores. The breakthrough curves generated by these experiments are sometimes indicative of retention by diffusion into a matrix with homogeneous characteristics, at least within the portion of the matrix accessed in the course of the experiment. In particular, such curves have tails with a characteristic slope of $t^{-3/2}$, as observed in the TRUE-1 experiments at Äspö [8]. These tail slopes are not, however, always observed. Those from the WIPP tracer tests, for example, showed slopes ranging from $t^{-2.1}$ to $t^{-2.8}$, indicating heterogeneous matrix characteristics. Even where a $t^{-3/2}$ slope is obtained, there may be disparate opinions among experts regarding the most appropriate conceptual model to represent matrix pore space [7]. Where the tails of breakthrough curves do not show the characteristic slope of $t^{-3/2}$, an unambiguous interpretation of breakthrough curves is likely to be even more difficult without substantial complementary information.

A further problem with using field tracer transport experiments to provide evidence of matrix diffusion for performance assessment purposes is that, over the long timescales of relevance to performance assessment, pore spaces may be accessed by radionuclides that are not accessed in the much shorter-term experiments [8]. This is associated not only with the distance of matrix pores from a fracture, but also with the variability in the size of matrix blocks, and the connectivity/tortuosity and constrictivity of pores [18,19]. Thus, field confirmation may be difficult to obtain for all of the matrix diffusion that may occur on the PA timescale and care must be taken when extracting diffusion parameters for performance assessment from experiments conducted over relatively short timescales in which the pores accessed by diffusion may be different from those accessed over performance assessment timescales.

3.3.2   *Process-level modelling of matrix diffusion*

As indicated by the above discussion, when modelling matrix diffusion in geologic media, the key issue to be addressed is the representation of matrix heterogeneity. A "representative elementary volume" over which heterogeneity can be averaged, and which can be used as the basis for a continuum model employing the concept of Fickian diffusion and treating the whole rock matrix as homogeneous, may exist for some media (e.g., some fractured clays). For many media, however, it does not [19]. The treatment of such media as homogeneous in the modelling of experimental results gives rise to scale dependence in the parameters characterising matrix diffusion. In other words, single values for the matrix diffusion coefficient and other relevant parameters cannot be defined for all relevant scales of space and time if the matrix is treated as homogeneous. This has been observed, for example, when diffusion coefficients have been derived by through-diffusion experiments conducted on Äspö diorite samples of varying thickness [18]. The degree to which matrix diffusion retards radionuclide transport also depends on flow conditions (as described, e.g., by the "flow-wetted surface"), and as such may be strongly influenced by heterogeneous groundwater flow.

Two broad approaches were presented at the workshop for the representation of heterogeneity in process-level models. One approach involves the characterisation of matrix heterogeneity via probability distributions of "matrix residence times". This approach has been applied, for example, for the interpretation of tracer tests in the Culebra Dolomite Member of the Rustler Formation at the WIPP site [19]. Another approach is to model diffusion into different rock matrix zones (altered and unaltered) explicitly [8], with different characteristics (porosities, diffusivities, sorption parameters) assigned to each zone.

The further development of process-level models of matrix diffusion is likely to require a better understanding of the geometry and connectivity of matrix pores. The development of novel techniques to allow the investigation of diffusion at larger time and spatial scales, such as those discussed by Working Group 2, would be particularly beneficial.

3.3.3   *Representation of matrix diffusion in performance assessment models*

The process modelling approaches outlined above require detailed information on, for example, small-scale matrix structure and the variability of parameters between matrix blocks. This information may not always be available to performance assessors. As mentioned in the discussion of the characterisation of matrix heterogeneity, above, it is sometimes easier to demonstrate the existence of connected porosity, accessible to matrix diffusion, in the wallrock immediately adjacent to fractures and, in particular, in altered zones adjacent to fractures, compared with the more distant unaltered wallrock. Performance assessments often do not need to invoke matrix diffusion over distances into the wallrock normal to fracture surfaces of more than a few centimetres in order for the geosphere to provide a highly effective transport barrier for many safety-relevant radionuclides. Indeed, diffusive transport into the wallrock is often so slow that many nuclides cannot diffuse more than a few centimetres into the matrix before they decay. Thus, if it is difficult to demonstrate the existence of connected porosity in unaltered wallrock, a performance assessment that invokes matrix diffusion only in the altered wallrock adjacent to fractures may nevertheless indicate an adequate performance of the geosphere as a transport barrier. Even if matrix diffusion in the more distant, unaltered wallrock is conservatively neglected, the possibility of additional retention in the unaltered wallrock can be cited in a safety case as a qualitative argument that safety margins will be higher than those indicated by performance assessment calculations.

Performance assessment models generally treat the diffusion-accessible matrix as homogeneous, but sometimes limited in extent to distances over which connected porosity can reliably be argued to exist. In the Finnish TILA-99 performance assessment, different sorption and matrix diffusion properties are assigned to altered wallrock adjacent to fractures and more distant, unaltered wallrock, and a geosphere transport code is employed that explicitly models these different structural components. In Switzerland, Nagra have also developed a code that allows different sorption and matrix diffusion properties to be assigned to discrete matrix zones [13]. It was noted at the workshop that, for strongly sorbing species, matrix diffusion distances are sometimes as little as around a millimetre. The representation of the matrix as a homogeneous medium with diffusion-dominated transport, separated discontinuously from a fracture with advection-dominated transport, is questionable for such small matrix diffusion distances. The sorbing species are, however, generally so well retained by the geosphere that the exact formulation of the geosphere transport model is unlikely to affect the overall insignificance of these species in performance assessment. Performance assessment models also assume the applicability of Fick's Laws.[7] In cases where the porosity in rocks is at or below the percolation threshold,[8] Fick's Laws do not correctly model diffusion.

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7.   The justification for neglecting solute-solute interactions when applying Fick's Laws was questioned in one of the poster presentations [20].

8.   As the porosity of a rock decreases toward the percolation threshold, pores become increasingly isolated from each other, tortuosity grows, and the pore space becomes a fractal [19].

There is, however, evidence from electrical conductivity work and field diffusion studies that, although deviations from Fick's Laws certainly occur, they may not be important over the scales of space and time generally of interest in performance assessment.

Surface diffusion has been recognised as a relevant process in some performance assessments, but has been conservatively[9] neglected. Anion exclusion has been included in many recent assessments, either through assigning element-specific diffusion parameters (diffusion coefficients/porosities), or by assigning single, conservative values to these parameters.

3.4   Colloid-facilitated radionuclide transport

3.4.1   Fundamental understanding of colloid-facilitated radionuclide transport and the evidence on which it is based

Colloid-facilitated radionuclide transport is recognised as an issue in recent performance assessments and has been the subject of considerable experimental and theoretical study in order to develop a fundamental understanding of the relevant processes, as discussed in Working Group 3.

Colloid-facilitated radionuclide transport is generally of concern in performance assessment only for the more radiotoxic nuclides. In addition [21]:

– Colloids must be able to compete effectively against immobile-phase solids in the sorption of safety-relevant radionuclides (i.e., colloids must be present in sufficient concentrations) and radionuclides must strongly sorb to (and/or slowly desorb from) these colloids.

– Colloids must be transported over considerable distances (i.e., colloids must be stable and filtration rates must be low).

Radionuclide-bearing colloids may arise from the sorption of radionuclides on natural groundwater colloids. For many such "symmetrical" systems, the refinement of sampling techniques in recent years has yielded a number of accurate estimates of colloid concentrations. Furthermore the chemical nature of these colloids is, in many cases, similar to that of immobile solid phases and, therefore, reasonably well understood. Radionuclide-bearing colloids may also, however, arise from processes associated with a repository (e.g., canister corrosion). These "asymmetrical" systems are often of most concern in performance assessments, which usually address geologic settings where the natural groundwater colloid concentrations are low (e.g., < 10 mg/L).

The mechanisms and degree of understanding of colloid generation, deposition, radionuclide uptake, and transport were discussed by Working Group 3 and are also covered in [21]. These aspects, though understood in general terms, are all subject to numerous uncertainties. Filtration theory, which describes colloid deposition, works well for systems of well-defined geometry in which there is no requirement to predict the effects of phenomena (e.g., changes in ionic strength and pH) that modify surface charges. It is, however, inadequate for many natural (chemically and physically heterogeneous) systems of interest. Understanding of desorption kinetics, which may be relevant in some systems where colloid transport is rapid, is not well advanced. With respect to transport, it has not, in general, been possible to demonstrate that radionuclide-bearing colloids will be immobile in natural systems, other than some dense clays (a highly compacted bentonite backfill constitutes a filter for colloids in the safety concepts of several disposal systems). Indeed, examples were presented in the workshop that

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9.   Surface diffusion, where it operates, increases the distance that cations diffuse into the matrix and enhances the retention due to matrix diffusion. Omitting surface diffusion from performance assessment models of matrix diffusion is thus conservative.

indicate the mobility, in some geologic settings, of both organic and inorganic colloids over considerable distances. Examples given for inorganic colloid-facilitated transport include colloidal plutonium migration over more than a kilometre at the Nevada Test Site, USA and bentonite (montmorillonite) colloid-mediated transport of tri- and tetravalent metal ions in crystalline rock at the Grimsel Test Site in Switzerland (e.g., [3]). On the other hand, none of the natural analogue studies conducted to date has provided clear evidence of colloid-facilitated radionuclide transport [3].

The role of natural organic matter (NOM) colloids in radionuclide transport has been relatively little studied in comparison to mineral colloids. Emerging evidence, however, suggests that NOM may, in some instances, enhance the transport of radionuclides through subsurface systems, both indirectly, through the ability of NOM to stabilise inorganic colloids with respect to deposition, and more directly, by forming radionuclide/NOM complexes [21]. In the Boom Clay in Belgium, field experiments have demonstrated the mobility of ^{14}C-labelled NOM and transport over a distance of the order of 0.5 m.

3.4.2   *Process-level modelling of colloid-facilitated radionuclide transport*

Working Group 3 observed that many systems are dominated by a specific class of colloids, where the classification is made according to the chemical nature of the colloids, e.g., hydrous metal oxides, and humic substances. The development of basic understanding and of process models thus has to be tailored for application to specific systems. It was also observed that, despite the uncertainties mentioned above, recent advances in the understanding of the role of geochemical heterogeneity in colloid transport and release suggest a promising avenue for improved understanding and more realistic modelling of colloid transport in real systems.

Process models for colloid-facilitated radionuclide transport include two that were presented at the workshop [22,23]. One [22] simulates colloid-facilitated radionuclide transport at Äspö, although it has not yet been tested against experiments. The other [23], which takes account of sorption kinetics, has been applied to colloid-facilitated europium transport in column experiments using humic colloids.

The Working Group identified a need for more high-quality datasets from relevant systems in order to test and further refine colloid-facilitated radionuclide transport models and a need to develop methods to upscale process models developed for laboratory systems to the field scale.

3.4.3   *Representation of colloid-facilitated radionuclide transport in performance assessment models*

Some performance assessments have explicitly included colloid-facilitated radionuclide transport in geosphere transport models, although such models are generally highly simplified due to the absence of relevant site-specific data and the complexity and consequent uncertainties associated with the systems under consideration. Other assessments have used a variety of lines of reasoning to argue that the process is unimportant for the particular system under consideration. In particular, as observed by Working Group 3, if the product of colloid concentration and the K_d that represents the equilibrium, reversible sorption of a particular radionuclide on colloids is sufficiently small, then colloid-facilitated transport will be of minor importance for that radionuclide. If, however, the interaction between the radionuclide and the colloid is irreversible or characterised by slow desorption/release kinetics, this simple argument is not applicable. The Group also concluded that performance assessment models for colloid-facilitated radionuclide transport exist, or can readily be developed, that are adequate given the current level of scientific understanding and availability of data, provided equilibrium reversible sorption can be assumed.

A question raised by Working Group 3 (but not discussed in detail), which is relevant to both process-level and performance assessment modelling of colloid-facilitated transport in fractured media, is whether colloids might diffuse into matrix pores, and thus be subject to the retardation process of matrix diffusion. Where colloid-facilitated radionuclide transport is explicitly included in performance assessment models, it is generally conservatively assumed that colloids are excluded from such pores.

3.5 Immobilisation

3.5.1 Fundamental understanding of immobilisation processes and the evidence on which it is based

The immobilisation of radionuclides in the bulk of a solid has the potential to provide a highly effective retention mechanism. Immobilisation cannot, however, be assumed to be permanent. Conditions may arise leading to the remobilisation of radionuclides (see below). Whether or not the period of immobilisation approaches (or exceeds) the timescales relevant to performance assessment depends on the nature and rates of remobilisation processes, and will thus be system- and site-specific. Highly effective immobilisation of ions in mineral phases in diverse environmental settings is widely observed in nature, although not all of the observed systems reflect the reducing conditions often expected in deep geologic repository concepts. Several examples were presented at the workshop, including estuaries affected by metalliferous mining in Cornwall, UK [4], the Oklo natural analogue in Gabon, and the formation of mineral deposits, including deposits of uranium, at suitable redox and chemical interfaces [3,24]. Laboratory and modelling studies, often integrated with analogue research, also support the development of basic understanding of immobilisation processes (e.g., [3,6,12]).

Incorporation of a radionuclide in a solid may occur during co-precipitation as a new phase from a supersaturated solution, during the re-crystallisation processes that all crystal surfaces undergo, or by solid-state diffusion, especially where defect density is high. Simple precipitation of a separate solid phase is possible, especially as coatings on pre-existing grains, but where radionuclides are present at low concentrations, formation of a separate phase is less likely than incorporation in a pre-existing one. Immobilisation by precipitation (e.g., of secondary uranium phases) and by co-precipitation in carbonates (e.g., calcite) and Fe- and Mn-oxyhydroxides are of particular importance in many natural analogues and are also likely to be important in many repository systems [3]. Working Group 4 considered that, under reducing conditions, the most important retention mechanism for the elements radium, strontium, selenium, and nickel, which are significant in many performance assessments, would be immobilisation by incorporation in calcite, pyrite, or Fe- and Mn-oxyhydroxides, rather than sorption, as generally assumed in performance assessment calculations. In the Boom Clay in Belgium, Wang *et al.* [25] conclude that geochemical conditions are such that uranium immobilisation by precipitation and filtration of uranium-bearing colloids are likely to play dominant roles. Furthermore, if radionuclides migrate to shallower regions where oxic conditions prevail, immobilisation may occur at geochemical interfaces.

Short-term laboratory measurements on bulk systems often do not allow slow immobilisation processes to be distinguished from the usually much more rapid sorption processes, and thus fundamental understanding of these immobilisation processes is, in many cases, poor [11]. High-resolution techniques, however, that allow the observation of subtle processes on the nanometre scale, offer the prospect of improved understanding in this area. Specific observations relevant to immobilisation include that [12]:

- Dynamic equilibrium constantly rearranges material, allowing incorporation of radionuclides by re-precipitation.

- Radionuclides adsorbed on surfaces can migrate into the bulk material by solid-state diffusion, where they are less available for release.

These are slow processes that may nevertheless be important in the context of immobilisation over the long timescales of interest in performance assessment.

The incorporation of radionuclides in a solid can, under some circumstances and over long timescales, be reversible. In particular:

- Ions trapped within solid solution can be mobilised again if the solid exsolves to make a mixture of two or more separate phases.

- Transformation of one mineral phase into some more stable phase may release radionuclides back into solution that were adsorbed, or incorporated in the original mineral as a solid solution (an example given at the workshop was the transformation of amorphous Fe-oxyhydroxides to crystalline varieties such as goethite and haematite [12]).

- Solid-state diffusion (especially where defect density is high) can not only immobilise adsorbed radionuclides by transporting them into the bulk of a mineral, but can also bring incorporated radionuclides back to the surface.

Furthermore, as discussed by Working Group 4 and in [3], the dissolution or erosion of solids incorporating immobilised radionuclides may occur as physicochemical conditions change due, for example, to the decrease in concentration of dissolved species (including radionuclides) originating from the repository, or to deep downward intrusion of glacial melt water and/or the upward movement of highly saline waters.

3.5.2   *Process-level modelling of immobilisation*

Mechanistic models based on thermodynamic formalisms have been mentioned in the context of sorption in Section 3.2.2. The difficulties encountered in modelling sorption also apply to the application of these models to immobilisation processes. In particular, until recently, the lack of high-resolution techniques has been an obstacle to process-model development. Nevertheless, Working Group 4 concluded that, with adequate information on groundwater chemistry and some additional thermodynamic data, current knowledge is adequate to perform simplified calculations of the likely magnitude of immobilisation processes in some systems. This would enable such processes to be compared in terms of their possible effectiveness with other (reversible) retention processes. Furthermore, Smellie [3] refers to the successful application of mechanistic models to describe uranium immobilisation in heterogeneous clay material at the Bangombé reactor at the Oklo natural analogue.

3.5.3   *Representation of immobilisation in performance assessment models*

In spite of the evidence for their widespread occurrence, immobilisation processes have not so far been taken into account in performance assessments in a quantitative manner, although many workshop participants recognised the benefits that could, potentially, result from the inclusion of immobilisation processes in performance assessment models. Not only could more credit be taken for the geosphere as a transport barrier, but the models would also better reflect current scientific understanding of the likely actual fate of any radionuclides released from a deep geologic repository.

The omission of immobilisation processes from performance assessment models is generally the result of the absence of relevant site-specific data and uncertainties associated with the slowness and complexity of the processes, and is usually justified on the grounds of conservatism. Care must, however, be taken regarding the treatment of phenomena that could lead to the later re-mobilisation of immobilised radionuclides (which may in some cases be concentrated at geochemical fronts), as discussed in Section 3.5.1, which may potentially lead to short-lived but higher releases of radionuclides to the biosphere.

Uncertainties are such that the prospects of including immobilisation processes in performance assessment models used to demonstrate compliance with regulatory guidelines in the near future appear low at present. Nevertheless, there are good prospects for some improvement in the understanding of these processes, which will at least improve qualitative arguments for the long-term retention of many safety-relevant radionuclides in the geosphere.

4. Recommendations

The following recommendations are based on the workshop presentations, discussions of the working groups, and general discussions.

1. *Database of observations relevant to retention processes*

It may be useful to compile a database of geological phenomena and laboratory observations that support, or provide information on, immobilisation processes in geologic environments (including important phases formed at solid/liquid interfaces), and also information on processes that can lead to remobilisation. Such a database could be used to provide qualitative arguments to support the effectiveness of the geosphere transport barrier in performance assessments. By providing a clearer understanding of the factors controlling immobilisation and remobilisation, it could also potentially provide the basis for simplified, but well-supported quantitative models of immobilisation processes to be used in future performance assessments.

2. *Up-scaling of laboratory data to field conditions and model testing*

Data on sorption for use in performance assessments are often derived principally from batch sorption experiments in the laboratory. Data relevant to colloid-facilitated radionuclide transport are also often obtained in the laboratory. There can, however, be unavoidable differences between the conditions under which studies are conducted in the laboratory and those that prevail in the field. Laboratory sorption experiments are often conducted on samples that have been mechanically disaggregated or ground up, thus potentially creating new sorbing surfaces. Furthermore, the chemical environment in the laboratory may be perturbed by the presence of air. Mechanistic sorption models can be useful in assessing the effects of differences in the chemical environment. *In situ* mass transport experiments (including those addressing colloid-facilitated transport) are, however, recommended as possibly the only way to test the assumptions associated with the upscaling of laboratory experiments to field conditions and, more generally, to test models of transport and retention processes under conditions relevant to performance assessment.

3. *Characterisation of fractured media for the modelling of matrix diffusion in performance assessment*

In order to support the modelling of matrix diffusion in performance assessments, there is a need to develop and refine methods to characterise the degree of channelling within fractured rocks (the flow-wetted surface) and the distance into the wallrock over which matrix diffusion can be expected to occur. Currently, significant uncertainties can arise in geosphere transport modelling due to lack of quantitative information on these characteristics. Methods for the characterisation of matrix porosity were presented at the workshop (in poster presentations) and discussed in Working Group 2.

In order to provide convincing site-specific evidence that matrix diffusion can be relied upon as a retention mechanism, it is advantageous to concentrate efforts on characterising any higher porosity altered zones adjacent to fractures, where the existence of diffusion-accessible porosity may be relatively easy to demonstrate. It is more difficult to demonstrate that matrix diffusion can occur in more distant and less porous,

unaltered wallrock. Furthermore, it may be unnecessary to invoke matrix diffusion in unaltered wallrock in order to demonstrate the effectiveness of the geosphere transport barrier (see also Item *5*, below).

When field tracer transport experiments are conducted, especially if they are to be used to derive parameters for performance assessment models, care must be taken to collect high-accuracy data from the tails of breakthrough curves, the form of which may reflect matrix heterogeneity (e.g., [8]). Where possible, derived parameters should be supported independently by non-tracer-test data.

4. Consideration of heterogeneity and variability in the modelling of retention processes in performance assessments

Several examples were presented in the workshop indicating the importance of carefully considering the possible implications of heterogeneity over a wide range of scales, and also of variability in time, when modelling retention processes in performance assessments. Averaging may have non-conservative consequences; it may not, for example, be appropriate to represent the whole of a heterogeneous geologic medium (which may contain, for example, fracture-infill material and altered zones around fractures) by a single K_d, single diffusion coefficient, etc., or by probability distribution functions for these parameters. The structure of relevant features over a range of scales should, therefore, be considered when developing and applying models in performance assessments, as should the possible consequences of variations of structure, mineralogy, and groundwater composition with time.

In this context, the use of semi-empirical functions to represent the dependence of K_ds on geochemical conditions can be useful in representing the effects of spatial heterogeneity and temporal variability of geochemical conditions on radionuclide transport. The use of such functions may be seen as a compromise approach between, on the one hand, the use of fixed K_d values (which may be over-simplistic in some circumstances) and, on the other, the incorporation of mechanistic equilibrium sorption models in radionuclide transport codes (which may lead to excessively complicated and non-transparent assessment models). The use of semi-empirical site-binding models in performance assessment calculations could also be considered, although this would require a greater emphasis to be placed on the site-specific characterisation of the mineral assemblages and variable groundwater composition along radionuclide transport paths.

5. Improved understanding of colloid-facilitated radionuclide transport

Working Group 3 concluded that performance assessment methods for colloid-facilitated radionuclide transport exist, or can readily be developed, that are adequate given the current level of scientific understanding and availability of data, provided equilibrium reversible sorption can be assumed. It is recommended, however, that the validity of the assumption of equilibrium reversible sorption should be more thoroughly investigated. In particular, the kinetics of desorption from colloids have not been addressed in most investigations to date. The mechanisms for inorganic colloid generation (e.g., by erosion of near-field materials and by changes in hydrogeological and geochemical conditions) also deserve more attention in future studies.

6. Dialogue and cross-fertilisation

Retention processes are, of necessity, represented in a simplified manner in performance assessment models. Dialogue is essential between regulators, performance assessors, and technical specialists in various scientific disciplines, in order to identify the features and processes that are most relevant to performance, and to identify where improved understanding is, and is not, required for performance assessment purposes (e.g., [14]). As mentioned in item *3*, above, matrix diffusion in more distant and less porous, unaltered wallrock could be an example of a process the operation of which is difficult to demonstrate, but for which feedback from performance assessment indicates that improved

understanding may not be essential. Dialogue between the groups is also required in order to ensure that model simplifications are well supported and acceptable to the regulators. The case of the U.S. Environmental Protection Agency (EPA) review of the WIPP Compliance Certification Application (CCA) provides an example of dialogue between performance assessors and regulators, leading to the iterative refinement of performance assessment models [14,15]. In some countries, the public and other interested groups may be asked to comment on any concerns they have. For the EPA review of the CCA, for example, public concerns were very important, and included technical comments related to the treatment of retention processes, as well as more general concerns [14].

Given that the importance of retention processes is recognised, and has been studied, outside the field of radioactive waste disposal in areas such as mining and the management of non-radioactive hazardous wastes, some scope for "cross-fertilisation" may well exist with these activities.

5. Concluding remarks

In conclusion, retention processes in the geosphere may be said to be generally:

(1) Well understood, at least in a qualitative sense, with this understanding supported by a wide range of observations.

Qualitative understanding of sorption, immobilisation processes, and matrix diffusion, as well as, to a lesser extent, colloid-facilitated radionuclide transport, is well supported by laboratory and field experiments, and by observations of natural systems.

(2) Sufficiently well understood to support realistic modelling of the processes in ideal media under controlled laboratory conditions.

In particular, mechanistic equilibrium models that may be applied to sorption and immobilisation processes are well developed for simple (clean) mineral/water interfaces. Diffusion models for simple solutes in homogeneous porous media have been successfully used in wide ranging applications and the basic mechanisms for colloid-facilitated radionuclide transport have been studied and, in many cases, successfully modelled in simple systems.

(3) Often insufficiently well understood to support realistic modelling of the processes in the geologic media, and over the scales of space and time, that are of interest in performance assessment – uncertainties often lead to the adoption of simplifying assumptions in performance assessment models, including the omission of immobilisation processes.

Due to the uncertainties associated with the complexity of geologic systems and the long timescales of interest, conservatively selected empirical partitioning relationships (usually K_ds) are widely used to represent sorption in performance assessment transport models. Furthermore, matrix diffusion is often modelled only in a limited part of the potentially accessible matrix (where connected porosity can be most readily shown to exist). Colloid-facilitated radionuclide is either treated in a highly simplified manner or omitted. Immobilisation processes have not so far been taken into account in performance assessments in a quantitative manner.

Whether the understanding of retention processes is sufficient for a performance assessment depends on the purpose of the assessment (and, in particular, the decision that the performance assessment supports), and is also site- and concept-specific. There was consensus that the current level of understanding appeared sufficient for the decisions at hand in the participating national programmes. The characteristics of the site and repository concept, and the degree to which these are understood, determines how much performance can be attributed to different retention processes, and how much needs to be attributed in order to meet acceptance criteria. The strategy to improve

understanding and to develop and refine models for performance assessments thus needs to be determined on a site- and concept-specific basis. Of key importance is the interaction between regulators, performance assessors, and technical specialists in the various scientific disciplines, in order that the full spectrum of possibilities is recognised in performance assessment, and in order to focus the efforts of scientific specialists on the most critical issues.

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STRUCTURE AND PROGRAMME OF THE WORKSHOP

1.   Introduction

The first three sessions of the workshop included sixteen technical presentations, each allocated a discussion period. The guiding theme for structuring the presentations and discussions was to review the theoretical bases and supporting evidence for the operation and modelling of radionuclide-retention processes, with emphasis on geological and field evidence, and the treatment of retention processes in performance assessment. This led to the following sequence of technical sessions:

I.   Fundamental Understanding of Individual Retention Processes.

II.   Geologic and Field Evidence for Retention Processes and their Representation in Models.

III. Consideration and Representation of Retention Processes in Performance Assessment and Justification of Treatment.

In addition, a poster session was organised that focused primarily on data collection and process modelling. The poster session included eight posters that provided a good complement to the oral presentations.

A key part of the workshop consisted of focused discussions within small *ad hoc* working groups on specific retention processes, namely:

1.   Sorption.
2.   Matrix diffusion.
3.   Colloid-related retention processes.
4   Immobilisation.

In addition, a fifth working group considered the lessons learnt from the complete GEOTRAP workshop series, and what follow-up actions may usefully be taken.

The outcomes of the working group discussions provided the basis for a plenary, concluding discussion and for the present synthesis.

For each session, each working group, and some individual presentations, the Programme Committee had established a series of key questions to be addressed. As in previous GEOTRAP workshops, this proved to be a very effective way of focusing the discussions and reaching practical conclusions and recommendations. The main elements of the workshop programme, including the key questions, are reproduced in the following section.

2.   Workshop Programme

Session I

Fundamental Understanding of Individual Retention Processes

Chairs: Ivars Neretnieks (KTH, Sweden) and Jan-Olof Selroos (SKB, Sweden)

This session addresses the mechanistic description of retention processes relevant to transport in the geosphere, the general understanding that is available, and current capabilities to model the processes.

The first presentation is intended to survey the topic of retention from the standpoint of geologists outside the specific field of radioactive waste disposal. Questions to be addressed include:

1.   What is the geologic significance of retention?
2.   What retention processes are recognised?
3.   Under what conditions do these processes occur?
4.   On what time and spatial scales are these processes thought to be active, and in what media of interest for waste disposal?
5.   Are the processes temporary, permanent, reversible, etc.?
6.   To what types of elements do these processes apply?
7.   What geologic observations support our belief in, and understanding of, these processes?

How Geologists View Retention
Mike Heath (University of Exeter, UK)

The following presentations have been chosen to cover a number of broad categories of retention processes. Both present-day knowledge and future developments and trends concerning improvement and extension of the experimental bases and modelling efforts will be taken into account. Questions to be addressed in all presentations are:

1.   What is the scope of the process or processes covered?
2.   What is the experimental basis (broadly speaking)?
3.   What are the possibilities for mechanistic modelling?
4.   What are the data needed for modelling?
5.   What is the range of applicability of models?
6.   Which processes/factors could affect the effectiveness of the retention process?
7.   What is your judgement about the reliability of our current understanding?
8.   What are the future prospects for resolving uncertainties?

Molecular Scale Observations and Models of Sorption Reactions
James Davis (USGS, USA)

Matrix Diffusion: Heavy-tailed Residence Time Distributions and their Influence on Radionuclide Retention
Roy Haggerty (Oregon State University, USA)

The Role of Colloids in Radionuclide Retention by and Transport Through Geologic Media
Bruce Honeyman (Colorado School of Mines, USA)

Immobilisation
Susan Stipp (University of Copenhagen, Denmark)

Isotope Fractionation Effects on Radionuclide Transport in Geologic Disposal of Nuclear Waste
William Murphy (California State University, Chico, USA) and David Pickett (CNWRA, USA)

Session II

Geologic and Field Evidence for Retention Processes and their Representation in Models

Chairs: Budhi Sagar (CNWRA, USA) and Peter Jürgen Larue (GRS, Germany)

This session addresses the evidence for, and understanding of, retention processes provided by field experiments, nature observations, and natural analogues, and how these processes can be represented in models. The temporal and spatial scales to which the various sources of evidence apply are to be emphasised. Also addressed is the degree to which it is possible to integrate retention processes in transport models.[10] Questions to be addressed by all speakers (except for the final presentation on integration) are:

1. How are the geologic and/or field data related to laboratory information?
2. What are the generic aspects of the information?
3. How have the needs of PA influenced the investigation?
4. What additional processes affect the processes under study? On what time and/or spatial scales?
5. How are the processes conceptualised or modelled?
6. How unique is the interpretation, and how might ambiguities be resolved?
7. What are the key uncertainties in the interpretation or model, including those related to the time and spatial scales of the observations?

Evidence for Retention Processes in the TRUE Experiments
Anders Winberg (Conterra AB, Sweden)

Do We See *In Situ* Sorption? – Can Useful Information Be Derived for Migration Modelling?
Juhani Suksi (University of Helsinki, Finland), Kari Rasilainen (VTT, Finland), Cécile Le Guern (BRGM, France) and Timo Ruskeeniemi (GSF, Finland)

Evidence for Matrix Diffusion in the TRUE-1 Block at Äspö Based on Fracture Characterisation and Modelling of Tracer Tests
Martin Mazurek (University of Bern, Switzerland) and Andreas Jakob (PSI, Switzerland)

Impact of Colloids on Long-term Performance Assessment of Nuclear Waste Disposal
Gunnar Buckau, Wolfgang Hauser, and Horst Geckeis (INE, Germany), Claude Degueldre (PSI, Switzerland), and Annie Kersting (LLNL, USA)

Solute Immobilisation: Observations from Natural Analogue Studies
John Smellie (Conterra AB, Sweden)

Questions to be addressed by the presentation on integration are:
1. Which processes can be integrated in transport models and which cannot?
2. What simplifications are required for this integration?
3. How well understood is the coupling among processes?
4. How confident can we be that all processes are treated either realistically or conservatively?
5. What are the prospects for improved understanding and more capable models?

Integration and Evaluation of Processes in Basin-scale Models of Radionuclide Transport
Jon Sykes, Ed Sudicky, Stefano Normani, and Robert McLaren (University of Waterloo, Canada) and Mark Jensen (Ontario Power Generation, Canada)

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10. We note that such detailed transport models may differ from the (often simplified) transport models used in performance assessment, and discussed in Session IV.

Session III

Consideration and Representation of Retention Processes in Performance Assessment and Justification of Treatment

Chairs: Pedro Hernán (ENRESA, Spain) and Richard Beauheim (NEA)

This session addresses how various retention processes are represented in performance assessment. Some processes are included within performance assessment models in a very simple manner (e.g., via the K_d parameter for sorption), or via a more complex approach. Other processes may be omitted from performance assessment models and discussed in a purely qualitative manner. Whatever the approach, its acceptability, e.g., to regulators and to technical reviewers, is likely to depend on careful justification.

The session includes an overview of the representation of retention processes in performance assessments carried out by waste-management organisations and an overview of how such representations (and the justifications for them) have been judged by regulatory authorities. A case study of the representation of retention processes in performance assessments leading up to licensing and for the future recertification of the Waste Isolation Pilot Plant (WIPP) in New Mexico, USA, is also given.

The Consideration and Representation of Retention Processes in Performance Assessments Carried Out by Waste-management Organisations – What Has Been Done and Why?
Jürg Schneider, Bernhard Schwyn, and Piet Zuidema (Nagra, Switzerland), Hiroyuki Umeki (NUMO, Japan), and Paul Smith (SAM Ltd., UK)

Questions to be addressed:
1. Which retention processes are normally included?
2. Which retention processes have been included quantitatively and which qualitatively?
3. What simplifications have been made for the purposes of performance assessment modelling; what are the motivations and justifications for these simplifications?
4. To what extent has geologic and field evidence (field experiments, observations of natural systems, etc.) been included in PA model representations of retention processes and in qualitative discussion of retention processes in PA; how is evidence transferred to temporal and spatial scales relevant to performance assessment?
5. What are the strengths and weaknesses of current PA models in terms of the representation of retention processes?
6. What future trends can be foreseen in how retention processes might be represented in PA (additional processes included in models, refinement of existing model representations, etc.)?

Representation of Retention Processes in Performance Assessment – A Regulatory Perspective
Budhi Sagar (CNWRA, USA) and Bo Strömberg (SKI, Sweden)

Questions to be addressed:
1. Is the current understanding of retention processes adequate for current and future PA purposes?
2. How important is the representation of heterogeneity and temporal variability viewed for the modelling of retention in PA?
3. To what extent should geological evidence (observations of natural systems) be used in PA?
4. How do regulatory bodies view the adequacy of simplifications that are made for the purposes of performance assessment modelling?
5. What are the strengths and weaknesses of current PA models in terms of the representation of retention processes?
6. What future trends can be foreseen in how retention processes might be represented in PA (additional processes included in models, refinement of existing model representations, etc.)?

The Consideration and Representation of Retention Processes in the WIPP Performance Assessment: Justification of Adopted Approaches and Interaction with the Regulator

Part I: Chemical Retardation of Dissolved Actinides

Laurence Brush, Charles Bryan, Lucy Meigs, Hans Papenguth, and Palmer Vaughn (SNL, USA)

Part II: EPA's Review Process and Approval Justification

Charles Byrum and Thomas Peake (EPA, USA)

Questions to be addressed:

1. Which retention processes have been included qualitatively and which quantitatively, in how much detail and with what justification?
2. What is the regulatory view of the treatment of retention processes in WIPP PA?
3. Did intervenors question the treatment of retention processes in PA, and were these questions taken into account?
4. What changes in the representation of retention processes can be foreseen in recertification?
5. How are the changes justified?
6. What is the role of a continuing research programme in recertification?

Session IV

In-depth Discussions by Working Groups

WG1:   Sorption
Chair: Scott Altmann (ANDRA, France)

WG2:   Matrix diffusion
Chair: Ivars Neretnieks (KTH, Sweden)

WG3:   Colloid-related retention processes
Chair: Jörg Hadermann (PSI, Switzerland)

WG4:   Immobilisation
Chair: Mike Heath (University of Exeter, UK)

These four working groups will discuss, in the context of each broad category of retention processes:

1.   What issues have been sufficiently resolved for current and future PA purposes?
2.   What future trends can be foreseen and in particular, what, if any, unresolved issues should still be addressed?

In addition, a special working group will discuss the lessons learnt from the complete GEOTRAP workshop series, and what follow-up actions may usefully be taken.

WG5:   Conclusions and synthesis of GEOTRAP and proposals for follow-up
Chair: Alan Hooper (Nirex, UK)

- This working group is to be attended, potentially, by members of the IGSC, GEOTRAP contact persons, and others.

- A discussion paper on lessons learnt from previous GEOTRAP workshops, and future possibilities, is to be prepared and circulated in advance of the fifth workshop.

Session V

Working Group Presentations and Final Discussions

Poster Session

Effects of Heterogeneous Porosity on Retention – Results from the TRUE Laboratory Experiments
J. Byegård, M. Skålberg, and H. Widestrand (GEOSIGMA AB, Sweden) and E.-L. Tullborg (Terralogica AB, Sweden)

Colloid Retention in Äspö Crystalline Rock: A Generic Computational Assessment
G. Lindgren and V. Cvetkovic (KTH, Sweden)

Immobilisation and Retention Processes of Uranium in Tertiary Argillaceous Sediments (Czech Republic)
A. Laciok and M. Hercik (NRI, Czech Republic) and U. Noseck and T. Brasser (GRS, Germany)

Comparison of Formation Factor Logs Obtained by Electrical Methods *In Situ* and at Laboratory
M. Löfgren, Y. Ohlsson, and I. Neretnieks (KTH, Sweden)

Modelling of Colloid Facilitated Contaminant Transport with the Computer Code TRAPIC: Theoretical Basis and Application
U. Noseck and D. Klotz (GRS, Germany)

Matrix Diffusion – Through-Diffusion Versus Electrical Conductivity Measurements
Y. Ohlsson (SWECO VBB VIAK, Sweden) and M. Löfgren and I. Neretnieks (KTH, Sweden)

Discordance in Understanding of Isotope Solute Diffusion and Elements for Resolution
C. Pescatore (NEA)

Determination of Natural Uranium Concentration in Boom Clay: Effect of Different Extraction Techniques
L. Wang, M. De Craen, N. Maes, and P. De Cannière (SCK/CEN, Belgium)

CONCLUSIONS OF WORKING GROUP 1

SORPTION

Chair: *Scott ALTMANN (ANDRA, France)*

Members
Laurence BRUSH (SNL, USA), Charles BYRUM (EPA, USA), James DAVIS (USGS, USA),
Eckhard FEIN (GRS, Germany), Andreas GAUTSCHI (Nagra, Switzerland),
Roberto GIL DE MINGO (CSN, Spain), Jürgen LARUE (GRS, Germany),
Emmanuel MOUCHE (CEA, France), Matthew RANDALL (BNFL, UK),
Masahiro SHIBATA (JNC, Japan), Juhani SUKSI (University of Helsinki, Finland)

The possible partitioning of total radionuclide mass between (i) mobile solution species and (ii) "immobilised" species (mass) associated with geosphere solid phases is considered in all performance assessment (PA) programs because of its potential significant effect on radionuclide mass transport towards dose evaluation points.

The Sorption Working Group (WG1) agreed that radionuclide sorption/desorption:

i)   Regards only formation and dissociation of radionuclide surface complexes or ion exchange species at the interface between geosphere pore or fracture water and the wetted surface of the rock matrix.

ii) Can be considered to be reversible, with effectively instantaneous forward chemical kinetics and potentially much slower reverse kinetics. (It was noted that mass-transfer processes might hinder attainment of sorption equilibrium with many geo-materials.)

iii) Can, for a given radionuclide (K_d), vary significantly depending on the chemical composition of the aqueous phase and of the wetted surface of the geo-matrix.

These basic characteristics led the group to propose the following "Guiding Principle" to aid in identifying and assessing GEOTRAP-relevant issues:

The way radionuclide solid/solution partitioning due to sorption (K_d) is represented in
PA models should be coherent with the way spatial and temporal variability of geosphere
chemical composition (water, rock) is treated in site-specific PA scenarios.

For example, if the PA case considers the geosphere to be homogeneous and constant in chemical composition, use of a single K_d value for a given radionuclide would be appropriate, if appropriately determined for that composition. Another example would be the case where a PA scenario considers radionuclide retention by sorption in far-field geological formations having significantly

different, but constant, groundwater or rock matrix compositions (e.g., reducing to oxidising conditions, changes in salinity, etc.). Here again, K_d values appropriate for the different geosphere regions should be determined experimentally and then used in the PA. On the other hand, if a PA case explicitly considers evolution in near field host rock pore water composition caused by substances released from waste packages or engineered-barrier materials (concrete, etc.), evolution in radionuclide K_d (increase, decrease) should also be explicitly considered. If sufficient information is available, this could be done using a chemical model to calculate radionuclide sorbed species concentrations as a function of groundwater composition. This approach would also be applicable for a PA case considering radionuclide retention in the far-field with constant rock matrix composition but varying (gradient) groundwater compositions, such as the total concentration of dissolved carbonate or pH.

In addition, the group also considered that a demonstrated understanding of radionuclide immobilisation processes in general, and the principal phenomena and physical-chemical factors determining the sorption K_d for a given radionuclide in site-specific contexts of interest to PA, to be critical for building confidence in the safety case. In most cases, such a demonstration will necessitate characterisation of sorption on real, complex geomaterials.

The Working Group then identified the following four key issues and attempted to come to a consensus as to whether or not they have been sufficiently resolved for PA purposes:

Issue 1: For a given geological context, is it possible to determine representative values for radionuclide sorption (K_d) experimentally?

The group considered that the state of the art was very different for the geological contexts of unconsolidated and fractured rock.

Unconsolidated formations: Extensive experience has been gained over the last decade or so in experimentally characterising and interpreting radionuclide (and non-radioactive trace element) sorption on rock samples from unconsolidated rock formations. More or less proven methodologies exist in the literature (e.g., [1] and included references) for (i) determining pertinent rock properties (specific surface area, effective porewater volume, etc.) and, in certain cases, sorption-determining solid phases in contact with formation porewater, (ii) identifying environmental chemical parameters likely to significantly influence the sorption intensity of a given radionuclide, and (iii) measuring K_d values on ground rock samples. The passage from batch K_d values to ones representative of the undisturbed rock can pose difficulties, but interpretation of results of diffusion or permeation experiments using coupled sorption-transport models can aid in making this "change of scale".

Fractured formations: The group felt that the representation of sorption processes is much less well understood in fractures. This is largely due to problems in characterising and modelling the spatial heterogeneity of such systems vis-à-vis the sorption-determining parameters (defining and attributing parameter values to sorption process-relevant representative volume elements). For example, it is difficult to identify those sorbing phases that will effectively influence radionuclide migration, this largely resulting from ambiguities in identifying fluid flow paths at certain spatial scales (i.e., wetted surfaces seen by radionuclide). For this same reason, it is also difficult to quantify key extensive parameters such as surface area per unit volume of fracture water for different sorbing materials. The group also noted that relatively little work has been done on these issues; the Palmottu natural analogue project was cited as an example where these issues were studied by examining its "recent" mobilisation/immobilisation and related geochemical redistribution along a defined groundwater flow path. In this particular case, selective extraction methods were found to be especially informative. The group felt that progress is being made to overcome many of these difficulties, the most important contribution probably coming from understanding gained from interpretation of well-designed field tracer tests carried out at different spatial scales

(e.g., experiments carried out at Äspö (TRUE), Grimsel, etc.) and of natural analogues (e.g., Palmottu). Laboratory tracer studies, combined when possible with *in situ* radionuclide distribution studies, were thought to be of considerable help in moving forward in this area.

Issue 2:   Are there significant deficiencies in our understanding of sorption processes?

The group's overall impression was that the scientific community has a good "feeling" for the major chemical (and physical?) processes responsible for sorption of radioelements, and this for a wide range of potential conditions of geological systems. It was felt that, given information concerning (i) the mineral (and organic?) phases in contact with porewater and (ii) the major chemical characteristics of the porewater (pH, alkalinity, major ion content, redox state, etc.), it would be possible to predict qualitatively for many radioelements (i) whether sorption was likely to be a significant process and (ii) the likely variation in sorption intensity (K_d) as a function of changes in certain porewater chemical parameters. This capacity to make "expert judgements" concerning sorption processes is a reflection of the good understanding that has been obtained concerning sorption mechanisms (mass action laws for ion exchange and surface complexation reactions; molecular structure and geometry of sorbed species from spectroscopy, etc.). Many of these aspects are described in the NEA sorption report and included references.

On the other hand, the group also identified a number of systems that need further study, in particular:

- *Sorption processes* for (i) iodide (I^-) on complex geological materials containing both inorganic and organic solid phases, (ii) actinide organic complexes, and (iii) actinide carbonate complexes, under

- *Specific system conditions*: (i) reducing, (ii) cement-water affected, and (iii) in the presence of organic components released by high organic matter containing wastes.

Issue 3:   In PA situations requiring representation of spatially or temporally variable sorption, can technically defensible models be developed?

The group evoked a number of different conceptual disposal facility situations where PA might require taking into consideration variable Radionuclide sorption over time (K_d = f(t)) for particular volumes of the geosphere. In most cases the changes were due to variations in pore water composition. Cited examples included changes due to (i) migration of solutes coming from disposal facility waste packages (e.g., salts, complexants, organics, etc.) or from the breakdown of engineered barrier materials (cement, etc.) and (ii) events external to the repository (e.g., injection of oxygenated water into granite fracture systems during deglaciation and post-glaciation periods).

The group was in general agreement that, if the general sorption-determining characteristics of geosphere solid phases remained relatively unchanged, estimation of the evolution in radionuclide K_d as a function of solution composition was feasible using surface complexation modelling-based approaches. This capacity results from the fact that radionuclide solid/solution partitioning (K_d) is explicitly described in these models in terms of dissolved and sorbed chemical species, the concentrations of each species being calculated for each potential porewater composition based on known or experimentally determined mass action laws.

Instances were also cited where PA might be required to consider spatially variable radionuclide sorption in the far-field geosphere due to significant variations in rock composition and/or natural porewater composition. These variations will certainly exist between the different geological formations included in the PA far-field model; they may also exist within the host formation if it

exhibits significant variations in lithology. The group considered that the capacity to accurately represent the effect of spatially variable sorption (K_d = f(x,y,z)) in PA is likely to be limited largely by the availability of a sufficient density of representative samples of geosphere solids and porewater. Where samples are available, K_d values can be experimentally determined, and this information can be used to justify the explicit consideration of the characterised geosphere volume in the PA model with its specific K_d value.

Issue 4:   When chemical modelling is needed for supporting the radionuclide sorption parameters used by PA: (i) what level of model is appropriate? (ii) can model input parameters be determined?

A large body of experience is available (e.g., [1]) showing that, given the availability of appropriate experimental data, chemical models can be constructed which are capable of describing radionuclide sorption onto many different geosphere materials, over a wide range of solution compositions. Experience also shows that different types of models can be proposed for interpreting and representing experimental sorption data, the main model differences being (i) the way sorption *site types* are defined and quantified based on available information concerning the composition and structure of the solid surface, (ii) the way *sorbed species stoichiometries and structures* are defined based on available data, and (iii) whether or not *electrostatic corrections* are included in the sorbed species mass action models.

An on-going question regarding the use of chemical sorption models for PA is: *what level of model complexity is most appropriate for supporting the sorption parameter values used for PA?*. In particular, since we are dealing with the geosphere, a more pertinent formulation might be: *given the chemical and physical complexity of most rock matrices at the sample dimension scale, in particular the existence of many non-ideal phases and impurities at mineral surfaces, and the spatial heterogeneity of rock properties at the dimensions of the geosphere volumes represented in PA models, are sorption models based on detailed conceptions of sorbed species molecular-scale characteristics justified?*

A clear consensus concerning the answer to this question is yet to be found. The Phase 2 of the NEA sorption project should, however, provide both useful input and an appropriate forum for moving forward on this issue.

As a final note, it was pointed out that in cases where a complete/complex sorption model is found to be excessively difficult to defend, PA modelling using a sampling of K_d values over an appropriately bounded range might be the only way out.

Reference

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CONCLUSIONS OF WORKING GROUP 2

MATRIX DIFFUSION

Chair: *Ivars NERETNIEKS (Royal Institute of Technology, Sweden)*

Members
*Alain GENTY (IPSN, France), Roy HAGGERTY (Oregon State University, USA),
Andreas JAKOB (Paul Scherrer Institute, Switzerland),
Martin LÖFGREN (Royal Institute of Technology, Sweden),
Martin MAZUREK (University of Bern, Switzerland), Yvonne OHLSSON (SWECO VBB VIAK, Sweden),
Bo STRÖMBERG (SKI, Sweden), Edward SUDICKY (University of Waterloo, Canada),
Eva-Lena TULLBORG (Terralogica AB, Sweden), Henrik WIDESTRAND (Geosigma AB, Sweden),
Anders WINBERG (Conterra AB, Sweden)*

Working Group 2 mostly discussed matrix-diffusion phenomena in low-porosity crystalline rocks, such as granites and gneisses, because of time constraints and because most participants were primarily familiar with those rock types.

1. *Topics for discussion*

The group discussed the following items.

- Does matrix diffusion exist?
- To what distance from fractures is porosity connected?
- Influence of rock stresses.
- Role of any alteration zone adjacent to a fracture.
- Heterogeneities of porosity and diffusivity.
- Geologic evidence for matrix diffusion in crystalline rocks.
- Measurement methods.
- Flow-wetted surface.
- Modelling of radionuclide migration and retention influenced by matrix diffusion.

Does matrix diffusion exist?

Yes, given that there is connected porosity and that the diffusing species is small enough to have access to the porosity. Colloids, for example, may not have good access.

To what distance is porosity connected?

The question is raised because although there is ample evidence that connected porosity has been found at distances of up tens of centimetres in laboratory measurements, fewer observation have been made in field experiments or observations where the rock stresses are virgin and have not been released before the experiment.

Observations in laboratory

There is a wealth of observations from laboratory measurements. However, due to the long times needed to perform diffusion experiments, most observations have been made at distances less than 5-10 cm. Other techniques, such as resin impregnation and electrical conductivity (EC) measurements, are also used to establish the extent of connected porosity. Some examples are given below. The distances are approximate maximum values.

- Through diffusion experiments   5 cm
- Electrical conductivity   50 cm
- Mercury intrusion   centimetres
- Resin impregnation (incl. PMMA)   5-10 cm
- Diffusion in samples re-stressed to 300 bar   centimetres
- Electrical conductivity in samples re-stressed to 300 bar   5 cm
- Gas diffusion   5-10 cm

Many of these experiments have found decreasing connectedness with penetration depth (through diffusion experiments, resin impregnation). To date, it is not clear in long samples (> 10 cm) whether electrical conductivity measures the connectedness of pores, or the connectedness of pores plus electrically conducting minerals such as metal oxides and sulphides. If EC measures only the conductivity of pores, then it provides strong evidence of pore connectedness over great distances. If, however, EC is biased by mineral conductivity, its usefulness over long distances is reduced.

Field observations, some under natural stress

- Resin impregnation test at Grimsel.
  In drift where excavation may cause stress release   5 cm
- Ventilation test at Grimsel.
  In drift where excavation may cause stress release   tens of centimetres
- Uranium fluorescence due to seeping an evaporating
  water through matrix   tens of centimetres
- Electrical conductivity in deep boreholes. Virgin stress   m
- Stripa *in situ* matrix-diffusion experiments. Virgin stress   5-30 cm
- Radon emanation. Virgin stress   0.5 cm
- Helium from α-decay. Virgin stress   ?

The representative from a regulating agency pointed out that because matrix diffusion is so very important in performance assessments, it would be prudent to have strong proof that it is active in a future site. The group concluded that although the observations as a whole make it credible that matrix diffusion occurs over long distances, i.e., several tens of centimetres, it must be demonstrated to exist in the site that will be used for a repository, and that reductions in pore connectivity over tens of centimetres either do not exist or do not influence the effectiveness of matrix diffusion.

Role of alteration zones and heterogeneities

There are many observations of alteration zones (AZ) adjacent to water-conducting fractures. It is found the AZs have higher porosities and diffusivities near the fracture surface. Values of porosities quoted are typically 1-1.5% as compared to the unaltered rock that has typical values of 0.2-0.5%. The diffusivity could also be higher. It has also been observed that sorption coefficients, the so-called K_ds, often are higher.

In the rock not immediately adjacent to the fractures, it has been found in laboratory as well as in the field tests in virgin rock in Stripa that the porosity and diffusivity can vary considerably over short distances. Typically, at a few centimetres to tens of centimetres, there can be variations of a factor of three or sometimes even more in porosity and diffusivity. It is thus not surprising that experiments on one 5-cm sample can give quite different results from another sample taken from the same core. However, the Stripa *in situ* measurements in a rock volume 3 m long more than 60 cm by 60 cm showed that in many portions the tracers had reached 30-35 cm distance from the injection hole. In other more-or-less randomly placed locations, the tracers had reached no more than 6-7 cm. The measurements included more than 2 000 individual samples in the rock volume. The observed variability highlights the role and effect of heterogeneities in the rock.

The WG concluded that there is little doubt that diffusion takes place and will take place in the AZ. The WG suggests that in a new site the frequency of the water-bearing fractures that have AZs be determined as well as the extent and properties of the AZs. It has been found in some performance assessments that an altered zone of a few centimetres adjacent to the water-bearing fractures can exert a very strong retardation on the sorbing nuclides. It was suggested by some in the WG that it may be easier to take credit for this retardation mechanism for a site than that of diffusion in the deeper parts of the unaltered matrix with present-day clearly proven techniques.

Geologic evidence for matrix diffusion in crystalline rocks

Besides direct measurements of porosities and in some cases of diffusivities and K_ds in the alteration zone, there have been quite a few measurements of U-series disequilibria. In these measurements, typically a zone 2-5 cm deep is found to have had mobilisation of uranium over the last hundred thousand to million years. This usually has taken place in the altered zone.

At the Poços de Caldas uranium mine in Brazil, there is very distinct evidence of diffusion over distances of tens of centimetres to metres that have taken place over tens of millions of years. This is evidenced by the clearly visible redox front in the unfractured parts of the rock. However, the crystalline rock matrix at Poços de Caldas has a much higher porosity than most granites and gneisses.

Measurement methods (over long distances)

Laboratory measurements, even on re-stressed samples, do not give sufficient proof that matrix diffusion will be active over long distances (several tens of centimetres) in virgin rock.

In situ measurements in virgin rock are very time consuming and expensive and are difficult to perform in many locations.

Recent electrical conductivity measurements in deep boreholes have given some very encouraging results as they indicate a connected porosity over metre distance and conductivities, that when translated to diffusivities, are close to those measured on the cores from the same boreholes. However, it cannot be entirely ruled out that electrically conductive minerals in the matrix contribute to the conductivity. This is at present being investigated.

Some additional techniques considered for the future

In situ electromigration. In this technique, a charged tracer would be "pulled" through the rock matrix by a DC current.

Leaching of cores adjacent to fractures in which fresh water is known to have flowed since e.g., the last ice age. This may give salt concentration profiles in the cores.

Flow-wetted surface

The flow-wetted surface (FWS) is a term used to denote the fracture surface area that is in contact with the flowing water in the rock. This is the contact surface over which mass transfer can take place between the flowing water and the rock matrix.

There are two common ways of defining this entity: The FWS per volume of fracture, a_w, and the FWS per volume of rock a_R. There has sometimes been some confusion using these terms as they have not always been clearly defined. In principle, they are easily related, provided the flow porosity ε_f is known. The relation is:

$$a_R = a_w \varepsilon_f$$

The problem is that the flow porosity is not easily measured, except by tracer tests, and that even these experiments are difficult to interpret unequivocally.

Modelling of radionuclide migration influenced by matrix diffusion

The use of the term FWS is an oversimplification and aimed primarily at conveying the concept. It must in practice always be related to a local flow rate. Consider a packet of water with the flow rate, q (m^3/s), in a stream tube. This packet of water contacts a certain FWS along its flow path. A nuclide travelling with this packet will be transferred to the matrix to a certain degree related to q/FWS. The rate of uptake into the matrix depends in a very non-linear way on q/FWS. This implies that it is not possible to consider the average flow rate in a large volume of rock and the average FWS in the same volume of rock when one wishes to assess how much nuclide has gone into the rock. The averaging must be made over the whole pathway that the packets of water containing the nuclide travel. The averaging must also include mixing of the small packages in order to account for the strong non-linear property of the retardation mechanism.

How this averaging is to be made properly is not yet fully agreed upon and some approximations are usually used in the different conceptual and computational models.

Another effect that can influence radionuclide migration along a flow path is that the rock properties vary along the path. This can include the diffusivity but also the penetration depth in cases where there is limited matrix diffusion. Present models of radionuclide transport along a flow path can handle such effects and also the more general case where the properties vary along the flow path as well as in the rock matrix at different distances from the fracture surface.

2.   *Recommendation to NEA*

There is a need for common terminology and a strict definition of terms used in the area of radionuclide interaction with the geologic media. Terms are frequently used incongruently by different researchers and agencies. This results in confusion, inefficiency, and difficulties in comparing and communicating research effectively. We recommend that NEA convene a panel to publish a unified terminology for matrix diffusion and parameters related to matrix diffusion (various porosities, tortuosity, flow-wetted surface, capacity coefficient, etc.).

CONCLUSIONS OF WORKING GROUP 3

COLLOID-RELATED RETENTION PROCESSES

Chair: *Jörg HADERMANN (Paul Scherrer Institute, Switzerland)*

Members
*Gunnar BUCKAU (FZK, Germany), Vladimir CVETKOVIC (KTH, Sweden),
Bruce HONEYMAN (Colorado School of Mines, USA), Marcus LAAKSOHARJU (GeoPoint, Sweden),
Ronald LINDEN (Golder Associates/USDOE, USA), Georg LINDGREN (KTH, Sweden),
Norbert MAES (SCK/CEN, Belgium), Tiziana MISSANA (CIEMAT, Spain),
Ulrich NOSECK (GRS, Germany), Divyesh TRIVEDI (BNFL, United Kingdom)*

Colloids are ubiquitous in groundwaters. The Working Group made a *tour d'horizon* in view of their impact in performance assessments.

1.   Classification

Colloids are defined on the basis of size (usually entities of 1 nm to 1 μm). This definition is not very helpful when the interaction of radionuclides with colloids, colloid stability and colloid interactions with rocks have to be considered. A more complete understanding of colloid behaviour must be based on physical and chemical properties of colloids.

In order to render the discussions concise, the Working Group participants classified the colloids primarily by their chemical nature (Table 1):

Table 1. **Classification of colloids by general physical/chemical nature.**

Organic colloids
Humic substances (humic and fulvic acids)
Well-defined organics* (e.g., polysaccharides)
Microbes*
Inorganic colloids**
Hydrous metal oxides
Clays
or
Fixed charge surfaces
Variable charge surfaces
"Real" radiocolloids* (e.g., actinide polymers)

*   The Working Group did not discuss these classes of colloids.

**   Two subclassifications were proposed. Due to time constraints, it was deemed unnecessary
       to go into more details and to bring out advantages/disadvantages of both

This classification is a very rough one with a view to their role in performance assessment. For more comprehensive information, the reader is referred e.g., to Stumm and Morgan [1].

Out of discussions of this classification came the first conclusion of the Working Group:

Many systems are dominated by a specific class of colloids.

See, for example, a recent overview by Degueldre *et al*. [2].

As a consequence, it does not make sense to address the impact of colloid-facilitated transport on a generic basis. It has to be investigated on a system and site-specific basis. Development of a basic process understanding and models is required for a tailored application at different sites.

2. Important factors for colloid-facilitated transport

2.1 Preliminaries

It was considered rather trivial that the first thing to do, at a particular site, is to measure colloid concentrations, their size distribution and to characterise relevant colloid properties (e.g., radionuclide binding groups; classification per Table 1). The resulting information will allow proximate estimates of the importance of colloid-facilitated transport: If the product of colloid concentration and distribution ratio, of a given radionuclide, between aqueous and colloid phase is sufficiently small, colloid-facilitated transport will be of minor importance. However, what is "sufficiently small" will depend on the reversibility of the radionuclide-colloid interaction, or more precisely on its kinetics. Broad advantage can be taken, here, from the understanding of the interaction of chemical elements with solid surfaces and with organic substances (presentations by G. Buckau and B. Honeyman at the Workshop).

2.2 Colloid stability

The general trends for colloid stability are known [3]. The global picture is: From a deep aquifer to the biosphere, the groundwaters generally change from high salinity to low salinity. As a consequence the colloid stability changes from lower to higher. However, a model for extrapolation and quantitative simulation is missing.

2.3 Colloid generation

Colloid generation is induced by chemical and physical gradients in the system. The effect of chemical gradients is directly related to the colloid stability, see above. Changing water velocities and erosion in water-carrying features of the aquifers were mentioned as physical gradients. Humic colloids originate from the soil layer (inflow with groundwater recharge), *in situ* generation (microbiological turnover of organic sediment constituents), and possibly release from clay backfill. The situation for model simulations is addressed below.

2.4 Migration distances

The question arises whether colloids can be transported over larger distances. Field experiments and field observations can help in answering this question, whereas laboratory experiments are *eo ipso* restricted to small scales.

With respect to humics, the measurement of concentrations of humics in a Bavarian aquifer (G. Buckau, this Workshop) has shown their stability and transport over large distances. In the Boom clay, field experiments have demonstrated the mobility of ^{14}C-labelled natural organic material and transport over a distance of the order of 0.5 m [4].

With respect to inorganic colloids, the situation is more complex. At the Nevada Test Site, migration of plutonium over a distance of 1.3 km was measured [5], albeit under conditions which are quite unrealistic for a repository system. The Working Group concluded that there is no unique field evidence for colloid-facilitated radionuclide transport over long distances under realistic conditions. It was mentioned that at the Grimsel Test Site a field experiment on colloid transport (CRR, Colloid and Radionuclide Retardation) is presently ongoing.

For performance assessment, an important result is that a dense bentonite backfill constitutes a filter for colloids and retains them quantitatively [6].

3.   Models for Performance Assessment

For humics, the colloid concentration can be estimated based on the average mass of fulvic and humic acid and dissolved organic carbon, DOC, concentration (typical range from 10^{17} to 10^{20} particles/macromolecules per litre). For inorganics, the colloid concentration is dependent on groundwater chemistry. However, no predictive models are available.

Transport models for performance assessment were presented at the Workshop [7, 8]. Based on these presentations and on literature, the Working Group concluded that the models available are adequate to our present understanding of colloid-facilitated transport and to the data available, provided an equilibrium approach is permitted.

4.   Progress made

The Working Group summarised the progress made in the past years in our understanding of colloid-facilitated transport.

First is the full awareness of the importance of the classification and site-specificity of colloid populations in groundwaters. Second, the understanding of interactions, on a mechanistic basis, between chemical elements and colloid surfaces has strongly advanced. It became also evident that sorption often shows a fast kinetics whereas desorption kinetics is often slow. Understanding of desorption processes is, however, still in its infancy.

The analytical methods and tools for colloid measurements and colloid-nuclide interactions have made progress. Especially mentioned were Laser-Induced Breakdown-Detection (LIBD), X-ray Absorption Spectroscopy (XAS), and Flow Field Fractionation (FFF).

In parallel, new measurements in the field were performed or are in progress. These include natural analogue situations as well as problem-tailored field experiments. At the same time, laboratory experiments are ongoing to increase the understanding of relevant processes and mechanisms.

The existing transport models were deemed, by the Working Group, to capture the main features of colloid-facilitated radionuclide transport. Two serious remaining aspects of the colloid-facilitated radionuclide transport problem are the development of upscaling techniques (e.g., the extension of laboratory models to the field) and the ability to account for system heterogeneities. It is evident that both of these aspects are not restricted to colloid-facilitated radionuclide transport.

The Working Group reconsidered B. Honeyman's Figure "Solving the Problem of Colloid-Facilitated Transport" and confirmed essentially the author's judgement. In some cases, the Group felt a need for introducing uncertainty bars and slight changes. The result is presented below:

What is needed

*not discussed in working group
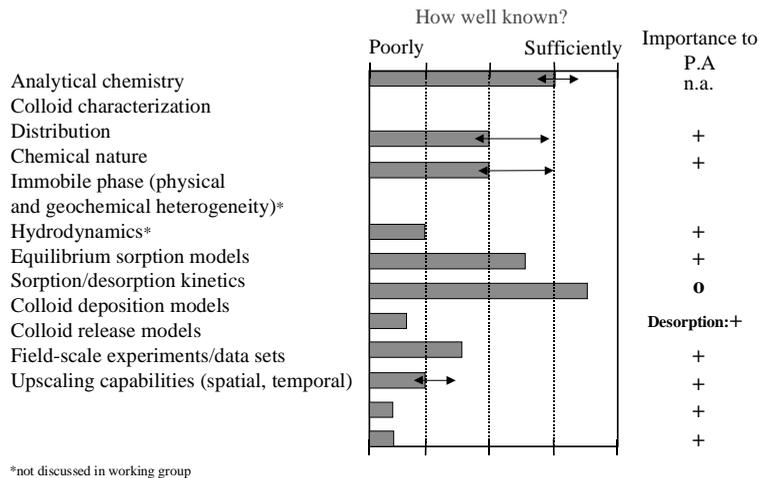
5. Overall conclusions of the Working Group

The Working Group came to two overall conclusions:

1. Colloid-facilitated radionuclide transport is an issue for performance assessment. It should be evaluated based on site-specific data and on the knowledge of radionuclide interactions with the specific colloid class.

2. There is, in general, no evidence for colloid retardation of radionuclides. Colloid retention is seen in specific systems; an important example is filtration in dense bentonite backfills.

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CONCLUSIONS OF WORKING GROUP 4

IMMOBILISATION

Chair: *Mike HEATH (University of Exeter, UK)*

Members
Jordi BRUNO (QuantiSci SL, Spain), Johan BYEGÅRD (Geosigma AB, Sweden),
María GIMENO (University of Zaragoza, Spain), Aleš LACIOK (Nuclear Research Institute, Czech Republic),
William MURPHY (California State University-Chico, USA), John SMELLIE (Conterra AB, Sweden),
Margit SNELLMAN (Posiva Oy, Finland), Susan STIPP (University of Copenhagen, Denmark),
Lian WANG (SCK/CEN, Belgium), Peter WIKBERG (SKB, Sweden)

Immobilisation processes, by which solutes are retained in the geological environment for long periods of time (relative to the timescales of interest for radioactive waste disposal), are commonly observed in nature [1,2] but mostly represent near-surface phenomena at suitable redox/chemical interfaces. There is a general lack of documented evidence from deeper, strongly reducing bedrock conditions that are more representative of a repository environment. Furthermore, the available data from all natural observations are difficult to characterise and quantify and are not incorporated into performance assessment (PA) models at present. Working Group 4 examined the main immobilisation processes that are familiar to geologists and explored the possibilities for making them more accessible to PA. Discussions focused mainly on fractured crystalline rocks as these were of greatest interest to the Working Group members.

1. Working Group Brief

Working Group 4 discussions focused on immobilisation processes, which were defined for the purposes of the workshop as "*processes ... by which solutes become incorporated within immobile solid phases ... (over the timescales of relevance to performance assessment)*". The discussion opened with a consideration of what kind of processes these might be and of the timescale over which they should continue to retain the solutes of interest.

Processes

Relevant processes include those that affect the surface (2D), which are commonly described using a distribution coefficient, K_d, and those that affect the bulk solid (3D). Because of the relative irreversibility of the 3D processes over long timescales, K_d alone is not a suitable parameter. The Working Group explored the possibility of deriving an additional term, analogous to K_d, that would be more realistic for describing 3D uptake for assessment modelling.

For the purposes of the discussion, the timescales of interest were agreed to be 10^5–10^6 years. Of particular importance here are fast flow paths (faults, fractures, etc.) through which radionuclides might be transported rapidly towards the human environment. It was suggested that ten half-lives of ^{239}Pu might provide a rule of thumb, suggesting around 250 000 years as a timescale to work with. However, Swedish PA requirements specify one million years.

2. Immobilisation processes

The key immobilisation processes of interest here (that is, processes that retain radionuclides within the geosphere over the timescales of interest to PA) include the following [3]:

- *Reprecipitation*: dynamic equilibrium between solid and liquid phases in which there is continual exchange of material between the phases. This results in no observable change at the macroscopic scale in the composition of either the solid or the solution, but at a molecular scale, one sees constant change in morphology as material moves on and off the surface. Available equilibrium constants describe behaviour of a wide range of commonly occurring minerals.

- *Co-precipitation*: incorporation of trace components by isomorphous substitution during the precipitation or reprecipitation of solid phases; equilibrium constants are largely unavailable for these processes.

- *Precipitation* as coatings or as colloidal-size particles where trace elements are an essential component of the phase. Uptake behaviour is poorly understood and many equilibrium and kinetic constants are unavailable.

Although these processes are observed in nature and can be described quantitatively, data are missing for many systems, and methods for incorporating them into PA modelling will require some work.

3. Immobilisation behaviour of key radionuclides

Despite the difficulties in quantifying immobilisation processes, can we speculate usefully about the way they might affect key radionuclides released from a leaking repository into the groundwater environment?

Immobilisation

The likely immobilisation behaviour of radionuclides under the reducing conditions of the repository environment was discussed with reference to the transport of a range of selected nuclides through a fracture system in crystalline rock, where the fracture linings are mostly composed of calcite, Fe oxides or sulphides, and clay, with the following tentative conclusions:

Radionuclide	Likely behaviour in the repository environment
Am, Np, Pu, Tc	Retained in the repository; if released, retention depends on equilibrium relations with colloids, complexes, etc.
U	Adsorbed with high K_d; behaviour could be better described along with that of Ra using a thermodynamic parameter instead of a high K_d.
Ra	Incorporated into calcite.
Cs	Adsorbed with high K_d.
Sr	Incorporated into calcite.
Se	Incorporated into pyrite.
Ni	Incorporated into pyrite, Fe/Mn oxyhydroxides, or calcite.
I	? (immobilisation possibilities seem limited for this key radionuclide).

It seems, therefore, that there is great potential for the immobilisation of a range of important nuclides, but might they be remobilised during the time period of interest to PA?

Remobilisation

Remobilisation of radionuclides would only occur if pH, Eh, the solution composition, and/or salinity changed over time. It was recognised, however, that the groundwater environment surrounding the evolving repository over the timescales of interest is poorly understood at present but that it would vary within the volume affected by the repository and would be likely to change with time. Of particular importance would be processes that would operate when solutes reach an environment that is oxidising in the repository host formation.

It was recognised that the groundwater surrounding a repository would be a complex mixture of solutes, making the behaviour of individual species difficult to predict, particularly as conditions changed.

4. Applications to performance assessment

During discussion, the need for an immobilisation parameter such as K_d was recognised. K_d, which describes *retardation*, meaning retention followed by release, is a time-dependent parameter. This makes it inappropriate for describing processes of immobilisation where retention is "permanent" over the timescales of interest to the repository.

A new term, provisionally labelled F_d, was considered to be needed to describe immobilisation. For the co-precipitation of a radionuclide R, F_d could be expressed as:

$$F_d = \frac{R_{coprecip}}{R_{aq}}$$

where $R_{coprecip}$ represents R immobilised by co-precipitation in the solid phase and R_{aq} is R remaining in the aqueous phase. This is analogous to K_d but the retention is "permanent" (over the timescales of interest).

The key question then is: can we determine F_d for key radionuclides? The tentative answer appears to be "probably", because F_d could be derived from:

- Existing thermodynamic data on some specific nuclides plus new data from further study.

- Information from site characterisation on groundwater geochemistry, etc.

An example of the derivation of F_d from thermodynamic and site data was given at the Workshop. F_d seems, therefore, to be a potentially useful term because it fits the format of current PA models and data for it could be determined for radionuclides of interest in the future even if the necessary data are not available at present.

5. Other factors

The Working Group's discussion time did not permit consideration of two other factors that are likely to affect radionuclide immobilisation, which are:

- Changing repository conditions over the timescales of interest, such as would accompany glaciation, notably changes in flow rates and salinity, redox conditions, and pH.

- Microbiological factors, which could be significant.

Time did not permit the further consideration of these or other factors that might affect immobilisation.

6. Conclusions

By the end of the discussion, we concluded that:

- Immobilisation phenomena are observed in nature, although mostly near the bedrock surface at redox/chemical interfaces; there are few documented observations from deeper, highly reducing environments, and further studies are recommended in order to assess the role of radionuclide immobilisation in the geosphere.

- The observed processes are potentially important within the repository environment and can be made accessible to performance assessment through a new term, F_d.

- Sufficient information is available or could be obtained from site characterisation or further research, focusing particularly on thermodynamic data, to provide F_d for key radionuclides.

- There is a need for a database of natural immobilisation phenomena from field and laboratory observations from which a clearer understanding of the controls of immobilisation and long-term behaviour of immobilised solutes can be obtained.

The discussions pointed the way toward the incorporation of immobilisation phenomena into performance assessment modelling and outlined an approach that could be adopted for the inclusion of these potentially important processes into quantitative models of repository systems.

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Annex 6

CONCLUSIONS OF WORKING GROUP 5

CONCLUSIONS AND SYNTHESIS OF GEOTRAP AND PROPOSALS FOR FOLLOW-UP

Chair: *Alan HOOPER (Nirex, UK)*

Members
Johan ANDERSSON (JA Streamflow AB, Sweden), Richard BEAUHEIM (NEA, France),
Peter FLAVELLE (CNSC, Canada), Erik FRANK (HSK, Switzerland), Aimo HAUTOJÄRVI (Posiva Oy, Finland),
Pedro HERNÁN (ENRESA, Spain), Kai JAKOBSSON (STUK, Finland),
Mark JENSEN (Ontario Power Generation, Canada), Patrick LEBON (ANDRA, France),
Claudio PESCATORE (NEA, France), Klaus RÖHLIG (GRS, Germany), Budhi SAGAR (CNWRA, USA),
Klaus SCHELKES (BGR, Germany), Jan-Olof SELROOS (SKB, Sweden), Paul SMITH (SAM Ltd., UK),
Hiroyuki UMEKI (NUMO, Japan), Jürgen WOLLRATH (BfS, Germany)

1.   **Introduction**

The Working Group discussed the following topics:

- The draft report, circulated to all members of the Group prior to the meeting, synthesising the outcome of the GEOTRAP Project up to the Fifth Workshop.

- The Group's view of the key outcomes of the GEOTRAP Project including the Fifth Workshop and of any key issues that are outstanding.

- Priorities for future international collaboration within NEA in terms of technical scope and implementation.

2.   **GEOTRAP Synthesis Report**

The Working Group was highly disciplined in not seeking to redraft the report but rather to give high-level guidance on how the report met the participants and others' expectations. The overall view was very favourable and several participants congratulated Rick Beauheim (NEA Secretariat) on his work in producing the draft. Several observations were made on how the report might be developed.

2.1.   *Extended synthesis*

Many participants felt that the report was an excellent summary of the reports on the proceedings of the workshops that had been held. However, they proposed that the final report should include additionally:

- More detail (in the conclusions) on the role(s) played by the geosphere in making a safety case.

- More detail on the integration between performance assessment and site characterisation that was evident in a number of workshops.

- A general description of the development of models and a commentary on the extent to which the issue of different conceptualisations of the natural system (with respect to radionuclide retention) had been addressed.

2.2. *Project evaluation*

A number of comments related to a desire to include an objective evaluation of the project in terms of both process and outcome. It was generally considered that a brief description should be given of the genesis of the Project, including its relationship to INTRAVAL, GEOVAL, and similar past initiatives. Several participants stated that the responses to the questionnaire distributed in October 2000 should be included.

Ideas were put forward as to other means of evaluating the Project. It was felt that a key objective of communicating understanding and issues to programme managers had been achieved but that communication to non-technical readers was not so successful. This might be addressed by the addition of a summary (see below). The participation of the academic community in the Project was viewed very positively and it was proposed that their views should be sought formally and recorded as part of the final report.

The value of the Project as a learning experience for the participants was not to be underestimated. A key question is whether it has been of such value to the national programmes. The questionnaire responses should help to answer that question, but it was also suggested that other methods, e.g., tracking the use made of the Project's reports as key references, should be pursued.

The view was expressed by some participants that the Project struggled to retain the declared focus on radionuclide transport and retention, and was drawn towards the better-trodden path of groundwater flow. It was felt that a realistic view should be presented as to whether this had reduced the success of the Project and, if so, how the focus might have been better retained. Possibly a related issue was the influence of programmatic decisions, taken to make workshops practical, where artificial separations were necessarily made between related technical topics, e.g., the holding back of much discussion on geochemical aspects until the final workshop. The participants were not making these comments as adverse criticisms on the outcomes of the Project (see in particular Section 3 below) but rather as pointers to how the working methods might be improved in the future.

2.3. *Summary and recommendations*

A high proportion of the participants made proposals that a summary should be added which would include key outputs and recommendations drawn from the Project. It was also proposed that such recommendations could be prioritised. In drawing out the recommendations, it was suggested that they should be explained in terms of the identifiable evolution of ideas that occurred within the timespan of the Project.

Particular value was attached to the inclusion of a summary of "field experiences" where the significant issues to be addressed should be identified, e.g., in tracer tests; computing/modelling capabilities.

2.4. *Additional contents*

It was suggested that the report should note the relationship of GEOTRAP to other international projects such as DECOVALEX, and to other NEA initiatives – in particular the highly relevant Spatial Heterogeneity Workshop and the Workshop on The Role of Conceptual Models.

2.5.   *Presentational point*

It was stressed that there should be even coverage, in terms of length, of the summaries of each of the five Workshops.

3.   Key outcomes

There was a good consensus for such a large group that the key outcomes of the GEOTRAP Project were as follows:

- Successful forum for exchange of information.

- Through good exchanges, the previously perceived controversies about transport processes had been reduced significantly; it is now possible to recognise that there is no such thing as "an unimportant process" in a general sense, but that importance can be determined in a specific application.

- Representatives of all key players in the scientific process had been able to interact successfully:
  - Experimentalists and modellers.
  - Site characterisation and PA specialists.
  - Workers on different geological media.
  - Scientists from within and without the radioactive waste "community".
  - Implementors and regulators.

- Realistic view of modelling capability balanced by an improved understanding of transport processes; this had led to the elimination of "fitting" of model parameters without a proper scientific basis evident in earlier work.

- Better understanding of the use of so-called "soft information" (with examples now of both quantitative and qualitative use), but this area still requires progress.

- Informs decisions on modelling strategy by identifying what needs to be taken into account when selecting the type/complexity of model to be applied.

- Firm scientific basis for the decisions at hand in most advanced national programmes, noting that this is a time-dependent statement and that "good science" is assessed always against prevailing standards.

4.   Proposed follow-up to GEOTRAP

The Working Group was strongly in favour of a follow-up to the GEOTRAP Project on the basis that the Group's discussions had identified a number of issues, highly relevant to national programmes, that could be addressed effectively through such international co-operation. It is important to note that the Working Group contained a high proportion of managers of technical programmes who have a direct responsibility for work in the relevant areas. The Group was able to formulate ideas on the overall objectives, the outline of the issues, and the modus operandi and practical points to be addressed. These are described in turn below.

4.1 Overall objectives

The new project should aim:

1. To achieve effective communication of ideas, information and issues, leading to personal learning by participants, who should be drawn from multiple disciplines and backgrounds. The involvement of the academic community, both associated with, and outside, radioactive waste management should be fostered.

2. To continue with a "forum approach" as in the current GEOTRAP Project, to achieve the required level of involvement.

3. To further develop the integration of field (*in situ* and laboratory) information and performance assessment.

4. To work in the framework of building and communicating confidence in key aspects of safety cases. This should include a conscious tracing of the development in understanding from previous international initiatives (HYDROCOIN, INTRAVAL, etc.).

5. To address a topic of active work and widespread interest within many national programmes.

4.2 Outline of issues to be addressed

The Group was able to identify five broad issues that should be addressed. In the time available, it was not possible to specify these in sufficient detail that, if required, a start could be made to work from the current definitions. Recommendations are made in Section 4.4 on how the required level of definition could be achieved.

4.2.1 How all types of field information (e.g., geophysical, hydrogeological, geological, geochemical) contribute to a description (or what may be called conceptualisation) of the geosphere (treating all lengthscales).

This topic would be covered by examining the following:

- The iteration and integration of field information and performance assessment – in particular to determine whether PA-relevant parameters are measured and the structural basis for these parameters.

- The traceability of field information in making a safety case and the use of multiple lines of geological evidence within a safety case.

- The development and application of alternative conceptualisations (conceptual models).

4.2.2 Implications of the geometry and evolution of the engineered system for radionuclide migration from the waste form/engineered barrier system into the geosphere: The Near Field/Far Field Interface.

This topic would involve the following:

- How to describe "early-time" transients in the disturbed part of the system, in particular with respect to disturbed geochemistry, leading to development of tractable evolution scenarios for use in safety cases.

- Demonstrating how understanding of migration into the geosphere under relevant scenarios informs the design, location and any monitoring decisions in relation to the engineered system.

If this topic were addressed successfully, it would provide the safety assessment context for the outputs from the international DECOVALEX Project.

4.2.3   *The PA-relevant evolution of geosphere characteristics.*

The Working Group noted that the GEOTRAP Project repeatedly had identified this as an important issue which had been excluded from its remit but which was of clear relevance to many of the subjects considered. It also noted the problems that had been experienced in NEA standing committees in defining an appropriate initiative on the topic. In outline, it was agreed that the topic should include:

- Identification of the changes that could occur in important physical and chemical properties over a period of order one million years.

- The implications of the observable past evolution of boundary conditions for the geosphere in terms of informing the degree to which there is a need to capture their possible future evolution as part of a safety case.

The Working Group stated firmly that any initiative in this area under the envisaged follow-up to GEOTRAP should not deal with scenario analysis *per se*; this was viewed as being dealt with under PA initiatives. What is required is the geoscientific understanding to give the relevance of this key aspect of a safety case.

4.2.4   *Understanding the issue of the geosphere/biosphere interface.*

The Working Group was of the opinion that treatment of the geosphere/biosphere interface could be viewed as deficient. Although acknowledging that an initiative would require more thought and access to information generated from other international projects such as BIOMASS, it was proposed that the topic should at least address:

- What are the important geosphere/biosphere interactions.

- Whether there is consistency of treatment within safety cases of similar processes in the geosphere and biosphere.

4.2.5   *Issues outstanding on radionuclide retention processes in the geosphere.*

The Group noted the success of this fifth Workshop in identifying very clearly the outstanding issues on sorption, diffusion, colloid transport and immobilisation. The outputs of the Working Groups 1-4 working in parallel with this one were expected to define the way forward on this topic. One aspect readily identified as requiring attention was the identification of field measurements that would be required to support the confident use of retention processes in safety cases.

4.3   *Modus operandi*

After lengthy discussion the Working Group determined that, with minor improvements, the current modus operandi of GEOTRAP was very successful and a good model for the proposed follow-up. The following features were highlighted.

4.3.1   *Workshops*

These should be held every 1-2 years (not more than one per year, not less than one per 2 years). A workshop should last around three days and should include working group sessions. The attendance should be limited to ensure effective dialogue and involvement, but a small expansion should

be envisaged to accommodate stronger representation of the academic community. (Methods such as a larger number of working groups, perhaps more than one addressing the same topic, were proposed).

The method of seeking responses to key questions was viewed as a particular success of GEOTRAP and should be maintained.

4.3.2   Published proceedings

The published proceedings are highly valued. They should include the presented papers, a synthesis, and working group reports, as previously.

4.3.3   Continuity

The need for continuity through a project of several years duration was emphasised. GEOTRAP had reasonable continuity, although improvements could be made. This has to come from the national delegations and ideally from a fixed contact person. That contact person should not be viewed as a fixed delegate to all workshops; the role of the contact person is to nominate the most appropriate participant, ensure he/she both understands the context and gives feedback. The achievement of continuity should be reviewed by the contact persons in national delegations and by the IGSC (with its programme management role).

4.3.4   Participation

Participation in workshops should be principally from:

- Staff from the relevant national, technical programme (implementors and regulators).

- Invited specialists:
  - Supporting national programmes.
  - From other relevant areas of application of the geosciences (e.g., academics).

Particular effort should be made to develop further the now-encouraging level of inputs from the regulators' programmes.

4.3.5   Links to other international initiatives

The proposed initiative should have strong, formal links to other relevant international initiatives. There is not sufficient resource to duplicate work. The information from other initiatives should be recognised in the documentation and, where appropriate, available to workshop participants.

4.4   Practical points

The Group identified the following practical points as requiring to be addressed in developing the specification for the proposed follow-up:

1. The proposed project is very broad and requires the commitment of a much wider range of inputs and disciplines. There needs to be evidence of their availability.

2. The proposed topics defined in Sections 4.2.1 to 4.2.5 are very large in some cases – almost individual projects in their own right. Some may require to be disaggregated, or at least reviewed, to make them practicable over a useful period of time.

3. The specification of all topics in Sections 4.2.1 to 4.2.5 is very much at the outline stage and requires considerable development to enable delegations to participate meaningfully. It was suggested that a good way forward would be for a small group (possibly the IGSC Core Group with invited specialists) to formulate a set of key questions to be addressed under each topic.

4. It was noted that NEA Secretariat resources were limited. In the event that the IGSC decided to deploy the secretariat to a different, new project, a different balance of management responsibilities might be required. It was considered practicable that a national programme (ideally comprising both implementor and regulator) hosting a workshop would supply the resources to organise and document the workshop as a possible way forward. It was noted that one model for a workshop could involve the presentation by the hosting national programme of its geosphere-related work including the approach to the topics, in particular how all types of field information contribute to the geosphere description.

5.   Summary

The Working Group showed considerable focus and discipline to generate, with a high level of consensus, a view of a valuable follow-up to the GEOTRAP Project. In particular, it was stressed by many participants that the NEA should retain a major initiative focused on the role of the geosphere barrier in contributing to the safe long-term management of long-lived radioactive wastes, even if a new approach to its management would be required (as proposed in 4.4 (iv), above). The IGSC members present, and in particular the Working Group Chairman, were charged with making the strongest representations of the Group's proposals for inclusion in the future programme.

PART B

WORKSHOP PROCEEDINGS

How Geologists View Retention

M.J. Heath
University of Exeter, UK

1.   Introduction

Retention processes will play a key role in controlling the behaviour of radionuclides released from an engineered radioactive waste repository into the geological environment. The effectiveness of these processes, which include mechanisms for radionuclide retardation and immobilisation, must be understood in establishing a safety case for any disposal system in which the geological barrier forms a major component.

In exploring the extent to which these processes of retardation and immobilisation are understood by geologists, two key questions must be addressed. Firstly, are the processes that are envisaged to contribute to the retention of radionuclides within the geological component of any multi-barrier waste isolation system actually observed in Nature? Secondly, are these processes likely to operate on timescales that are relevant to radioactive waste disposal in deep geological repositories?

2.   Processes

The processes of interest here include mechanisms for both retardation and immobilisation and are well known in relation to the mobilisation/immobilisation behaviour of metals in the environment [1].

The key *retardation* mechanisms of interest here (that is, processes that delay the time taken for solutes to traverse the geosphere) include both sorption (that is, adsorption and ion exchange, expressed in terms of a distribution coefficient, K_d) and (for fractured media) matrix diffusion (the transfer of radionuclides by diffusion between flowing groundwater in fractures to stagnant water in rock matrix pores, expressed as a diffusion coefficient). Retardation processes simply slow the rate of release and may be reversible as conditions surrounding the repository change with time.

Immobilisation processes are those by which solutes are retained within the geosphere for long periods of time (long, that is, in relation to the time scales of relevance to performance assessment, which lie in the range of 10^5-10^6 years). These processes include precipitation and co-precipitation of the nuclides of interest as immobile solid phases. It is of interest to note here that the same retention processes, often described in terms of retardation and K_d, operate in the environment of a landfill or other hazardous waste disposal or contaminated site, and are important in controlling the "attenuation" of hazardous substances leached from such sites into the geological environment [2].

3.   Controls of retention

The effectiveness of these retention processes in controlling the release of any specific radionuclide in any specific geological environment will depend on a range of properties of both the radionuclide itself and of the environment into which it is released. Among key factors to consider here

are the chemical properties of the element itself (whether in solution as cation or anion, if complexed with other molecules, if occurring in different valency states), the pH and Eh of the groundwater environment, the nature of surfaces with which the radionuclides of interest might come into contact (whether of clay or any other geological or non-geological material), and the presence of other dissolved substances (such as organic or inorganic complexation agents or competing species) and/or of suspended material to which radionuclides might become attached (including colloids and other suspended particles).

Other processes taking place simultaneously with these retention mechanisms will also influence the dispersion of radionuclides within the geosphere. Notably, hydrodynamic dispersion will allow dilution of radionuclides as they disperse in large volumes of water within fracture systems or within the matrix of porous rocks. This will affect radionuclide concentrations and their ability to participate in retention processes. Isotopic fractionation (the separation of different isotopes of the same elements) will also influence the overall behaviour of specific elements (notably uranium) and can lead to isotopic disequilibria (which might provide useful information on the mobilisation and retention behaviour of these elements [3]).

## 4.   Geological evidence for retention on timescales of interest

Given that many of these retention mechanisms operate simultaneously, it is difficult to identify the individual roles of specific processes, and the results of field migration experiments, for example, are often difficult to interpret in relation to specific retention/dispersion processes.

As the timescales of interest to radioactive waste disposal are long (say, 10^5-10^6 years), it is possible that, during the lifetime of a repository (throughout which it must continue to meet its design performance criteria), significant changes will take place in the key rock properties that influence retention processes. Changes in groundwater chemistry (including pH, Eh, and presence of complexation agents), changes in rock matrix porosity and permeability, and changes in rock mass hydraulic conductivity and hydraulic gradient might all be anticipated over the timescales of interest. Each of these changes might influence the retention of radionuclides in the geosphere and thus compromise the performance of the geological barrier.

Important to our understanding of these retention mechanisms is the geological evidence that these processes operate in Nature and do so on the timescales of interest. Here, of particular interest is the permanent retention of metals in the natural environment in the form of metalliferous mineralisation. That some of these mineralisation processes are rapid (that is, on a timescale of hundreds of years) is demonstrated by the immobilisation of metals through diagenetic precipitation of solid mineral phases in estuaries affected by metalliferous mining in Cornwall. Figure 1 shows diagenetic zinc sulphide and sulphate cements nucleated on detrital quartz and carbonate grains in sediments that cannot be more than 130 years old according to historic evidence from an adjacent abandoned quay [4].

Evidence for temporary retention in the natural environment in also seen in the rapid precipitation of Fe/Mn oxyhydroxides from leachate seeps and minewaters as ochre slimes to which trace metals become "bound" by sorption, co-precipitation or precipitation [5]; "uranic ochres" were described long ago in the mines of Cornwall [6] while Fe/Mn oxyhydroxides have also been shown to scavenge uranium at El Berrocal [7]. Other natural migration phenomena include a range of alteration and weathering processes that entail the bulk migration of ions and the formation of new phases within rock matrices and fracture systems (associated, for example, with the kaolinisation process, which may be accompanied by leaching and redeposition of uranium [8]).

Figure 1. **Scanning electron microscope images of diagenetic zinc sulphide/sulphate cements nucleated on detrital quartz and carbonate grains; the lower image is an enlargement of part of the upper image showing the structure of cements rimming a detrital quartz grain [4].**
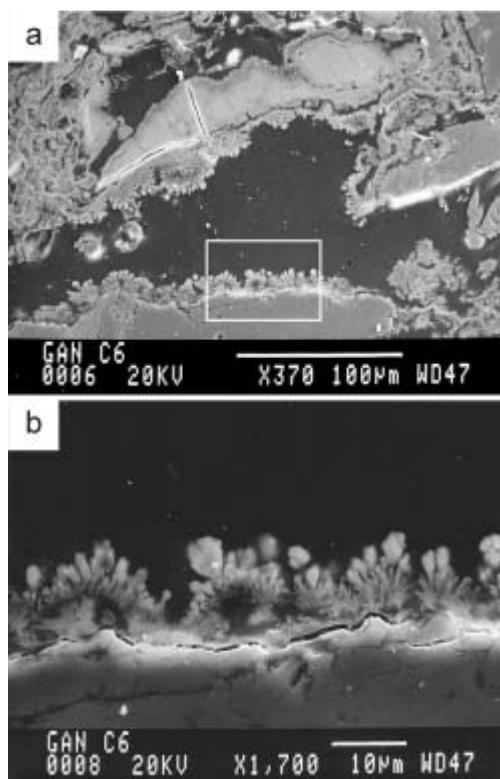
5.   Remobilisation

As physicochemical conditions change over the 10^5-10^6 years of interest, many of these processes might show themselves to be reversible. Rock matrix diffusion, for example, might be expected to be reversible as elemental concentration gradients between fracture waters and porewaters change with time (as a pulse of radioelement contamination passes through a fracture system, for example). Sorption and ion exchange might also prove reversible where chemical conditions change (notably in response to changes in pH and the presence of other dissolved constituents, whether complexation agents or simply competing species). Precipitation/co-precipitation might also be reversible as conditions (especially redox conditions) change with time. Microbiological factors, not considered here, might also become important in the evolving environment of a radioactive waste repository.

6.   Conclusions

The geological evidence shows that the processes envisaged as playing a key role in radionuclide retention are indeed observed in Nature, though they may be described in different terms by different disciplines. There may still be difficulties in extrapolating the results of studies of these natural systems to the environment of a repository, and from geological timescales to those of interest for performance assessment, but many of the geological phenomena observed do appear to operate on timescales of relevance to radioactive waste disposal.

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Molecular Scale Observations and Models of Sorption Reactions

James A. Davis

U.S. Geological Survey, Menlo Park, California, USA

Sorption is one of many processes that can contribute to the retention of radionuclides in the geosphere. In the environmental sciences literature, sorption is generally defined as a loss of a chemical species from a solution to a contiguous solid phase. There are several mechanisms by which a sorption process can occur, for example: (a) *adsorption*, an accumulation of matter at the interface between a solution and a solid adsorbent, without the development of repeating three-dimensional molecular structures [1], (b) *ion exchange*, a special type of adsorption, in which counterions accumulate at the interface of a solid adsorbent with permanent structural charge, (c) *surface precipitation*, the growth of a solid phase exhibiting a primitive molecular unit that repeats itself in three dimensions on the surface of a different contiguous solid phase [1-4], (d) *surface polymerisation*, a special type of adsorption, in which multinuclear surface species are formed [5-6], (e) *surface substitution,* the formation of a solid solution in the surficial layers of a contiguous solid phase by exchange of elements between solution and the solid phase structure [4,7-9], and (f) *absorption*, the diffusion of a species from solution into nanoscale pore spaces of a solid phase [10].

From the variety of possible mechanisms, it should be obvious that a clear distinction between sorption and immobilisation processes is problematic, as a continuum of possible bonding geometries and dimensions of surface structures exists. On the time scales of interest in many performance assessment calculations, all such processes may be reversible. The easiest distinction can probably be made on the basis of physical dimensions of surface structures, with surface precipitate formation and surface substitution categorised as immobilisation, and the formation of the smaller surface structures categorised as sorption processes. The focus of this paper will be on the latter, with particular emphasis on the adsorption and ion-exchange processes.

The quantitative description of adsorption as a macroscopic phenomenon is achieved through the concept of *relative surface excess* [11]. For accumulation of solute i at the solid-water interface, the relative surface excess, Γ_i, or adsorption density of solute i may be defined as:

$$\Gamma_i = n_i/A$$

where n_i is the moles of surface excess of solute i per unit mass of the solid phase, and A is the specific surface area of the solid phase. The adsorption density can be measured by a variety of experimental techniques, but is most commonly determined by batch experiments in which a suspension of the solid phase is mixed with an aqueous solution. The molecular structures of adsorbed species, however, cannot be determined from measurements of macroscopic uptake on solid phases. The details of bond distances, co-ordination numbers, and stoichiometries of surface reactions can only be determined from spectroscopic techniques [1-9].

The experimental basis for our understanding of adsorption and ion-exchange reactions relies primarily on laboratory data collected for time scales on the order of days to weeks [11]. In the longer

time scales considered in performance assessment, slower processes can also occur, such as the dissolution and precipitation of secondary mineral phases during chemical weathering of rocks. The longer time scale makes it more likely that other sorption processes can occur, such as absorption, surface substitution, and surface precipitation. The occurrence of such processes makes it experimentally difficult to quantify the amount of radionuclide that is adsorbed versus that which is associated with the solid phase by a different mechanism. This does not mean that adsorption-desorption models are not valid over long time scales. However, it does mean that adsorption-desorption models may need to be coupled with other models that also describe radionuclide association with solid phases via the slower processes. Our fundamental understanding of the slower processes is still poor and the conclusions reached in the literature have generally not been confirmed with spectroscopic evidence.

At least three types of models for describing the equilibria of adsorption-desorption reactions of radionuclides at mineral surfaces can be distinguished: (a) empirical partitioning relationships, (b) mechanistic models that describe the details of chemical species formation at mineral surfaces using thermodynamic formalisms, and (c) semi-empirical site-binding models that utilise concepts from the first two model types [12-13].

Empirical relationships include distribution coefficients, adsorption isotherms, and partitioning equations, each of which is capable of expressing adsorption as a function of a concentration variable or variables [11]. The empirical modelling approaches have the advantage that the collection of experimental data is relatively simple and straightforward. Distribution coefficients are defined as:

$$K_d = RN_{ads} / RN_{aq}$$

where RN_{ads} refers to the quantity of radionuclide sorbed and RN_{aq} refers to the aqueous concentration of the same radionuclide. The relationship implies that a constant ratio is obtained between these two quantities, as in a linear isotherm. There are many types of adsorption isotherms. The most common, the Langmuir isotherm, is defined as:

$$K_L = RN_{ads} / (RN_{aq})(\Gamma_{free})$$

where K_L is a constant and Γ_{free} refers to the quantity (or concentration) of available surface sites. The Langmuir isotherm accounts for the decrease in radionuclide adsorption that occurs as the surface becomes partially saturated with increasing aqueous radionuclide concentration. The relationship is usually determined for a specific set of constant chemical and physical conditions as the radionuclide concentration is varied. More general empirical relationships include partitioning equations, such as:

$$K_{part} = (RN_{ads})(H^+)^x / (RN_{aq})(\Gamma_{free})$$

These relationships are capable of describing radionuclide adsorption as a function of radionuclide concentration and variable pH.

The parameters of all empirical partitioning relationships are conditional, and should not be utilised to describe radionuclide partitioning beyond the experimental conditions. This is a major drawback to the empirical modelling approach. For example, it has been shown that the distribution coefficient for adsorption of uranium(VI) on sediments and pure mineral phases may vary by more than 8 orders of magnitude over a wide range of chemical conditions [14]. Figure 1 shows how the distribution coefficient for uranium(VI) varies as a function of pH for ferrihydrite, quartz, and sediments collected from a shallow alluvial aquifer near Naturita, Colorado (USA).

Figure 1. **Distribution coefficients for uranium(VI) adsorption as a function of pH on the pure ferrihydrite and quartz surfaces and on an alluvial aquifer sediment (total U(VI) concentration of 10^{-6} M; air equilibration).**
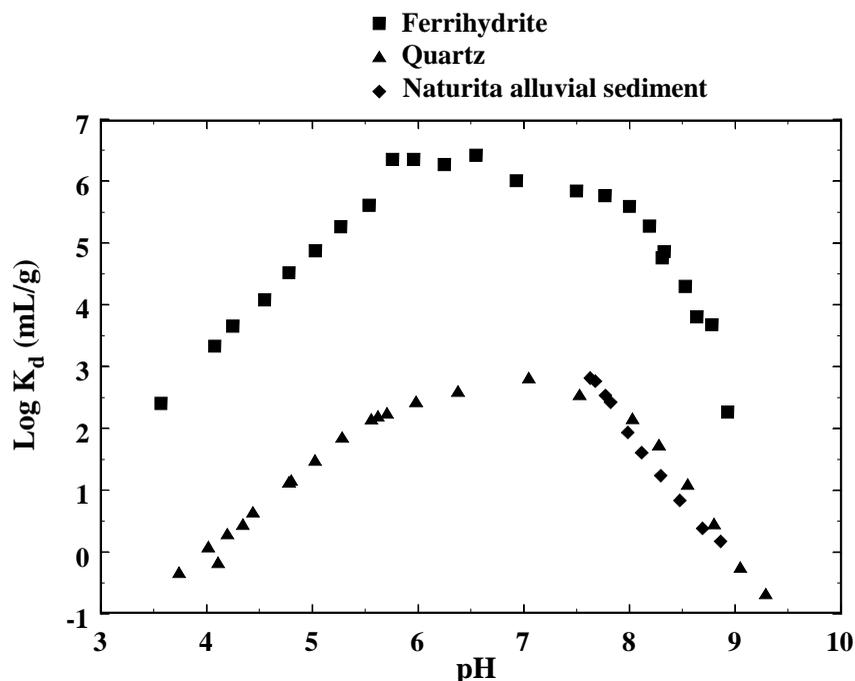
Mechanistic models use the surface complexation concept to describe adsorption. The possible advantages of applying the surface complexation concept to describe radionuclide sorption in nuclear waste performance assessment (PA) include the following factors:

1. The modelling approach provides a thermodynamic framework to describe adsorption reactions of radionuclides,

2. The stability constants for the adsorption reactions can be included as part of an overall network of chemical reactions in chemical equilibrium or coupled reactive transport models, and thus coupled with the NEA thermodynamic database,

3. The modelling approach allows predictive calculations for a wide range of geochemical conditions without adjustment of the values of the stability constants for radionuclide adsorption as geochemical conditions are varied in space or time, unlike the condition-dependent empirical relationships

4. The modelling approach can be included efficiently in transport simulations (or PA scenarios) in which there are chemical gradients in space or time.

Ideally, mechanistic models use spectroscopic evidence to confirm the existence of surface species used in the mass laws, and therefore require the collection of considerable data. However, these models have the advantage of ***predictive*** calculations over a wide range of chemical conditions. In mechanistic modelling, mass laws are written that describe adsorption as a function of aqueous chemical conditions, thus taking into account changes in chemical speciation, competitive adsorption,

and other multi-solute interactive chemical effects. Some examples of mass law equations that might describe the adsorption of uranium(VI) on an iron oxide surface include:

$$K_{ads1} = (\equiv FeO_2UO_2)(H^+)^2 / (UO_2^{2+})(\equiv Fe(OH)_2)$$

$$K_{ads2} = (\equiv Fe(OH)OUO_2)(H^+) / (UO_2^{2+})(\equiv Fe(OH)_2)$$

$$K_{ads3} = \frac{(\equiv FeO_2UO_2CO_3^{2-})(H^+)^3}{(UO_2^{2+})(HCO_3^-)(\equiv Fe(OH)_2)}$$

where $(\equiv Fe(OH)_2)$ represents the activity of unoccupied iron oxide surface sites, (UO_2^{2+}) and (H^+) are the aqueous activities of the divalent uranyl cation and the proton, $(\equiv FeO_2UO_2)$ is the activity of the surface complex formed between the iron oxide surface site and the uranyl cation, and K_{ads1} is the mass law constant for the reaction, including correction for electrostatic interactions. The surface species postulated should be supported with spectroscopic evidence [5]. The total adsorption of uranium(VI) is the sum of all U(VI) surface complexes formed. The mass laws allow for a description of adsorption as a function of variable aqueous chemical conditions, such as pH, carbonate concentration, and all other aqueous compositional changes. The presence of complexing ligands at variable concentrations in water, such as carbonate, can have large effects on the values of empirical parameters like the distribution coefficient (see Figure 2).

Figure 2. **Distribution coefficients for uranium(VI) adsorption on the pure ferrihydrite surfaces as a function of pH and the partial pressure of carbon dioxide gas (total U(VI) concentration of 10^{-6} M).**
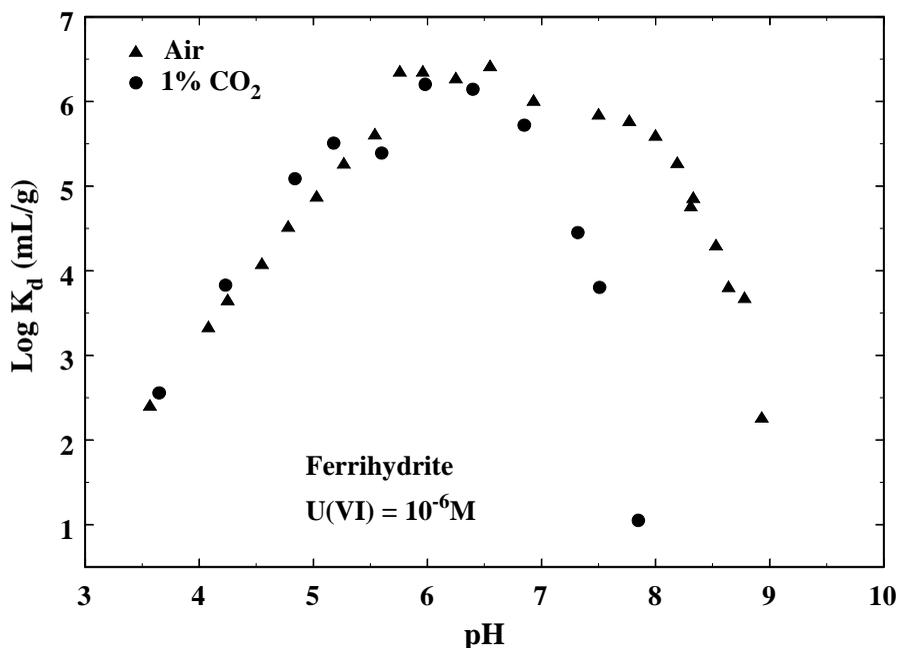
Adsorption calculations in mechanistic models that employ electrical double-layer terms are highly sensitive to the double-layer parameters in the general case of the formation of a charged surface species. For example, in the case of uranium(VI) adsorption on hematite, it is known from spectroscopic studies that the major surface species formed is a ternary surface-uranyl-carbonato complex [5]. Within the context of a triple-layer model for the hematite surface, Figure 3 shows how the adsorption calculations are sensitive to the location of charge within the surface complex. The net

charge of the surface species is –2, but for the purpose of calculating the electrostatic potential contribution to the free energy of adsorption, the charge could be located at the surface plane (σ_o), the mean plane of adsorbed ions (σ_β), or it could be distributed between the planes. As shown in Figure 3, a nearly even distribution of charge between the planes provides the best description of the adsorption data, assuming that only this surface species contributes to the uranium(VI) adsorption.

Figure 3. **Adsorption of uranium(VI) on hematite as a function of pH (air equilibration).**
Dots are experimental batch data for the system conditions shown in the legend.
Curves are triple-layer model simulations for formation of the species, $\equiv FeO_2UO_2CO_3^{2-}$,
with three different assumptions as to the distribution of net charge
within the electrical double layer (triple-layer model).
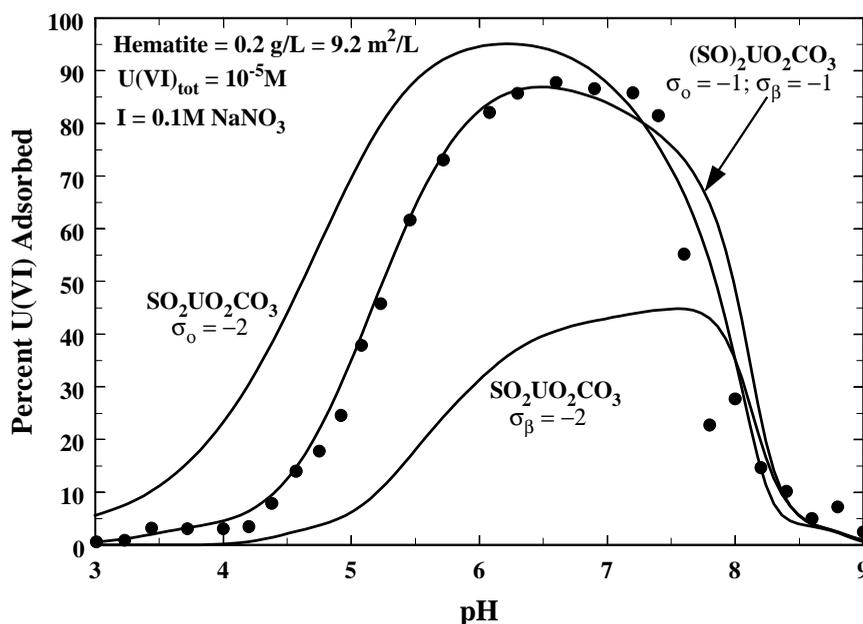
The sensitivity to the electrostatic terms illustrates a significant practical problem in extending detailed mechanistic models directly to simulate radionuclide adsorption on complex mineral assemblages in the environment. Mineral surfaces in the environment are coated with poorly crystalline secondary mineral coatings and natural organic materials (fulvic and humic acids), making it extremely difficult to assess quantitatively the electrostatic contribution to the free energy of adsorption. Clearly, an assumption that the electrical double layer properties of pure mineral phases studied in the laboratory are the same for these minerals in the environment is incorrect. Thus, the challenge in model application is to simplify the model such that the adsorbed quantities are still calculated with mass laws that are coupled with aqueous speciation, while lumping parameters that are difficult to characterise in the environment in with other parameters. This modelling approach can be achieved with semi-empirical, site-binding models [12,13,15].

Mechanistic and semi-empirical site-binding models represent two extremes of surface complexation modelling [12]. While mechanistic models need to be validated with spectroscopic evidence and other detailed data to confirm surface speciation, semi-empirical site binding models represent a less rigorous and applied modelling approach. This "engineering" approach to surface complexation modelling has not been widely used to date, but it may represent a good compromise in

terms of data collection needs and the capability to predict radionuclide distributions over a range of chemical conditions [13,15]. Table 1 compares the modelling approaches and their data needs.

Table 1. **Characteristics of Surface Complexation Modelling Approaches for Environmental Adsorbents.**

MECHANISTIC MODELLING	SEMI-EMPIRICAL MODELLING
Predict adsorption from thermodynamic constants and known surface species	Simulate (fit) adsorption data collected with site-specific adsorbent samples, using chemically plausible surface reactions
Surface sites are unique and defined for each specific mineral phase present in environmental samples	Generic surface sites, assumed to have average chemical characteristics
Surface site densities quantified by characterisation of the surface of environmental samples	Surface site densities quantified by measurement of specific surface area and fitting of experimental adsorption data for environmental samples
Apparent stability constants and reaction stoichiometries obtained from studies of adsorption by specific mineral phases present in environmental samples	Apparent stability constants and reaction stoichiometries fit to experimental adsorption data for environmental samples
Overall adsorption predicted by the sum of adsorption for each specific mineral phase present in environmental samples	Numbers of surface site types and chemical reactions increased as necessary to achieve good model simulations and to meet modelling objectives

The range of applicability of the semi-empirical site binding models with respect to chemical variation is determined by the type and amount of experimental data collected. As an illustration of this modelling approach, Figures 4 and 5 show the values of uranium(VI) distribution coefficients for adsorption onto sediments collected from a shallow alluvial aquifer near Naturita, Colorado, as a function of uranium(VI) concentration, pH, and the partial pressure of carbon dioxide gas in equilibrium with the aqueous phase. These are the major aqueous chemical variables that influence the adsorption of uranium(VI) and its transport within the shallow aquifer. The Naturita site is the location of a former uranium mill in Colorado (USA), operated between 1947 to 1963, which contaminated the subsurface alluvial aquifer with uranium and vanadium. The major minerals composing the sediments are quartz, feldspars, and calcite. Figure 4 shows the distribution coefficients for uranium(VI) sorption on the < 3 mm grain size fraction of the aquifer sediments. Because of the presence of calcite, only one equilibrium pH value could be obtained for each partial pressure of carbon dioxide gas used in the experiments. Figure 5 shows the uranium(VI) distribution coefficients for the < 3 mm grain size fraction, after dissolution of the carbonate minerals in a sodium acetate solution held at pH 4.7. After dissolution of the calcite, it is possible to achieve a variation of pH for a single gas phase equilibrated with the aqueous phase.

Figure 4. **Distribution coefficients and semi-empirical model simulations for uranium(VI) adsorption onto the Naturita alluvial aquifer sediments. Experimental points are shown as symbols for various chemical conditions. Model simulations are shown as curves.**
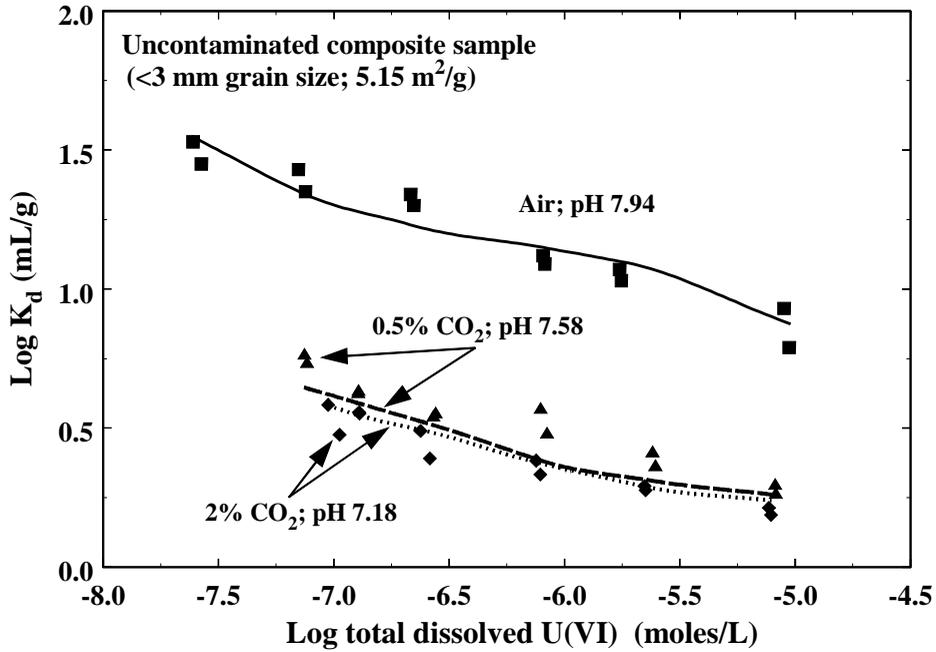

Figure 5. **Distribution coefficients and semi-empirical model simulations for uranium(VI) adsorption onto the Naturita alluvial aquifer sediments after dissolution of the carbonate minerals. Experimental points are shown as symbols for various chemical conditions. Model simulations are shown as curves.**
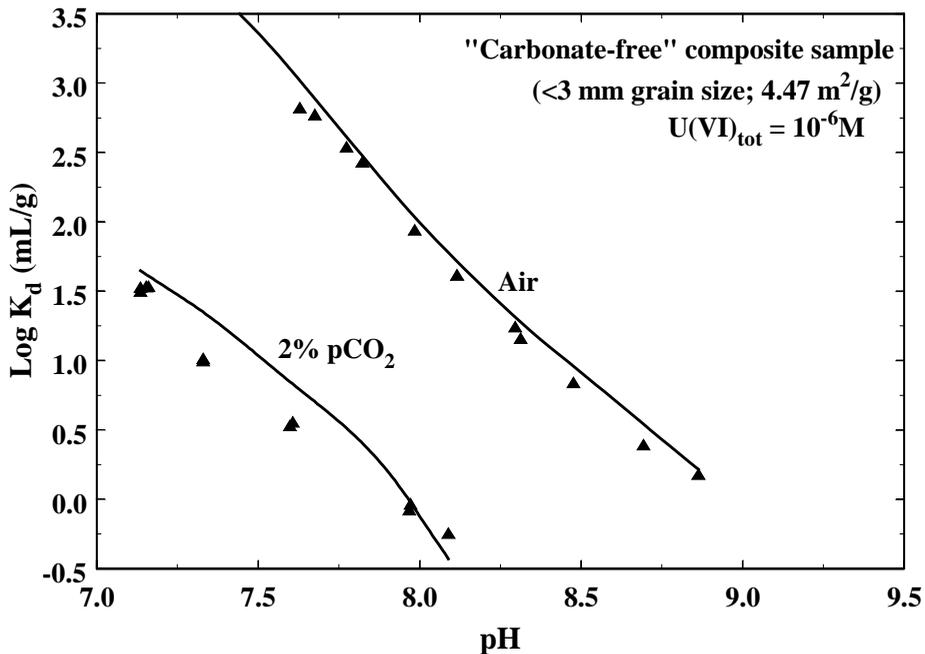
In the semi-empirical modelling approach, a minimum number of surface reactions is proposed to describe the adsorption data over the range of chemical conditions considered relevant to the modelling scenario [12,13,15]. If possible, the electrical double-layer terms are neglected to simplify the model. In Figures 4 and 5, the adsorption data are described by this approach with only two mass law equations and no electrical double-layer modifications to the binding constants:

$$K_{ads4} = (\equiv SO_2UO_2)(H^+)^2 / (UO_2^{2+})(\equiv S(OH)_2)$$
$$K_{ads5} = \frac{(\equiv SO_2UO_2HCO_3^-)(H^+)^3}{(UO_2^{2+})(H_2CO_3)(\equiv S(OH)_2)}$$

where $(\equiv S(OH)_2)$ represents the concentration of free generic surface sites. The solid curves in Figures 4 and 5 represent the model simulations.

Our current understanding and models for sorption as a retention process are well advanced at the molecular level, but our knowledge and the models become increasingly uncertain as the physical scale increases. The inherent heterogeneity of environmental systems makes application of the truly mechanistic adsorption models difficult at present, even at the microscale level [12, 15]. However, in the author's opinion, the current operational paradigm that employs constant distribution coefficients for individual radionuclides introduces more uncertainty than is necessary to our understanding of retention by sorption, at least for some radionuclides. It appears that the uncertainty could be reduced in the future with the use of the semi-empirical site-binding models [12, 13]. This would require a greater emphasis placed on site-specific characterisation of the natural mineral assemblages expected to be encountered along major flow paths away from nuclear repositories. Data collection for such studies could be focused on those radionuclides that are expected to be important contributors of dose in the far-field regime. From a practical point of view, the limiting factor in applying either type of modelling approach is the knowledge of the spatial and temporal variation in aqueous chemical conditions and mineral surfaces exposed along flow paths in PA scenarios.

Conclusions

1. Fundamental understanding of sorption processes and mechanistic modelling are well developed for clean mineral-water interfaces.

2. Fundamental understanding and modelling are improving for geologic media – technical problems exist due to coatings (organic and poorly crystalline precipitates) and the electrical double layer.

3. Using constant or a range of K_d modelling approaches can add to model uncertainty with respect to sorption. The importance of this uncertainty depends on the aqueous speciation of the radionuclides and the modelling scenarios.

4. Semi-empirical surface complexation modelling can reduce model uncertainty with respect to sorption. Alternatively, the models could be used in the PA process to support the evaluation and choice of technically defensible K_d values. This is a viable approach to link adsorption modelling with the NEA thermodynamic databases for aqueous speciation and mineral solubilities.

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Matrix Diffusion: Heavy-tailed Residence Time Distributions and Their Influence on Radionuclide Retention

Roy Haggerty

Department of Geosciences, Oregon State University, Corvallis, Oregon, USA

Matrix diffusion is frequently assumed to be both Fickian and effectively homogeneous over space- and time-scales relevant to radionuclide retention. However, evidence suggests that one or both of these assumptions may be invalid in some rocks and at some scales. Both non-Fickian diffusion and heterogeneous matrix properties may lead to heavy-tailed (i.e., power-law) residence time distributions for tracers and radionuclides. Under some scenarios, such behaviour may lead to non-conservative estimates of radionuclide retention in Performance Assessment.

Evidence for heterogeneous matrix properties includes geologic information about pore structure and matrix geometry, formation factor, and measurements of pore diffusivities. This variability may be compounded for sorbing solutes by heterogeneity in the distribution coefficient or kinetic rate coefficients. Evidence for non-Fickian diffusion is less well established, but includes depth-dependent pore diffusivities, fractal pore geometries in some rocks, and the likelihood that the matrix of some rocks may be very close to the percolation threshold at the pore-scale. Lab- and field-scale tracer tests have resulted in heavy-tailed breakthrough curves and have yielded estimates of characteristic retention times that scale with the duration of the experiment. These test results are consistent with the presence of either or both of heterogeneous matrix properties and/or non-Fickian diffusion. At the same time, there is evidence from electrical conductivity work and field diffusion studies that non-Fickian diffusion may be negligible at larger scales, so important questions remain.

There is little doubt that at the smallest scales, matrix diffusion is affected by both heterogeneity and some form of non-Fickian behaviour. Consequences on radionuclide retention largely depend on the spatial and temporal extent of these. If the scales extend beyond those measured in the lab and field, then the consequences may include one or more of the following. (1) A single pore diffusivity and block size will not be able to represent the diffusion process at all time- or space-scales. Lab/field values may need to be different than PA-scale values. (2) The effective diffusion rate coefficient used decreases with time- and space-scales. (3) The retention capacity of host rocks may be smaller than apparent in lab and field tests because all of the pore space is not accessible via diffusion over the PA-scale transport time. (4) Certain experimental designs and/or parameter estimation techniques may be particularly susceptible to non-conservative parameter estimates, and should be avoided.

Challenges to addressing heavy-tailed matrix residence times include lack of knowledge of pore geometry, pore connectivity, and matrix residence time distributions in many host rocks, difficulties with extremely long and expensive matrix diffusion experiments, and the ubiquitous issues of sparse data and uncertain parameters. Although models of heavy-tailed matrix residence times at the lab-scale (i.e., one-dimensional models with homogeneous parameters with respect to flow) are now available, incorporation of these effects into models that address flow and transport at the field

scale has not been achieved. Effort should be directed toward both the experimental and modelling challenges presented by heavy-tailed matrix residence time distributions.

1.   Introduction

Matrix diffusion is one of the primary retention mechanisms for radionuclides in existing and proposed geologic repositories. Since the pore volume of rock in which water is essentially immobile is typically many times larger than the fracture volume through which water is moving, the average rate of transport of conservative solutes is much lower than the rate of transport of water in the fractures [1]. Additionally, since most radionuclides are strongly sorbing, the net rate of transport is much slower than that of a conservative solute.

The properties of rock affecting matrix diffusion are commonly assumed effectively homogeneous in space. Matrix block size (a) is typically assumed to be uniform. Matrix tortuosity (τ) and constrictivity (δ_D) are assumed to be single-valued. Parameters characterising sorption (typically a distribution coefficient, K_d) are also commonly assumed single-valued. All of these properties are included within a single parameter group within solutions to the diffusion equation. This parameter group is (assuming for the moment that all pores are connected, thus ignoring dead-end pores):

$$\frac{D_a}{a^2} = \frac{D_w \delta_D}{\tau^2 a^2 \left(1 + \frac{\rho}{\varepsilon} K_d\right)}$$

Equation 1

where other variables represent apparent diffusivity (D_a); aqueous diffusivity (D_w); bulk density (ρ); and matrix porosity (ε). The pore geometry of the matrix is assumed to be well-connected and effectively Euclidian such that diffusion is Fickian. Note that for a non-sorbing species, $K_d = 0$ and the apparent diffusivity is equivalent to the pore diffusivity (D_p). For further discussion and explanation of diffusion terminology, see work by Ohlsson [2,3].

In this paper, we discuss cases where these assumptions may not be valid and what the consequences may be for modelling and Performance Assessment.

2.   Brief introduction to mathematics of heavy-tailed residence time distribution

The behaviour of a solute (tracer, radionuclide, or other pollutant) within the matrix may be characterised by its residence time distribution $g*(t)$. This is a probability density function (pdf), and is the probability that, given entrance to the matrix at time $t = 0$, a molecule will be released from the matrix at time t. The pdf is sometimes referred to as the probability of first return or distribution of first passage times [4]. In conventional matrix diffusion, the matrix residence time distribution is given by:

$$g*(t) = 2v \frac{D_a}{a^2} \sum_{j=1}^{\infty} \exp\left(-A_j \frac{D_a}{a^2} t\right)$$

Equation 2

where v and A_j are geometry-dependent coefficients [5, 6]. The only possible heavy-tailed residence time for conventional matrix diffusion is the case of an infinitely large matrix block, where:

$$g*(t) \sim \sqrt{\frac{D_a}{t}}$$

Equation 3

In this paper, we will examine more general cases where $g*(t)$ is defined by a power-law, i.e.:

$$g*(t) \sim t^{1-k}$$

Equation 4

where k is a positive number.

The relationship between the matrix residence time distribution and the behaviour of a concentration at late time given a pulse injection of linearly-sorbing or non-sorbing solute is a simple function [5]:

$$c = t_{ad} \beta_{tot} \frac{M}{Q} \frac{\partial g^*}{\partial t}$$

Equation 5

where c is the concentration; t_{ad} is the advection time between the injection and measurement points; M is the mass of the pulse injected into the stream-tube that is measured; Q is the flow rate of the water in which the solute is measured (e.g., the pumping rate of a well); and β_{tot} is the capacity coefficient, which is the ratio of the mass in the advecting water to mass in the matrix at equilibrium.

Three points need to be made about equation (5). First, it is valid when time is much greater than both t_{ad} and the length of the injection pulse and the mean residence time in the matrix is much greater than t_{ad}. If more than one streamline is sampled, it also assumes that the standard deviation of advection times (t_{ad}) along sampled streamlines is small compared to the mean residence time in the matrix. Second, equation (5) is insensitive to heterogeneity along streamlines provided that the residence time distribution and velocity fields are uncorrelated.

Third, equation (5), in conjunction with (4), indicates a key identification technique for matrix diffusion (either heavy-tailed or not), which is the measurement of late-time concentration breakthroughs from a tracer injection. They also suggest an important problem if matrix diffusion provides a heavy-tailed breakthrough curve: scale-dependent parameters.

3.   Sources of heavy-tailed behaviour in matrix diffusion

Broadly speaking, there are two sources of heavy-tailed behaviour in matrix diffusion. The first is a power-law distribution of D_a/a^2 (hereafter referred to as the diffusion rate coefficient) and the second is a fractal pore geometry. Both lead to heavy-tailed residence time distributions within the matrix, and we discuss both briefly. We also review a literature summary of evidence for heavy-tailed matrix diffusion.

3.1.   *Power-law distribution of D_a/a^2*

Over the time-scale of observations available, a power-law distribution of the diffusion rate coefficient (D_a/a^2) is practically indistinguishable from a distribution with a large variance. A uniform distribution, for example, is a power-law distribution. Consequently, we will consider arguments that suggest that the distribution of the diffusion rate coefficient is either large-variance, or truly power-law.

Block size is frequently large-variance or power-law. Turcotte [7] reviewed a number of cases where block size in fragmented media was found to vary as a power-law. Expressed as a pdf of block sizes, $p(a) \sim a^{3-2k}$, Turcotte found k ranging between 0.72 and 1.77 for different material. Such a distribution necessarily leads to a power-law residence time distribution (see Appendix). For example, a uniform distribution $p(a) \sim a^0$ yields $k = 3/2$. The residence time distribution in this material would be $g^*(t) \sim t^{-1/2}$ and a tracer test would have late time concentrations $c \sim t^{-3/2}$. This heavy-tailed behaviour would be maintained between times of a_{min}/D_a and a_{max}/D_a where a_{min} is the minimum block size and a_{max} is the maximum block size.

Data on the tortuosity and constrictivity suggest that these may vary over a narrower range than block size, and in most rocks may contribute less to overall variability in the diffusion rate coefficient. Fleming and Haggerty [8] noted a lognormal distribution of the formation factor (presumably due to variability in tortuosity and constrictivity) in the Culebra dolomite, with a log-standard deviation of 0.7. Data from electrical conductivity in crystalline rock (e.g., [3,9,10]) suggest

smaller variability in the formation factor. Measurements in sedimentary materials, once effects of non-linear sorption and diffusion into organic materials are factored out, suggest that the variability of tortuosity and constrictivity also vary over a moderate range [11] and are correlated to porosity. Since it is likely that tortuosity and constrictivity are uncorrelated to block size, they act to increase the overall variability in the diffusion rate coefficient.

3.2. *Anomalous diffusion*

The case of large (but "uniform") tortuosity deserves special mention. While the discussion above assumes the pore-space of a matrix block is well-connected, not all pores are necessarily well-connected to all other pores. (Fluid inclusions within minerals are an obvious example of this.) More importantly, some low-porosity rocks may achieve very large tortuosity. Archie's Law states that the tortuosity (ignoring effects of constrictivity) is inversely proportional to porosity [12]:

$$\tau^2 \sim \left(\varepsilon - \varepsilon_0\right)^m$$

Equation 6

where ε_0 is a percolation threshold. Such a relationship suggests that rocks close to the percolation threshold are likely to have extremely large tortuosities. In the limit as $\varepsilon \rightarrow \varepsilon_0$, the pores become increasingly isolated from each other (transport distances between pores becomes very large), tortuosity grows, and the pore space becomes a fractal. This is the case of a percolation network at the percolation threshold. Rocks chosen for geologic disposal may, by choice, be close to this threshold out of a desire to minimise permeability.

In cases where rocks are at the percolation threshold, the (Fickian) diffusion equation will not correctly model or predict diffusion, and the diffusion coefficient becomes dependent upon the time- and space-scale of measurement. Such diffusion has been termed "anomalous" (i.e., non-Fickian) [4,13]. Within such a geometrically complex or disordered pore-space, the apparent diffusivity can be shown to change in the following manner [14]:

$$D_a \sim t^{1 - 2/d_w}$$

Equation 7

where d_w is the walk dimension of the fractal. Diffusivities also scale with length. Similarly, it can be shown that [15] the residence time distribution in such an object is a power-law:

$$g*\left(t\right) \sim t^{d_s/2 - 1}$$

Equation 8

where d_s is the spectral dimension of the fractal. In a Euclidian geometry (i.e., conventional medium), $d_w = 2$, and D_a would be constant. However, in a three-dimensional percolation network (for example) near the percolation threshold, $d_w \approx 3.8$ and $d_s \approx 4/3$ [16]. Therefore measurements of D_a would change approximately as $t^{-1/2}$, residence time scales as $t^{-1/3}$. Interestingly, the residence time distribution is close enough to the behaviour of an infinite matrix block, that the two behaviours could be mistaken for each other, but have different implications for Performance Assessment.

Anomalous diffusion is clearly present in crystalline rocks over very short length-scales micrometers to millimetres). The pore diffusivity within a single pore ($< \mu m$) is equal to the aqueous diffusivity. However, over scales of mm and larger, the pore diffusivity is reduced by factors of between 5 and 300. Over these length scales (and the corresponding time-scales), the pore and apparent diffusivity will scale in a fashion similar to equation (7). At larger scales (millimetres to centimetres), there is a modest amount of evidence that diffusion is anomalous. Three studies in Fenno-Scandian granitic rocks [17-19] have found diffusivities that decrease with the length-scale of measurement, an observation that is consistent with anomalous diffusion. (Note, however, that these studies found exponential decreases with length scale, whereas diffusion in fractal media would have a power-law decrease.) Work using electrical conductivity [3] suggests that diffusivity may decrease

over a few centimetres, but then stabilises to a constant value (within constraints imposed by heterogeneity). Probably the strongest evidence against anomalous diffusion to date in crystalline rock is from the field experiments in the Stripa mine [20], where migration by diffusion extended in some cases as much as 400 mm. However, this penetration was non-uniform, and it is possible that such penetration could occur in a non-Fickian manner. An open question, therefore, is whether anomalous diffusion is truly present at intermediate scales (centimetres) and if so, whether it continues at larger scales (tens of centimetres to metres). Research remains to be done on this topic.

A set of example breakthrough curves is shown in Figure 1 for the case of anomalous diffusion. The matrix residence time distribution is as shown in Equation 8, with $d_s = 4/3$. For a pulse injection of solute, this yields a breakthrough curve with late-time concentrations scaling as $t^{-1.33}$.

Figure 1. **Breakthrough curves for pulse injection of solute into medium with anomalous diffusion and resultant matrix residence time distribution scaling as a power-law. Vertical axis is normalised by 0th moment of injection (i.e., M/Q) and advection time (L/v) so that power-law scaling of the breakthrough curve is most easily seen.**
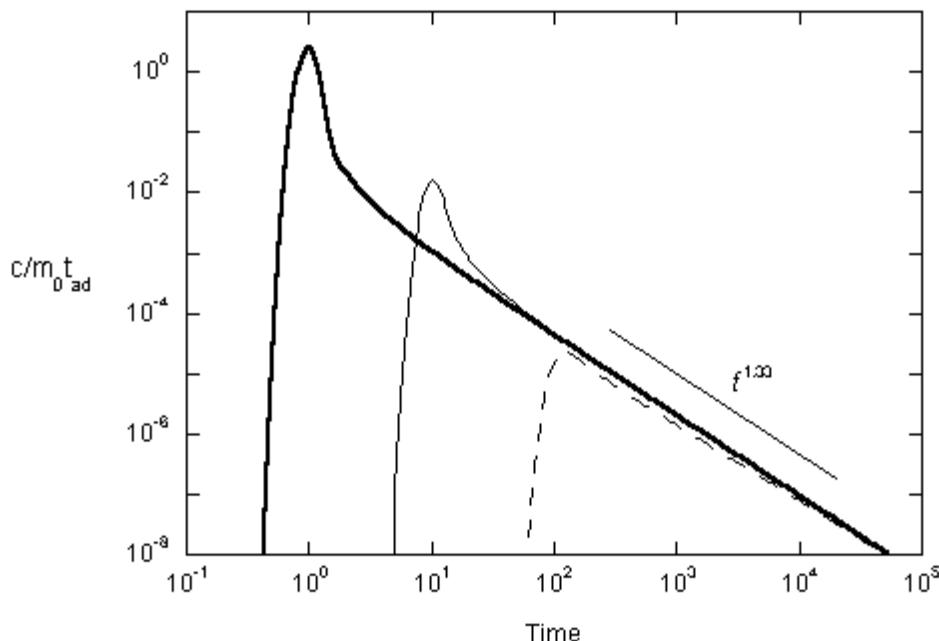
3.3. *Literature survey of scale effects in matrix diffusion*

One of the primary effects of heavy tails in matrix diffusion will be scale-dependent estimates of mean residence time if the method of estimation does not account for the heavy tails correctly. Due to the type of scaling discussed in the sections above, experimental estimates of matrix diffusion (as well as granular diffusion in porous media) that assume that diffusion is described by a single diffusion rate coefficient will be dependent upon the time-scale of observation. To examine the issue of time-dependence, we compiled a number of studies where the mean residence time in the matrix or immobile domain were estimated from batch, column, and field tracer tests. In all cases the models used either diffusion into uniform matrix blocks or a linear driving force model (i.e., first-order approximation). We

calculated the mean residence time from the parameters given in each paper (e.g., $a^2/15D_a$ in the case of diffusion into spheres, $a^2/3D_a$ for diffusion into layers, etc.) The results are displayed in Figure 1. The mean residence time is plotted on the vertical axis, and the duration of the experiment on the horizontal axis. Data from 130 experiments are shown. We see that, in general, large rate mean residence times, which represent small estimates of D_a/a^2, are estimated from long experiments, and vice versa. A longer-duration experiment in the same medium is likely to experience apparently slower matrix diffusion, while a shorter-duration experiment is likely to experience apparently faster matrix diffusion. Using a conventional matrix diffusion model to produce an accurate prediction of solute transport for any time-scale other than that of the original experiment, we must know what apparent rate of matrix diffusion will dominate at the time-scale of our prediction.

4. Data needs and other challenges

Challenges to addressing heavy-tailed matrix residence times include lack of knowledge of pore geometry, pore connectivity, and matrix residence time distributions in many host rocks, slow and expensive matrix diffusion experiments, and the ubiquitous issues of sparse data and uncertain parameters. Although models of heavy-tailed matrix residence times at the lab-scale (i.e., one-dimensional models with homogeneous parameters with respect to flow) are now available, incorporation of these effects into models that address flow and transport at the field scale has not been achieved. Effort should be directed toward both the experimental and modelling challenges presented by heavy-tailed matrix residence time distributions.

Research is needed to investigate the geometry and connectivity of pores, particularly within crystalline rock. Due to the small size of these pores and the fact that fluid movement in low-permeability rocks has been of little economic value, very little is known about the pore geometry of low-permeability rocks. Advances in imaging technology, supported by high-end computational techniques could and should be coupled with pore-scale modelling to understand diffusion at the microscopic to mesoscopic scale, particularly in crystalline rocks.

New techniques to investigate diffusion at larger time- and spatial-scales need to be developed. The use of late-time/low-concentration breakthroughs in conventional tracer methods should allow us to better understand the matrix residence time distribution. Diffusion of gas within large, unsaturated samples may allow us to overcome the inherently slow rate of aqueous diffusion, and should be further exploited. Where existing outcrops have known geochemical histories (e.g., salinity changes, trace element changes, etc.) in the recent and geologic past, samples should be taken to measure and map concentration, allowing us to overcome some of the difficulties associated with slow rates of diffusion. Geophysical techniques, particularly those analogous to diffusion, should be further developed to understand diffusion over longer time- and spatial scales.

5. Consequences for performance assessment and conclusions

There is little doubt that at the smallest scales, matrix diffusion is affected by both heterogeneity leading, in some cases, to large-variance distributions of diffusion rate coefficients. Some form of non-Fickian behaviour is also well-established at very small spatial scales. Consequences on radionuclide retention largely depend on the spatial and temporal extent of these. If the scales extend beyond those measured in the lab and field (to date), then the consequences may include one or more of the following.

First, a single pore diffusivity and matrix block size will not be able to represent the diffusion process at all time- or space-scales. As shown in Figure 2, the estimated mean matrix residence time scales over several orders of magnitude and appears to be dependent upon experimental observation

time. If similar behaviour continues at larger scales, then conventional models (single diffusivity, single block size) require scale-dependent parameters to correctly predict breakthrough response. The inappropriate use of small-scale parameters for large-scale prediction could result in over-prediction of waste retention and therefore non-conservative Performance Assessment calculations.

Second, (and more specifically) the scale-dependent diffusion rate coefficient used decreases with time- and space-scales. Figure 2 shows that the estimated mean matrix residence time increases with experimental observation time. This is caused by the effective (scale-dependent) value of D_a/a^2 decreasing with time-scale of observation. This has the potential to cause overly-large values of D_a/a^2 to be ascribed within Performance Assessment calculations. The consequence of this is a potential underprediction of the release of radionuclides to the accessible environment.

Third, the retention capacity of host rocks may be smaller than apparent in lab and field tests because all of the pore space is not accessible via diffusion over the PA-scale transport time. Some host rock is likely to be accessible by diffusion relatively quickly, while other host-rock is likely to be accessible by diffusion over much longer time-scales. This is due not only to distance from a fracture, which conventional models include, but also variability in matrix block size, pore-connectivity/tortuosity, and constrictivity. Short-term experiments, however, may be biased towards identification of the most quickly accessible host rock. The risk for Performance Assessment is that the (correct) parameters for the quickly accessible rock are incorrectly ascribed to the entire host rock. In effect, this results in an over-estimation of the volume of host rock available to retain waste via diffusion and sorption.

Figure 2. **Means of matrix residence time distribution vs. time-scale of experiments from which they were measured. Data include sorbing and non-sorbing tracers, lab- and field-scale tests.**
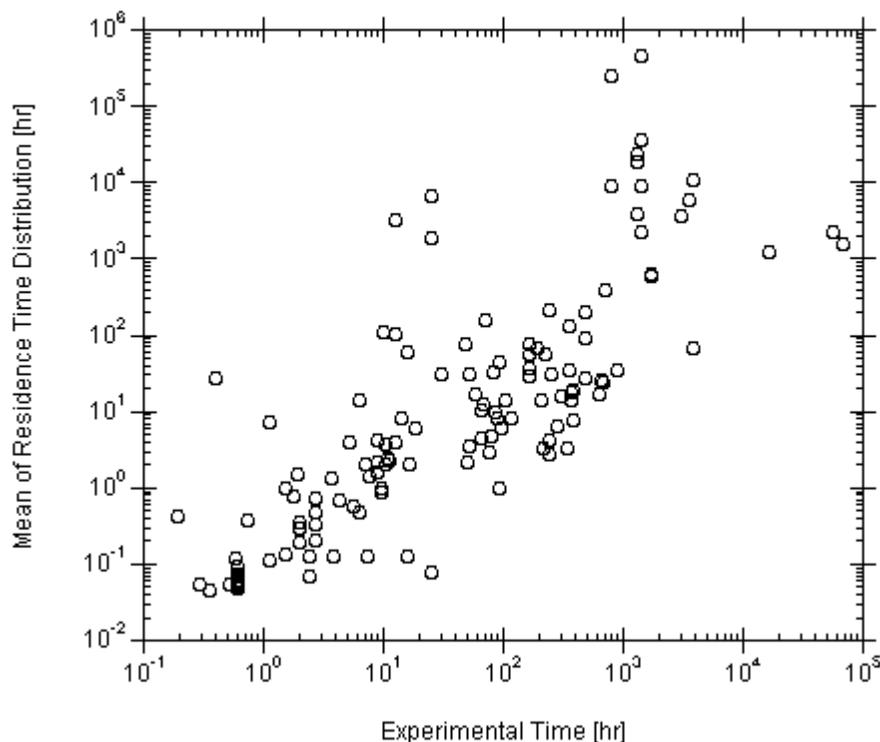
Fourth, certain experimental designs and/or parameter estimation techniques may be particularly susceptible to non-conservative parameter estimates, and should be avoided. The "worst-case" (non-conservative) scenario for Performance Assessment is to ascribe matrix block sizes that are too small or pore diffusivities that are too large to the entire medium. Such a worst case scenario could happen if parameter estimates are determined primarily from small-scale short-term tracer experiments. Problems with small-scale tracer tests may be compounded by the use of single, uniform values of matrix diffusion parameters and by not collecting or adequately using late-time/low-concentration data. In particular, estimates of pore diffusivity and matrix block size must be obtained via different methods than relative volumes of matrix and fracture. All parameters should be supported independently and by non-tracer test data. When tracer tests are performed, care must be taken to collect high-accuracy data from the tails of breakthroughs and to fully use these data within models.

Appendix

In this appendix we derive the relationship between a power-law distribution of matrix block sizes and a power-law residence time distribution.

The residence time distribution for a single spherical matrix block is given by:

$$g*(t) = 6\frac{D_a}{a^2} \sum_{j=1}^{\infty} \exp\left(-\pi^2 j^2 \frac{D_a}{a^2} t\right) \qquad \text{Equation A1}$$

Note a simple way of deriving Equation A1 is that $g*(t)$ is the derivative of the mass uptake at time t divided by the mass uptake at $t \rightarrow \infty$ given a constant boundary concentration. Also note that the choice of spherical grains is not important, but only gives a specific example to work with. The expression for such mass uptake is given by several authors [21,22]. By superposition, the residence time distribution for a distribution of spherical blocks is:

$$g*(t) = 6\frac{D_a}{a^2} \int_0^{\infty} p(a) \sum_{j=1}^{\infty} \exp\left(-\pi^2 j^2 \frac{D_a}{a^2} t\right) da \qquad \text{Equation A2}$$

Let the distribution of block sizes be a power-law:

$$p(a) = B\, a^{3-2k}, \quad a_{min} < a < a_{max} \qquad \text{Equation A3}$$

where B is a constant (units $L^{2(k-2)}$) determined by the requirement that $p(a)$ integrates to 1 and the values of a_{min} and a_{max}. Also, let us make the variable change $\alpha = D_a/a^2$. Incorporating these into Equation A2 we get:

$$g*(t) = 6BD_a^{2-k} \sum_{j=1}^{\infty} \int_b^c \alpha^{k-2} \exp\left(-\pi^2 j^2 \alpha t\right) d\alpha \qquad \text{Equation A4}$$

where $b = D_a/a_{max}$ and $c = D_a/a_{min}$.

In general, Equation A4 must be evaluated numerically. However, our purpose here is simply to show the relationship between the power-law block-size distribution in Equation A3 and a power-law residence time distribution in Equation A4. Consequently, we summarise the behaviour of Equation A4 as follows:

$$g*(t) \sim t^{1-k}, \quad c^{-1} < t < b^{-1} \qquad \text{Equation A5}$$

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The Role of Colloids in Radionuclide Retention by and Transport Through Geologic Media

Bruce D. Honeyman
Colorado School of Mines, Golden, Colorado, USA

1.   Introduction: Colloids and the "Colloid Problem"

The idea that colloidal forms of contaminants may exhibit enhanced transport through geologic media, relative to dissolved forms, has been the subject of much concern and debate for the last fifteen or so years. While many details of colloid-facilitated contaminant transport need to be resolved, several principles of the phenomena can be outlined (modified from Kretzschmar *et al.* [1]):

1. Colloids must be able to compete effectively against immobile-phase solids for the contaminant.

2. Colloids must be transported over substantial distances (i.e., slow deposition rates).

3. Because transport by colloids will be limited, the contaminant must have adverse health effects at low concentrations/activities.

Point 1 has two sub-principles:

a. Colloids must be present in sufficient concentrations; and,

b. The contaminant must strongly sorb to, and slowly desorb from, colloids.

The following sections describe some of the attributes of Points 1 and 2, above. Point 3 is not considered here.

2.   Colloid-/immobile-phase competition

Figure 1 is a schematic illustration of the interactions relevant to point 1, above. At its simplest, and for illustration here, systems of interest consist of three phases: an immobile phase consisting of soil or aquifer materials, a dissolved phase, and the colloid phase. Most evidence suggests that the chemical nature of the colloids and the immobile phases is similar, e.g., [2], at least for most natural systems. Similarity of colloids and immobile-phase sorptive properties in a three-phase system I define as a *symmetrical* system. It is likely, though, that processes occurring in a waste repository (e.g., corrosion of waste containers) will result in the generation of colloids with physico-chemical properties markedly different from those of the immobile phase. Such a system is accordingly an *asymmetrical* system.

Figure 2 compares radionuclide partitioning to colloids in hypothetical symmetrical (2a) and asymmetrical (2b) systems. The geometric characteristics of the two systems are identical; only the chemical identity of the immobile phase (IP) is different in the examples. The radionuclide/colloid partitioning parameter is dimensioned in terms of reciprocal area concentration [4] (e.g., L m^{-2}). In the case of the asymmetrical system, ferrinol sites are considered to be better complexants for the metals

Figure 1. **Schematic illustration of the interactions relevant for Point 1 of the Principles of colloid facilitated contaminant transport. The small spheres represent a target radionuclide and the large sphere is a colloid. Subscripts *f* and *r* designate forward and reverse rate constants, respectively.**
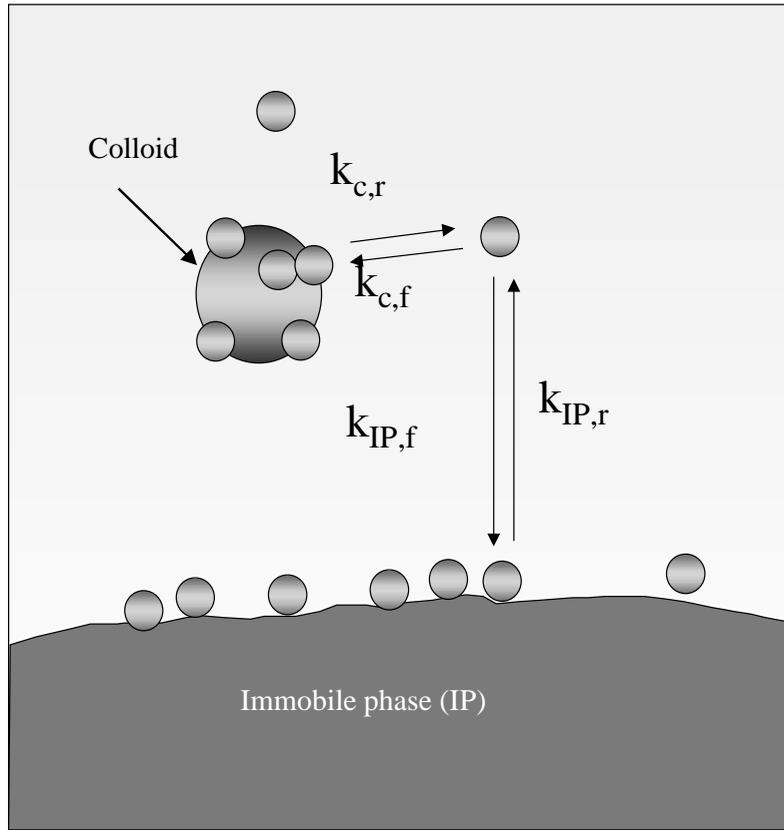
Figure 2. **Hypothetical partitioning [3] of selected metals between a stationary aquifer phase (porosity = 0.4, particle size = 0.3 mm, surface area 30 m^2 m^{-3}) and a colloid phase (17 m^2 g^{-1}, colloid diameter = 70 nm). *a*). The site types for both the immobile- and colloid-phase surfaces are ferrinol. For this example, the partitioning coefficient (K: m^2 L^{-1}) is written as normalised to surface area rather than mass. *b*) Ferrinol colloid sites; silanol IP sites.**
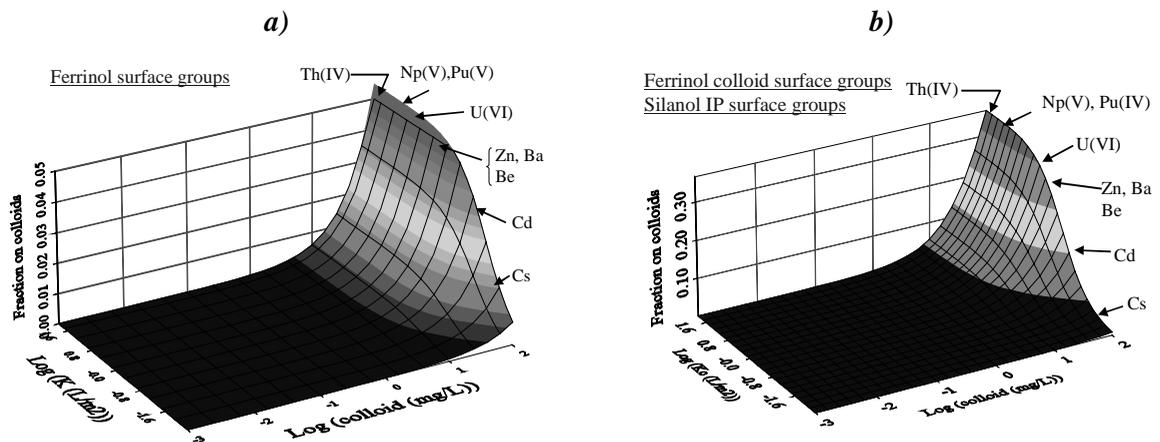
ion than are silanol sites. As a consequence, Figure 2b shows enhanced partitioning of the metal ions to the colloidal phase than in the symmetrical case (Figure 2a).

The analysis presented above is based on a simple mass balance for metal-ion partitioning in a three-phase system:

$$M_T = [M_c] + [M_{IP}] + [M_d] \qquad \text{Equation 1}$$

$$f_c = \frac{[M_c]}{[M_c] + [M_{IP}] + [M_d]} = \frac{K_c S_c}{1 + K_c S_c + K_{IP} S_{IP}} \qquad \text{Equation 2}$$

where f_c is the fraction of M (the target metal ion) associated with the colloid phase. K_c and K_{IP} are metal-ion partitioning coefficients ($dm^3\ m^{-2}$) and S is surface area concentration ($m^2\ dm^{-3}$). If, for a given surface type, K_c and K_{IP} are not dependent on system geometry, then the f_c will depend on the ratio of S_c to S_{IP}. For many systems, the crucial factor in determining the amount of M associated with colloids is the colloid concentration (Point 1a).

The refinement of colloid sampling techniques in recent years has yielded a number of accurate estimates of colloid concentrations in a range of systems (e.g., [5]). There is enormous variation in colloid concentrations between systems. While most systems of interest for radioactive waste disposal exhibit relatively low colloid concentrations (i.e., less than 10 mg L^{-1}), concentrations exceeding 100 mg L^{-1} are not uncommonly reported [6]. Of course, the important aspect of colloid concentration is not simply its absolute value but its value relative to immobile-phase sites. In their analysis of the importance of colloids to repository performance assessment, Contardi *et al.* [7] derived immobile phase/colloid surface area ratios ranging from 63 to 3.2×10^4 using the data of Kingston and Whitbeck [6]. However, when the strongest sorbing radionuclides are considered (e.g., Am(III)), the effect of colloids on radionuclide transport is maximised even at colloid concentrations as low as 1 mg L^{-1} or less.

This latter observation brings us back to the issue of the chemical identity and characteristics of the sorbing phases. While there is some evidence that mineral surfaces as a group behave relatively similarly when sorption data are normalised to specific site concentration or surface area [4], the extent to which such observations can be generalised to include surfaces that are not those of inorganic minerals. Data from the field suggest that in most cases colloids are derived from the existing IP materials and limited evidence suggests that the chemical heterogeneity of IP and colloidal materials is similar [5,8]. Indeed, the systems likely to be of greatest concern for colloid-facilitated radionuclide transport, or retention for that matter, are systems for which the colloid phase is of a different chemical character than the immobile phase, i.e., asymmetrical systems. Figure 3 is a comparison of the U(VI) sorptive behavior of three surface "archetypes": a Gram-negative bacteria (*Desulfovibrio vulgaris*), a natural organic matter (NOM): Suwannee River humic acid and a colloidal metal oxide: hematite (α-Fe_2O_3). Sorption data are normalised to surface sites. Note that: 1) the surfaces dominate the sorption of U(VI) at different pH values and 2) the surfaces are markedly different in their ability to sorb U(VI). Because the relative ability of a surface to compete against other sorbents for a radionuclide is a function of the product of the interaction parameter (e.g., P or K_c) and the site concentration (e.g., Equation 2), Figure 3 suggests, for example, that *Desulfovibrio vulgaris* could be an effective colloidal transport agent at substantially lower concentrations than in the cases of the NOM and hematite.

A final point with respect to the competition issue is desorption kinetics. Thus far, this discussion has focused on colloid/IP competition under equilibrium conditions. However, the effect of colloidal species on radionuclide transport can be enhanced if the desorption of the radionuclide from the colloid is kinetically slow. This aspect of colloid-facilitated contaminant transport has been explored in several papers; the simulation results shown in Figure 4 are characteristic of computational results found in the literature.

Figure 3. **Comparison of U(VI) binding to three surface types, as a function of pH. I = 0.01 M.**
Relative sorption intensity is expressed in terms of partitioning coefficient
in which the data are normalised to site concentration. *Desulfovibrio vulgaris:*
a Gram negative bacteria in a resting stage (from Landkamer *et al.,* unpublished);
Suwannee River humic acid (data from [9]); hematite [data from 10].
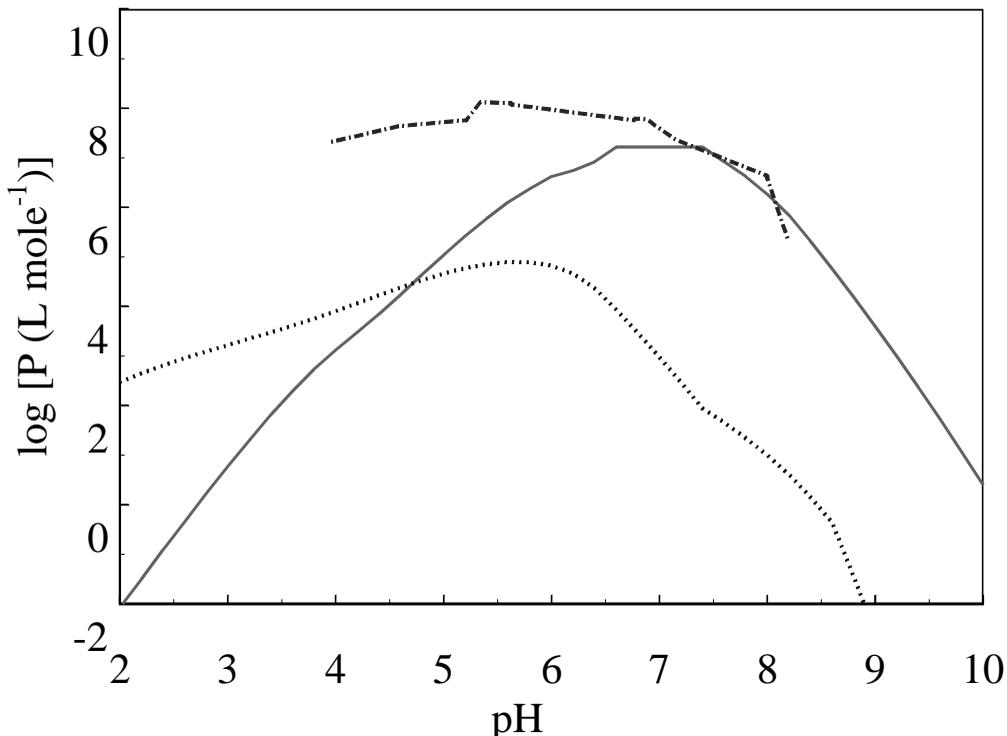
Figure 4. **Evaluation of the effect of local equilibrium and kinetic formulations**
on colloid-facilitated 1-D contaminant transport in porous media [11].
The *y*-axis is the relative total mobile contaminant concentration at the outlet
of the mathematical column. "LEA" is the local equilibrium assumption and
K_{sm} **is the first-order release rate for the contaminant from the colloids.**

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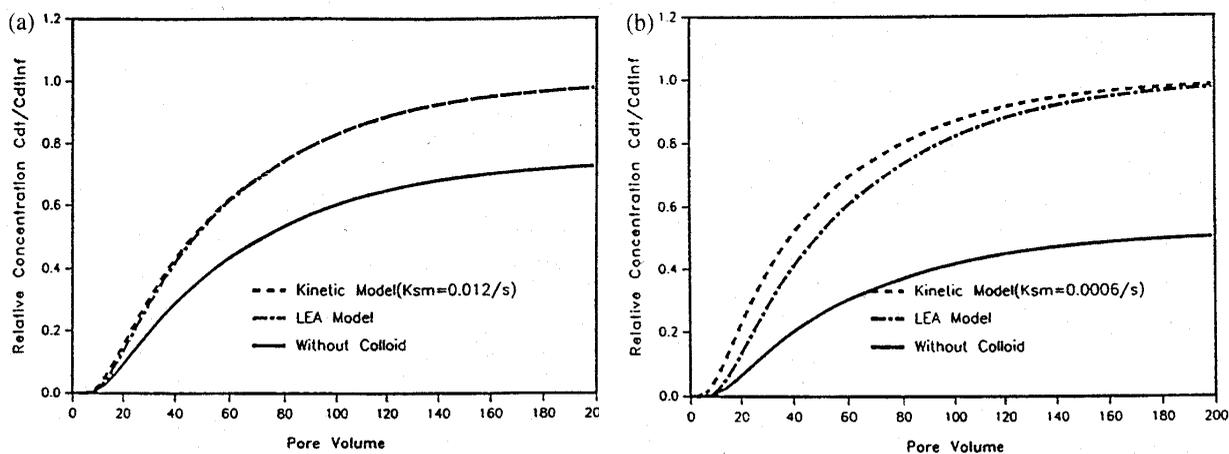
The simulation results of Figure 4 [11] show that, for this case, the presence of colloids enhances contaminant transport relative to the colloid-free case. If K_{sm}, the first-order rate constant for the desorption of the contaminant from the mobile colloids, is relatively large in value, the simulation results for the local equilibrium assumption (LEA) case and the kinetic case are the same. However, if the rate of desorption of the contaminant is relatively slow (in these cases 0.012 s^{-1} *v.* 0.0005 s^{-1}), desorption kinetics has the effect of enhancing colloid-facilitated contaminant transport.

3.   Colloid generation, deposition, and transport

Several excellent reviews on colloid generation, deposition and transport are available in the literature (e.g., [1,12]. Most studies of colloid behavior have focused on inorganic colloids, although organic macromolecules and biocolloids have been studied to a limited extent.

Inorganic colloids are generated by two primary mechanisms: 1) *in situ* precipitation and 2) the mobilisation of existing colloids. As pointed out by Ryan and Elimelech [12], the precipitation mechanism is relatively uncommon for natural systems, although it may be a dominant process in the near-field of waste repositories where gradients in pH and Eh may be expected. In addition, bacteria may under certain circumstances produce inorganic colloids as in the reductive precipitation of U(VI) to U(IV) by some sulphate-reducing bacteria (e.g., [13]). Under constant physical and chemical conditions, the release rates of existing inorganic colloids are relatively small. Unlike the case for colloid deposition, where theory is relatively well developed, models for the release of inorganic colloids are few. In general, inorganic colloids are released through DLVO effects; colloid release is regulated by system conditions that affect mineral surface charge (pH, ionic strength, the specific sorption of solutes). Colloids may also be generated through chemical processes that destroy cementing agents [14] or through hydrodynamic effects such as shear brought on by rapid pumping.

Biocolloid release is also be regulated by DLVO type interactions or through non-electrostatic mechanisms (hydrophobic bonding in the case of viruses). Bacteria can attach to immobile surfaces through excreted biopolymers (e.g., Extended DLVO theory); subsequent destruction of the biopolymers can result in bacterial release. Bacteria may also produce organic macromolecules, such as acid polysaccharides, which are strong complexants for actinides [15]. Such molecules may themselves attach to immobile surfaces thereby retarding associated radionuclides or, under other system conditions, act to facilitate radionuclide transport.

By far, the greatest amount of theoretical and experimental work on colloid attachment or deposition has as its roots DLVO theory, e.g., [1,12] and references therein. Filtration theory [e.g., [16]) which is usually expressed in terms of a single collector (i.e., the immobile phase) efficiency works well for systems with well-defined geometry and in which repulsive double layer interactions are absent, that is, for fast deposition. Although filtration theory quickly evolved to include DLVO type interactions (i.e., repulsive forces and slow deposition), large discrepancies between experimental results and theory typically arise if double-layer interactions are required (e.g., [17]). As a consequence, predicting colloid deposition in response to changes in ionic strength, pH (for surfaces where the proton is a potential-determining ion) or other surface-charge regulating processes is problematic with filtration theory as typically applied.

An additional problem with applying models of colloid deposition to the field is the inherent heterogeneity of systems of interest. Although there are a number of aspects to the heterogeneity problem as it applies to colloid transport, recent advances in understanding the role of geochemical heterogeneity in colloid deposition and release suggest a promising avenue for understanding and predicting colloid transport in real systems (e.g., [18]).

Figure 5 [19] illustrates one part of the "dynamic" heterogeneity problem: deposition site blockage by deposited colloids. In this example (5a), natural soil colloids are injected until breakthrough occurs. Water is injected and no colloids are released. A second pulse of injected colloids is eluted coincident with a conservative tracer suggesting that sites for colloid deposition are already occupied. A lower concentration of injected colloids (5b) results in a slower rate of breakthrough as it takes longer in the experimental runs with a lower colloid concentration for the colloids to occupy favourable colloid deposition sites.

The deposition of colloids onto immobile-phase sites favourable to the deposition of colloids, and the eventual filling up of those sites by the deposited colloids, will, in principle, result in the eventual fostering of colloid facilitated contaminant transport. Dynamic blocking functions have been developed to account for the decrease in deposition rate with increasing fractional coverage of favourable deposition sites by colloids [20].

Figure 5. **Experimental evidence of colloid deposition site blocking, from Kretzchmar *et al.* [19]. The data are for the transport of natural soil colloids through undisturbed saprolite columns.**
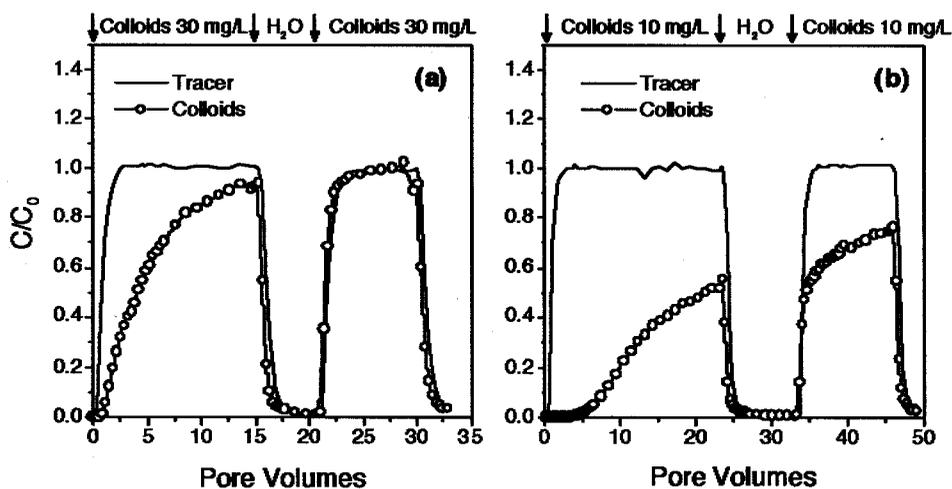
Collector surfaces in real systems contain a mixture of favourable and unfavourable sites for colloid deposition. Which category a site falls into depends on the nature of the colloid. For example, iron oxide colloids would likely be favourably deposited onto negatively charged immobile-phase surfaces such as quartz (i.e., under circumneutral pH conditions). While geochemical heterogeneity has been identified as an important parameter for predicting colloid deposition, evaluating heterogeneity is more elusive. Relatively few studies exist in which the nature of sorbent (for adsorption) or collector (for colloid deposition) has been systematically ascertained. Indeed, a framework for characterising collector heterogeneity has yet to be thoroughly developed. For example, suggestions are that the extent of heterogeneity is relatively narrow (a few percent? [21]). However, the nature of the distribution of the heterogeneity (regularly-distributed or random) appears to be as important as extent of the heterogeneity, itself. Furthermore, it appears that techniques such as measuring the average ζ (zeta) potential of a collector leads to problems with theoretical predictions of colloid deposition [22].

3.1 Organic colloids

Although the existence of natural organic matter (NOM) colloids in soil and groundwaters has been recognised for many decades, the role of NOM in contaminant transport has been relatively under-studied compared to mineral colloids. To a certain extent, the de-emphasis of NOM on

contaminant transport is due to a general belief that NOM acts to enhance metal-ion binding to mineral surfaces. However, emerging evidence indicates that NOM, in many instances, may be an effective means of transporting metal ion and radionuclides through subsurface systems [23], not only through the direct transport of metal ions in the form of metal-ion/NOM complexes (e.g., [24,25]; Figure 6) but also indirectly through the ability of NOM to stabilise inorganic colloids with respect to deposition [5,26]. Additionally, recent data [27] indicate that fulvic acid may remain stable in solution for thousands of years.

Figure 6. Elution of Np(V) from a granite column in the presence and absence of humic material [25]. URL = Underground Research Laboratory of AECL. The addition of humic substances results in the enhanced transport of Np(V) relative to the humic-substances-free case. Note, also, the effect of humic acid type on transport results.
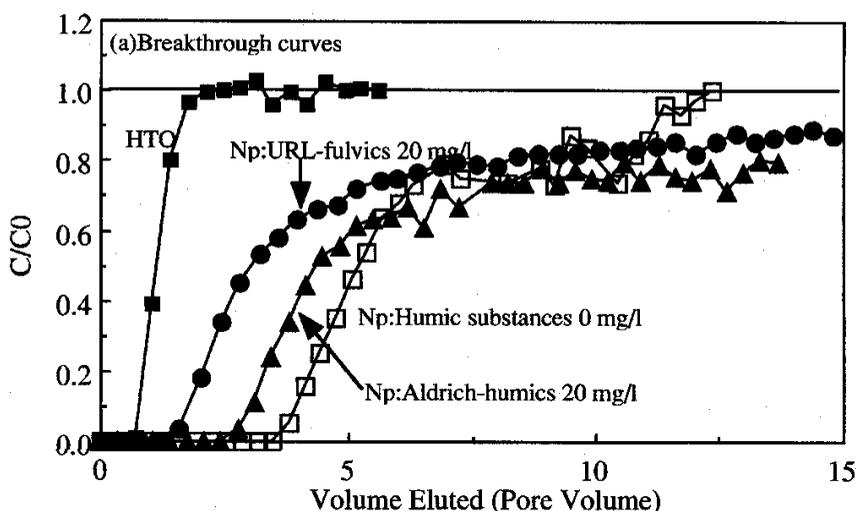
4.   Summary

Most systems of interest as sites for nuclear waste repositories will be "symmetrical", at least in the far field. Near-field systems are likely to become "asymmetrical" with time. Colloid-facilitated radionuclide transport in symmetrical systems will likely be minimal. The current uncertainty over the importance of colloid-facilitated radionuclide transport is associated with a substantial lack of knowledge of system heterogeneity.

4.1   Research needs

- Evaluation of colloid-facilitated radionuclide under field conditions:
  - More data sets are needed for developing and testing models.
  - Methodologies are needed for upscaling.
  - Potentially asymmetrical systems need to be identified.

- Greater understanding of the influence of chemical and physical heterogeneity on colloid-facilitated radionuclide transport (with particular emphasis on the immobile phase).

- Greater understanding of the role of minor components and kinetics on the sorption of radionuclides by colloidal- and immobile-phase materials.

- A greater emphasis needs to be placed on organic- and bio-colloids.

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Immobilisation: Molecular Scale Observations of Processes Relevant to Attenuation of Radioactive Contaminants

Susan L.S. Stipp

Interface Geochemistry, Geological Institute, Copenhagen University, Denmark

Abstract

Currently, performance assessment (PA) modelling for nuclear waste repositories relies heavily on the K_d approach which empirically averages contaminant retardation over a range of conditions in the hope that uncertainties are treated conservatively. Mechanistic approaches are rare or non-existent, often because of lack of information. However, recently developed high-resolution, surface analytical techniques offer direct observation at nanometre scale, meaning we are now able to observe molecular-level processes and describe them conceptually. This information could be incorporated to make PA models more realistic by considering processes that immobilise (on relevant time-scales) rather than simply retard contaminants. Processes responsible for contaminant uptake include adsorption, co-precipitation, and the formation of solid solution. Release processes include desorption and dissolution. Exsolution of components of a solid solution and transformation of a mineral to a more stable phase can make previously incorporated contaminants more available for release again. Immobilisation occurs when the rates of the release processes are negligible compared to the rates of the uptake processes.

High-resolution techniques show that: dynamic equilibrium constantly rearranges material, allowing incorporation of trace components by reprecipitation even on dry surfaces; a contaminant can adsorb to a surface that is actively dissolving; co-precipitated compounds can be liberated during mineral transformation; trace components can hide in colloidal-size particles or as thin coatings that are impossible to detect with classical methods; and material adsorbed at surfaces can diffuse into the bulk where it is less available for release and the rate of movement depends on the defect density of the solid. Examples for illustration were chosen from the work of our group on the Fe-(oxy)hydroxide and Ca-carbonate systems because of the common occurrence of these minerals in the environment and because of their ability to take up radioactive components.

1.   Introduction

For handling radioactive waste, an attractive possibility would be to immobilise it in a form that is stable forever. The question is, however, "What is forever?" Immobilisation implies permanence but the degree of immobility depends on the time-scale upon which we look. Would it be safely locked away for 100 years? 1 000? 1 million? Over geological time-scales, nothing is permanent. All materials, geological and man-made, are eventually broken down by physical, chemical, and biological weathering processes, given the right conditions of temperature, pressure, solution composition, and enough time. However, some locations are better hiding places for dangerous components than others. Some minerals are more resistant to remobilisation processes and in general, storage within the bulk of a mineral is more effective than sorption at surfaces where desorption is possible. The purpose of this paper is to describe some of the chemical processes responsible for uptake and release, to provide mechanistic evidence from high-resolution analytical techniques, and to discuss the relative potential impact of these processes on immobilisation for radioactive components over periods of relevance for performance assessment.

Faced with the challenge of predicting the behaviour of radionuclides, one can choose between several modelling strategies. Grouped by common advantages and limitations, one can choose between the empirical, thermodynamic, or mechanistic approach for simulating experimental results and for predicting contaminant transport. Empirical models, such as the K_d approach, can be used to extend from experimental observations of specific samples or conditions, but problems of scaling from lab to field and the assumptions required about homogeneity over long distances, as well as constant chemical conditions over long times, are serious limitations. Thermodynamic models can describe major phase composition and behaviour quite well, but for trace components, they are inadequate. In part, our inability to describe the behaviour of trace components results from lack of data for their uptake within major phases as solid solution. Moreover, one of the most cited limitations of thermodynamic models is our inability to account for kinetic control during the approach to equilibrium. A mechanistic approach is more realistic but also more complicated. It absolutely requires a correct conceptual model of molecular-scale behaviour and a great deal of data. For most geochemical systems, these are not yet available and, unfortunately, such fundamental scientific studies are not generally popular when research funding is distributed.

If our aim is, however, to develop mechanistic models, thorough understanding of the basic geochemical processes is essential. We cannot model them if we cannot demonstrate how the atoms behave at a local scale. Furthermore, without understanding at the molecular level, we cannot make simplifying assumptions about the relative importance of the various processes. This is necessary for building performance assessment models that are as realistic as possible while still being of a size and complexity that are manageable. We absolutely require enough information about some specific systems so that we can use them as a base for making generalisations for other fluid/solid combinations, especially for those that are impossible to experiment upon, and for determining the relative importance of competing processes.

Uptake from solution to a solid surface begins by adsorption and, depending on the properties of the solid and the composition of the solution, an adsorbed ion can become part of the bulk either during co-precipitation of a new phase from a supersaturated solution or during the recrystallisation process that all crystal surfaces undergo (dynamic equilibrium, Figure 1). In either of these cases, a contaminant can sit in a regular position in the atomic structure, often substituting for an ion with a similar size, charge, and bonding preference. Simple precipitation of separate solid phases is possible, especially as coatings on pre-existing grains, but from solutions where radionuclides are present at extremely low concentrations, formation of a separate phase is less likely than incorporation in an already existing one.

Effectiveness of contaminant uptake depends strongly on the relative rates of competing processes. For example, adsorbed ions can be considered immobilised provided the rate of desorption is slow relative to the time-scale of decay of the component. We often hear this referred to as "irreversible sorption" in the K_d approach. Ions trapped within a solid solution can be mobilised again if the solid exsolves to make a mixture of two or more separate phases. Transformation of one mineral phase to some more stable phase often releases material back to solution that was adsorbed on or incorporated within as a solid solution. Diffusion through the solid is generally considered to be slow, but for minerals where defect density is high, diffusion can hide adsorbed material or it can bring buried material back to the surface. Finally, change in temperature or solution composition can result in dissolution.

Figure 1. **Atomic force microscopy (AFM) images of Iceland spar calcite showing the effects of dynamic equilibrium. Lighter shades represent parts of the surface that are closer to the viewer; darker, further away. The images were taken within 10 minutes of each other. They are 10 μm across; terrace steps are one molecular layer or 3 ångströms (0.3 nm) high. From the macroscopic perspective, there is no change in overall composition of the solution or surface, but that contrasts strongly with the behaviour we see here at the nanometer-scale. Locally, dissolution makes step edges ragged and produces holes in some terraces while at the same time, precipitation decorates other step edges and deposits new material on terraces.**
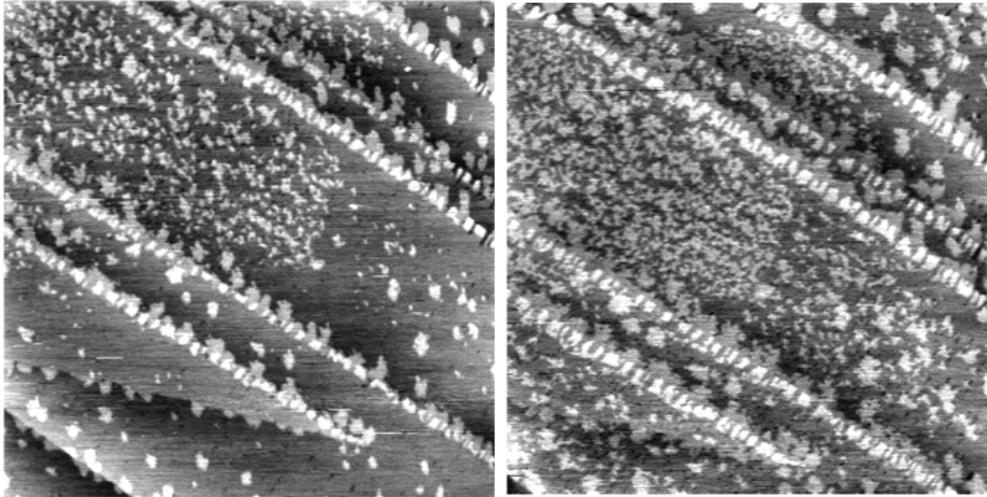
Over the past decades, we have made good progress in defining uptake and release processes thermodynamically but there is still a great deal of data missing, especially for trace contaminants. One disadvantage with thermodynamic studies is that they describe the average over the whole of the bulk system. The measurements are macroscopic. During precipitation, for example, we measure that material leaves the solution phase and becomes associated with the solid. However, we tend not to think about the dissolution that always goes on simultaneously, at the local scale, because our observations show the average over the whole system. The averaging can mask one or several processes aside from the one that we think we are observing.

For example, in a system where material is disappearing from solution but X-ray diffraction (XRD) does not show the development of a new phase, we interpret adsorption. However, locally, a separate phase may have precipitated as surface coatings or as colloids with particle size so small that the material appears amorphous to X-rays. Identification of the true nature of the process responsible for immobilisation in such a case can have important consequences to a model if the material in adsorbed form is easily desorbed but the small particles are relatively insoluble, or if the particles have the possibility to be transported with the groundwater. Another process that could be masked by averaging over the whole system is solid-state diffusion. Material adsorbed at the surface diffuses into the bulk by ion-by-ion replacement driven by the concentration gradient but the loss of the component from solution is interpreted only as "the fast process" which is often named adsorption and "the slow process", often ascribed to co-precipitation or to diffusion into dead-end pore spaces. The volume of material immobilised per unit time by solid-state diffusion is much smaller than that taken up by adsorption in the early stages, so uptake by diffusion is not observed directly in the macroscopic measurements. However, movement of a contaminant from surface sites, where it is available for desorption again, into the bulk makes it less mobile and liberates surface sites for further adsorption. The consequence of neglecting solid-state diffusion in short-term

predictions (hundreds of years) is insignificant, but over the very long time-frames required for prediction of radionuclide transport ($> 10^5$ years), even low diffusion coefficients would result in differences in estimates of immobilised material.

2. High-resolution techniques

Information about physical and chemical properties at the interface between solid and solution can give insight into the processes that take place there. However, until recently, resolution limits prevented investigation of the two-dimensional boundaries between phases. Now, techniques borrowed from physics and materials science make it possible to collect nanometer-scale information. Combination of data from macroscopic methods with that from high-resolution techniques can bring us further toward developing the conceptual models we need for understanding uptake processes, and can point to areas where better data are needed for development of more realistic predictive tools. There are many high-resolution techniques. Three of them have been used for the data presented here, and they provide complementary information about morphology, composition, and structure.

One technique that is especially good for seeing at molecular-scale resolution is scanning probe microscopy (SPM), which provides images of the change of physical properties on the surface of a solid. Lateral resolution is on the order of a couple of ångströms (10^{-10} m) and vertical resolution is limited at about 0.2 Å. One of the family of SPM techniques, atomic force microscopy (AFM), allows observations on insulating as well as conducting solids, without coatings, under solution or during exposure to air or gases, in real time. Chemical identity and bonding information are available from X-ray photoelectron spectroscopy (XPS), which is particularly sensitive to the top few nanometres of a solid surface. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) gives chemical maps of the top two or three atomic layers of a solid with resolution of about a micrometer laterally. These techniques, as well as a number of others, allow us to make direct observations beyond our normal limits of resolution which is about the range of a micrometer, into the four orders of magnitude leading to the atomic scale. SPM can be used *in situ*, in real time, so that time-dependent studies during changing solution conditions are possible. Morphology and molecular-scale structure can be collected as images, but chemical information is difficult to achieve. The chemical techniques, XPS and TOF-SIMS, require ultra-high vacuum, but experience shows that surfaces retain evidence of their history even when the fluid is removed. More information about these techniques and their application to geological materials can be found in [1-5] and references therein.

3. Uptake and Release Processes

3.1 Adsorption

Immobilisation by adsorption is discussed in this volume by colleagues who are much more experienced in that field than I. However, one point should be made about the topic that to some people seems to be a contradiction. Ions can be adsorbed to a solid even while it is dissolving in a highly undersaturated solution. An example is an experiment with single cleavage flakes of Iceland spar calcite ($CaCO_3$), such as that shown in Figure 2a. The sample was exposed to a solution of 10^{-3} M $Ni(ClO_4)_2$ where pH was about 3. Such a solution is unsaturated with respect to Ni-carbonate and Ni-hydroxide as well as calcite. After exposure for 1 minute, the solution was removed physically by a jet of N_2 to avoid evaporation and precipitation of salts. AFM offered clear evidence of the formation of dissolution pits on the calcite surface (compare Figures 2a and c) but XPS showed the development of small peaks representing adsorbed Ni^{2+} (compare Figures 2b and d). More details of this study are available in Hoffmann and Stipp [6].

Figure 2. *a*) **An AFM image of a calcite surface immediately after cleavage.**
The triangles result from pressure tangential to the observed surface.
The image is 1 μm wide and step edges are one atomic layer high.
b) **XPS spectrum of a similar freshly cleaved sample.**
The peaks representing Ca, C, and O appear as expected for calcite.
c) **AFM of a similar sample immediately after exposure for 1 minute to a Ni-bearing solution.**
Dissolution is verified by the appearance of monolayer-deep etch pits. Image width is 4 μm.
d) **XPS spectrum of a similar sample analysed soon after exposure to the Ni solution.**
The peaks representing calcite have been joined by a small peak from adsorbed Ni
(from Hoffmann and Stipp [6]).
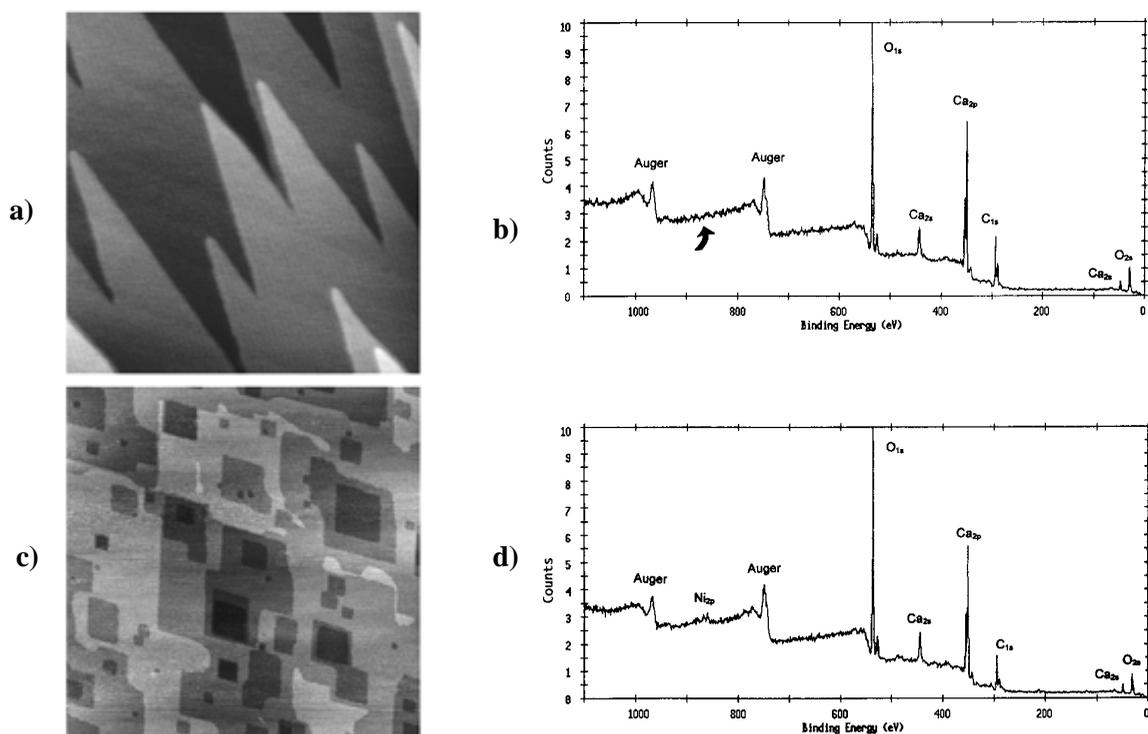
The apparent conflict can be resolved by thinking of the two processes, adsorption and dissolution, separately. During exposure to the Ni-bearing solution, Ni^{2+} adsorbs and desorbs from the surface but more ions come to the surface than leave in the initial stages. Thus, the processes look like adsorption. Likewise, during exposure to solution, the solid's own Ca^{2+} and CO_3^{2-} leave the surface and go into the solution and then some attach again to the surface. Macroscopically, we see more leaving than attaching (so we call it dissolution) but *both processes occur simultaneously*. The sites of adsorption or dissolution of the ions at the surface are determined by the energy relationships between the atoms of the solid and the ions in solution and it is not necessarily true that the same sites are equally active for ions going on and those coming off. Thus, for our nickel on calcite example, Ni^{2+} is attracted and sits in some sites while at the same time, Ca^{2+} is released from others.

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3.2   Co-precipitation

The iron-oxide system provides a good example of immobilisation by co-precipitation followed by release again by mineral transformation. When Fe(III)-hydroxide precipitates following oxidation of Fe(II), ferrihydrite forms (Figure 3a) and trace elements such as Pb^{2+} are incorporated by the colloidal-size particles. In a recent study using AFM and XRD [7], we have observed that ferrihydrite grows into hematite or goethite (Figure 3b, c) by aggregation of the primitive $Fe(OH)_3$ particles. The phase favoured depends on solution composition and temperature. In one study of ageing in solution at 70°C, we found that at low concentrations (< 100 ppm), Pb^{2+} released back to solution during transformation was undetectable with atomic absorption spectroscopy. Other studies where dry ferrihydrite was transformed by heating showed that some Pb^{2+} could be leached from the transformed product, but that which had been incorporated within hematite and goethite as solid solution was resistant to release even during exposure to somewhat violent leachate conditions [8,9].

Figure 3. **AFM images of Fe(III) oxides before and after transformation.**
***a*) 2-line ferrihydrite (FeOH)$_3$ within a day of precipitation.**
Identity was verified with X-ray powder diffraction with Rietveld refinement [7].
Image width is 500 nm. Particle height is about 5 Å and they are probably spherical,
but they appear wider laterally because of convolution of tip size and shape.
***b*) Hematite forms during exposure to solutions at 70°C and dominates after a few days.**
Some ferrihydrite (small particles) is still present. Image width is 1.5 μm.
Hematite aggregate height is about 50 nm.
***c*) Goethite characteristic crystal form which formed from ferrihydrite**
that was aged in solution at pH $\geq$ 12. Image width is 1.2 μm.

a)   b)   c)
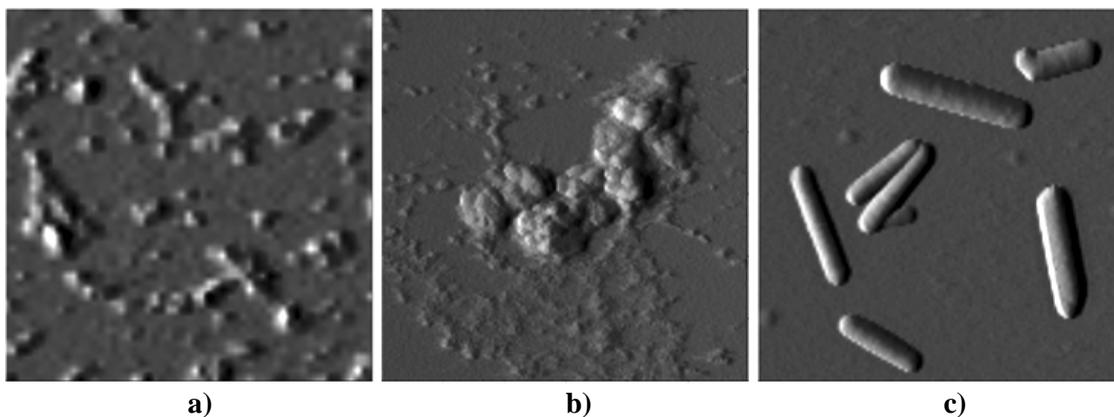
3.3   Colloids and coatings

In systems where the dangerous components represent a very small fraction of the mass, they can hide in colloidal particles or surface coatings as a separate phase. An example comes from a study of Cr(VI) immobilisation by a reactive barrier containing sand, bentonite, and Fe(0) [10]. As the iron was oxidised first to Fe(II) and then to Fe(III), Cr(VI) was reduced to Cr(III). It was expected that $Fe_xCr_{(1-x)}$-hydroxides would form and we found some evidence for their presence. However, TOF-SIMS revealed a Ca-Cr(III)-oxide phase that appeared as coatings only a few atomic layers thick on the bentonite particles (Figure 4). Such a phase was not visible with XRD because of its small particle size and extremely low relative abundance. Although such a phase can be synthesised with high Cr and Ca concentrations in the laboratory, there are no reports in the literature of it ever having been considered previously in geochemical modelling. Similar, currently unknown associations for radionuclides are possible.

Figure 4. **TOF-SIMS chemical maps of a sample of reacted barrier material
containing 90% quartz sand, 5% Fe(0), and 5% bentonite, and exposed to solutions
containing Cr(VI), which reduces to Cr(III) while Fe(0) oxidises to Fe(III).
High relative intensity is denoted as white, background is black.
Image width in all cases is 180 μm and the data represent the top few atomic layers
of the surface. The top row of images representing Si, Al, and K have very similar patterns
and are interpreted to represent clay particles covering the quartz sand.
The Fe pattern resembles the clay pattern in most areas, suggesting that Fe sits as coatings
over the clay. Cr was expected to follow the pattern of Fe in $Fe_xCr_{(1-x)}$ co-precipitates and
some of it does, but Cr is more closely associated with Ca as a CaCr-oxide coating (from [10]).**
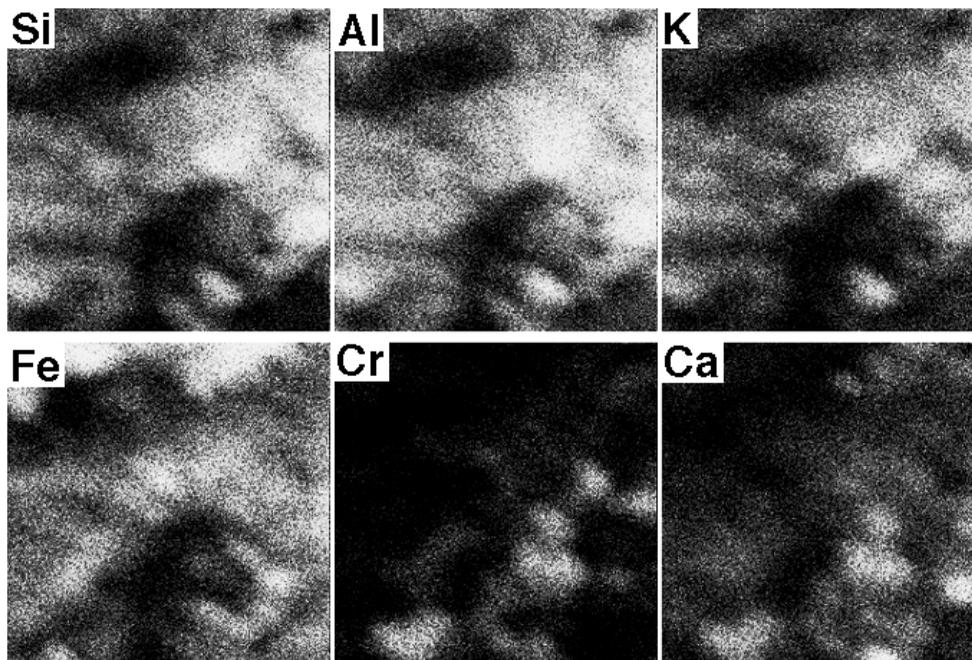
3.4   *Solid-state diffusion*

An example of the role played by solid-state diffusion in contaminant uptake is offered by calcite. Experiments with Cd^{2+} in undersaturated solution showed that it was taken up at the surface during dissolution. XPS showed clear peaks for Cd on freshly prepared samples, but on samples that had been stored for a few days in air, the Cd had disappeared [11]. Other experiments, where $CdCO_3$ was grown epitaxially over $CaCO_3$, showed that the Cd/Ca ratio representing relative surface composition decreased as a function of time, meaning that Cd^{2+} moved into the bulk calcite while Ca^{2+} moved out (Figure 5). Exchange of Ca for Cd in the metal sites in the atomic structure, under ultra-high vacuum (10^{-10} atm), in the absence of a solution phase, provides evidence for the development of solid solution by a mechanism other than reprecipitation and co-precipitation from solution. Rates of diffusion within the bulk were estimated at nanometres in weeks. Experiments with Zn^{2+} [4] showed the same behaviour but the rate was slower. For Ni^{2+}, diffusion into the solid was extremely slow [6].

Figure 5. **XPS spectra from a layer of CdCO$_3$ that is more than 100 Å thick, grown epitaxially over CaCO$_3$.**
a) In the spectra taken immediately after removal from solution, peaks representing Cd are intense,
b) whereas the peaks representing Ca are very weak because the CdCO$_3$ layer is nearly thick enough to mask the underlying calcite. The initial Cd/Ca intensity ratio was 63:1.
c) After the sample was stored for a month in ultra-high vacuum (~10^{-10} atm), relative Cd intensity had decreased while
d) Ca intensity increased; the peak intensity ratio changed to 3:1. By this time, some of the Ca has moved into the range detectable by XPS while some of the Cd has moved beyond it. More details can be found in [11].
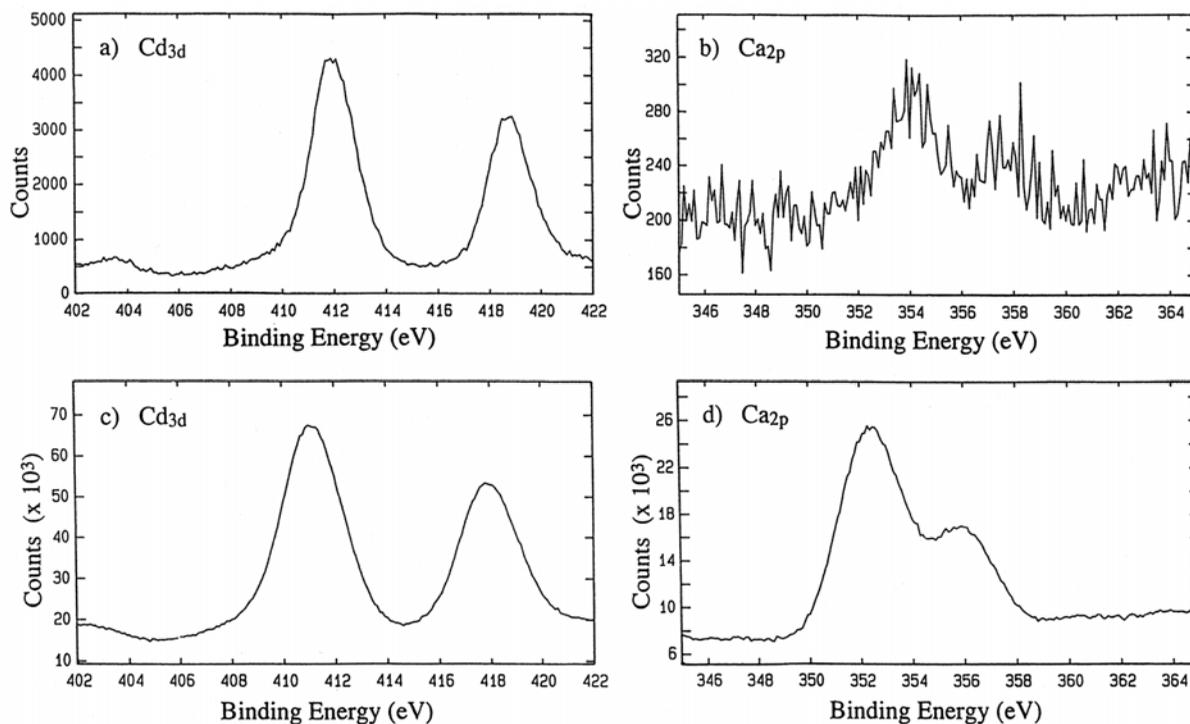
AFM studies of dry calcite surfaces have suggested two mechanisms by which material adsorbed or precipitated could move away from the surface and into the bulk, in the absence of visible liquid water. One is by surface mixing and burial; the other is by solid-state diffusion, probably along linear defects. Calcite (and similarly all mineral surfaces) is coated by a layer of water that adsorbs from the humidity in air. In this layer, calcite dissolves and reprecipitates so that over a period of minutes to hours, the surface recrystallises [12]. At high humidity, such as on a warm summer day, the process is rapid. Figure 6a is an AFM image taken on the same sample as shown in Figure 2a, 8 hours later (at a slightly different location). The 3-Å-high step edges are preserved, but now the terraces and edges are rough. Figure 6b shows that even at humidity of only 5% or less, mixing can rearrange the surface. This image was taken from a slightly different site on the sample shown in Figure 2c after 18 days storage in a desiccator. Pit edges that were originally straight have become rounded and dissolution pits have begun to fill in. Adsorbed material, such as the Ni^{2+} in this case, can be incorporated into the calcite bulk as the surface rearranges. This mechanism has the possibility to move significant material from surface sites, where it is susceptible to desorption, into more secure bulk sites. However, there is no evidence yet to suggest that this mixing process affects more than about the top ten molecular layers.

Figure 6. **AFM images of calcite.**
a) A different site on the sample shown in Figure 2a, after 8 hours exposure to air at 50% humidity.
The sample has not been exposed to liquid water, but the surfaces have spontaneously recrystallised.
b) During exposure to dry air in a desiccator (≤ 5% humidity) for 18 days,
the same sample shown in Figure 2b has recrystallised.
Surface rearrangement fills some pits and rounds step edges.
c) A sample that looked like Figure 2a immediately after cleavage; it was smooth
with no evidence of defects. After exposure to distilled water (pH = 5.6) in equilibrium with CO_2
in air for one minute, shallow and deep etch pits formed.
The one-atomic-layer-deep pits are the generally observed dissolution features.
The series of dark holes aligned along one of the cleavage directions formed because the water
selectively attacked at the sites of linear defects running into the calcite surface [13].
a) **b)** **c)**
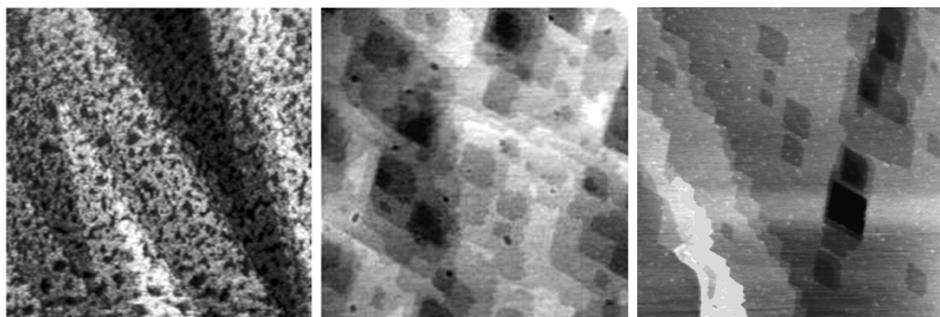
In experiments in ultrahigh vacuum, XPS shows that liquid water is not retained on the surfaces [14], suggesting that surface mixing is not a viable explanation for the rapid and effective movement of elements that disappear rapidly into the bulk, such as for Cd. A previous study of the movement of the monovalent ions K, Na, and Cl out of calcite suggested solid-state diffusion along linear defects running into the surface at a high angle [13]. Such defects have never been observed on freshly cleaved surfaces (such as Figure 2a) but their presence affects the appearance when water is added. The defects enhance formation of deep pits on surfaces exposed only for one minute to distilled water (Figure 6c). Using the approximate rates of disappearance into calcite for divalent Cd, Zn, and Ni as well as for the expulsion of the monovalent ions, one could roughly estimate movement of about a monolayer of adsorbed material from the surface of calcite into the bulk at rates in the range of a day to several years, depending on the element's properties, the contact solution's composition, and the defect density of the solid.

4.   Conclusions

We can learn a lot by complementing laboratory and field results with observations from surface analytical techniques. The relative difference between the metre scale – in the world where we live – and the Ångström scale – in the world of atomic distances – is ten orders of magnitude. That is roughly equivalent to sitting on the moon with very strong glasses and observing the identity and structure patterns of the heads of an audience sitting in a lecture theatre. Previous resolution limits are commonly considered to be about a micrometer. The four orders of magnitude of higher resolution that surface-sensitive techniques give us offers a huge new volume of worlds to explore, and the power to determine directly the chemical mechanisms that control uptake and release.

We have only begun to study processes at the molecular level. Parameterisation is the next step. Then, simulation and prediction based on mechanistic modelling will increase validity of risk

assessment models and long-time or long-distance predictions. A sounder scientific base will promote increased confidence on the part of other scientists and the public. At the stage we are at now, more data are needed so that we can determine which processes are most important in given conditions and to provide parameters for modelling. Data required include information about bulk properties for phases that are not common in natural systems, but that are key to controlling concentrations of trace components. This includes data for thermodynamic properties for dissolved species and for solid solutions and it includes information about some of the more dynamic parameters such as diffusion coefficients and transformation rates.

Experiments are currently underway in the Interface Geochemistry Laboratory to explore the uptake of Eu^{3+} by calcite and its ability to move into the bulk by solid-state diffusion. Eu^{3+} provides a convenient safe analogue for the trivalent actinides. Some of the handicaps that we face in defining behaviour include a general lack of standard parameters for the Eu^{3+}-bearing solids such as values for molar volume and surface free energy. Furthermore, in order to quantify diffusion coefficients, we must find a way to determine defect density of minerals at a local scale. To determine uptake capacity in general, chemical analytical methods for measuring low concentrations with very high spatial resolution are necessary. Techniques exist, but if funding for instruments for basic research remains scarce, future prospects for filling in currently unknown information look bleak.

Acknowledgements

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Isotope Fractionation Effects on Radionuclide Transport in Geologic Disposal of Nuclear Waste

William M. Murphy

Department of Geosciences, California State University, Chico, California, USA

David A. Pickett

Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, Texas, USA

1.   Introduction

Understanding the behaviour of radionuclides in geochemical systems is essential to demonstrating the safety of geologic disposal of nuclear waste. Geochemical phenomena such as aqueous speciation, solubility, solid solution, colloid formation, and surface complexation depend primarily on the electronic properties of atoms and not on their isotopic mass. Hence, aside from differing radioactivities, performance assessments for geologic disposal of nuclear waste reasonably neglect differences in chemical properties of isotopes of the same element. Nevertheless, isotopes are fractionated in geochemical systems. Fractionation is due to kinetic or equilibrium mass effects during phase transitions, molecular transformations (which may be enhanced in biogeochemical processes), and diffusion. These effects are negligible for heavy isotopes, including most that are of concern in nuclear waste. For radioisotopes, fractionation also occurs due to radiation effects including decay and alpha recoil. Chemical variations due to isotopic fractionation are generally subtle compared to those resulting from differences in geochemical characteristics such as oxidation-reduction potential, pH, ionic strength, and mineralogy.

So why consider isotopic fractionation in the context of geologic disposal of nuclear waste? This paper examines two general reasons. (i) Information on transport characteristics of geochemical systems can be revealed by isotopic variations. In particular, information on the degree of openness or closure of the system and the timing of chemical fluxes can be revealed in the systematics of radionuclide activities in the uranium and thorium decay series. Also, chemical transport properties (such as mineral-water distribution coefficients) of elements composed of multiple radionuclides may be determined, in principle, from natural system data on the chemical behavior of the isotopes. For example, *in situ* sorption and desorption rates may be deduced in theory by solving simultaneously mass conservation equations for the distribution of several isotopes of the same element having the same sorption reaction properties but different half lives and fractionation effects due to nuclear processes. (ii) Fractionation phenomena, which are particular to individual radioisotopic systems or processes, may affect radionuclide release and transport in a repository system. For example: (a) The stability of colloidal plutonium depends on its isotopic composition because of radiological effects on colloid formation and degradation. (b) Release rates of alpha-decay products from solid matrices are enhanced because of alpha-recoil effects, leading to isotopic fractionation that could affect performance. (c) Dilution effects due to mixing cause variations in isotope ratios and could affect releases and transport of individual radionuclides. Differential isotopic behavior in waste disposal may be especially significant if dose conversion factors vary among isotopes.

2.   Natural analogue data from Peña Blanca

The Nopal I uranium deposit at Peña Blanca, Mexico, has been extensively studied as a natural analogue of the proposed geologic repository for high-level nuclear waste at Yucca Mountain, Nevada [1,2,3,4,5]. Silicic volcanic rocks similar to those at Yucca Mountain host a natural uranium deposit at Nopal I. The hydrologic environment of the uranium deposit is presently unsaturated and the chemical environment is oxidising, which are also the conditions at Yucca Mountain. Uranium at Nopal I was initially reduced uraninite (UO_{2+x}) analogous to spent nuclear fuel, but it is now almost entirely oxidised. An estimated limit on the oxidation rate of uraninite at Nopal I has been used as a constraint in alternate performance assessment source-term models for Yucca Mountain [6]. The distribution and fractionation of uranium and uranium decay series isotopes at Nopal I have been useful in characterising transport phenomena and in judging the validity of transport modelling for performance assessment of the proposed repository at Yucca Mountain. Uranium decay series data from Peña Blanca [5,7,8,9] can be used to illustrate the utility of studying isotope fractionation to characterise geochemical transport phenomena.

Uranium isotope and daughter nuclide fractionation in rocks and waters were also used in the Alligator Rivers Analogue Project, with varying success, to help constrain quantitative, time-dependent release and transport models [10]. For example, the models allowed for differential release rates for ^{234}U and ^{238}U due to recoil and related effects.

3.   Hydrogeochemical system characterisation

3.1   System closure

In a system that is closed on a time scale that is long relative to half-lives of the daughters, the activities of radionuclides in the uranium and thorium decay series become equal. This secular equilibrium is an indication of geochemical system closure, which is a favourable natural system characteristic for geologic isolation of nuclear waste. Radioisotope disequilibrium (decay-series activity ratios other than unity) indicates open system behavior. Geochemical mechanisms of openness of a system in radioisotope disequilibrium may be interpreted based on the chemical properties (e.g., solubility, speciation, sorption) of the radionuclides and variations in the hydrogeochemical environment. Natural groundwaters are commonly enriched in ^{234}U relative to ^{238}U (i.e., they have $^{234}U/^{238}U$ activity ratios greater than 1) because of radiation effects such as alpha recoil [11]. Daughters of alpha decay may be ejected from stable crystallographic sites or left in damaged and preferentially reactive sites. These daughter isotopes are released preferentially to solution. (^{234}U depletions in groundwater, which are less common than ^{234}U enrichments, are generally attributed to changes in environmental conditions leading to dissolution of previously ^{234}U-depleted source materials.) Preferential release of alpha-decay products is a primary mechanism for fractionation of heavy radioisotopes.

Uranium decay series isotopes in the geologic and hydrochemical environment of the uranium deposit at Nopal I are commonly out of secular equilibrium. $^{234}U/^{238}U$ activity ratios in present groundwaters at Peña Blanca range up to 5 [12]. $^{234}U/^{238}U$ ratios up to 2.4 in rocks and fracture-filling materials outside the primary uranium deposit at Nopal I are due most likely to precipitation of uranium from solutions enriched in ^{234}U by interactions with uranium-rich source rocks [5,9]. Uranium decay series disequilibrium in fracture-filling materials and rocks at Peña Blanca reveals multiple-stage processes of radionuclide release, transport, deposition, and remobilisation [9]. Another uranium-series study at Nopal I [7] concluded that uranium mobility has been limited during the past 300 000 years, although radium mobility was indicated. Similarly, uranium-series isotopic disequilibrium in fractured granites from the Lac du Bonnet batholith, Manitoba, Canada, has been interpreted to represent open system behavior, whereas isotopic equilibrium in the unfractured granite marks a closed system [13].

Potentially, system closure as demonstrated by uranium and thorium decay series secular equilibrium could be evaluated as a quantitative criterion for performance characteristics of the natural hydrogeochemical system of a nuclear waste repository site. This approach would be particularly useful for radionuclides with half-lives comparable to the regulatory time scale. For example, consider a hypothetical repository in which containment of radium is a safety concern within a 10 000-year time frame. The ^{226}Ra half-life of 1 600 years is comparable to this period. In a closed system after 10 000 years, disequilibrium between ^{226}Ra and its relatively immobile ^{230}Th parent (e.g., ^{226}Ra depletion in rock due to mobilisation) would evolve to within about one percent of equilibrium. Therefore, a ^{226}Ra/^{230}Th activity ratio in repository host rock outside a few percent from unity would indicate that radium was mobile under site conditions within the past 10 000 years and would be likely to be mobile during the regulatory period. Decay-series radioisotope secular equilibrium criteria would be specific to individual chemical species, and acceptable limits could be based on safety and geochemical considerations, such as the magnitude of initial disequilibrium. Separate but complementary criteria could be developed for other decay-series nuclides with contrasting geochemical characteristics, and generalisations could be developed to apply to anthropogenic species.

3.2   *In situ K_d*

Performance assessments for geologic repositories for nuclear waste commonly and conveniently invoke constant mineral-water distribution coefficients for individual radioelements to simulate retardation of radionuclide migration. A theoretical framework has been developed relating distribution coefficients for radioelements in the uranium and thorium decay series to the activities of radionuclides in natural water-rock systems (e.g., [14]). Mass-balance relations for each of the multiple isotopes of individual chemical elements in the uranium and thorium decay series (notably isotopes of Th, Ra, and Pb) provide multiple constraints for each element on chemical properties such as distribution coefficients. Chemical properties such as equilibrium constants, diffusion coefficients, and precipitation rate constants vary insignificantly among isotopes of the same element in these series. Thus, mass-conservation relations, involving dissolution, precipitation, sorption, radioactive decay, and migration, can be written for each of the isotopes and solved simultaneously to determine the chemical properties. For example, Ku *et al.* [14] present equations relating activities of five thorium isotopes, which can be solved simultaneously for the five parameters: dissolution rate, precipitation rate, adsorption rate, desorption rate, and surface area. The distribution coefficient or *in situ K_d* is in turn related to the ratio of the sorption and desorption rate constants.

Extracting *in situ K_ds* from natural system data is complicated by the characteristic complexity of nature relative to models. Critics note the complexity of processes that control the distribution of chemical species among the aqueous phase, sorption sites, and bulk solids, as well as ambiguities associated with analytical methods. Processes neglected or incompletely represented in various theoretical approaches and interpretations of data include non-linear sorption, sorption site saturation, precipitation, co-precipitation, colloid formation and transport, and disequilibrium between sorbed species and the bulk solid. In particular, McKinley and Alexander [15] warn against potentially dangerous applications of distribution coefficients or retardation factors in performance assessments for radioactive waste disposal systems when the coefficients cannot be shown to provide conservative results. Nevertheless, evaluation of *in situ K_ds* provides an alternate line of evidence that may be used to judge laboratory-based data.

4.   Fractionation effects on release and transport

4.1   *Preferential release and transport*

In nuclear waste repositories, aqueous release is influenced by the phase setting and radiolytic history of particular radionuclides. Daughter radionuclides may occupy crystal sites that

have been damaged by alpha and beta emission and alpha recoil. For example, [239]Pu in spent fuel that has grown from alpha decay of [243]Am (half-life 7 400 years) may occupy more damaged crystal sites than other Pu isotopes, and so may be preferentially released. The projected proportion of [239]Pu atoms in these sites could be calculated from [243]Am decay; availability of these [239]Pu atoms to solution could be predicted based on theoretical considerations and comparison to natural systems and laboratory studies using shorter-lived parent-daughter pairs. Effects on radionuclide release due to damage during reactor operation could be tested by analysing for individual isotopes during laboratory leaching/degradation studies. Analogous preferential release leads to common [234]U activity enrichments in natural groundwaters. Occurrences of [234]U/[238]U activity ratios up to 5 in groundwaters from Peña Blanca [12] suggest that fractionation leading to isotopic disequilibrium could have an important effect on ultimate doses due to radionuclide release to the biosphere. Release models in performance assessments should not necessarily assume isotopically proportional release from solid waste forms.

Differential isotopic stability of plutonium colloids is also due to alpha-recoil effects [16]. [239]Pu, with a half-life of 24 110 years, shows negligible effects of colloids in PuO_2 solubility studies. In contrast, [238]Pu, with a half-life of only 88 years, shows appreciable effects. Alpha recoil is believed to foster generation of colloids from hydroxide precipitates of [238]Pu causing enhanced solubility effects. In natural geochemical systems, plutonium may also be transported by sorption on groundwater colloids, which tend to be destroyed by alpha-recoil effects [16]. Therefore, relative to [239]Pu-bearing colloids, isotope fractionation due to alpha recoil enhances formation of [238]Pu-bearing hydroxide colloids and diminishes stability of natural colloids with sorbed [238]Pu.

4.2   *Isotopic dilution*

The isotopic composition of a radioactive contaminant can also be altered by mixing with a naturally or artificially occurring source of the element. This mixing could result in isotopic dilution of the contaminant radionuclide and could mitigate contaminant migration under certain circumstances. For example, depleted uranium (predominantly [238]U) has been proposed as a chemical buffer material for disposal of spent nuclear fuel [17,18]. If mixing of the two components results in a concentration at the geochemically imposed solubility limit, then precipitation of the mixed element would limit contaminant transport. Under other circumstances, transport of the contaminant could be augmented if the addition of the natural component leads to saturation of sorption sites. In general, mixing under natural geologic conditions is unlikely to lead to high aqueous concentrations, because the concentration in the mixture will be intermediate to that of the two components, and isotope dilution will not mitigate or enhance contaminant transport. In any case, radioelements such as plutonium that are rare in nature would not be subject to isotope dilution by natural sources.

5.   **Implications for performance assessment**

Radionuclide fractionation is most likely to affect performance of a geologic repository for nuclear waste through the preferential release of alpha-decay products or differential isotopic release from multiple phases. Natural system data show that preferential release can lead to activity ratios in solution several times that occurring in source minerals.

A survey at the GEOTRAP 5 meeting of practitioners of performance assessment for geologic disposal of nuclear waste indicates that isotopic fractionation effects have been neglected in performance assessment models. Improved understanding of isotopic fractionation in nuclear waste disposal is likely to come primarily from observations of natural geologic occurrences of radionuclides and interpretations of experimental data. If significant processes are identified, including them in performance assessment models should be practical. For example, modelled radionuclide release rates

could be isotope-specific, and sensitivity of dose to isotope fractionation could be tested by varying differential isotope release rates in performance assessment models.

Acknowledgements

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Evidence for Retention Processes
in the Tracer Retention Understanding Experiments (TRUE)

Anders Winberg
Conterra AB, Sweden

1.   Introduction

For the Operating Phase of the SKB Äspö Hard Rock Laboratory (HRL), the Swedish Nuclear Fuel and Waste Management Company (SKB) initiated the Tracer Retention Understanding Experiments (TRUE) with the objective to improve the understanding of radionuclide transport and retention processes in fractured crystalline rock. Overall objectives included enhancement of confidence in models for transport of sorbing radionuclides in performance assessment (PA), and to show that pertinent transport data can be obtained from site characterisation or field experiments, and that laboratory results can be related to retention parameters obtained *in situ*. A basic drive from PA has been to obtain *in situ* data on transport and retention of sorbing radionuclides at different length scales. In addition, addressing the multiple scales embedded in TRUE is relevant to taking the step from experimental scales to site scale (100-1 000 m). Is retention more profound at a larger scale given larger transport distances, a higher degree of heterogeneity and longer transport time (linear effects of equilibrium surface sorption not taken into account)? Can the knowledge integrated from laboratory, detailed and block scales be used to improve predictive capability on a site scale? Yet another PA drive has been to obtain estimates of parameters equivalent to the "flow-wetted surface area".

2.   Specific objectives of performed in situ experiments

The first test cycle, TRUE-1, which has recently been concluded [1], focuses on transport and retention in an interpreted single fracture in the detailed scale (< 10 m). This scale may be seen to represent the environment experienced by a released radionuclide in the immediate vicinity of a deposition borehole. Included in the objectives of this test cycle was a demonstration of transfer of tracer-test techniques and methodologies to the ambient hydraulic pressure and chemical situation at a depth of 400-500 m at the Äspö HRL. A secondary objective was development of *in situ* techniques for pore-space characterisation using epoxy resin. The performed *in situ* experiments with radioactive sorbing tracers have been complemented by laboratory batch sorption and through-diffusion experiments, and analytical and numerical modelling.

In the TRUE Block Scale experiment [2,3] the experiences from TRUE-1 have been transferred and tested on a larger length scale and somewhat longer transport times. The specific objectives were to increase understanding of transport and retention in a network of fractures in the block scale (10-100 m), thereby increasing the ability to make model predictions over longer length and time scales. Further objectives were to study the relative importance of retention processes in a fracture network and, finally, to study the potential for using hydraulic data for making predictions of transport phenomena. After a series of characterisation and experimental stages [3], the TRUE Block Scale is presently in an evaluation and reporting stage and final reports are due in early 2002.

3. Characterisation and building of hydrostructural models

Over the duration of the TRUE programme, successive refinements and modifications of the characterisation and experimental methodology have been made, but overall the important components in the basic characterisation remain the same. It was identified early on that the basis for successfully designing, performing, and evaluating *in situ* tracer tests over the length scales considered is a sound and robust hydrostructural model complemented by a good hydraulic understanding of the studied system. In building these models, the key elements have been integration of cross-hole pressure responses (from drilling and interference tests), borehole TV imaging (BIPS), and results from high-resolution borehole flow-logging [4]. Fractures which could not be assigned to deterministic structures/fractures interpreted to extend between multiple boreholes were assigned to a stochastic background fracture population. The material properties, e.g., in terms of transmissivity, have been obtained through various types of single hole and cross-hole hydraulic tests. Hydraulic boundary conditions have been inferred either from larger scale numerical models or from measurements of hydraulic head in packed-off borehole sections.
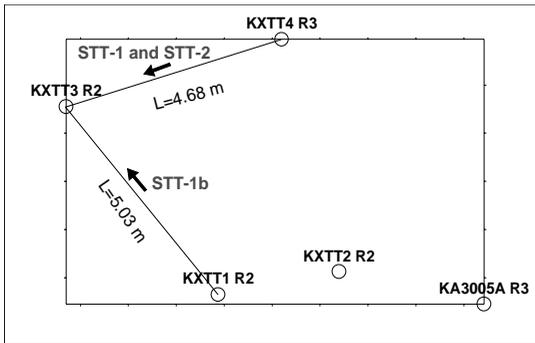
Figure 1. **TRUE-1 : Configuration of sink and source sections in the plane of studied the interpreted Feature A.**
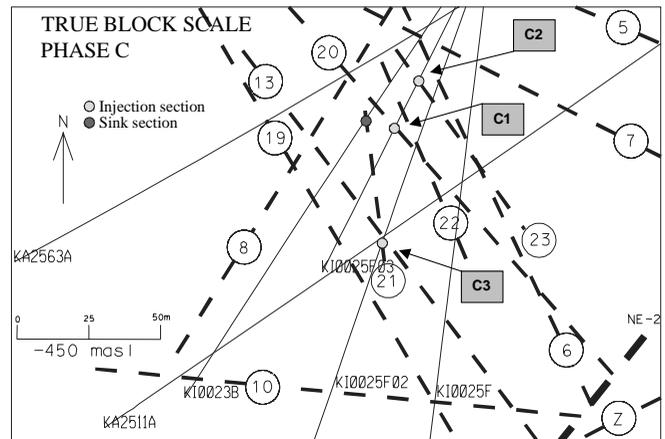
Figure 2. **TRUE Block Scale Phase C : Plan view of configuration of sink and source sections in the network of deterministic structures.**

4. Tracer tests with radioactive sorbing tracers

In total, five different source-sink pairs have been investigated using radioactive sorbing tracers, two at the TRUE-1 site (L = 4.7-5 m, [1], cf. Figure 1) and three at the TRUE Block Scale site

(L = 17-100 m, [4, 5], cf. Figure 2). Radioactive sorbing tracers used included ^{22,24}Na, ^{47}Ca, ^{85}Sr, ^{83,86}Rb, ^{42}K, ^{131,133}Ba, ^{57,58}Co, and ^{134,137}Cs. Conservative tracers used for non-reactive reference included ^{82}Br and ^{131}I, ^{186,188}Re, ^{82}Br, HTO, fluorescent dye tracers (primarily uranine) and various metal complexes. The selected source-sink pairs in the case of TRUE Block Scale are interpreted to involve transport in 1 to > 3 of the interpreted deterministic structures. It should be emphasised that the identification of suitable source and sink (injection and pumping) sections for the tests was the result of comprehensive efforts in terms of pre-tests and tracer-dilution tests employing conservative tracers. For the flow paths subsequently tested with radioactive sorbing tracers, the mass recovery in the case of TRUE-1 was > 90% and in the case of TRUE Block Scale > 80%, for the conservative species. Tests with radioactive sorbing tracers at the TRUE-1 site were carried out at two pumping rates, 0.4 and 0.2 L/min. Sufficiently high mass recovery rates could only be accomplished at the TRUE Block Scale site at a maximum possible pumping rate, 2.1

L/min. In TRUE Block Scale, a series of pre-tests was also performed with dissolved He-3 gas. The results compared to a reference conservative dye tracer showed a marked retardation for the more diffusive He tracer compared to the dye, interpreted as a manifestation of diffusion [5].

5.   Laboratory investigations

Investigations in the laboratory included batch sorption and through-diffusion experiments, primarily made on unaltered Äspö diorite samples [6]. Sorption experiments have been conducted on different size fractions and, likewise, through-diffusion measurements have been made on variable sample thicknesses, 1-4 cm [6]. Site-specific retention data on fracture wall rock samples are primarily related to TRUE-1. No sorption or diffusivity data are at present available for fault breccia/fault gouge material. However, in the case of TRUE Block Scale, where fault breccia has been collected from relevant structures, K_d values have been evaluated from cation-exchange capacities estimated from the mineralogy in combination with the ambient hydrogeochemistry [4]. Additional laboratory work includes measurement of porosity and porosity distributions using water saturation and impregnation of rock samples with ^{14}C-labelled polymethylmethacrylate (^{14}C-PMMA) [7].

Figure 3. **TRUE-1 : Conceptual model of interpreted Feature A [1].**
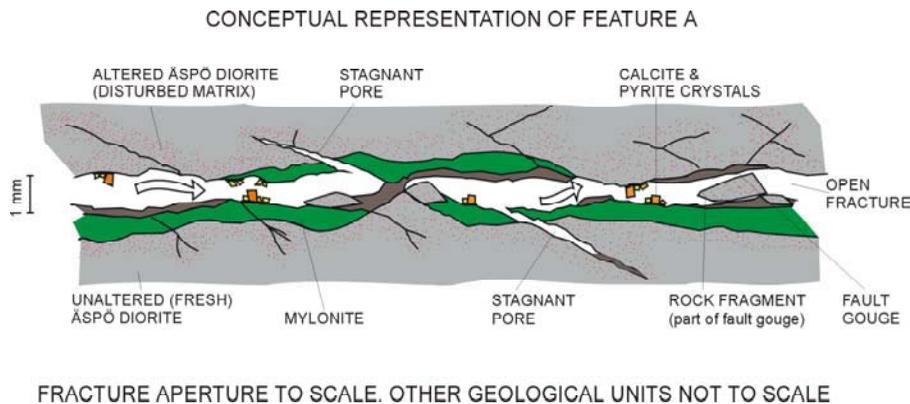
6.   Conceptual models of conductive fractures

Fractures at Äspö have typically been subject to variable amounts of tectonisation (indicated by the occurrence of cataclasites and/or mylonites) and variable degrees of chemical alteration (alteration of biotite to chlorite, saussuritisation of plagioclase, oxidation of magnetite to hematite, etc.). Almost all studied structures/fractures show alteration and tectonisation of the wall rock, and most intercepts follow mylonites. Conceptual model development for fractures and their immediate surroundings has been concentrated to fractures exposed in tunnel openings and on the ground surface [8], to the Feature A studied in TRUE-1 [1], and the structures involved in the tests with sorbing tracers in TRUE Block Scale [4]. Some of the latter structures are comparable to Feature A, although they are slightly more complex, more transmissive, and wider. Feature A is interpreted to comprise a fracture that follows a mylonitic brittle precursor, cf. Figure 3. It may either be made up of a single undulating fracture plane over a distance of some 10-20 m, or be constituted of a number of connected fracture planes with slightly variable orientation. Support for the interpreted "singularity" of Feature A is provided by the fact that all borehole sections interpreted to lie within it respond preferentially to pressure disturbances created within it, as well as by a distinctive hydrochemical signature compared to the surrounding. However, hydraulic flow dimensions > 2 suggest 3D networking effects. Evaluated flow dimensions between 3-3.5 from a test of Feature A in KXTT4 can alternatively be interpreted as an effect of a constant-head boundary or a leaky aquifer system [9].

The total width of the altered zone around Feature A is estimated at 0.05-0.09 m. Although gouge material was not collected from the six boreholes intercepting the feature, it cannot be ruled out that gouge material is present in Feature A. PMMA studies indicate a porosity of about 1-2% in the rim zone close to the fracture surface (locally the porosity is much higher) and a sharp gradient towards the interior where the porosity is about one order of magnitude lower some 1-2 cm from the surface of Feature A [10]. A high porosity gradient and an increased pore connectivity near fracture surfaces may result in markedly increased diffusivity and sorption capacity compared to intact rock away from the fracture surfaces [10]. Fault breccia has been recovered from some structures in the TRUE Block Scale studies. PMMA analyses performed on fault breccia pieces (1-3 cm) and fault breccia fragments (1-2 mm) show porosities in the order of 0.4-0.8% (with small areas with highs of about 10%), cf. Figure 4, and 1.3-11%, respectively [4]. In general, the porosity constitutes micro-fractures and porous mineral phases (secondary or altered minerals).

Figure 4. **TRUE Block Scale :**
Composite showing a cut surface of a centimetre-sized PMMA-impregnated fault breccia piece, the associated autoradiograph, and a histogram accounting for the area distribution of porosity. The total porosity assessed from the exposed surface is 0.8% [4].
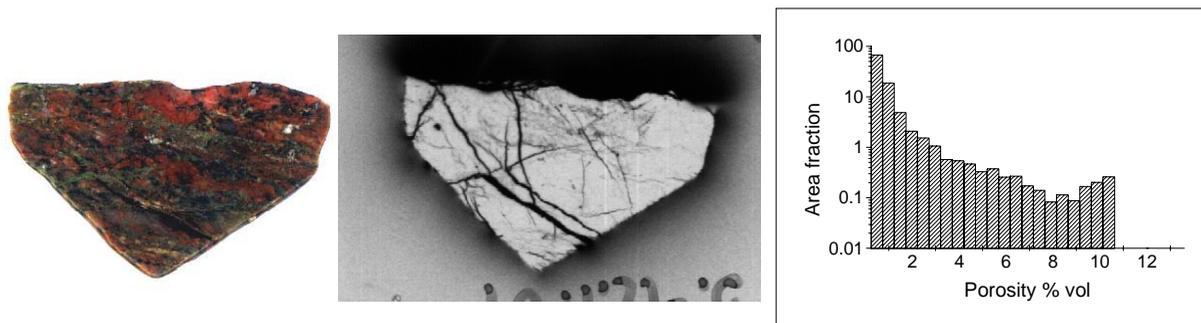
An alternative conceptual model for TRUE-1 that describes "Feature A" as a cluster of interconnected shorter fractures concentrated along a mylonitic precursor has been presented [11]. This model features diffusion-accessible porosity in the fault rock, which includes fine-grained fault gouge and cataclasite with clay minerals (smectite layers) which are attributed a high sorption capacity.

Remaining uncertainties relevant to experimental time scales, include the geometry of the tested flow paths along involved fractures, the distribution of altered bedrock (primarily high porosity), mylonite (primarily low porosity), mineralogy, and porosity distribution along the studied flow paths, and/or effective values that integrate the variability. In addition, the distribution *in situ* of fault breccia, its fraction of fine-grained fault gouge, and the *in situ* porosity of the infilling material along studied flow paths are unknown.

7.   Predictive capability of numerical models

The TRUE-1 experiments have been subject to blind model predictions and subsequent evaluation as part of the Äspö Task Force on Modelling of Groundwater Flow and Solute Transport, [12,13]. Following the modelling process from the blind prediction of the first sorbing tracer test, the models at first generally underpredicted the breakthrough times of the sorbing tracers. As a consequence, matrix diffusion/sorption (i.e., diffusion into the matrix and associated sorption on inner matrix surfaces) was incorporated in most models for the next set of predictions where the models showed improved predictive capability, cf. Figure 5, albeit with substantial differences between different models.

Figure 5. **TRUE-1 STT-2: Comparison of model predictions using various model approaches and experimental breakthrough [13], cf. Figure 1.**
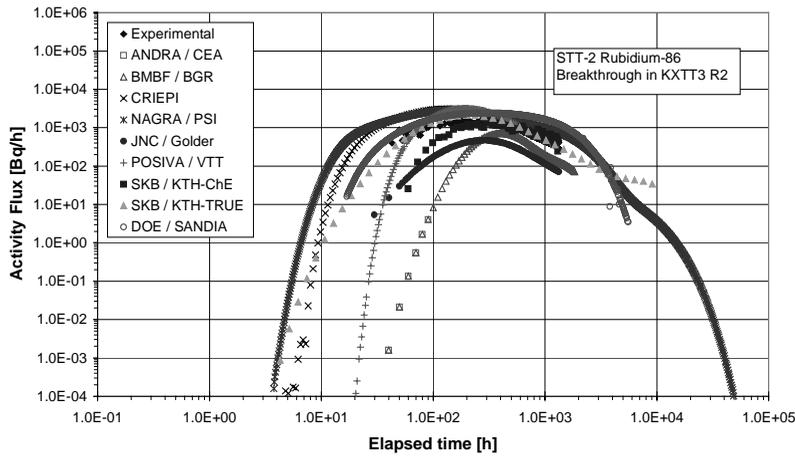
The ability to make reasonable predictions on a 15-m length scale was demonstrated when some of the models used in TRUE-1 were applied to the shortest and least complex of the block-scale source-sink pairs, cf. Figure 6a. In the case of the longer and more complex source-sink pairs, they performed less well, cf. Figure 6b. The block-scale tracer tests are presently subject to evaluation using the different model approaches which include stochastic continuum, discrete feature network, channel network, and two approaches which are more PA-related, the LaSAR approach extended to the block scale [14] and the so-called POSIVA approach [15].

Figure 6. **TRUE Block Scale:**
Comparison between predicted cumulative normalised mass recovery (%) and the corresponding experimental breakthrough. *a*) C1 (Cs-137), *b*) C3 (Sr-86), cf. Figure 2.
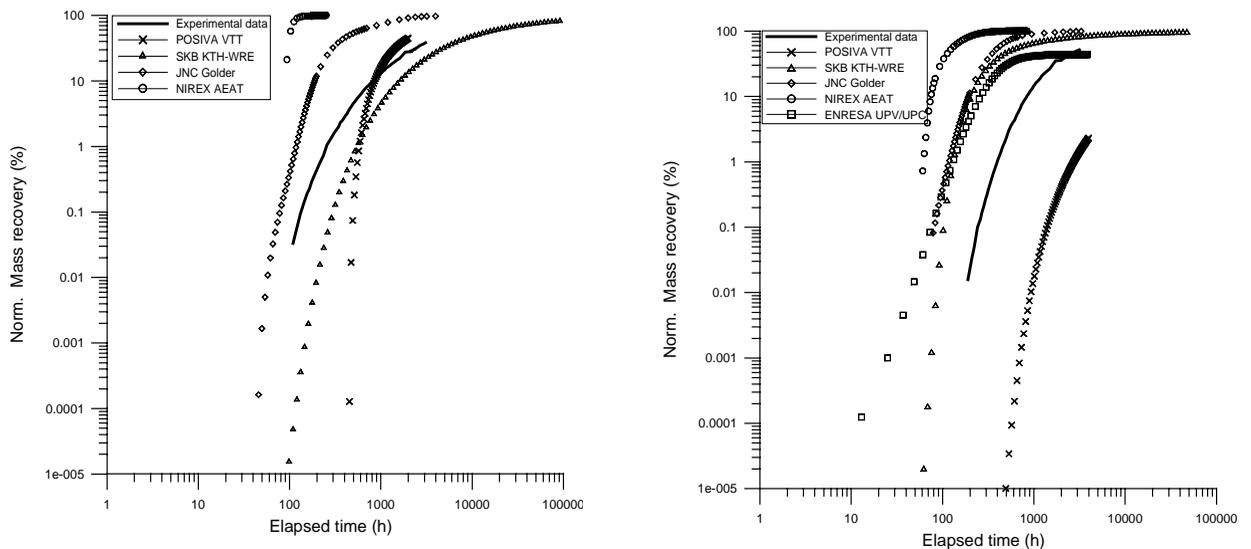
8. Relative importance of retention processes and effects of time and scale

The results of the TRUE-1 *in situ* experiments [1, 16] show that for radioactive sorbing tracers of the alkali and alkaline metal groups (for which ion exchange is the main sorption mechanism), over transport distances of about 5 m, Na, Ca, and Sr were transported only slightly retarded compared to the reference conservative tracers, whereas Rb and Ba were moderately retarded, and Cs and Co were strongly retarded. A similar relative order of retention was also noted in the laboratory. In TRUE Block Scale, a similar pattern emerges for a single-structure flow path over a length scale of about 15 m (C1). However, no breakthroughs of [83]Rb (C3) and [137]Cs (C2) have been observed after some six months of pumping for the two longer and more complex TRUE Block Scale flow paths, 35 and 100 m long, respectively, cf. Figure 2. This in contrast to performed model predictions which overall projected breakthrough. The recovery of ^{137}Cs in the case of TRUE-1 (STT-1) was about 37% after some 11 000 hours, indicating that 63% of the mass still remained sorbed in the injection section and in the fracture [1]. Continued sampling and employment of developed techniques to lower the measurement limit are expected to reveal whether the observations made in TRUE Block Scale in fact are true indications of a more pronounced retention on a larger scale, compared to the detailed and laboratory scales. Possible explanations for the observed discrepancy may arise from differences in mineralogy, or alternatively from more pronounced effects of fault breccia compared to conditions prevailing in Feature A at the TRUE-1 site.

The results of the modelling of the TRUE-1 experiments show that different (combinations of) processes can be used to explain the experimental results [13]. Diffusion/sorption is considered to be the most important retention process and (matrix) diffusion has indeed been manifested in the - 3/2 slope observed in the tailing of some of the breakthrough curves. However, there are disparate opinions about the pore space that actually is involved. These alternate conceptual models include: multi-rate diffusion [17], diffusion into stagnant pore spaces [18, 19] and diffusion/sorption in fault gouge [11]. Cvetkovic *et al.* [16] compared different retention processes and concluded that only unlimited diffusion/sorption in the rock matrix suffice to explain the experimental data from TRUE-1, cf. Figure 7.

Figure 7. **TRUE-1: Assessment of model sensitivity; Pure surface sorption [∅],**
pure first-order kinetic sorption [∇], and pure unlimited diffusion/sorption [x] in matrix for:
***a*) Ba-133 and *b*) Cs-137, both from STT-1 [16], cf. Figure 1.**
Best fit [o] includes combined effects of diffusion/sorption and first-order kinetic sorption.
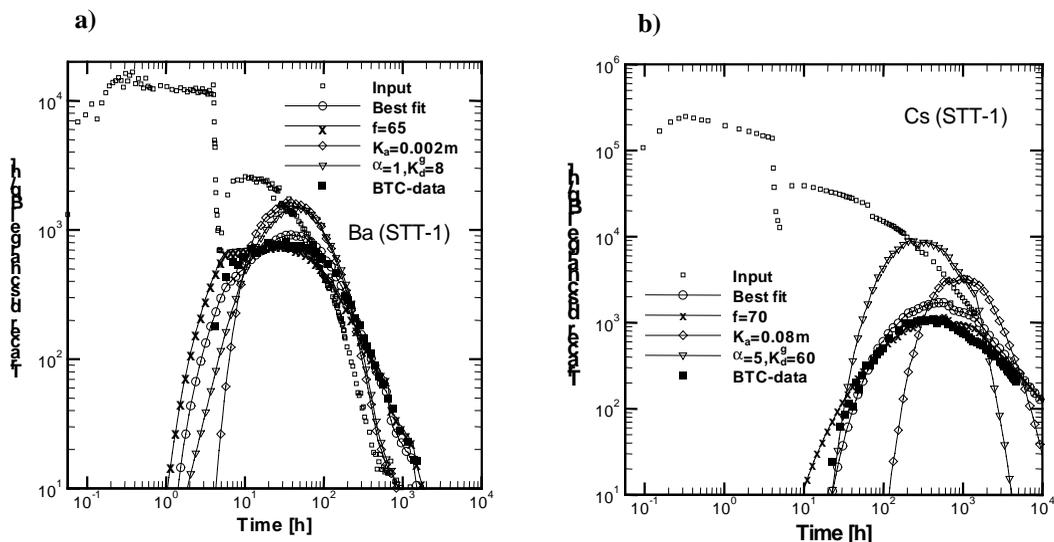
Some of the models identify that the laboratory-derived D_e and K_d, primarily representative of unaltered Äspö diorite bedrock, are too low and not representative of the observed retention in Feature A and its rim zone. Alternative explanations for the noted enhanced retention include effects of complex (3D) flow paths including fracture intersection effects [19, 20] which could provide the necessary larger flow-wetted surface, or heterogeneous, multiple sandwiched flow paths in the fracture plane [11,19].

Over the time scale of the three TRUE-1 experiments with radioactive sorbing tracers, approximately 1.5 years, the observed drop in salinity of the groundwater in the investigated fracture system (particularly in $[Ca^{2+}]$) from about 1 700 mg/L to about 1 000 mg/L was expected to increase sorption (K_d) by a maximum of 70% [1].

9. Outlook and measures to resolve conceptual and parametrical uncertainties

In order to resolve the conceptual difficulties associated with the pore space providing retention over the spatial and temporal scales of the TRUE-1 experiments, the developed *in situ* resin-injection technology will be employed. A performed pilot test at Äspö HRL demonstrated the capability of the methodology to statistically characterise fractures with physical apertures in the order of 240-270 microns [1]. This technology applied to the TRUE-1 site would provide not only a more detailed spatial description of the pore space, but also a more detailed description of the interior constitution of Feature A including its altered rim zone along relevant parts of the flow path. In addition, a possibility would open to map diffusion penetration depths and preferential sorption sites for the radionuclides that have not decayed, e.g., ^{137}Cs. Such an exercise would also shed light on possible 3D effects (including the role of intersecting fractures) and the existence of multiple channels (heterogeneity).

An improved understanding of the retention properties of gouge material is required in order to improve conceptual models of conductive fractures and improve predictive capability of models used for experimental time scales. Although the laboratory database on intact unaltered bedrock samples from TRUE-1 may not be fully applicable to the experimental time scales employed, it is projected that the laboratory database is relevant to PA time scales. If this can be demonstrated and generalised, and further that no account is necessary for the available pore space for limited diffusion (provided by the fault breccia/fault gouge) to make the PA safety case, the need to characterise flow paths in detail in site characterisation can be relaxed. Experiments of the TRUE type at different scales can typically be used to demonstrate site specific understanding of processes and phenomena relevant to experimental time scales.

Estimation of the flow-wetted surface needs to be better resolved, possibly through a combination of *in situ* tests (e.g., from emission of naturally occurring gases) and numerical modelling. The SKB project team, from the analysis of the TRUE-1 tests, provided an estimate of the "flow-wetted surface (per volume of water)" of about 3 000-6 000 m^{-1}, which lies within the range suggested in the literature.

10. Conclusions

The TRUE experiments performed at Äspö have successfully demonstrated the possibility to run well-controlled quantitative experiments with radioactive sorbing tracers in interpreted single structures and networks of deterministic fractures/structures over length scales < 100 m.

Prerequisites for design, performance and associated model prediction and evaluation of such tests are robust hydrostructural models of the studied networks of structures. Of special importance in building such models in fractured crystalline rock are observations of connectivity as obtained from pressure responses together with borehole TV images and detailed flow log data. Tracer dilution tests have been identified as crucial for identification of candidate source sections for tracer tests in the borehole arrays, and also as a means to verify hydrostructural models.

Numerical modelling of the TRUE experiments have been performed with a wide range of approaches/concepts ranging from analytical models, through stochastic continuum, discrete fracture network and channel network models, to more performance assessment type model approaches. The results indicate successful outcome of model predictions in relation to experimental data on a length scale < 15 m. The evaluation of the TRUE Block Scale experiments is expected to help increase predictive capability on a 100-m length scale.

Unlimited diffusion/sorption is regarded as the most important retention process for the TRUE experimental time scales. However, in the case of the TRUE-1 experiments, no unambiguous proofs exist as to whether the accessible pore space is provided by the rock matrix (altered rim zone including fault breccia pieces/fragments) or possible fine-grained fault gouge. Impregnation of TRUE Block Scale wall rock and fault breccia pieces/fragment samples with ^{14}C-PMMA have helped reveal characteristics and distributions of porosity of important constituents of the studied transport paths. A "*post-mortem*" injection of epoxy resin with subsequent excavation and analysis is regarded as the principal means to reveal the internal structure of tested fractures/structures (including Feature A) and their relation to the surrounding fracture network. Such an analysis will also assist in assessing the relative importance of pore spaces, thereby reducing the uncertainty associated with conceptual and numerical modelling of transport and retention in fractured rock at Äspö HRL.

Acknowledgements

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Do We See *In Situ* Sorption?
Can Useful Information Be Derived for Migration Modelling?

Juhani Suksi
University of Helsinki, Finland

Kari Rasilainen
VTT Energy, Finland

Cécile Le Guern
BRGM, France

Timo Ruskeeniemi
Geological Survey of Finland

1.   Introduction

Distribution coefficient K_d, expressing the equilibrium partitioning of an element between solid and liquid phases in a laboratory batch experiment, is in routine use in PA migration models. An inherent limitation is that a K_d is valid for only one set of conditions (under which it was determined). To further develop the applicability of the K_d, researchers have generated K_d values that vary as a function of additional environmental parameters. They include the look-up table K_d, the parametric K_d and the mechanistic K_d [1]. A more limiting factor, however, is our lack of knowledge as regards variations in physico-chemical conditions (aqueous, solid and gaseous phases) and exposed mineral surfaces along migration routes. Indeed, future geochemical evolution can only be postulated.

In the Fennoscandian shield, which is a future host of at least two spent nuclear fuel repositories, major changes in surface environment are expected to occur during the next glaciation cycle, as deduced from current climatic models. The most drastic changes should occur during the culmination points at the glaciation-deglaciation period. Impacts on hydrogeology are also expected. In terms of hydrogeochemical conditions, such a future period will be roughly similar to the corresponding preceding cycle. Natural analogue studies appear thus meaningful for predicting future migration of radionuclides from spent nuclear fuel repositories [2].

In this paper we consider U migration/retardation in terms of past changes. Long-term partitioning of U between rock and groundwater is discussed in the light of observations made at the Palmottu natural analogue site [3].

2.   Uranium as an indicator of spatial and temporal changes

Understanding processes that have affected radionuclide migration in the *past* is important in developing modelling approaches for migration in the future. The term "past" is defined here as a time interval between the present and the onset of the latest glacial cycle, i.e., some 150 000 years ago. This time period is important for three reasons. First, it encompasses changes on the ground surface that might occur during a similar period in the future. Secondly, it overlaps the best application range of the U-series disequilibrium (USD) technique, an important method in natural radionuclide migration studies. Thirdly, this time period is considered most important in the Finnish PAs for spent nuclear fuel disposal [4]. A natural radionuclide migration study is meaningful in a PA if the occurrence of migration processes in relevant time scales can be shown to be understood.

Valuable information is obtained by studying modes of occurrence of natural U and measuring decay series disequilibria. Indeed, the time period needed to equilibrate any disequilibrium is not more than one million years and, further, the radioactive disequilibria always reflect changes in ambient condition [5]. Valuable information of spatial and temporal changes in bedrock conditions may be derived from the combined body of evidence from three types of observations. These are observations from (1) shallow versus deep bedrock conditions, (2) from flowing channels versus lower transmissivity fractures, and (3) from the behaviour of redox sensitive U. Some evidences of these changes at Palmottu natural analogue site are presented in Figure 1. They all describe U migration and retardation events that have occurred during the last 300 000 years and within a relatively small bedrock volume (0.002 km^3).

Figure 1. **Recent U mobilisation at the Palmottu natural analogue study site [3].**
Upper left: **U-series data from fracture coatings plotted on a Thiel's diagram show general trend of U accumulation.**
Lower left: **Model age distribution of the single-event U accumulations indicated in the upper left figure.**
Right column: **USD profiles in drill core samples measured away from water-carrying fractures. Activity ratios of Th-230/U-234 exceeding the equilibrium value of unity indicate significant U removal from rock to fracture. High values (exceeding 2) further reflect much more recent removal than the time period needed to equilibrate the Th-230/U-234 activity ratio to unity (*i.e.,*~300 000 years). Generation of such large activity ratios requires significant amounts of labile U on pore surfaces (susceptible to groundwater leaching).**
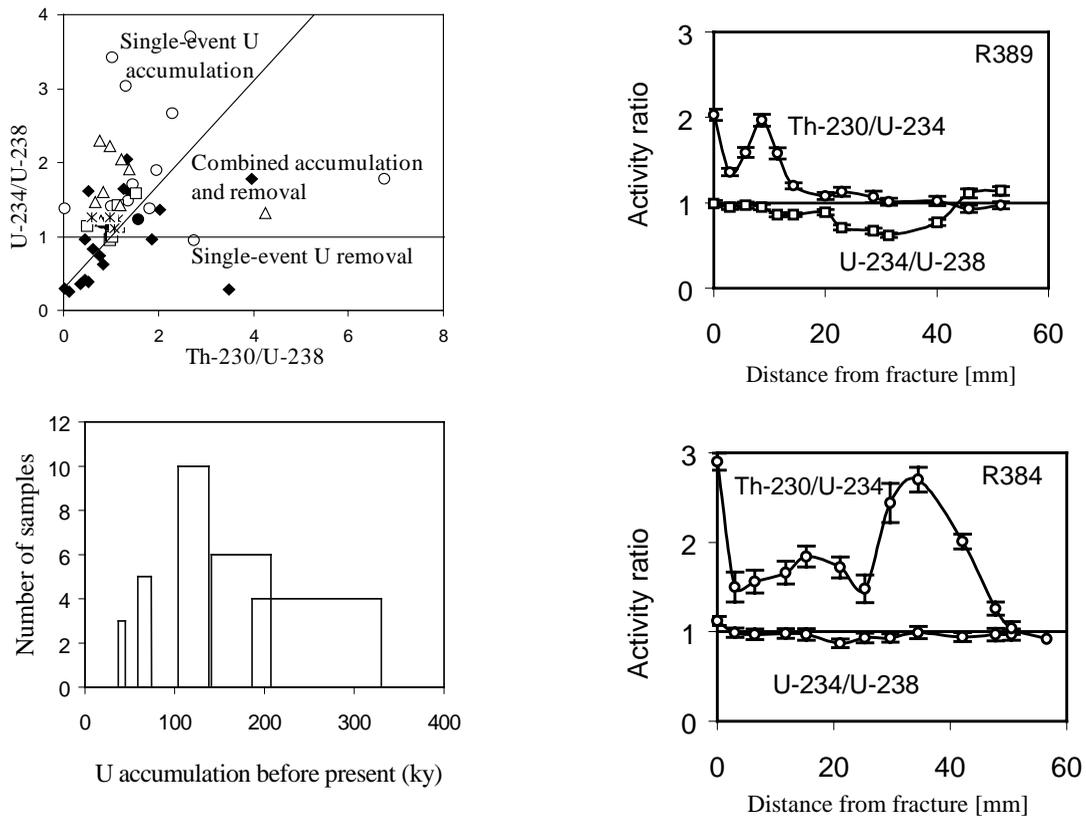
3.   Laboratory K_d versus *in situ* partitioning

Radionuclide concentration in groundwaters is determined by the geochemical nature of its source (amount, rate of release, aqueous and solid processes). Dissolution/precipitation and adsorption/desorption are the most important processes. Prolonged time may cause other processes to occur, such as diffusion, absorption, surface substitution, and surface precipitation, which may be considered irreversible in the sense of the K_d concept. The occurrence of such processes makes it difficult to quantify the adsorbed amount. To obtain a distribution coefficient more representative to natural conditions, an *in situ* K_d value has been suggested as it is obtained by dividing the *in situ* concentration of a radionuclide in solid phase by that in the corresponding liquid phase.

There have been in-depth discussions in the literature of means to separate the inventory sorbed reversibly *in situ* from those fixed more permanently [6]. From experimental point of view, this discussion stems from the fact that the used experimental method, i.e., selective chemical extractions, provides merely operationally defined inventories that are difficult to link directly to any single geochemical process, like adsorption. On the other hand one should keep in mind that the laboratory-based K_d could neither be linked to any single *in situ* process. Both approaches are therefore needed. Figure 2 describes the basic difference between the two approaches.

Figure 2. **Solute distribution between solid and liquid phases in laboratory (K_d) and in natural environment (*in situ* K_d).**
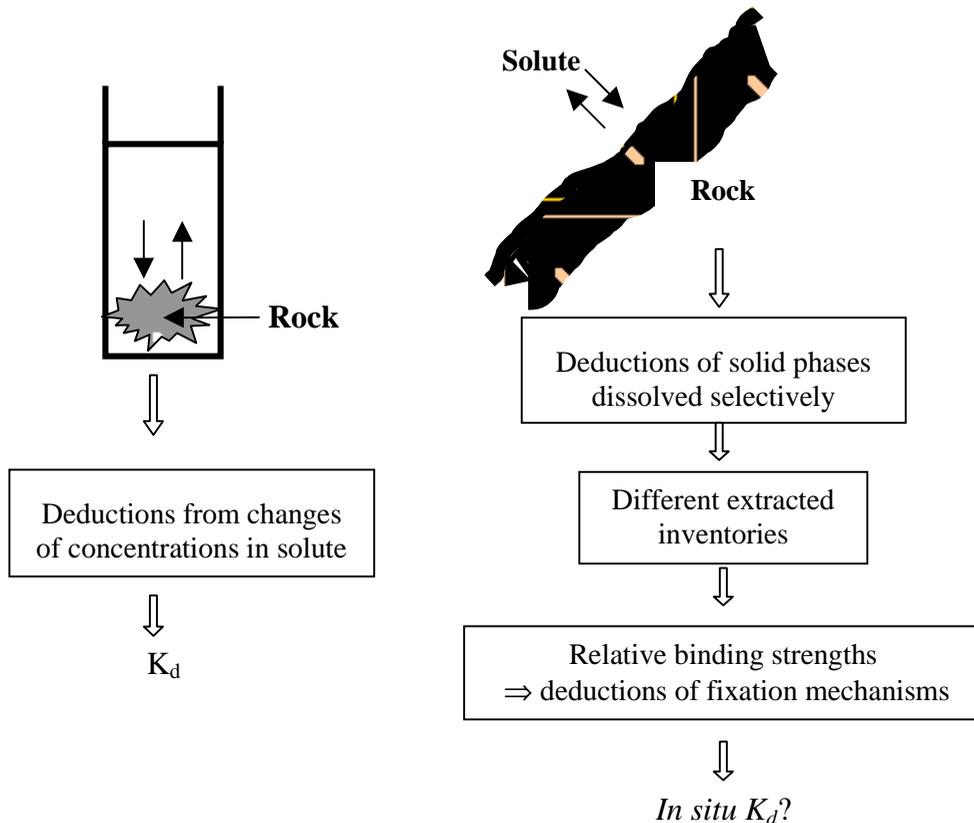
The problem of incompatibility of the experimental concept of sorption (i.e., we attempt chemically separate reversibly fixed phase) and the modelling concept K_d (which describes equilibrium partitioning in laboratory) is considered in Figure 3. The *in situ* inventory in the solid phase has been divided into two co-located components in terms of K_d and irreversible attachment.

Figure 3. **Schematic concept of partly irreversible sorption.**
The quantity accumulated into the irreversible sink is replaced instantaneously by
an equal amount from the aqueous phase [7]. The total *in situ* inventory in solid is $C_{total} = C_1 + C_2$.

Batch experiment => K_d

C_1^+

C_1
Sorption equilibrium

$\lambda' C_1$

C_2
Irreversible sink

In situ accumulation
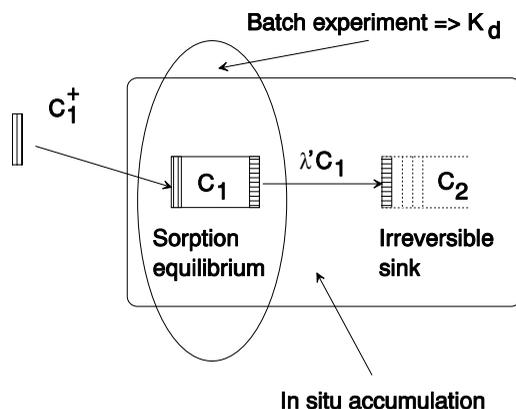
The first inventory, C_1, represents the inventory always in adsorption equilibrium with pore water or groundwater. This inventory is the adsorbed amount represented by the K_d concept. The second inventory, C_2, represents a gradually increasing inventory that is more and more isolated from the groundwater. There is a slow mass flow from C_1 to C_2. At the onset of adsorption, C_2 equals zero, but with time it slowly increases, and may eventually dominate the *in situ* inventory ($C_2 \gg C_1$). Using the above concept, the problem of quantifying only the reversibly fixed inventory can be illustrated as separating C_1 from C_{total}. Experimentally, the separation is difficult to do because irreversible inventories may be extracted as well, and the extraction results are, thus, somewhere between C_1 and C_{total}.

4.   Can natural adsorption be quantified by the extractions?

The use of the extraction technique is based on the idea of reversing natural fixation by selectively dissolving the fixed inventory. The choice of reagent for dissolution is based on operationally defined target phases, e.g., the adsorbed phase is separated with the excess of competing ions (works for ion exchange and physical adsorption), and (co)precipitations are dissolved selectively [8]. The extraction technique has been widely used to study the geochemical association of natural radionuclides. Several alternative extraction procedures, depending on sample material, have been applied for U [e.g., review in [9]]. Extracting differently fixed U phases from various sample materials has received a fair amount of attention in the literature [10].

Reversible *in situ* fixation of trace elements is extremely difficult to quantify technically. In fact, selective extraction technique may be the only way to do it. Though various surface spectroscopic techniques are available, their greatest value is to study the occurrence of adsorbed species and their bonding on mineral surfaces. Combination of these techniques would be most useful. Good examples of parallel use of these two techniques and surface analyses can be seen in a recent NRC report [11].

Figure 4 shows a typical extraction result. In this case, information of U fixation was attempted by examining the relative binding strength of U in fracture-coating material by successively dissolving by a set of reagents [12].

Figure 4. **Natural partitioning of U in four different calcite-bearing fracture coatings (presented as different bars), modified from Suksi *et al.* [12].**
Each sample was successively extracted by the same set of reagents.
Reagent 1 = **strong electrolyte (here 0.5M CsCl, pH ~7;**
later replaced by 1M CaCl$_2$ prepared in groundwaters).
Reagent 2 = **NH$_4$OAc buffer solution (pH = 4.8).**
Reagent 3 = **TAO (oxalic acid-oxalate mixture, pH = 3.6).**
Reagent 4 = **total dissolution (HF + HCl + HNO$_3$ mixture).**
First bar represents material rich in kaolinite. A distribution of differently fixed U inventories was obtained indicating that *vis-à-vis* the concept in Figure 3. C$_1$ can be distinguished, but C$_2$ has a more detailed inner structure.
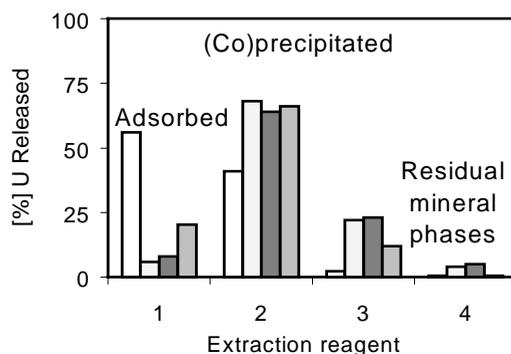
Does the result of strong electrolyte extraction (first four bars in Figure 4) represent adsorbed U? This can not be answered for sure. To scrutinise the extraction, a subset of crushed rock was "washed" with ammonium acetate to remove *in situ* adsorbed species and to "clean" sorption sites. Distribution coefficient K_d was then determined for both "washed" and untreated natural batches of the same rock using laboratory batch experiment. Systematically larger sorption for "washed" rock material was obtained, indicating that U sorption sites can be wet chemically controlled [13].

Synthetic U-ferrihydrite and U-lepidocrocite systems were prepared to study in more detail the extraction capability of 1M CaCl$_2$. Lepidocrocite was prepared as a crystalline reference material for the amorphous ferrihydrite. Ferrihydrite is commonly seen on fracture surfaces, indicating interaction in oxic environment. Precipitation of minerals was carried out in a system mimicking their natural formation [14]. The minerals were confirmed by XRD. Uranium was sorbed on both minerals into the structure during their formation. After formation the minerals were taken to standard batch experiment with U-236 as tracer U to quantify their sorption capacity on the external surfaces. This mimics the process of extra U interacting with the minerals (e.g., U released from a repository). Aliquots were prepared for the analysis. The extraction of U sorbed during the formation of the minerals was studied with the first aliquot (Figure 5). Then extraction of U-236 and the effect of isotope exchange were studied for the second aliquot (Figure 6).

Extraction results clearly indicate strong and weak fixation for U. Furthermore, different types of surface reactions may be deduced (sensitive to CaCl$_2$ and NH$_4$OAc, respectively). Because of the high ionic strength of 1 M CaCl$_2$, the extraction results may be used to consider whether the inner sphere or outer sphere surface complexes are present. One should keep in mind, however, that the used experimental conditions (1 M CaCl$_2$ was prepared in synthetic groundwater, pH ~ 8) favour highly charged carbonate complexes. The activity of these is significantly affected by ionic strength [15], probably affecting the extraction result. In any case we have seen reversible sorption, but more detailed studies could reveal the fine inner structure of the adsorbed component.

Figure 5. **Extraction of structural U from lepidocrocite and ferrihydrite using successively**
1M CaCl$_2$ (20 min) and NH$_4$-acetate buffer solution (5 and 50 min) AAc5 and AAc50, respectively.
N.B. Only part of U was removed by the extraction (the rest remains more strongly fixed).
The crystalline mineral appears to release its U contents more easily.
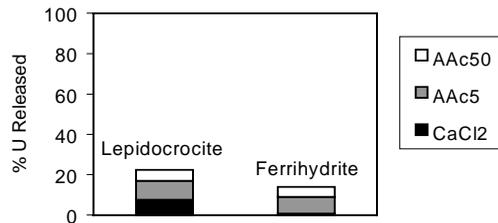
Figure 6. **Extraction of tracer U from lepidocrocite and ferrihydrite by successively applying**
Allard water for 4 days (dark bar) and 1 M CaCl$_2$ for 20 minutes (white bar).
The easily extractable inventory (sensitive to CaCl$_2$) is seen to be bigger for the tracer U
than for the original U in Figure 5. However, all tracer U attached is not easily extractable,
but has been fixed to stronger sorption sites (insensitive to CaCl$_2$).

Figure 7.   **Experimental set-up for natural fracture surface (NFS) approach [16].**
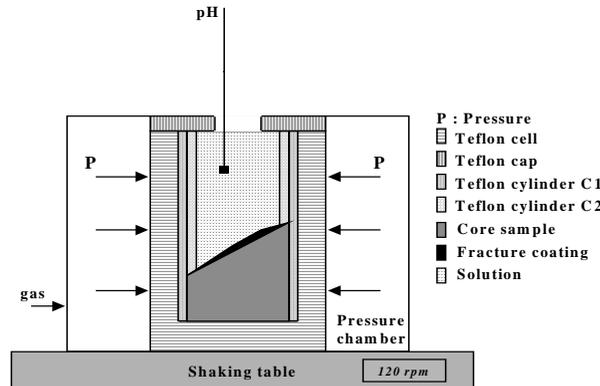
5.   Towards more realistic adsorption modelling

Development of models capable of describing adsorption to single mineral phases has been considerably advanced in recent years [1,11]. Natural mineral assemblages, however, appear so complex that alternative, more generalised modelling approaches have been considered [11]. Realistic adsorption modelling was also the aim in the Palmottu Natural Analogue Project. In addition to the extraction studies, a new experimental, natural fracture surface (NFS) approach was started to study *in situ* sorption. In the approach, chemical exchange between the liquid phase and a well-characterised natural fracture surface (optical microscopy, SEM) is monitored (Figure 7). A reconnaissance study to examine

the feasibility of the NFS approach was carried out using fracture surface samples from water-conducting fractures [16]. The chemical exchange was monitored by analysing U, major species, and pH in the liquid phase (synthetic groundwater) as a function of time. In the preliminary modelling, we used Specific Chemical Simulator (SCS) under Allan-Neptunix modelling environment [17]. The main chemical species and minerals were taken from the field observations at Palmottu ([3] and references therein), preliminary thermodynamic calculations (EQ 3-6) [18] and literature data [9,15,20,21]. Acid-base complexation and ion exchange were used as surface reactions. Model fit was obtained by varying the total number of reaction sites for the surface reactions. For U mass balance calculation, the adsorbed U (i.e., weakly attached) was quantified by extraction with 1 M $CaCl_2$.

In all studied fracture surfaces, a rapid release of U was observed initially during each equilibrium (desorption) step. The rapid U release was followed either by a steady-state or a slower rate of U release. The final U concentration in water was close to that determined in independent groundwater analyses. The modelling gave a fairly good reproduction of the observed initial rapid U release. An example is given in Figure 8 where observed desorption of U is compared to the modelling result.

Figure 8. Calculated and measured evolution curves for U desorption from fracture surface in synthetic U-free groundwater (sample R318). Model fit was obtained in each desorption step by varying the total number of sorption sites [16].
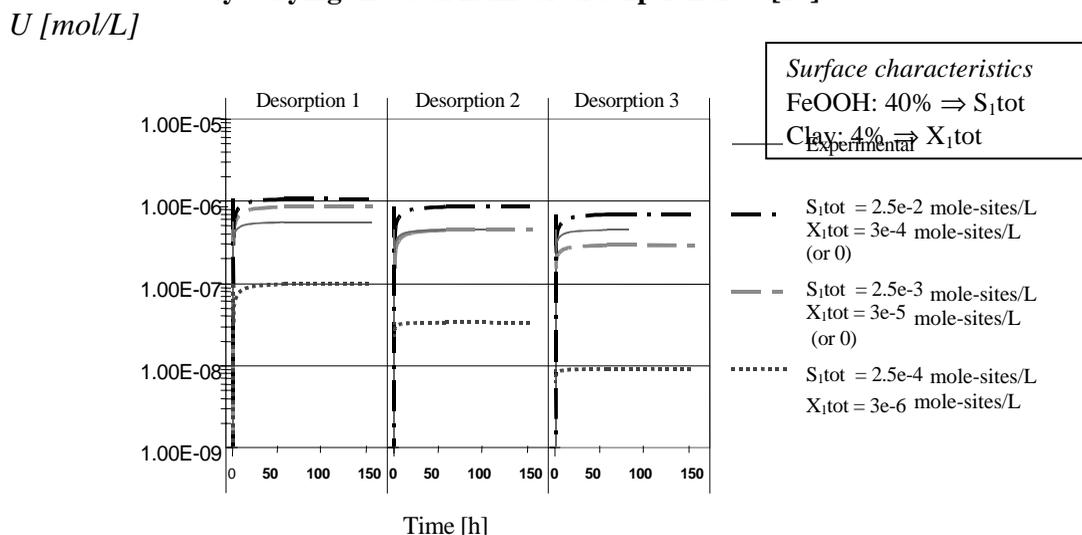
The preliminary results were encouraging and demonstrate the feasibility of the approach in producing information of naturally occurring adsorption phenomena. Knowing this is needed in developing more detailed modelling approaches for sorption.

6. Concluding remarks

It appears that there is a great potential in using chemical extractions to obtain qualitative and quantitative information of the traces of long-term *in situ* sorption. After a more systematic scrutiny of the extraction technique, significant contribution to developing mechanistic sorption modelling may be expected. Extraction technique may be of great use in examining how and to what extent complex natural material should be characterised in order to obtain conceptually more rigorous mechanistic sorption models.

Observations of U attachment at the Palmottu natural analogue site clearly show that the long-term partitioning of U is difficult to interpret using K_d because reversibly attached inventory is only a small part of the whole *in situ* inventory of U. By definition, K_d applies only for the reversible subinventory. This important finding may be used to quantify the degree of conservatism in K_d selection for PAs.

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Evidence for Matrix Diffusion in the TRUE-1 Block at Äspö Based on Fracture Characterisation and Modelling of Tracer Tests

Martin Mazurek

GGWW, Institutes of Geology and of Mineralogy and Petrology, University of Bern, Switzerland

Andreas Jakob

Waste Management Laboratory LES, Paul Scherrer Institute, Villigen-PSI, Switzerland

Abstract

In situ tracer tests using uranine and differently sorbing radiotracers over distances of metres in fractured granitic rock were conducted in the Äspö Hard Rock Laboratory (Sweden) at 400 m below surface. These tests were accompanied by: (1) a detailed structural and petrological characterisation of the test volume, and (2) a modelling effort to identify the most relevant transport and retardation processes and to constrain parameter values. Due to the short duration of the experiments (hours-days), tracers interact with a very limited volume of the rock, and thus tracer retardation due to matrix diffusion and sorption may occur exclusively in the fracture-filling fault rocks, specifically in fault gouge and, to a lesser extent, in adjacent cataclasite. On the other hand, the unaltered and undeformed bulk rock is not expected to interact noticeably with the tracers over the timescales of the experiments.

The flow field was characterised on the basis of a simple 2D-streamtube formalism with an underlying homogeneous and isotropic transmissivity field. Tracer transport was modelled applying the dual porosity medium approach, which is linked to the flow part of the model by the flow porosity. Calibration of the model was done using the data from one single uranine breakthrough (PDT3). The analysis of the PDT3 test clearly showed that matrix diffusion had to be included in the model, evidenced by a characteristic shape of the breakthrough curve.

Blind-predictions were made for the breakthrough curves of a number of tracers, considering advection/dispersion in fractures as well as limited matrix diffusion and sorption in fault gouge. After the disclosure of the measurements, the predictions were compared with the experimental findings and turned out to be very good for non-sorbing species but somewhat less precise for sorbing tracers, most likely due to the limited knowledge of the diffusion and sorption characteristics of fault gouge. It is concluded that matrix diffusion into fault gouge is likely to be a relevant process even over the short experimental timescales. However, the tracer tests do not yield information with regard to matrix diffusion into the undeformed wallrocks because of the limited timescales of the experiments. The extrapolation of the findings to larger scales in space and time is not straight-forward, because tracer retardation will be dominated by different rock types at different times. While fracture-filling gouge materials are very efficient in retarding tracers at early times, their volume is very small and, with time progressing, retardation will be dominated by altered wallrock and, finally, by fresh granite. In such fresh granitic wallrock, both porosity (and therefore the effective diffusion coefficient) and sorption K_ds are more than one order of magnitude smaller compared to fault gouge, thus indicating that radionuclide retardation is expected to be present but less pronounced.

1. Introduction

Geological and hydraulic properties of faults and fractures of different sizes were studied in the Äspö Hard Rock Laboratory in granitic rock of SE Sweden (general overview in Stanfors *et al.* [1]) at depths of 0-450 m below surface. A number of regional water-conducting faults that extend over kilometres were penetrated by the 3 700 m long tunnel system. The quantitatively largest part of visible water inflows into the tunnel is related to faults extending over distances in the decametre scale. Even smaller hierarchies of water-conducting fractures (metre scale) are identified in boreholes, even though, in general, their transmissivity is lower and so they do not visibly discharge into the tunnel. The understanding of the mechanistic principles of the faulting process, together with a detailed characterisation of the hydrothermal water/rock interactions experienced by the rocks, are important for the description of the geometry of the fracture network on all scales, as well as of the geochemical properties of the rocks.

The geological investigations are used as support of the quantitative evaluation of dipole tracer tests that were conducted in the framework of the Tracer Retention Understanding Experiment (TRUE-1 [2]). TRUE-1 consists of a number of *in situ* hydraulic and tracer tests conducted on a scale of metres, using conservative, weakly and moderately sorbing radioactive tracers.

The objectives of this paper include

- To demonstrate how hard and soft geological field data can be used to constrain conceptual models that are needed for quantitative predictions of tracer transport and parameter evaluation, either for short-duration dipole tracer tests or the long-term and large-scale contaminant transport through fractured granitic rock.

- To identify the relevant transport and retardation processes that govern tracer migration during the short-duration tracer experiments, and also to identify the rock domains in and around fractures in which these processes occur. In specific, the role of matrix diffusion is addressed.

2. Geological investigation methods

In a first stage, the geometries and rock domains of decametre-scale water-conducting features were investigated by the following methods:

- Detailed data acquisition and mapping of water-conducting features in the tunnel.

- Mapping of faults in surface outcrops at Äspö island on a scale of 5-20 m.

- Drilling of large-diameter (20 cm) boreholes through the central parts of water-conducting faults in the tunnel, followed by epoxy impregnation.

- Laboratory programme to characterise the detailed anatomy and pore-space distribution in water-conducting faults (mostly based on the analysis of resin-impregnated rock slabs and thin-sections) and the nature and spatial arrangement of fracture infills and wallrock domains (mineralogic analysis, porosimetry).

In a second stage, investigations were focused on smaller-scale water-conducting features (with sizes in the range of decimetres to metres) in the so-called "TRUE-1 block", i.e., to the rock volume at 400 m depth in which the tracer tests were conducted. While these fractures are less transmissive than the larger faults (none of them visibly discharges water into the tunnel), hydraulic borehole tests indicate that they make part of an interconnected fracture network [2]. The investigation methods included:

- Detailed geological core logging.

- Analysis of BIPS (Borehole Image Processing System) images of the borehole walls.

- Mapping and line counting on tunnel walls (scale of metres).

- Downscaling of information derived from the investigation of larger faults.

- Deterministic and stochastic visualisation of the fracture network in the test volume.

3. Geological characterisation of water-conducting features

3.1 Geometry of faults with lengths in the range of decametres

Close to 100 decametric water-conducting features (i.e., those cross cutting the entire tunnel profile) were studied and mapped that visibly discharge water into the tunnel [3]. The analysis indicates that they are mostly related to steeply dipping faults. While flat-lying structures (fractures, joints) also exist in the tunnel, their sizes are more limited, and their transmissivities are in general not sufficient to result in water inflow points.

Figure 1. **Fault geometries of five types of water-conducting features on a scale of metres.**
The sketch in the lower right corner schematically illustrates the evolution of the growth and linkage of master faults and splay cracks, resulting in fault steps and locally different fault geometries.
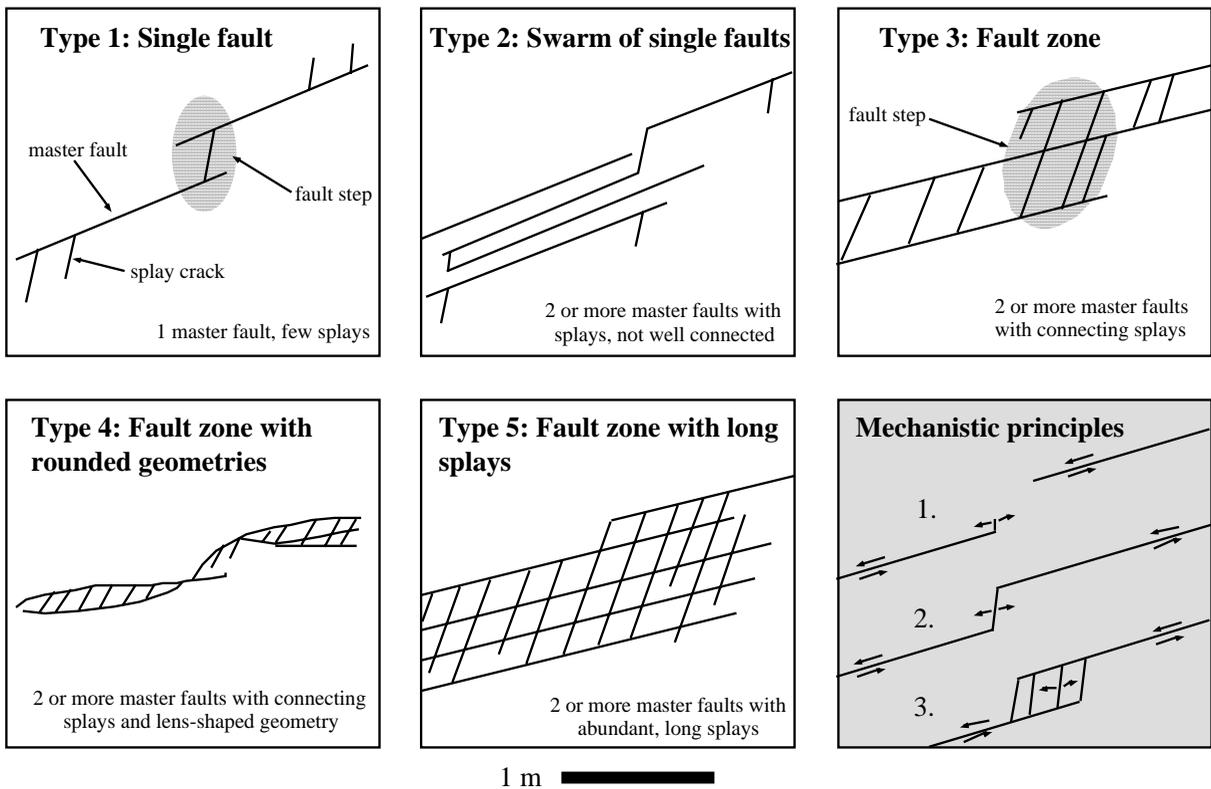
Based on their geometry, five different types of faults can be distinguished and are shown in Figure 1. Each of these types of faults consists of two different elements, namely

1) *Master faults* along which shear displacement occurred and which are often associated with cohesive or incohesive fault rocks (such as cataclasites, fault breccias or gouges, see below).

2) *Splay cracks* that are tensile structures (joints) and typically have an angle of circa 30° to the master faults. Because no shear displacement occurred along these, they are in general devoid of fault rocks.

Figure 1 shows that the geometric variability of the faults is substantial, ranging from simple structures such as single faults with only few splays (type 1) to highly complex networks consisting of several parallel master faults connected by splay cracks (e.g., type 5). The strike direction of all faults

is predominantly NW-SE, and there is no discrimination among different fault types with respect to orientation. During fault growth, adjacent master faults may link together via splay cracks, which results in fault steps which consist of interconnected arrays of master faults and splay cracks (Figure 1). The observed fault geometries are consistent with the mechanistic principles of fault nucleation, propagation and linkage derived by Martel and Pollard [4]. Along strike, the fault anatomy is heterogeneous and includes geometrically simple segments (types 1 and 2 in Figure 1) alternating with segments of more complex geometries, which contain several master faults connected by densely-spaced splay cracks (e.g., in complex fault steps; types 3-5 in Figure 1). The length of simple and complex segments within the faults lies in the order of metres to few tens of metres according to surface investigations of large outcrops. Thus the geometric patterns of faults shown in Figure 1 characterise the variability along strike of the faults rather than fundamentally different families of faults.

3.2   Fault rocks

Many of the faults clearly document recurrent events of deformation and related hydrothermal alteration/cementation. At least three major deformation styles and types of fault rocks can be distinguished:

1) *Mylonites:* Ductile deformation at elevated temperature (> 400°C), leading to locally foliated to mylonitic zones in the otherwise massive granites. Due to dynamic re-crystallisation (which is inherent in the definition of a mylonite), no discrete fractures developed, and so mylonite zones per se are hydraulically no preferential flow paths today. Due to re-crystallisation of the fabric and the reduction of grain-size, matrix porosity of mylonite is even lower than that of undeformed granite.

2) *Cataclasites:* A first stage of brittle deformation at elevated temperature led to brittle faulting and the development of fault breccias and gouges in the central parts of the faults. The deformation was followed by hydrothermal activity, leading to a partial cementation of the faults rocks (mainly by epidote, quartz and chlorite) and an alteration of the wallrocks. Cementation restored the cohesion of the fault rocks, thus resulting in cataclasites. There are indications that such events of faulting, followed by hydrothermal water/rock interactions, occurred recurrently throughout the long history of the Precambrian granites.

3) *Fault breccias and gouges:* Some of the younger stages of faulting were no longer related to events of hydrothermal water/rock interaction, such that brittle fault rocks which resulted from the shearing process remain as incohesive fault breccias and gouges today. Incohesive rocks have been observed in most of the investigated faults.

Faults observed today in the Äspö laboratory contain the integrated record of deformation and alteration events that affected the rocks over the last 2 Ga. Because older structures represent pre-existing mechanical heterogeneities for younger deformation events, the same structures were reactivated recurrently and so contain different types of fault rocks. Thus the lithological heterogeneity is substantial within faults, and mylonites, cataclasites, fault breccias/gouges and wallrocks in various stages of hydrothermal alteration may occur along any single profile across a fault. The different rock units have highly contrasting properties, and relevant parameters such as porosity and sorption capacity may vary over orders of magnitude.

3.3   Detailed-scale anatomy of decametric faults

Dedicated large-diameter boreholes (circa 1 m long, 25 cm in diameter) were drilled for the characterisation of the anatomy of master faults on a detailed scale. In order to minimise core damage, the drilling axis was chosen parallel to the fault strike, with the master fault centred in the core. In the laboratory, the recovered cores were first evacuated and then impregnated by fluorescent resin under a pressure of 10 bars. Rock slices and thin-sections were prepared and used for the characterisation of the detailed geometries of rock types and pore spaces.

Figure 2. **Small-scale architecture of decametric faults.**
Left: **Structural elements record recurrent activity (mylonite-cataclasite-fault gouge).**
Right: **Core impregnated by fluorescent resin highlights present-day fluid pathways (UV light illumination).**
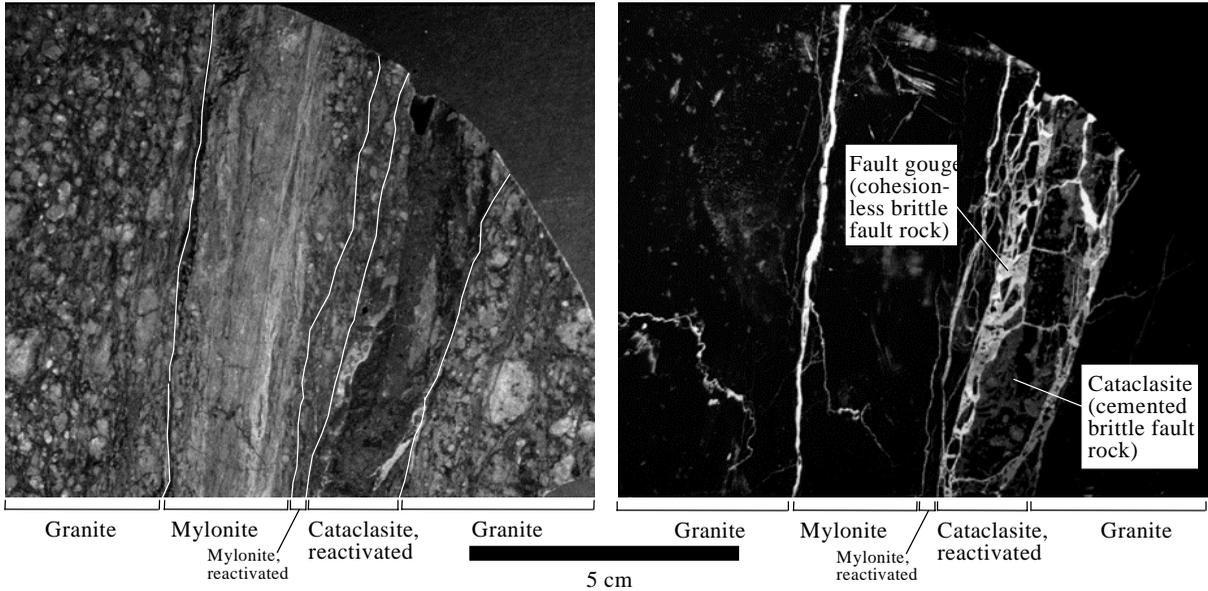
Figure 2 shows the distribution of different rock units and of fractures in a profile across the fault plane. The fault was active during different deformation events and contains a variety of different fault rocks, ranging from mylonites to cataclasites and incohesive fault gouges. It can be seen that most of the open fractures through which flow may occur are located along the contacts of different rock types, in specific along cataclasite and fault gouge horizons.

On a microscopic scale (Figure 3), it is seen that the bulk mass of the fault gouge is highly porous but discrete open fractures are located along the contact to the wallrock. Figure 3 suggests that flow may occur at the interface of fault gouge and wallrock, while the highly porous gouge material is accessible to diffusion. On the basis of the impregnated thin-sections, fault gouge porosity can be roughly estimated at 10-30 volume %, whereas direct measurements are not available (and would be difficult to obtain).

Figure 3. **Microscopic pore-space geometry observed in impregnated thin-sections (UV light).**
Interface between fault gouge (top) and wallrock (bottom), showing a naturally open microfracture with idiomorphic crystals on the walls. Width of micrograph 0.5 mm.
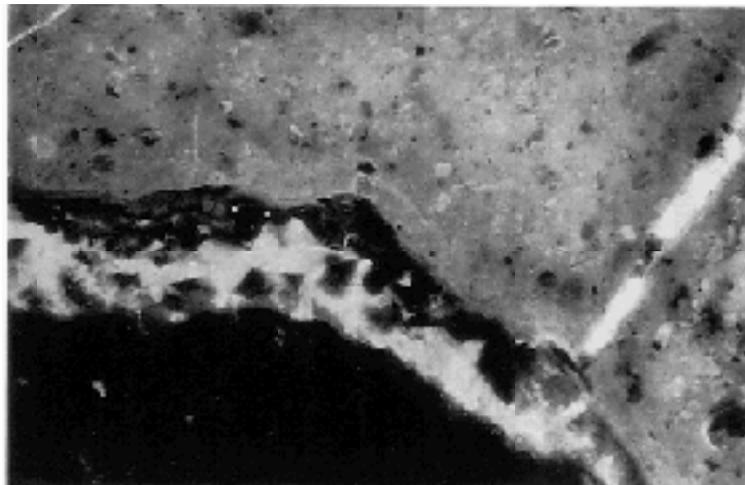
It is obvious from Figure 2 that the rock types adjacent to the actual flow paths are mostly fault rocks (fault breccia/gouge, cataclasite, mylonite) and not granite. Over typical timescales of dipole experiments (hours-days), tracers are likely to interact with the immediate surroundings of the fractures. Due to their enhanced porosity and higher sorption capacity due to the presence of clay minerals, the dominant interaction is most probably with fault gouge and cataclasite. While granite constitutes the largest part of the bulk rock volume, its role for water/rock interaction during tracer tests is very subordinate.

3.4   *Fracture geometries in the TRUE-1 block (with lengths in the range of decimetres-metres)*

The so-called TRUE-1 block has been chosen as the target volume for dipole tracer testing because it is devoid of decametre-scale faults as the ones described above (these structures actually bound the block). The circa 50 m long tunnel section through the TRUE-1 block is entirely free of visible water discharges or moisture zones. However, tunnel mapping (Figure 4) and borehole evidence clearly indicate that it contains a network of smaller-scale fractures and faults with trace lengths in the range of decimetres to metres. Fracture patterns and orientations are less regular than on the larger scale, and a mechanistic explanation is less straightforward. Most likely, the fracture pattern was determined by the local stress field generated by movements along the larger faults that bound the block.

A series of boreholes was drilled through the TRUE-1 block, and their positions are shown in Figure 5. Transmissivities were calculated from single-packer tests (measurement of differential outflow) and relate to intervals of 0.5 m length along hole. 65% of all intervals have a transmissivity above the detection limit (circa 10^{-10} m^2/s), with a maximum value of $2 \cdot 10^{-6}$ m^2/s [2]. Thus in spite of the absence of large faults, the whole TRUE-1 block is characterised by a very dense network of hydraulically active fractures. In some of the boreholes, a positive correlation with fracture frequency can be identified.

Figure 4. **Structural tunnel-wall map in the TRUE-1 block.**
Shaded areas indicate mylonitic zones, later reactivated by fracturing.

2965   1 m   2970
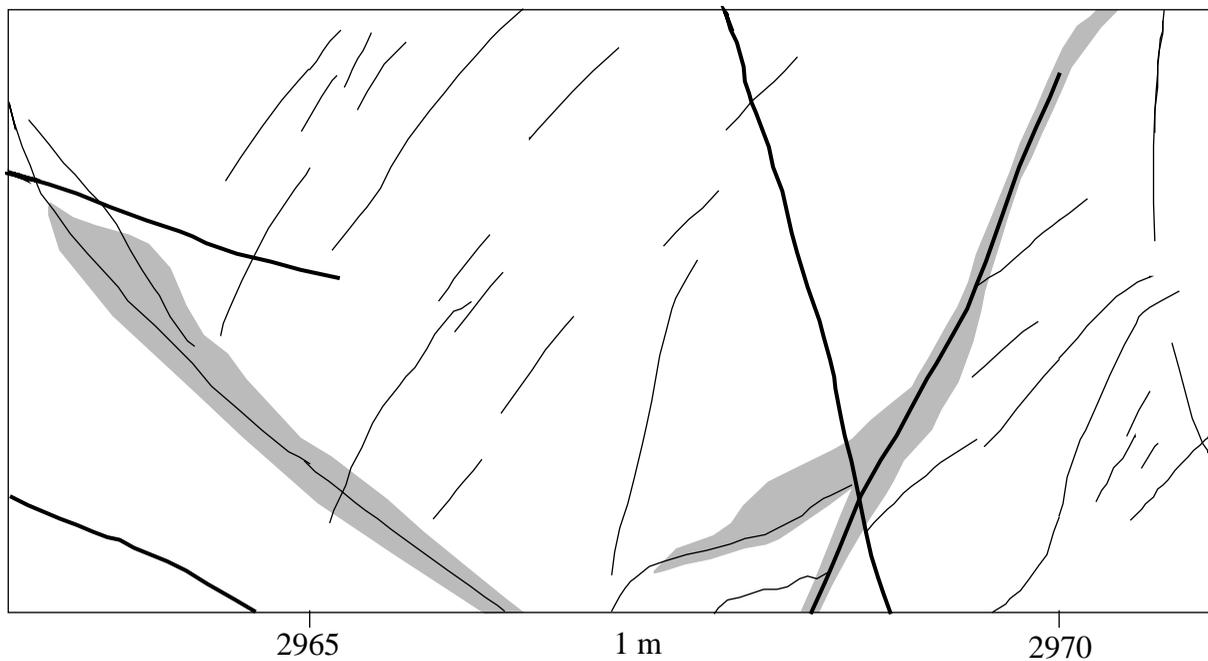
Larger-scale faults as described above often occur along pre-existing mylonitic zones. Such mylonites also occur within the TRUE-1 block, accounting for 16% of the total core material. BIPS

borehole-wall imaging indicates that the average fracture frequency in mylonitic zones is around 7 m^{-1}, which is substantially higher to the overall average of 4 m^{-1}. Thus similarly to the large scale, mylonites tend to focus and concentrate brittle fracturing. Moreover, as shown in Figure 4, fractures along pre-existing mylonites tend to be longer than fractures outside mylonitic zones (whose trace lengths are mostly below 1 m). On the basis of structural evidence, it is concluded that mylonites are potential zones of enhanced fracture connectivity.

While no clear distinction of interval transmissivities in and outside mylonites exists, hydraulic interference testing [2] indicates that crosshole responses are specifically high within the most prominent mylonite zone penetrated by the boreholes. This zone is 1-2 m thick and can be identified in all boreholes. The large part of this zone is only weakly affected by mylonitic deformation, resulting in the development of a planar fabric (foliation). Very strong mylonitic deformation, producing fine-grained, mica-rich fabrics, is concentrated to a limited number of discrete horizons (typically 3-6), each of which is only a few centimetres thick. These horizons focus the development of younger, brittle structures, such as cataclasites and open fractures, as illustrated in Figure 6. Because of their enhanced connectivity on a scale of metres at least, structures of this type have been chosen as the target for crosshole tracer testing that will be dealt with below.

Figure 5. **Structural model of the TRUE-1 block in cross-section (plane dipping 40° towards ENE, i.e., parallel to the KXTT boreholes that are shown in grey).**
Thick lines represent mylonite zones containing interconnected networks of fractures.
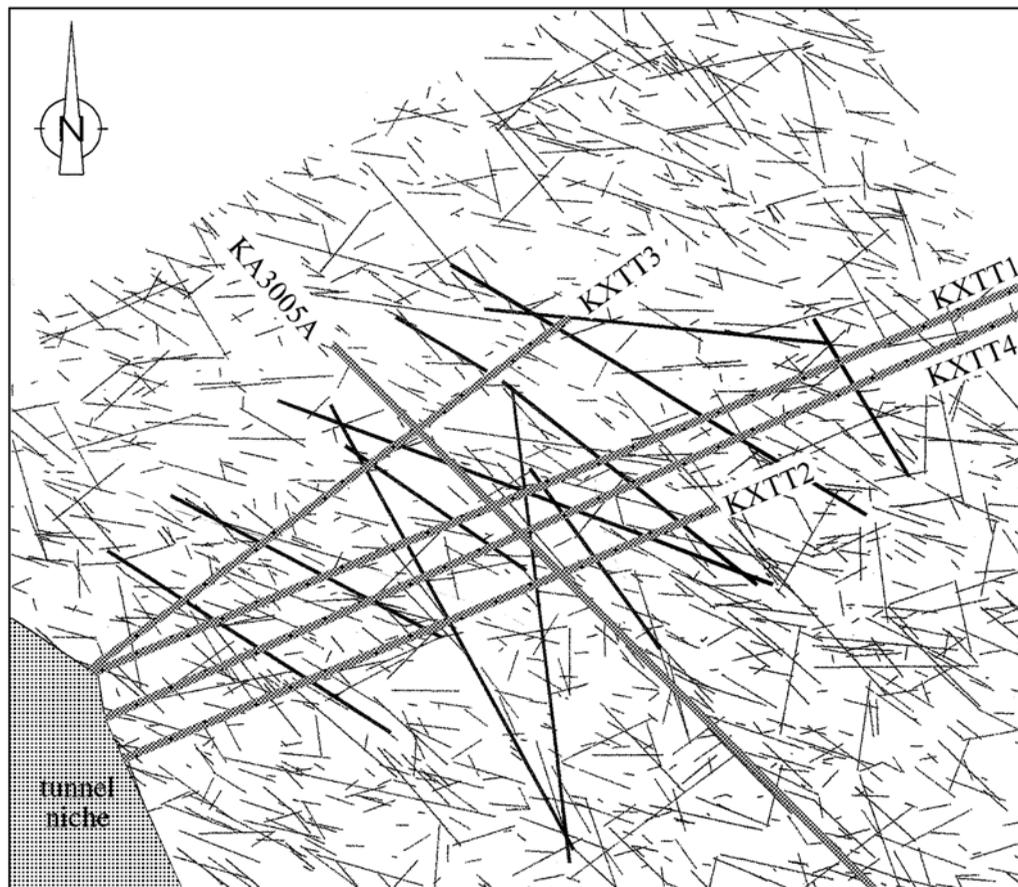
3.5 Structural model of the TRUE-1 block

A structural model of the TRUE-1 block was derived on the basis of geological and hydraulic information from the boreholes and from the adjacent tunnel wall and is shown in Figure 5. In the immediate surroundings of the boreholes, deterministic information based on core and borehole logging was used. However, the larger part of the model volume had to be described stochastically (based on discrete fracture network modelling) because individual fractures are mostly shorter than 1 m and cannot be extrapolated over larger distances away from their intersections with boreholes. The only structures that can be correlated between different boreholes are fracture systems that follow mylonitic zones, and these are represented by thick lines in Figure 5. The density of fractures in the model volume is enormous. As the majority of all fractures is transmissive, it is concluded that the TRUE-1 block represents a hydraulically well-connected fracture network, with mylonites representing the zones of maximum fracture frequency and connectivity.

Figure 6. **Image of the borehole wall in the TRUE-1 block showing the fracture subjected to crosshole testing (scale in m along hole).**
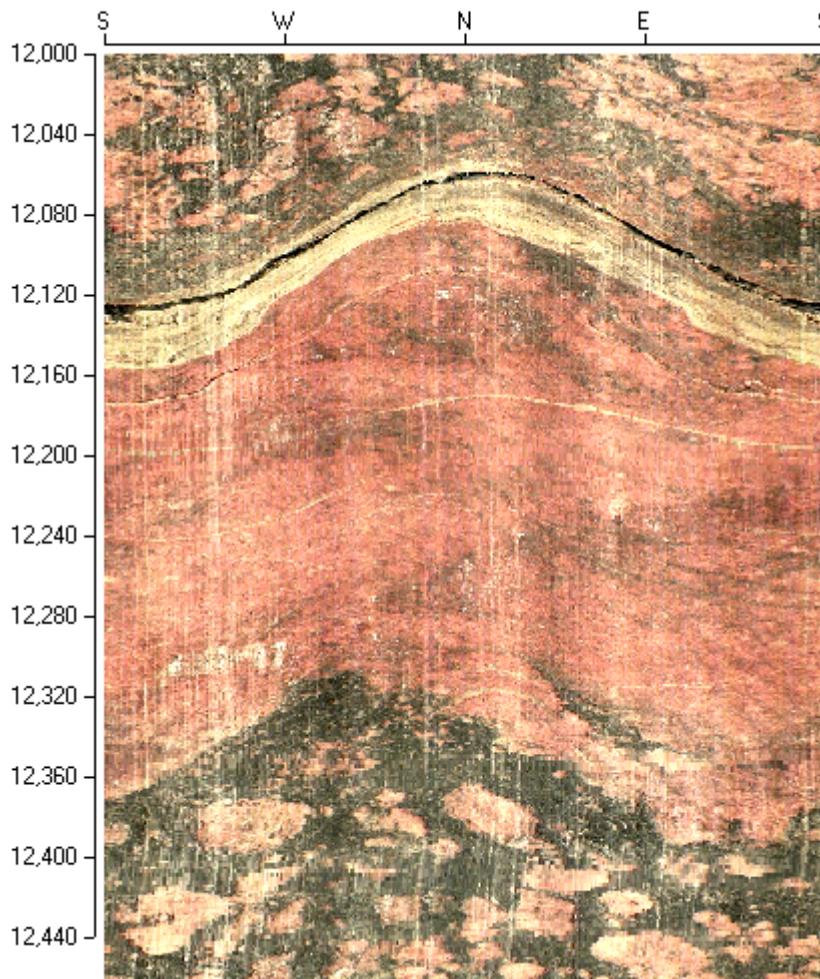
3.6 Conceptualisation of the structures used for crosshole tracer testing

Figure 6 shows a 360° borehole-wall image of the intercept of the mylonite-hosted fracture that was subjected to crosshole tracer testing. While this structure belongs to a smaller size hierarchy

when compared to the larger structure shown in Figure 2, the anatomy of both structures is remarkably analogous, reflecting the same geological evolution with recurrent deformation/alteration events that result in the same types of fault rocks. The structure in Figure 6 consists of a mylonitic zone that was recurrently reactivated by faulting. Thus it contains cataclasite as well as uncemented, open fractures. The only difference is the fact that no fault gouge was observed. In principle, this can be due either to the absence of gouge *in situ*, or due to washing out of the friable gouges during the drilling process. From a geological point of view, it appears very likely that gouge materials are present in situ (even though probably less in quantity) because of the analogy of the fault anatomies and deformation processes at both scales. Thus the presence of gouge in the target structure for tracer testing is inferred by downscaling observations made on faults of a larger size hierarchy.

For the sake of understanding and quantifying tracer transport and retardation in the tracer tests that were conducted in the TRUE-1 volume, a detailed-scale geometric conceptual model of representative fractures was developed and is shown in Figure 7. It integrates direct evidence from core and borehole logging, insights based on the understanding of the deformation mechanisms and information derived from larger-scale faults at Äspö.

Figure 7. **Small-scale conceptual model of fractures subjected to tracer testing in the TRUE-1 block.**
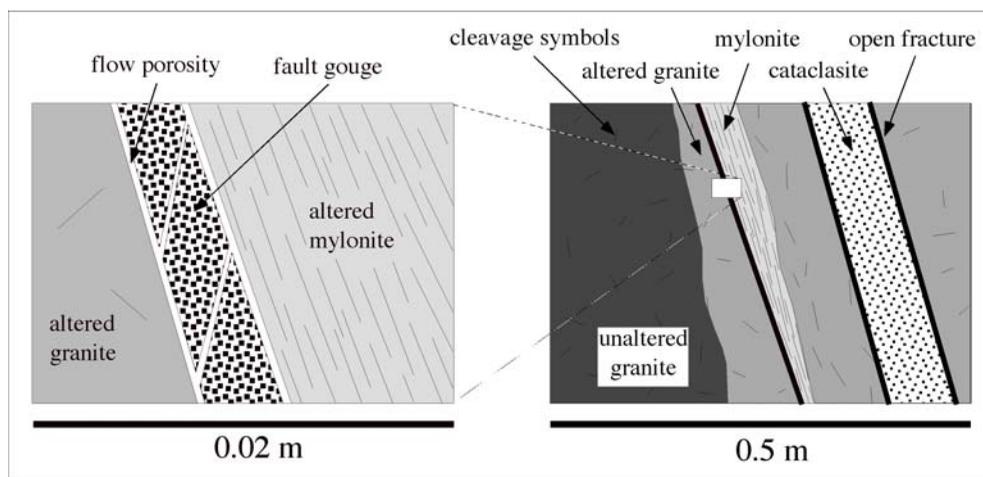
Table 1 lists the mineralogical compositions and matrix porosities of all rock domains that are represented in the model. Porosity varies over orders of magnitude between different rock types, and the presence of clay minerals in fault gouge (± cataclasite) suggests that sorption characteristics of these brittle fault rocks are most likely contrasting to those of the other rock types. The combination of high porosities and expected high sorption K_d-values, together with the occurrence along open fractures through which water flow occurs, suggests that fault gouge and, to a lesser degree, cataclasite, are the rock types that dominate tracer retardation during the short-duration tracer tests.

4.   Modelling framework

4.1   *Rationale*

A series of crosshole tracer tests, using different radioactive tracers, were conducted in the reactivated mylonitic structure described above. In this paper we focus on the first tracer test STT1 only with a distance of circa 5 m between the injection and extraction borehole. For this test, tracer breakthroughs were predicted blindly, i.e., without knowledge of the actual experimental results. The main objective of TRUE-1 was to test the adequacy of different models from various modelling teams

(including the choice of processes to be considered) as well as of field and laboratory-derived parameters. Input data that were provided to the modellers included:

- Test results from a previous dipole test (PDT3) in the same test interval, including the injection distribution function, test conditions and the uranine breakthrough data.
- The tracer injection function and the injection/extraction rates of the STT1 test.
- Laboratory-derived measurements for pore diffusion coefficients D_p and sorption K_d-values for fresh granite.

Table 1. **Average mineralogical compositions and matrix porosities of rock types occurring in the neighbourhood of open fractures. (+ = occurrence in trace amounts)**

Data in wt%	Fresh granite	Mylonite	Cataclasite	Fault gouge
Quartz	17	15	10	12
Plagioclase	44	30	14	7
K-feldspar	13	21	14	11
Biotite	13	23	+	0
Epidote	5	5	45	4
Chlorite	+	+	14	44
Fe-oxides	0	0	+	+
Calcite	+	+	+	4
Accessories (titanite, opaques, sericite)	5	3	2	3
Clay minerals	0	0	+	12
Porosity, vol. %	0.3	0.05	0.5-3.0	10-30

4.2 Geometry of the flow field and model calibration

By analysing the time-dependent uranine injection distribution in the PDT3 test, a value for the time-independent injection flow rate Q_i of 0.659 mL/min could be determined. For the calibration run PDT3 as well as for the subsequent tracer test STT1 a fixed pumping rate Q_e of about 400 mL/min was installed as the down-stream boundary, hence, the ratio $Q_e/Q_i = 607$ generated a monopole-like radial flow field (see Figure 8). It was concluded that the flow domain would remain strongly restricted and heterogeneities on the decimetre or even metre-scale would play only a very minor role. Thus, in spite of the structural complexity shown in Figure 5, the flow field is almost 1-dimensional and does not characterise the network characteristics of the TRUE-1 block. Calculations in the frame of the 2D-streamtube model with an underlying homogeneous and isotropic transmissivity field and taking into account the influence of a natural background flow field indeed supported such an assumption.

4.3 Role of matrix diffusion

Matrix diffusion is an important retarding and dispersing transport mechanism for solutes carried by groundwater in fractured porous media. It retards solutes by:

a) Spreading them from the flowing groundwater into the diluting reservoir of the interconnected pore space of the rock matrix.

b) Providing an increased surface for sorption processes.

Matrix diffusion has been studied either by small-scale laboratory (e.g., [5,6]) or larger-scale field tracer experiments (e.g., [7,8,9,10]).

The uranine breakthrough of the PDT3 test (Figure 9) clearly reveals a relatively simple structure with a pronounced tailing. In a log-log representation a $t^{-3/2}$-dependency could be observed, which is considered to be diagnostic for a marked effect of matrix diffusion. In addition, an additional hump on the trailing edge could be seen which was interpreted as a possible spatial limitation (boundary) of the porous rock accessible to matrix diffusion.

Figure 8. **The flow and transport domain for the PDT3 and STT1 tracer tests represented by 10 streamlines of the capture zone (right part is a close-up in the vicinity of the injection borehole). Due to a weak background flow field the capture zone is slightly deformed, very narrow and has a width of only a few centimetres. The high pumping rate in the extraction borehole ensures full tracer recovery in the model.**
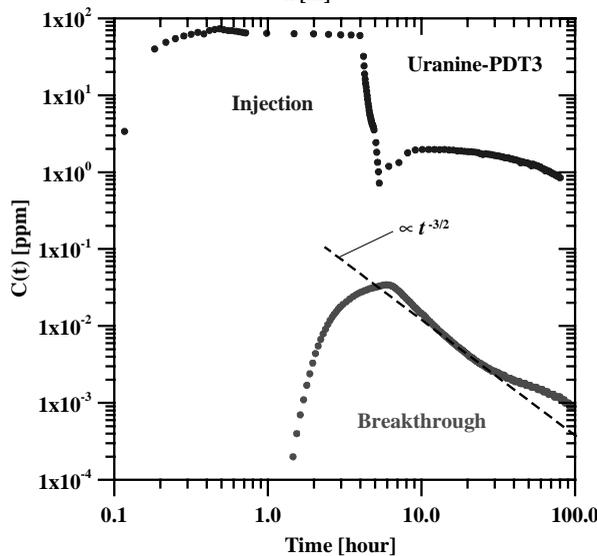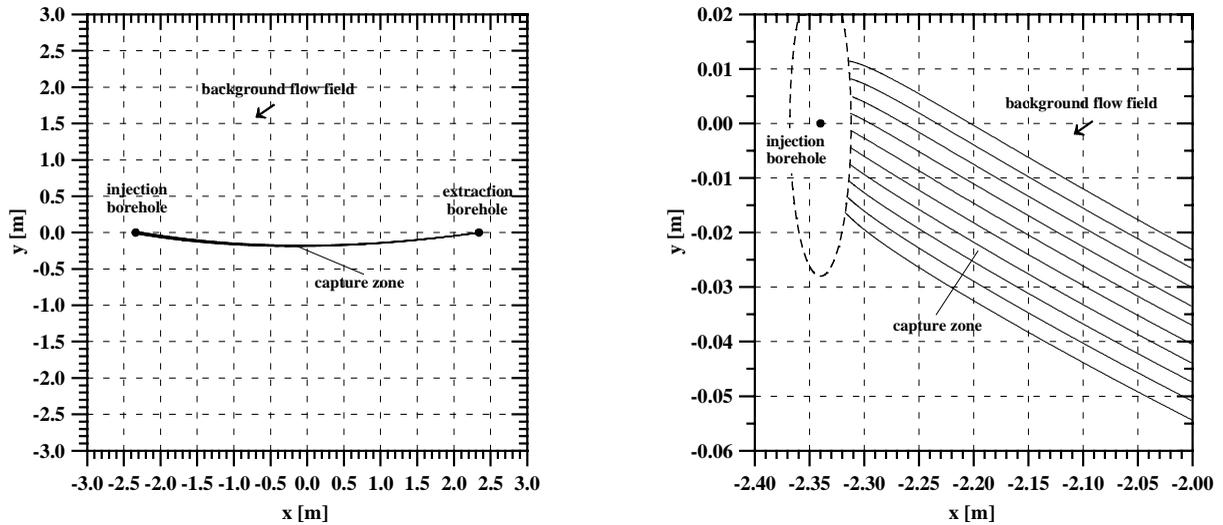
Figure 9. **Measured uranine injection and breakthrough concentration versus time for tracer test PDT3. The straight dashed line illustrates the $t^{-3/2}$-dependency of a part of the trailing edge of the breakthrough curve which is indicative for matrix diffusion.**

In order to test the assumption that matrix diffusion has cogently to be taken into account, the attempt was made to model the measured breakthrough curve with the help of a simple 1D-advection/ dispersion model where the only freely adjustable parameters are the flow-width and the Peclet number. The flow-width roughly accounts for the peak arrival time, and the shape of the breakthrough curve is mainly influenced by (longitudinal) dispersion. The best-fit value for the flow-width is 1.4 mm, which is equal to the fracture aperture of Andersson *et al.* [11, Table 1-2]. Furthermore, a best-fit value for the longitudinal dispersion length a_L of 0.45 m could be determined. However, as shown in Figure 10, the

shape of the breakthrough curve is only very roughly reproduced and the predicted peak maximum is 1.6 times too high, irrespective of the choice of the value for the dispersion length. It is concluded that an advection-dispersion model alone cannot explain the measurements.
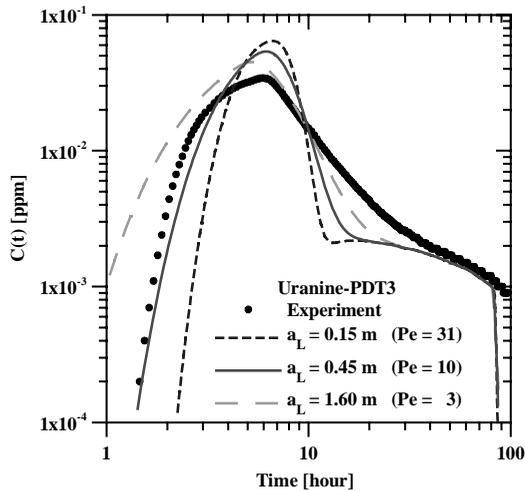
Figure 10. **Influence of the longitudinal dispersion length a_L in the frame of the 1D advection-dispersion model on uranine breakthrough of tracer test PDT3.**

According to the geological conceptual model of the migration pathways in the TRUE-1 block (Figure 7), brittle fault rocks occur adjacent to the fractures in which flow occurs, namely fault gouge and cataclasite. Specifically the former has a very high porosity (Table 1) and therefore is of potential relevance for matrix diffusion. Thus both the shape of the uranine breakthrough curve in test PDT3 and independent geological information indicate that matrix diffusion into fault rocks needs to be considered for modelling purposes. In contrast, advective water flow in the fault rocks is most likely negligible due to the very small pore apertures and therefore low permeabilities.

Figure 11 shows examples of the meso- and microscopic fault geometries. Individual water-conducting channels constitute a complex interconnected network bounded either by highly porous fault gouge or cataclasite. Consequently the flow-wetted surface will largely exceed that of a single planar fracture. Some micro-fractures are completely filled with fault gouge and so flow is expected to be restricted only in a fraction of the network.

As shown in Figures 7 and 11, the thickness of the fault rocks is limited to some millimetres, which limits the rock volume into which diffusion may take place. Because the rock types unaffected by brittle deformation (e.g., mylonite, granite) have porosities that are orders of magnitude lower compared to fault gouge, they can be assumed as inaccessible over the timescales considered in the experiment (hours-days). Thus matrix diffusion is expected to reach a physical boundary, eventually resulting in saturation (i.e., similar solute concentrations in the fracture and in the porous matrix). Once the concentrations in the fracture decline, this will result in an increased solute back-flow, followed by a rapid drop once the reservoir is drained. In the breakthrough curve, such a boundary effect is recognised by a second hump (the so-called tail-end perturbation) that modifies the $t^{-3/2}$-slope of the trailing edge. Unfortunately, due to the shape of the experimental injection function, the analysis of the uranine breakthrough curve of PDT3 was inconclusive with respect to such boundary effects. A second prominent tracer-injection pulse after about 6–10 h (Figure 12, left) masked a possible tail-end perturbation completely, although the tracer release was by a factor of 35 smaller compared to the main tracer injection. In the right part of Figure 12, the solid line represents the calculated breakthrough using the full dataset concerning uranine injection, and the dashed lines only consider the tracer release up to 5.5 h. It can be seen that the second injection signal has a substantial effect on the shape of the breakthrough curve, making the recognition of physical boundary effects of the porous material impossible.
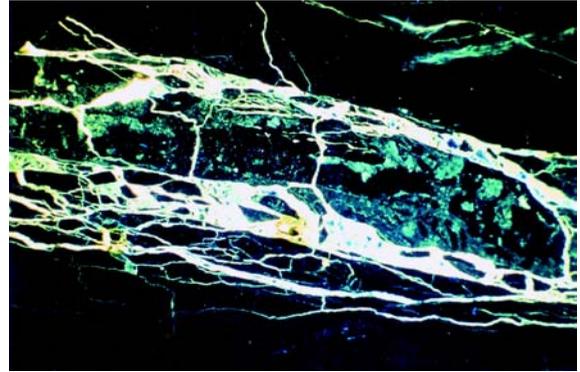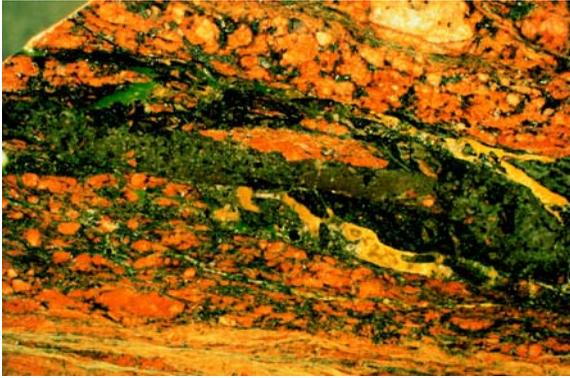
Figure 11. **Photographs of a cross-section through a resin-impregnated fault.** *Top:* **Visible and UV light photographs of the same area. Width of the photographs: 4 cm.** *Bottom right:* **Micrograph, width 0.2 cm.**
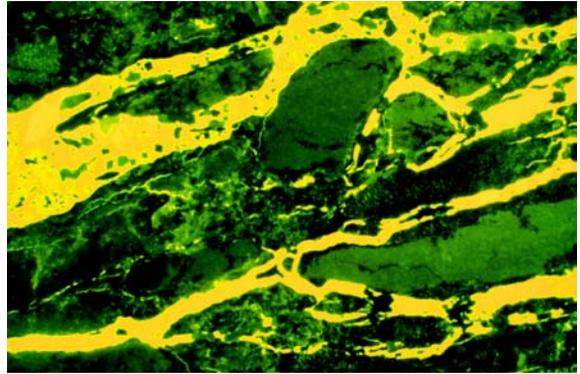
Figure 12. **Influence of tracer release on uranine breakthrough of PDT3.**
The left plot shows the uranine release as a function of time.
After about 5.5 hours, a first tracer pulse is followed by a second, 35 times less pronounced pulse.
The right plot shows a series of calculated tracer breakthrough curves,
where different parts of the injection function were considered.
The strong decrease in the tail (solid line) for times larger than 80 h is caused
by missing data of the second part of the injection distribution. ("md" = matrix diffusion).
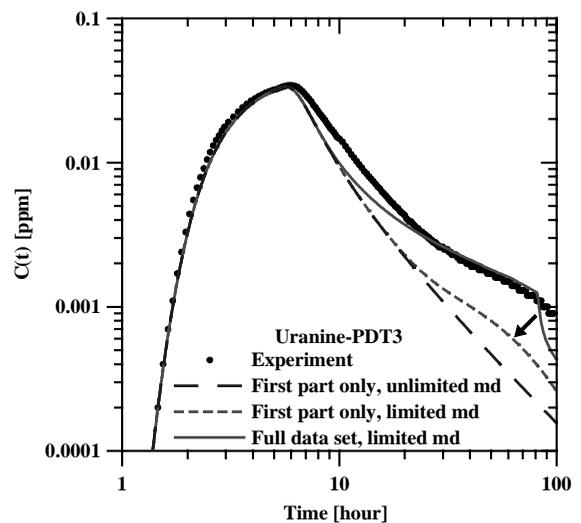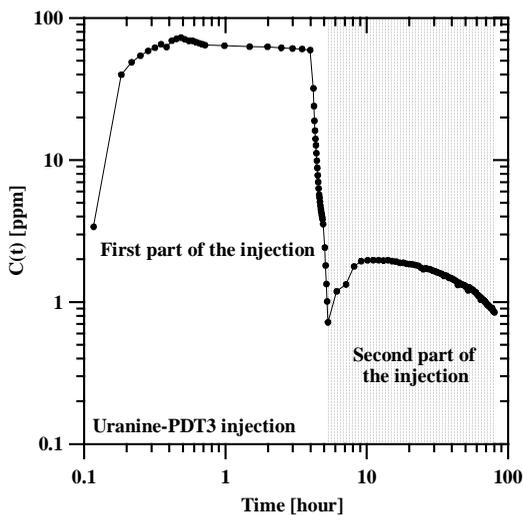
5. Blind predictions of tracer breakthrough curves in test STT1

5.1 Introduction

For the blind-predictions, matrix diffusion into the cataclasite was neglected for the sake of simplicity. However, a value for the extent of the fault gouge had to be specified for the calculations. As already outlined from the uranine-PDT3 breakthrough curve a value for the limited extent of the fault gouge could not be extracted and was therefore based on geological evidence which suggest thicknesses in the range of 1 to 5 mm. Scoping calculations using both bounding values yielded a slightly better fit for 1 mm. Therefore, this value was applied for all the predictions for the STT1 tracer test.

After having fixed the tracer-independent flow and transport parameters, some tracer-dependent parameter values had to be defined for the blind-predictions. Remaining parameters were the pore-diffusion coefficient D_p, the surface-based sorption equilibrium distribution coefficient K_a and the mass-based sorption equilibrium distribution coefficient K_d. Some of them were obtained from laboratory investigations of Andersson $et\ al.$ [12], even though they refer to fresh granite and not fault gouge.

- For the values of the pore diffusion coefficient it was assumed that the geometric factor G [-], which is a measure for both the constrictivity and the tortuosity of the fault gouge, is identical for all tracers. From the best-fit value obtained from the uranine-PDT3 breakthrough and the value in free water (where $D_w = 5.0 \cdot 10^{-10}$ m^2/s [13]), a value of $G = 5.56 \cdot 10^{-2}$ was extracted. Using this nuclide-independent value for G, the laboratory values given in [12] were rescaled for D_w according to $D_p = D_w\ G$.
- For the values for K_a, it was decided to use laboratory data obtained from batch sorption experiments using crushed Äspö diorite [12].
- Due to the much stronger impact of K_d on the predictions, the laboratory data of [12] were also rescaled, in order to account for the different properties of fault gouge when compared to fresh granite that was investigated in the laboratory. Further details can be found in Jakob $et\ al.$ [14].

5.2 Results of blind predictions and comparison to experimental breakthrough curves of the STT1 test

Predicted breakthrough curves are shown in Figure 13 for four of the eight tracers that were considered.

For the following discussion, the tracers will be grouped according to their sorption capacity:

- Conservative tracers: uranine and tritium (HTO).
- Weakly sorbing tracers: sodium (^{22}Na$^+$), strontium (^{85}Sr^{2+}), and calcium (^{47}Ca^{2+}).
- Moderately and more strongly sorbing tracers, such as rubidium (^{86}Rb$^+$), barium (^{133}Ba^{2+}), and caesium (^{137}Cs$^+$).

For uranine, an excellent agreement between blind-prediction and measurement was obtained, and it was concluded that the flow field had not undergone major changes between the two tracer tests PDT3 and STT1. Tritium was only very slightly retarded when compared to the uranine breakthrough, with a measured peak-arrival time of about six hours. However, in our blind-predictions we accounted for a much stronger delayed breakthrough for tritium. Hence, this is an indication that the simple assumption of a nuclide-independent geometric factor G for the pore diffusion coefficient – at least for tritium as tracer – is not appropriate.

In the group of weakly sorbing tracers, the retardation with regard to the peak-arrival time was predicted quite precisely, but the peak height was always overestimated by a factor of about two. Due to mass-balance considerations and because the rising edges of all these tracers were predicted quite accurately, the calculated trailing edges of the breakthrough curves decreased much faster than observed in the field experiment. This is most likely due to the underestimation of the effects of matrix diffusion. Due to the relatively large values for the pore-diffusion coefficients of the sorbing tracers applied for the blind-predictions, matrix diffusion acts rather as a surface sorption than as a real diffusion process. However, a larger value for the thickness of the fault gouge could have improved the prediction.

For rubidium and barium but not for caesium of the third tracer group, the peak heights were predicted correctly, but the calculated retardation was overestimated by a factor of 2 to 5 for all three tracers. All these tracers show a fast tracer breakthrough not predicted by the model. Discrepancies in the shape of the breakthrough curves are evident especially in the trailing edges. As outlined previously, this can be explained by an inappropriate description of the effects of matrix diffusion.

Figure 13. **Predicted and measured breakthroughs of selected tracers in the STT1 experiment. For illustration purposes the tracer injection distributions are also shown.**
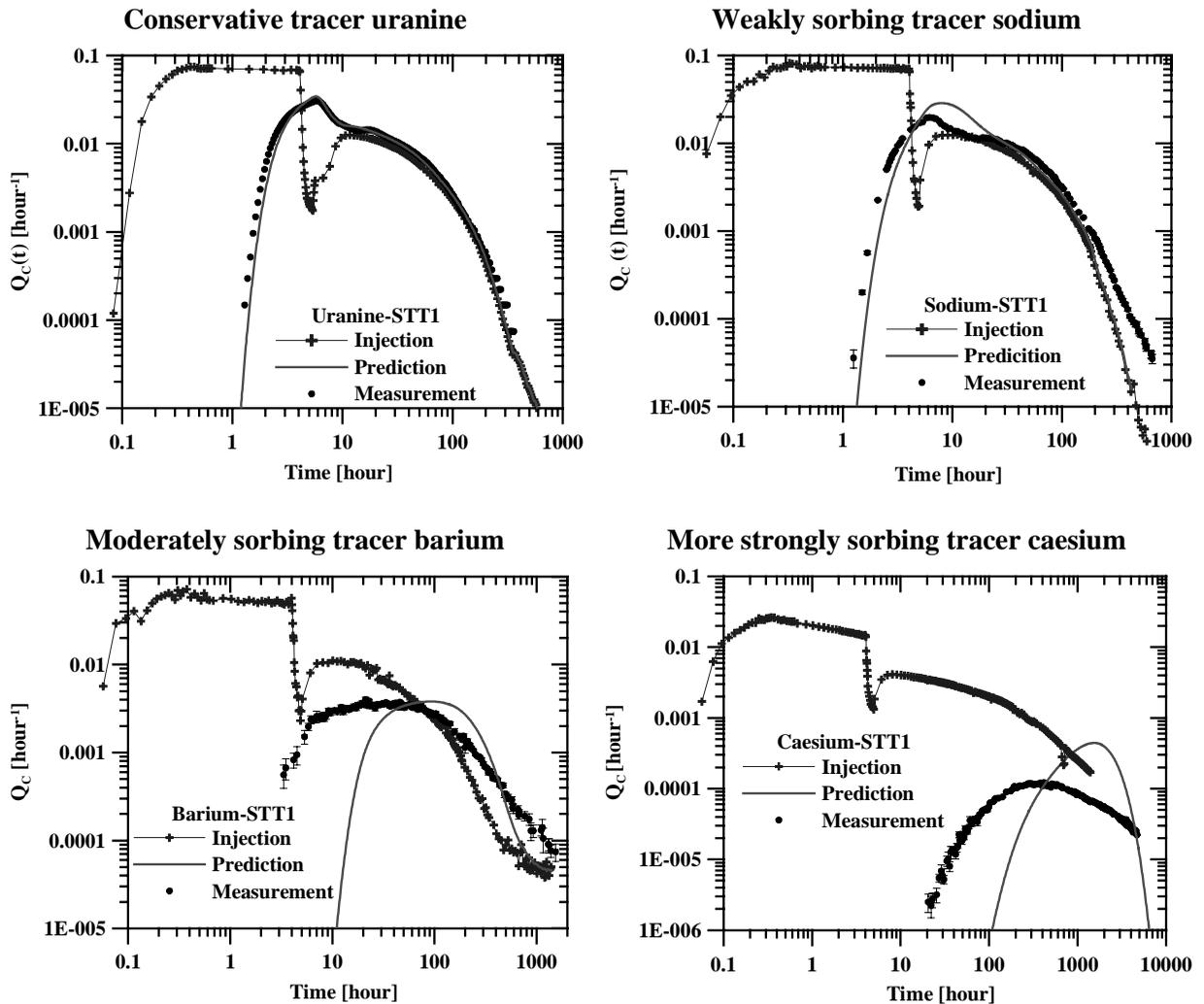
5.3   *Lessons learnt*

- The flow field had not changed significantly between the two subsequent tracer tests PDT3 and STT1.

- Although a clear indication for more than one preferential flow path in the measured breakthrough curves was not identified, the early tracer breakthroughs of the more strongly sorbing tracers rubidium, barium and caesium could be interpreted as being due to a second pathway.

- The quite accurate predictions for the conservative and weakly sorbing tracers show that the chosen nuclide-independent parameter values, such as e.g., the flow width and a_L (or Pe, respectively) are appropriate. On the other hand, the maximum penetration depth for matrix diffusion d of 1 mm is not well constrained and needed consequently a revision in the subsequent analysis.

- Except for barium and, much more weakly, for rubidium, the measured breakthrough curves showed hardly anything of the $t^{-3/2}$-dependency that would be indicative for unlimited matrix diffusion. From analysing the injection distribution of uranine-PDT3, it was clear that the second tracer release not only masked a possible tail-end perturbation but also the signature of (unlimited) matrix diffusion, especially for the conservative and weakly sorbing tracers.

- Due to the short half-life of the applied rubidium isotope, the measurements could not be extended to relevant times where matrix diffusion would strongly affect the trailing edge and where the influence of the tracer injection distribution would have become insignificant. For caesium, the relevant breakthrough data in the trailing edge could have been obtained only after several years.

6.   Conclusions

- Matrix diffusion was clearly identified as a process that occurs even over the short timescales of the experiments.

- Fault rocks, even though occurring in small proportions, dominate the tracer/rock interactions over the experimental timescales. Rock types unaffected by brittle deformation, such as mylonite or granite, do not interact noticeably with the tracers, even though they account for the largest part of the rock volume. The consistency of the experimental breakthrough curves and the model predictions is an independent confirmation of the geological inference regarding the presence of fault gouge in fractures.

- For the modelling work, a simple model was used. The flow part consisted of a 2D-streamtube model with an underlying homogeneous and isotropic transmissivity field considering in addition the weak influence of a homogeneous, steady-state background flow field. The transport part of the model was based on a 1D double porous medium approach linked to the flow part by the flow porosity, i.e., one single number. In spite of this, the blind-predictions were fairly good for most of the tracers, and this is due to the fact that the effects of the flow field were mainly dominated by those of important transport processes. Hence, heterogeneities on a decimetre or even on a larger scale played only a very minor role and could be successfully taken into account by 1D-dispersion. However, on the centimetre or millimetre scale, heterogeneities had a crucial impact on tracer breakthroughs. This recognition was an essential motivation to focus geological studies towards the millimetre-centimetre-scale structure of the flow paths.

- In order to get an appropriate model structure, detailed geological information was cogently needed. The input included the mineralogies and porosities of all relevant rock domains, and, even more importantly, the geometric conceptual model of representative flow paths. The recognition about the existence of fault rocks, such as fault gouge and cataclasite, turned out to have dominant effects on the model results and their interpretation.

- A good system understanding helped to formulate necessary constraints to reduce the parameter space.

- For high-quality predictions as they are required in the frame of field tracer tests, at least one breakthrough curve for model calibration purposes is needed.

- The laboratory characterisation of the rock materials was performed on fresh granite, whereas tracer/rock interaction is most significant in fault gouge. For this reason, laboratory data had to be re-scaled to account for the much larger surface of fault gouge. Therefore it is strongly recommended to measure sorption and diffusion parameters both on fault gouge material and cataclasite.

- The irregular shape of the tracer injection distribution masked important information on the rock/nuclide interaction in the trailing edge of a breakthrough curve. Hence, for future tracer experiments, the techniques of tracer injection have to be improved.

- In addition, it would be highly beneficial to measure the trailing edge of a breakthrough curve down to very low values and longer times, in order to record the effects of a possible tail-end perturbation and thereby further constrain the models parameter space.

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Solute Immobilisation: Observations from Natural Analogue Studies

John A.T. Smellie
Conterra AB, Uppsala, Sweden

1.   Introduction

Natural analogue studies have been in vogue for some 15-20 years, initially including investigations loosely focused on far-field geochemical processes (e.g., radionuclide retardation) expected to occur under long-term repository conditions. In the mid 1980s, mainly under the auspices of the European Commission (Natural Analogue Working Group, NAWG), a concerted effort was made to link analogue studies more directly to Performance Assessment (PA) requirements. This has involved the active participation of PA personnel at all stages of planning, execution, and interpretation of data. In addition, to further quantify interpretation and, therefore, its use in PA, analogue studies increasingly are being integrated with laboratory and in situ field experiments. The major strength of natural analogue studies is that many of the features, events, and processes (FEP) of importance to PA can be studied under natural geological conditions and over timescales more in tune with the nature and expected lifespan of a repository system (i.e., thousands to hundreds of thousands of years).

This article is based mainly on the Swedish SR-97 Canister Defect Scenario [1] which concerns low-temperature ($< 100°C$) solute release and transport within the geosphere. For discussion, it is assumed that a heterogeneous (both physically and chemically) fractured crystalline bedrock comprises the far-field geosphere environment. Under repository conditions, the near-field groundwater environment is expected to be strongly reducing prior to, during, and following corrosion and penetration of defective metal containers. Following corrosion, the dissolution of radionuclides, actinides, and other trace elements from the spent fuel will be solubility limited. Although radiolysis reactions will also occur, the large quantity of reducing species from corrosion of the steel liner (mainly $H_2(g)$ and Fe(II)), and the redox buffering capacity of the spent fuel itself, will effectively neutralise the oxidants produced resulting in some formation of secondary phases. Therefore, as a result of highly reducing conditions and near-field retardation processes, the dissolved solutes subsequently released into the geosphere will be at the saturation levels of these secondary phases and subsequently low.

2.   Solute immobilisation

Solute (e.g., radionuclides, actinides and other trace elements) retention mechanisms which are chemical in nature include adsorption, ion-exchange, precipitation, and mineralisation [2]. Adsorption and ion-exchange are often referred to as sorption, which is generally considered a reversible process. Precipitation and mineralisation result in structurally fixing or immobilising solutes in new mineral phases. It is often difficult to differentiate between precipitation and sorption, although sorption might be expected to dominate at low solution concentrations of solutes; at increased concentrations, precipitation and mineralisation might be expected. However, the groundwater chemical environment will play an important role. For example, at relatively low uranium concentrations, the mobility of U(VI) in water/rock systems depends on its tendency to form insoluble precipitates or adsorb to solid substrates. Strong aqueous complexes under moderately alkaline conditions (e.g., uranyl carbonate complexes) tend

to be weakly adsorbed, thus promoting greater U(VI) mobility. Contrastingly, the presence of phosphate (as ternary uranyl phosphates) greatly increases U(VI) adsorption on ferrihydrite (due to the tendency of phosphate to bind to Fe(III) oxyhydroxide surfaces) and possibly on kaolinite in the acidic pH region, thus limiting U(VI) mobility. Ultimately, however, in all cases of radionuclide retardation and/or immobilisation, a change in solution concentration or in groundwater composition may lead to a release of solutes into solution from dissolution and desorption processes.

The picture is predictably more complicated in a natural setting. The mineral-filling sequence in a granitic fracture zone, from the host rock towards the fracture aperture, very often consists of early mineral phases of hydrothermal origin (e.g., epidote, chlorite, calcite, Fe-oxyhydroxides etc.) followed by later, low-temperature precipitations of new, and often similar, mineral phases or coatings/layers (e.g., calcite, Fe-oxyhydroxides) on existing minerals. At the groundwater interface, sorption and ion-exchange processes are active; the precipitated layer may, therefore, include examples of both immobilisation and sorption processes, thus emphasising the difficulty in discriminating between them.

3.   Natural analogue studies

Natural analogue studies have the advantage of locating sites, usually uranium deposits, where key performance assessment processes and mechanisms can be investigated with relative ease since normally there is an abundance of radionuclides (and other trace elements of importance) which greatly facilitate identification and analysis. These radionuclides and other trace elements (e.g., REEs) are not directly analogous to the radionuclides and actinides which may be released into the geosphere from a defective canister, but they can be used indirectly as close chemical and isotopic analogues (Figure 1). Analogue studies are designed also to integrate laboratory and/or *in situ* field experiments to help constrain boundary conditions; furthermore, they provide the opportunity to test and develop PA-related models [3]. As referred to above, analogue observations of solute immobilisation are mostly at suitable redox and chemical interfaces and usually relate to shallow, oxic groundwater conditions (< 100 m depth). Described below are examples taken from a wide range of natural analogues with emphasis on the natural reactor environment at Oklo (Gabon).

There are many examples in the geological literature relating to solute immobilisation at suitable redox and chemical interfaces, the most obvious evidence being the formation of mineral deposits. With respect to uranium deposits, examples exist in northern Sweden were small-scale redox environments have effectively trapped/immobilised uranium, forming enhanced uranium concentrations [4]. Here, oxidative alteration of a rhyolite/ignimbrite sequence mobilised and transported uranium through the rock as uranyl carbonate complexes until encountering small ilmenomagnetite phases up to 500 μm in diameter. As a result, the ilmenomagnetite underwent oxidation to rutile/leucoxene/anatase and the uranium was precipitated/co-precipitated as UO_2 (pitchblende) both on and adjacent to these secondary Fe-Ti oxides; complex uranotitanates were also formed from further alteration of these Fe-Ti oxides.

Large-scale immobilisation of uranium (tens of metres) characterises the uranium mineralisation at Poços de Caldas (Brazil). The formation of redox fronts formed by oxidative weathering of alkaline volcanic rocks (e.g., phonolites) resulted in the precipitation of pitchblende nodules ahead of the propagating redox fronts in the reduced bedrock [5]. In the oxidised bedrock, uranium is closely associated with ferrihydrite formed from the oxidation of pyrite.

Figure 1. **Periodic table of the elements.**
Some examples of chemical or isotopic analogues are illustrated:
a) natural [226]Ra for waste [226]Ra; *b*) fallout ^{137}Cs for waste [135]Cs; *c*) stable I for waste [129]I;
d) Re as an analogue for Tc; *e*) Eu or any lanthanide as an analogue for a trivalent actinide, e.g., Am;
f) Th as an analogue for Pu(IV); *g*) U under oxidising conditions as an analogue for Pu (VI) [2].

3.1 The Oklo study

3.1.1 Direct evidence of solute immobilisation

Examples of radionuclide, actinide, and REE immobilisation in mineral phases have been reported from natural reactor studies at Oklo [6], for example, during the coffinitisation and phosphatic coffinitisation of uraninites, and coeval with the formation of apatites (e.g., Cs, I), zircon, and chlorite in the reactor zones. Unfortunately, these processes have occurred at temperatures much in excess of those expected in most repository concepts (< 100°C), such that their applicability to low-temperature conditions is limited. However, it does demonstrate how effective and robust these retention mechanisms can be.

There are, however, many relevant examples of low-temperature immobilisation reactions at Oklo relating to shallow, oxic conditions, particularly at the Bangombé reactor mineralisation (~ 12 m depth) where redox processes accompany present-day groundwater recharge (e.g., weathering fronts). Here, in the upper weathered zone, the abundance of secondary uranyl sulphates and phosphates emphasise the importance of sulphur and phosphate during migration and retention of uranium and REEs. For example, a La-florencite (Ce-Al phosphate) was shown to contain 27-30% fissiogenic Nd and 67-71% fissiogenic Sm [6].

The evolution of uranium behaviour with increasing depth at Bangombé has been well documented [7]. In the upper oxidised zone, some 30-50% of the uranium (< 20 ppm) in the weathered clays is associated with amorphous phases, some 8-20% as exchangeable and/or on carbonate-bound fractions, and around 25% with co-precipitated crystalline Fe-oxides (e.g., goethite). At greater depths through the redox front into the black shales, the uranium content increases to around 500 ppm and is mostly exchangeable with 50% readsorbed onto chlorite and up to 20% associated with amorphous phases. At still greater depths characterised by Fe-rich brown shales (containing 170-540 ppm U), the Fe(III)/U(VI) system dominates and up to 40% uranium is mainly co-precipitated with goethite and phosphate, up to 30% exchangeable on clays or related carbonates (e.g., calcite, dolomite, siderite), and up to 20% on amorphous phases such as Fe and Mn-oxyhydroxides. The behaviour of REEs, important since they are useful chemical analogues to trivalent actinides (Figure 1), also show widespread mobilisation (mainly as carbonate complexes) and retention at Bangombé. In the oxidised zone, HREEs are preferentially leached and accumulate at greater reducing depths, mostly in association with Fe-oxides (some with phosphates). The accumulation and distribution of LREEs seem to be controlled largely by clay minerals.

3.1.2   *Indirect support for solute immobilisation*

Indirect support for solute immobilisation is indicated from laboratory experiments and modelling exercises in connection with several natural analogue studies. Based on work at Bangombé, integrated field and laboratory studies provide additional evidence of the important role of uranium co-precipitation with Fe(III) oxyhydroxides as potential sinks of radionuclides in the oxidised zone [8]. Furthermore, there has been the successful implementation of surface complexation and thermodynamic models to describe the sorption/precipitation behaviour of U(VI) on the heterogeneous clay material characteristic of Bangombé. Most pertinent for this discussion is the thermodynamic modelling which simulated the behaviour of uranium and U-retention during the alteration of the black shales (pelites) under oxic weathering conditions. This showed that: a) the simulated sorption/precipitation sequence is consistent with field observations, b) adsorption of uranium on clays under acidic weathering conditions are not efficient processes for retention, and c) dissolution/precipitation processes may be more efficient for uranium retention.

The so-called Blind Prediction Modelling (BPM) exercise carried out at Bangombé [9] confirmed field observations that uranyl carbonate complexes dominate the aqueous uranium speciation. In addition, the uranium concentrations measured in more reduced groundwater samples are better explained by assuming equilibrium with U(IV) coffinite and /or uraninite, and that in the more oxidised groundwater samples the uranium concentrations are better explained by assuming the precipitation of secondary U(VI) silicates such as uranophane. This further supports field observations. Other BPM modelling results show that the groundwater redox potential is mainly controlled by the Fe(II)/Fe(III) couple whilst in some localities the Mn(II)/Mn(IV) couple is operative. With respect to the U-Fe system, the association of uranium to Fe(III) oxyhydroxides as co-precipitates is able to explain more convincingly the measured aqueous uranium in the oxidised groundwaters. This conclusion is also supported from similar modelling exercises documented from other analogue localities.

3.2   *Other analogue evidence*

As presented, the Oklo studies underline the importance of radionuclide and REE immobilisation at suitable redox and chemical interfaces, in particular associated with the precipitation of carbonates (e.g., calcite) and Fe/Mn-oxyhydroxides. The importance of these phases is reflected also in several other important analogue studies. For example, there is evidence from studies at El Berrocal (Spain) and Palmottu (Finland) of low-temperature calcites and Fe($\pm$Mn)-oxyhydroxides containing uranium and, in cases, accompanied by REEs and thorium; Fe-oxyhydroxides from

Alligator Rivers (Australia), Poços de Caldas, and Oklo also show similar associations. At Tono (Japan), significant radionuclide retention has been observed in association with Fe-oxyhydroxides, pyrite, and carbonates. These analogue data have been documented also from site characterisation studies at Äspö (Sweden) and further supported by laboratory studies where immobilisation of uranium by calcite has been demonstrated [10]. Here, U(VI) was successfully co-precipitated with calcite using pre-prepared samples, although it was concluded using natural samples that the formation of U(VI)-calcite solid solution is not a major immobilisation mechanism.

Studies at Äspö [11, 12] considered the incorporation of REEs, Sr, Th, and U in calcite to be significant, suggesting that the precipitation rate may influence (i.e., increase) the amount of Sr (and other elements) in calcite. In the Palmottu study [13], the immobilisation potential of calcite was investigated in the laboratory using natural fracture-filling samples [14]. Here, sequential leaching of layered calcite indicated that in addition to calcite, the uranium was associated also with separate U-bearing phases. At Palmottu, therefore, uranium immobilisation in association with calcite was explained by adsorption, co-precipitation, and as occlusions or inclusions; simultaneous co-precipitation as a dominant mechanism was excluded (see further discussion in Suksi *et al.;* this volume). Laboratory sequential leaching results from El Berrocal [15] showed that uranium was mainly precipitated in mineral phases and/or co-precipitated with carbonates, although the main retention mechanism operating in the site was U(VI) co-precipitation with Fe(III) oxyhydroxides as a result of the pyritic quartz vein oxidation.

Additional solute immobilisation issues to be considered in the upper 50-100 metres of bedrock at the oxic/reducing interface include the potential role of microbial and/or colloidal/organic mechanisms. For example, the sulphate in solution at these depths is often reduced to sulphur by sulphate-reducing bacteria (SRB) which facilitate the precipitation of secondary pyrite. Radionuclides may become incorporated in such pyrite as demonstrated with uranium at Poços de Caldas. SRBs can also produce HCO_3^- and subsequently the local formation of calcite [11] that may involve immobilisation of radionuclides. However, bacteria themselves are not considered to have the capacity to influence radionuclide migration.

With respect to colloids/organics, preliminary results from on-going *in situ* radionuclide retardation experiments at Grimsel (Switzerland) seem to indicate that actinide(IV) colloids can migrate quite readily with groundwater. Low molecular weight organics such as humic substances can either stabilise radionuclides in solution by complexation, or enhance the mobility of radionuclides by aqueous and/or colloidal complex formation. Furthermore, they can also contribute to the radionuclide mobility by coating the active mineral surfaces and blocking potential sorption sites. However, to date none of the natural analogue studies (e.g., Poços de Caldas, Palmottu, Oklo) has been able to identify a clear mobilisation role of radionuclides due to organic and or colloidal transport.

3.3   *General conclusions*

Natural analogue studies have indicated the following:

- Examples of solute immobilisation are widespread in the natural bedrock environment at suitable redox and chemical interfaces.

- These data provide the opportunity to understand further the mechanisms of solute retention.

- Precipitation (e.g., U-secondary phases) and co-precipitation (e.g., Fe/Mn-oxyhydroxides and carbonates) are particularly relevant to solute immobilisation.

- Field evidence is supported by laboratory studies and model predictions.

4.   Substrate transformation and U(VI) partitioning

It has been shown that amorphous Fe-oxyhydroxides function as very efficient sinks for radionuclides and, in cases, REEs. These amorphous varieties are, however, thermodynamically unstable and, with time, transform into higher crystalline varieties such as goethite and haematite or a mixture of these [16]. Transformation to goethite is a dissolution/reprecipitation process whilst transformation to haematite is via an aggregation of ferrihydrite particles. The first important effect of transformation is to produce a more stable substrate which has a much reduced tendency to adsorb uranium when compared to ferrihydrite; this has been convincingly supported by laboratory experiments [17]. During transformation, there is some incorporation of adsorbed uranium that makes it more resistant to leaching. In addition, transformation may be accompanied by the release of previously adsorbed/incorporated uranium and REEs.

5.   Long-term hydrochemical instability

Repository groundwater conditions may change during climatic change, in particular during glacial events. This may give rise to the deep downward intrusion of glacial melt water, and/or the upward movement of highly saline groundwaters. Such hydrochemical changes may dissolve and reprecipitate, for example, earlier formed calcite and Fe/Mn-oxyhydroxide phases, thus releasing previously adsorbed radionuclides/REEs etc. into the aqueous system. However, since it is believed that neither scenario will result in oxidising groundwaters reaching repository depths, such changes are not considered a major threat to the overall long-term efficiency of the natural geosphere barrier system [18].

6.   Summary and conclusions

Assuming that present climatic conditions will prevail during the lifespan of the repository, solute transport through the geosphere will be characterised by reducing groundwater conditions, at least until shallower levels are reached (< 100 m) whereupon a transition to more oxic conditions is to be expected.

This is the environment where the immobilisation mechanisms will be most active when the pH decreases, Eh and HCO_3^- increase, and there is precipitation of calcite and Fe-oxyhydroxides; an increase in ion-exchange reactions may also be expected. Furthermore, there will be an increase in microbial activity and in the amounts of colloidal and organic species present which may also influence immobilisation mechanisms. Important from a PA perspective is that since Fe-oxyhydroxides and carbonate phases constitute the most dynamic phases at ambient temperature, their characteristic dissolution/precipitation times will be in the range of the groundwater residence times and, potentially, within repository timescales [19].

It is within such a groundwater redox/chemical interface environment that much of the above-described analogue data are directly relevant. However, what is largely unknown are the solute retention processes which are operative deep in the bedrock during the anticipated long radionuclide transport times (tens of thousands of years) through the geosphere to this geosphere/biosphere interface point. It may be that immobilisation, rather than sorption, on a micron scale (or less), is the dominant solute retention mechanism that should be considered in PA. However, the lack of high-resolution detection techniques has been an obstacle in this area of study and measured data are lacking. Nevertheless, technical advances have been made and it may soon be possible to produce quantitative data from this highly reducing bedrock environment [20].

To conclude, and from a PA perspective, solute immobilisation usually is not explicitly considered. However, from analogue studies, immobilisation can be: *a*) observed in natural systems, *b*) predicted by modelling, and *c*) supported by laboratory and *in situ* field experiments. The main PA drawbacks include:

- Many of the field observations do not reflect closely expected repository conditions at depth where the groundwater environment is highly reducing.

- Field observations that may reflect repository conditions at depth are qualitative and cannot be measured to the accuracy and precision required.

The main PA strengths include:

- Field observations mostly reflect oxic groundwater discharge conditions near the geosphere/ biosphere interface; such conditions will also occur in the repository host rock environment.

- $Fe(\pm Mn)$-oxyhydroxides and carbonates, which are expected to be present in the repository host rock, constitute the most dynamic solid phases at ambient temperatures and have been shown to play an important role in immobilisation processes.

- The characteristic dissolution/precipitation times of $Fe(\pm Mn)$-oxyhydroxides and carbonates are in the range of groundwater residence times and, potentially, within repository timescales.

- Understanding immobilisation mechanisms provides the opportunity to develop and test PA-related models.

Furthermore, substrate transformation with time from amorphous to crystalline Fe-oxides results in:

- The release of previously adsorbed solutes (i.e., negative PA implication)

- The partial incorporation of solutes (i.e., positive PA implication)

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The Consideration and Representation of Retention Processes in Performance Assessments Carried Out by Waste Management Organisations: What Has Been Done and Why?

Jürg Schneider, Bernhard Schwyn and Piet Zuidema
Nagra, Switzerland

Hiroyuki Umeki   **Paul Smith**
NUMO, Japan   SAM Ltd, UK

1.   Introduction

Waste management organisations generally carry out several performance assessments in the course of the stepwise planning and development of a repository. Performance assessments are used to test, as far as possible at a given stage, the suitability of a given site and design from the point of view of safety, and to guide future stages. Typically, such assessments involve:

–   The collation of scientific understanding (which evolves in the course of planning and development).

–   The identification of the most safety-relevant phenomena and the uncertainties in current scientific understanding to which the evaluated repository performance is most sensitive.

–   The development of arguments, based on current scientific understanding, that repository performance will be acceptable, from the point of view of safety, provided the spectrum of possibilities for the characteristics and evolution of the repository and its environment lies within certain bounds.

Complementary arguments are sought, e.g., from science and engineering studies, to provide evidence that the spectrum of possibilities does, in fact, lie within these bounds.

In order to develop convincing arguments for safety, it is important that safety-relevant phenomena and uncertainties are identified and evaluated in a cautious and systematic manner. Waste management organisations need to identify not only the phenomena that are expected to provide safety, which include the class of phenomena known as retention processes, but also events and processes that may adversely affect their operation. This paper reviews the typical treatment of retention processes in performance assessments carried out by waste management organisations, with particular emphasis on the processes of matrix diffusion and sorption.

2.   Inclusion of retention processes in performance assessments

Most performance assessments carried out for deep geological repositories employ quantitative models of geosphere transport that incorporate sorption as a retention process. Furthermore, for those assessments considering disposal in fractured geological media, matrix diffusion is also taken into

account. For these two retention processes, there exists wide-ranging evidence from observations of natural systems and laboratory experiments that the processes do indeed occur, and there is generally enough site-specific data to support quantitative modelling. Sorption and matrix diffusion can provide a substantial contribution to the safety functions of:

- Containment and decay.

- The "spreading in time" of released radionuclides within the geosphere.

Uncertainties are often such, however, that a wide range of parameters is required to cover the spectrum of possibilities of system behaviour.

Wide-ranging evidence also exists for the occurrence of a range of other processes that are likely to contribute to the containment and decay of radionuclides in the geosphere. These include the incorporation of radionuclides in solids by for example, precipitation or co-precipitation. For such processes, however, the detailed understanding and data to allow their inclusion in assessment models has, up to now, not been available and their omission has been justified on the grounds of conservatism. The recognition of such retention processes in performance assessments does, however, provide a qualitative argument that the performance of the geosphere as a transport barrier is likely to exceed that indicated by quantitative assessment model results.

3. Information requirements for performance assessment modelling

A range of information is required in order to characterise retention processes adequately for performance assessment, including an evaluation of processes and events that have the potential to adversely affect their operation. Ideally, in the case of sorption and matrix diffusion, the information that is required for assessment modelling includes:

1. Information on the characteristics of potential transport paths from repository to biosphere, such as (for media with advection-dominated transport):

   - The constituent types of water-conducting features.

   - The small-scale structure of these water-conducting features (including, for example, fracture coatings, fracture infill and altered zones around fractures).

   - Information on the interconnectedness of porosity within these different structural components.

   - Any time-dependence of the extent and properties of water-conducting features.

2. Element-specific datasets for sorption, diffusion and effective porosities, with one dataset for each structural component of the water-conducting features. The derivation of these databases itself requires a range of information, including, the geochemical properties of the surfaces available for sorption and of the porewater, with an emphasis on pH value and redox conditions.

4. Meeting the information requirements

The availability of information on retention processes evolves in the course of a repository project. Thus, in practice, the requirements of performance assessment are adapted, to some extent, according to the information that is available at a particular state of a project, with a conservative approach usually adopted where there are gaps in the information base. For example, typical steps in the development of a sorption database include:

– Laboratory investigations on relevant solid phases (rock samples and relevant pure minerals) with selected safety-relevant elements.

– Use of a variety of means (thermodynamic calculations, application of surface complexation models and expert judgement) to extend the results of laboratory investigations to all safety-relevant elements and to adjust the results to *in situ* conditions.

In the early stages of a project, however, sorption datasets (K_ds[1]) from other projects or from published tables may be all that is available, while at later stages, information from site-specific laboratory measurements and the results of mechanistic modelling studies is likely to have been obtained. Furthermore, at later stages, it may also be possible to test the resulting database with complementary field studies, including tracer tests, in URLs in the relevant geological environment. This, for example, can confirm that the methodology used for transferring sorption data derived in the laboratory or by modelling studies to *in situ* conditions is adequate.

Analogue information and field experiments have proved useful, in some cases, in demonstrating the existence of a zone of interconnected porosity near to fractures within which matrix diffusion may occur. Figure 1 shows an example of the use of resin impregnation to demonstrate the existence of interconnected porosity in weakly altered feldspars in granodiorite at the Kamaishi Mine in Japan.

Geological arguments may be used to assess the likelihood of significant changes in rock and groundwater properties. In the case of matrix diffusion, the possible existence of anomalous "fast paths" (or paths that are, or may become, coated with minerals that lack connected porosity) that are undetected, but cannot be excluded on the basis of field investigations, may be a particular concern. Geological arguments can sometimes be used to assess the likelihood of the occurrence of such features. The possibility of such features arising from the presence of the repository (e.g., gas fractures) or from future human activities has to be assessed on a system-specific basis.

5. Treatment of retention processes in performance assessment models

The treatment of retention processes in performance assessment models varies in detail depending on the degree of site-specific information available. Some general observations may, however, be made regarding the treatment of sorption and matrix diffusion.

Sorption is typically modelled as a rapid, reversible process, characterised by element-specific K_d values, which are usually assumed constant in time. Sometimes non-linear sorption, represented, for example, by a Freundlich isotherm, is also considered (for example in the Kristallin-I safety assessment [2]). In such cases, explicit account is taken of the way in which the sorption of an isotope is affected by the overall concentration of the corresponding element ("isotopic dilution"[2]). The K_d concept is a rather simplified representation of sorption, but it has the advantage of transparency and can easily be applied (in a conservative manner) in transport codes. Furthermore, the inclusion of more complex and detailed information is often complicated by the high degree of variability and uncertainty in natural systems. Although performance assessors thus often refrain from

1. Sorption isotherms tend to be available for only a few safety-relevant elements.

2. In principle, isotopic dilution may also be taken into account in assessing whether solubility limits are exceeded in the geosphere (e.g., at geochemical fronts). Whether or not the precipitation that occurs if solubility limits are exceeded provides a retention process depends on the nature of the solids that are produced (e.g., if stable and mobile colloids are produced, then precipitation may lead to more rapid radionuclide transport). In practice, most repository programmes develop arguments based on the characteristics of the site and design that such geochemical fronts will not arise.

replacing the K_d concept by more complicated models, a proper translation of information from laboratory experiments and mechanistic models into K_d values is essential (see Section 4, above).

Figure 1. **Impregnation of weakly altered feldspars from the Kurihashi granodiorite, Kamaishi Mine, Japan (from [1]).**

Feldspars in crossed polarised light
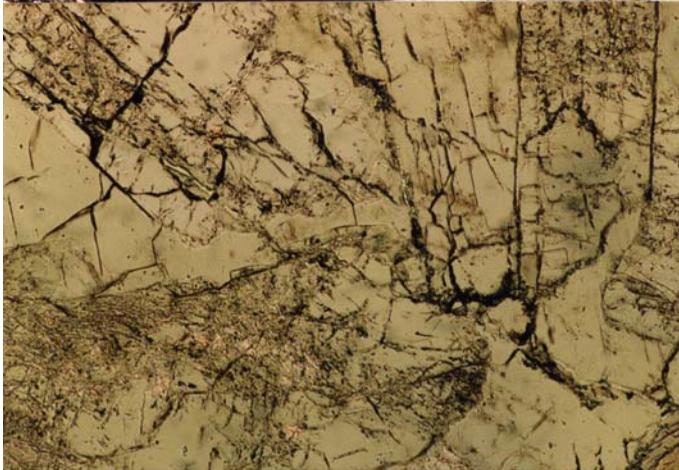
Same field in plane polarised light
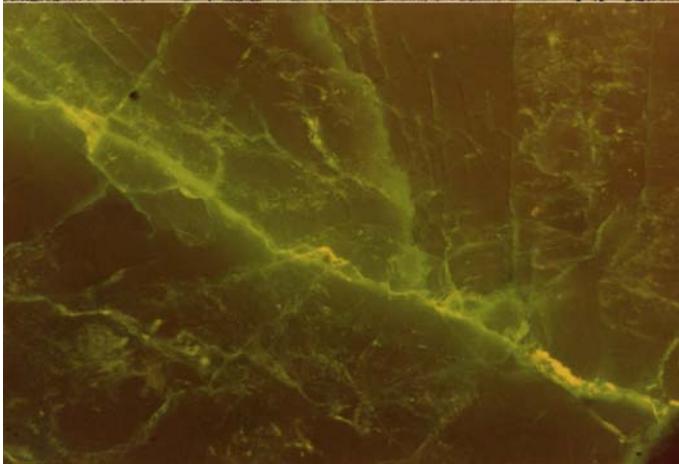
Same field in fluorescent light. The fluorescing dye in the resin shows very fine features in the order of 1 to 10 μm (field of view approx. 10 mm)

Matrix diffusion modelling also typically assumes time-independent properties. Small-scale heterogeneities in sorption- and matrix-diffusion-relevant properties are often "averaged over". In some assessments, such small-scale structure is, however, taken into account. For example, in TILA-99 [3], different sorption and matrix diffusion properties are assigned to altered wallrock adjacent to fractures, and more distant, unaltered wallrock and a geosphere transport code is employed that explicitly models these different structural components. Nagra has also developed a code that allows spatially variable sorption and matrix diffusion properties to be assigned [4].

6. Conclusions

Performance assessments are used by waste management organisations to test, as far as possible at a given stage of a project, the suitability of a given site and design from the point of view of safety. They also guide future stages by providing feedback to siting, site characterisation, design and other areas of research and development. This guidance comes not only from the results of quantitative modelling but also from the systematic consideration of all safety-relevant phenomena, and the assessment of the information that is available on these phenomena, which are also part of performance assessment.

The retention processes of matrix diffusion and sorption have the potential to contribute greatly to the performance of the geosphere. The level of scientific understanding and information is generally adequate to allow performance assessments to take quantitative credit for these retention processes, although a reduction in key uncertainties is desirable. Uncertainties are associated with the characterisation of features where retention phenomena occur. For example, information on mineralogy and porosity may be available on bulk materials, whereas, for sorption, it is the properties of surfaces that are of importance. On a larger scale, there may be anomalous "fast paths" that are subject to less retention than more typical transport paths, and have the potential to dominate geosphere performance. Uncertainties are also associated with the processes themselves (for example, the effects of colloids and the sorption of more complex species).

The strategy for the reduction or avoidance of these uncertainties generally needs to be determined on a site- and system-specific basis. Of key importance, however, is the interaction between performance assessors and technical specialists in the various scientific disciplines, in order that the full spectrum of possibilities is recognised in performance assessment and in order that the efforts of scientific specialists are focused on the most critical issues.

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The Consideration and Representation of Retention Processes in Performance Assessment: A Regulatory Perspective

Budhi Sagar

Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, USA

Bo Strömberg

Swedish Nuclear Power Inspectorate, Sweden

1. Introduction

Processes that prevent or delay the migration of radionuclides in the geosphere relative to ambient water velocity are called retention processes. These processes can be chemical (e.g., ion exchange, sorption, and mineral precipitation) or physical (e.g., matrix diffusion from fractures into rock matrix or filtration of colloidal particles). Such retention processes can significantly delay and reduce the rate at which radionuclides are released to the biosphere and, hence, reduce the dose to biota, including humans. In most countries, retention processes are considered important components of the safety case (e.g., radionuclide delay in the unsaturated and saturated zones). For example, retention processes are listed as principal factors in the U.S. Department of Energy Repository Safety Strategy [1] for the proposed Yucca Mountain site, and significant performance was ascribed to the retention processes in recently completed performance assessments in Sweden [2] and Finland [3]. In this paper, we discuss the perspective from the United States and Swedish regulators on retention processes, with specific examples related to ion exchange (or sorption) and matrix diffusion.

2. Basis of regulatory perspective

The regulatory perspective on any topic related to safety, including retention processes, is formed in response to the primary regulatory mission of gaining reasonable assurance (or determining that the same cannot be gained) that public health, safety, and the environment will be protected. While the implementor alone is responsible for the design, construction, operation, and closure of a repository, once such a facility is approved (or licensed) by the regulator, the public views the regulator as responsible for the integrity of the facility as well as the implementor. The public can easily lose confidence in the regulator's competence and effectiveness if the safety of an approved facility is questioned. Therefore, it is the regulator's job to evaluate potential vulnerabilities in the implementor's safety case. The intensity of regulatory scrutiny of the retention processes will depend on the importance of these processes to the implementor's safety case. Specifically, the depth of examination of these processes during regulatory reviews will depend on their contribution to meeting the performance objectives (e.g., see [4] for a discussion of importance analysis).

Because repository safety is to be assessed for thousands of years after closure, simulation of repository behavior through mathematical modelling is an essential element of a safety case. The conceptual model of the engineered and natural barriers, mathematical formulation of the retention processes including coupling with thermal and hydrological processes, estimation of model parameters, and numerical implementation of the model including consideration of both the model and parameter uncertainties are components that must be examined to determine if incorporation of the retention processes in the safety case

is acceptable. The regulatory approach envisions an adequate description of the retention processes consistent with their contribution to the safety case [5,6]. In a regulatory review, greater uncertainties may be acceptable if the retention processes have a small effect on the overall safety of the repository.

While it is preferable to have as realistic a description of the various processes in performance assessment as possible, a wholly realistic description is not absolutely necessary to support regulatory decisions. For example, from a regulator's perspective, it will be acceptable to entirely neglect (not take credit for) retention processes in a safety case even though this may not be a realistic assumption. In such a situation, so long as it is assured that neglecting retention processes does not negatively affect repository performance (see the SFR repository example below), and so long as other regulatory requirements (e.g., defence-in-depth, multiple barriers, or both) are satisfied, it should be acceptable to the regulator even though the overall system performance estimated using this assumption will itself not be realistic (i.e., it will tend to overestimate radionuclide releases to the biosphere). Such assumptions can contribute to a safety margin – the difference between the unknown realistic value and the estimated conservative value of the performance measure such as radiation dose. Multiple barriers and other defence-in-depth measures also contribute to safety margins. It is a good idea for the implementor to provide qualitative arguments whether an assumption in the safety case adds to or detracts from the safety margin, if quantitative estimation of the safety margin is not feasible.

The regulatory approach in Sweden, the United States, and other countries focused on developing an independent modelling capability to evaluate the relative importance of various parameters and processes and to apply this capability in reviewing site selection, adequacy of site characterisation, and various safety aspects of a proposed repository. Regulators have explored uncertainties related to both flow and transport by comparing alternate model conceptualisations and by various parameter sensitivity analyses. In the future, additional work will be done to judge the acceptability of the top-level abstracted (or simplified) models used in performance assessments. Greater regulatory emphasis on proponents' quality assurance of data and models and transparency of documentation is expected as the programs approach the licensing phase.

3. Adequacy of current understanding of the retention processes

The physical and chemical structure of a natural geological material is quite complex, thereby complicating the description of processes operating in it. The question of adequacy of understanding the retention processes can be thought of as two end members on the complexity scale: one for perfectly known simple ideal materials in ideal transport conditions and the other for imperfectly known complex actual sites with complex migrating mixtures of dissolved and suspended particles. We believe that the thermodynamics of the first end member are reasonably well understood [e.g., see review in [7] and references sited therein]. At the present time, most of the knowledge gained for the end member is extrapolated for application to the second end member, introducing large uncertainties. More uncertainties are introduced because of the dynamic nature of the repository system (albeit evolving slowly), introduction of engineered materials, and introduction of a thermal source. Clearly, we don't understand every (or even most) detail of the retention processes in such a system under ambient conditions or during its evolution for thousands of years in potential future environments. But, do we understand enough to make decisions about repository safety?

The answer to this question is site- and performance-assessment specific. If only a small amount of credit is taken for the retention processes in the performance assessment, then one can say with relatively high confidence that we have enough understanding of these processes. This may be the case for several European programs that estimate the nominal life of a copper container in a chemically reducing environment to be approximately one million years. In these programs, only in disruptive conditions, where the containers may not sustain their nominal performance is a degree of reliance on the

retention processes required to demonstrate safety, although greater reliance may be needed to demonstrate multiple barriers. Obviously, for such extensive container life times, understanding the container degradation processes is of much greater importance than understanding the retention processes. The current published estimates of the nominal container mean life in the Yucca Mountain program vary from 30 000 [8] to more than 100 000 years [9]. This period, although much greater than the regulated life of the repository (10 000 years), is nevertheless much shorter than the million years life estimated in the European programs. To determine the relative contribution of retention processes to performance, a sensitivity study of Yucca Mountain was conducted by the Center for Nuclear Waste Regulatory Analyses (CNWRA) and the U.S. Nuclear Regulatory Commission (NRC) [10]. In this study, the peak of the time versus total effective dose equivalent during 10 000 years after closure was estimated to be 0.023 mSv (2.3 mrem). When the sorption process was turned off in the model, this dose was calculated to be 0.125 mSv (12.5 mrem) – approximately a five-fold increase.

Many assumptions underlie the calculation reported above. The dose in the first 10 000 years is due to premature failure of initially defective containers. No mechanistic way of estimating the number of such initially defective containers has been developed yet. A certain number of containers are assumed to be initially defective, and the result for the 10 000 years is strongly dependent on this assumption. Furthermore, only selected radionuclides are tracked. A linear, reversible, and constant K_d-based sorption model (with parameter uncertainty modelled through assigning probability distributions to the K_ds) is used in the calculations. A $K_d = 0$ (to turn off the sorption process) for all radionuclides is not realistic and would imply existence of strange geochemical conditions that, if assumed, would alter other calculations in the model. All other processes except the sorption process were assumed to operate normally, and no attempt was made to make the model self consistent in this way. Also note that both the calculated doses are below the limits of 0.15 mSv (15 mrem) set by the U.S. Environmental Protection Agency (EPA) [11], although the 0.125 mSv (12.5 mrem) calculated without sorption is rather close to the 0.15 mSv (15 mrem) limit.

The system-level model used for these calculations is made up of many modules representing in a simplified manner the various thermal, hydrological, chemical, and mechanical processes. This model has more than 800 parameters, and more than 250 are designated as stochastic and are sampled during Monte Carlo simulations. In the sensitivity study cited previously, an effort was made to select the top 10 parameters to which the peak mean total effective dose equivalent was sensitive. For the 10 000-year period, the K_ds did not appear in this list. However, the K_ds for americium and neptunium were included in the list for the 50 000-year period. For the 10 000-year period, parameters related to determination of the container life were the most important. At 50 000 years, most of the containers failed in these particular simulations, and the retention processes gained more importance.

The sorption process is tightly coupled to water flow. For Yucca Mountain, in the unsaturated zone, the flow occurs mainly in the fracture zones, and an assumption of zero sorption in fractures is generally made [12]. Fracture zones are also present in the saturated zone, but non-zero K_ds are assumed for these zones. Flow paths enter alluvium in the far field and sorption may occur in this porous material. Based on all these factors, understanding of the sorption process is sufficient to determine the safety of the proposed repository at Yucca Mountain. However, questions remain about the validity of the K_d values used in the analyses and especially about their probability distributions obtained through expert elicitation.

For the fractured crystalline rock being investigated for a repository in Sweden, the primary difficulty lies in obtaining detailed site characterisation data. Nevertheless, present knowledge of the retention processes is probably sufficient for simplified and conservative calculations, with the caution that the knowledge may not be straight forward to assess the conservativeness of an assumption, and it should be appropriately tested. An example of the latter case is the SFR repository for low and intermediate level waste located at Forsmark close to the shoreline and 50 m (164 ft) below the Baltic Sea. A condition in the license granted in 1992 required preparation of an updated performance

assessment after every 10 years of operations. In preparing for review of the updated performance assessment, the Swedish Nuclear Power Inspectorate (SKI) is adapting a compartment model (AMBER software) to model radionuclide transport in various components of the system (near and far-field and biosphere). Although the model is simplified, it includes the most important retention processes and allows the identification of important issues that SKI should consider in its review.

From the preliminary calculations performed so far, it appears that the SFR repository is affected to a significant degree by changes in the level of the Baltic Sea caused by the ongoing land uplift. As the land rises and the sea retreats, the hydrologic regime and the biosphere will change. It is important to represent this time-dependency in performance assessment where early rapid releases when seawater is covering the site may have smaller impacts on human dose than at later times when fresh water may be extracted from a well close to the repository. Preliminary calculations suggest that near-field sorption on engineered materials is a key contributor to safety. A seemingly conservative assumption of zero sorption will allow the radionuclide inventory to be depleted earlier, leading to a potentially non-conservative estimate of dose at a later time. Thus, retention processes should not be viewed in isolation, but should be considered in the context of the complexity that is the total system.

To assist the NRC in conducting its regulatory review, CNWRA used detailed surface complexation models [13] to study the effect of geochemical factors on sorption. In this study, sorption was found to be a strong function of pH and total carbon. Two methods for incorporating this functional dependence in the performance assessment models were suggested: (i) based on the expected range of pH and total carbon along the flow paths, derive ranges of K_ds for each radionuclide for inputting into the performance assessment model; and (ii) include the dependence of K_d on pH and total carbon for each radionuclide in the performance assessment model directly through the use of regression equations. Instead of assigning a probability to K_d, assign probability distributions to the pH and total carbon. These suggested approaches avoid incorporation of computationally intensive complexation models directly into the performance assessment model, yet make the simplified K_d approach more realistic. The NRC intends to implement these suggestions into its total system code called TPA, which will be used to review the U.S. Department of Energy analyses.

A similar analysis [10] showed a decrease in dose from 0.023 mSv (2.3 mrem) to 0.0073 mSv (0.73 mrem) in 10 000 years when matrix diffusion is included in the analysis (all other factors being the same). Note that matrix diffusion is introduced in an empirical manner rather than modelling it mechanistically, hence, results may differ from other assumptions. While it is clear that the natural phenomenon of diffusion from the mobile phase in fractures to the relatively immobile phase in the adjoining rock matrix is always operative, its magnitude is problematic to determine-diffusion being dependent on the diffusing species, chemistry, pore structure, fracture spacing, and flow rates [14]. The subject has been studied for volcanic tuffs both in the laboratory (e.g., [15]) and in the field (e.g., [16]). In our opinion, the basic process of matrix diffusion is understood reasonably well, but site-specific experiments may have to be performed to get reasonable assurance regarding parameter values employed in the safety case.

The porosity of the unaltered granitic rock in Sweden is generally low, so diffusion of solute from fractures to rock matrix is the only mechanism for transport in the rock that can significantly enhance the sorption capacity. However, there are significant uncertainties related to the rate of diffusive transport that depend on whether the pores are connected beyond a few centimetres. A modelling parameter known as the flow wetted area strongly affects the uptake and subsequent release of radionuclides from the flowing groundwater in the fractures. This parameter, which has a large influence on estimated matrix diffusion and rock sorption, is not an intrinsic property but is related to the prevailing hydrologic regime and is difficult to measure. If significant performance is allocated to retention processes, then this key parameter has to be evaluated carefully and constrained.

4.   Representation of heterogeneity and temporal variability

The major part of radionuclide migration occurs along the flow paths. The flow and transport paths from the source to the far field are largely dependent on the spatial heterogeneities of the geologic system and (possibly time-dependent) boundary conditions. The geochemical conditions that affect retention processes (e.g., pH, mineral surface area, and total inorganic carbon) also vary along the flow paths. Heterogeneity exists at many scales, and the extent to which these scales must be included in performance assessment depends on the scale of modelling and its objective. Any feature that has the potential to affect the estimate of the performance measure significantly should be included in the analysis.

As part of the site selection process, performance assessment studies have been presented in Sweden [2], and Finland [3]. SKI, the Swedish regulator, also presented a study with the objective of demonstrating an independent performance assessment capability to be used for regulatory reviews [17]. All these studies have one thing in common; they consider relatively rapid transport pathways from the repository to the biosphere. Therefore, a consequence of heterogeneity is that it is difficult to rule out rapid advective transport pathways, which suggests there may be a limit for the level of safety that can be allocated to geosphere retardation processes. While the effects of rapid pathways may be reduced by judicious siting and appropriate placement of waste emplacement boreholes, experience indicates that significant uncertainties remain in conceptualisation of the flow and transport processes [17].

An illustration of the estimated flow paths from the proposed location of the repository at Yucca Mountain to the far field is shown in Figure 1. This figure represents the expected two-dimensional flow paths at a scale of tens of kilometres and assumes the hydrogeology is made up of homogeneous layers. The flow paths are, of course, three-dimensional. At present, one of the significant uncertainties in estimating flow paths is the location at which the flow paths (and, hence, the transport paths) enter the relatively shallow alluvium. Because the retention behavior of radionuclides in a porous medium-like alluvium is quite distinct from that in the igneous fractured rock, the calculation of dose can significantly depend on the length of the alluvium flow path. Representation of this heterogeneity in performance assessment, therefore, is important for regulatory decision making. The investigation of "fast flow paths" both in the unsaturated and saturated zones is another important heterogeneity that should be adequately represented. These fast flow paths, generally associated with smaller-scale discrete features (fracture zones and faults), have the potential to decrease the effectiveness of the sorption process, while at the same time, may enhance the delay through matrix diffusion.

While the detailed modelling of sorption processes differs from site to site and from program to program, most generally the K_d approach is employed in performance assessment. In the K_d approach, the complex physicochemical sorption processes are simplified to a single parameter that partitions a solute into the sorbed and unsorbed fractions. It is defined simply as:

$$K_d = \frac{M_{rs}/M_s}{M_{rl}/V_l}$$ Equation 1

where M_{rs} and M_{rl} are the masses of radionuclide on solids and in liquid, M_s is the total mass of solids in contact with the solution, and V_l is the total volume of the solution. From Equation 1, the units of K_d can be deduced to be (L^3/M). Equation 1 assumes that sufficient time is available for the solution to reach equilibrium with all solids it contacts. Most commonly, K_d is determined in laboratory batch experiments in which a known amount of M_s is allowed to react with a known amount of V_l until equilibrium is reached, at which point M_{rl} is measured. Turner and Pabalan [18] suggest improving Equation 1 by replacing M_s with A_s, where A_s is the effective surface area of the solid, which better represents the number of available sorption sites. Turner and Pabalan [18] called this modified partitioning coefficient K_A (= K_d/δ, where δ is the surface area per unit solid mass) with units of length.

The advantage of K_A is that it normalises the effects of mineral type while retaining sorption as a function of geochemical parameters like pH and total inorganic carbon (C_T).

Figure 1. **Location of the proposed high-level waste repository at Yucca Mountain (modified from Turner [19]).**
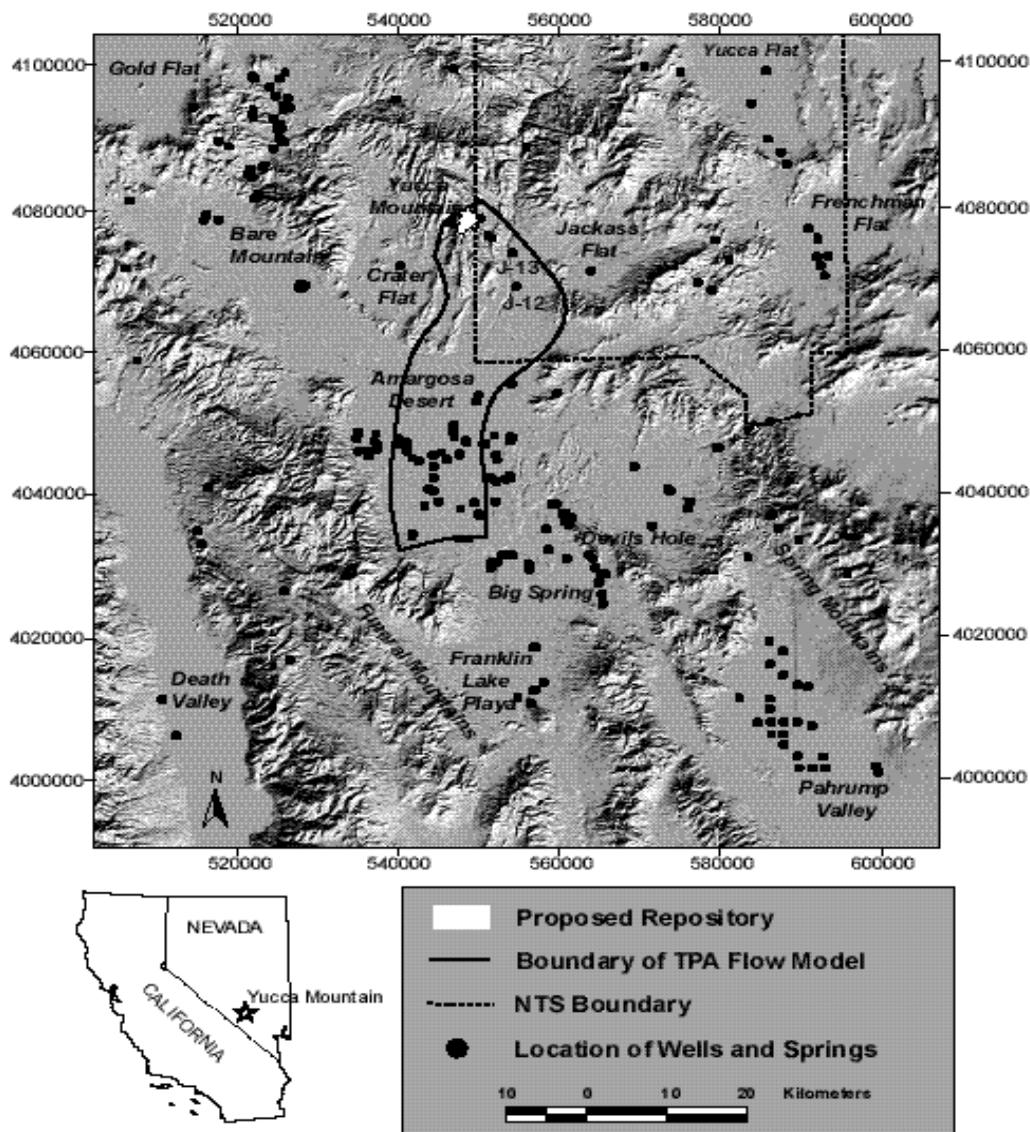
The geochemical conditions along the transport path will not only vary in space but would also evolve with time. Perfect *et al*. [19] have gathered and analysed chemistry data from more than 4 700 wells throughout more than an 80 000-km^2 area in the Yucca Mountain region. To estimate the potential effect of geochemical heterogeneity and variability on sorption, Turner and Pabalan [18] made the basic assumption that a subset (460 values) of the data in Perfect *et al*. [19] bounds the range of heterogeneity and variability in chemical conditions along the future transport paths. While this assumption is reasonable for bounding spatial heterogeneity, palaeochemical conditions may have to be

considered to bound the variation in time. In any case, Table 1 reproduces the Turner and Pabalan [18] estimate of various statistics of chemical parameters. The sorption coefficients calculated using a Double Layer Surface Complexation model implemented in MINTEQA2 are shown in Table 2. The ranges of K_d and K_A shown in Table 2 are much larger (by orders of magnitude) than those obtained from batch experiments using waters from the tuff aquifer in Well J–13 and Palaeozoic aquifer in Well UE–25 p#1, which are generally considered to bracket expected water chemistry at Yucca Mountain.

As stated previously, K_d values are functions of prevailing geochemical conditions that may be different in the future, for example, due to climate change (especially for coastal sites in Sweden). In addition, sorption properties of granitic rock are related to pore-structure and mineral distribution [20]. Therefore, the spatial and temporal evolutions of retention processes can be important considerations in the safety case.

Based on the above discussion, it can be concluded that spatial heterogeneity and temporal variability have a significant effect on retention processes and, hence, on the potential human dose. Therefore, the regulator would certainly require these effects be investigated by the implementor and that the implementor justify the model as well as the parameter values used.

Table 1. **Descriptive univariate statistics of measured groundwater chemical parameters based on application of screening criteria to hydrochemical database of [19].**

	pH (std units)	C_T (mg/L)	Log $P(CO_2)$ (atm)
Mean	7.83	295.76	− 2.50
Median	7.8	245.0	− 2.45
Standard Deviation	0.45	525.99	0.54
Kurtosis	1.75	270.67	3.73
Skewness	0.43	15.03	− 1.30
Minimum	6.3	6.80	− 5.08
Maximum	9.6	10 140.0	− 0.77
Count	460	460	460

Table 2. **Univariate statistics of calculated Np(V) – and U(VI) – Montorillonite sorption parameters.**

	Log $K_{A, Np(V)}$ (mL/m^2)	Log $K_{D, Np(V)}$ (mL/g)	Log $K_{A, U(VI)}$ (mL/m^2)	Log $K_{D, U(VI)}$ (mL/g)
Mean	0.74	1.73	− 0.03	0.96
Median	0.77	1.76	0.002	0.99
Standard Deviation	0.42	0.42	0.98	0.98
Kurtosis	26.58	26.58	12.93	12.93
Skewness	− 3.56	− 3.56	− 2.32	− 2.32
Minimum	− 3.26	− 2.28	− 6.84	− 5.85
Maximum	1.88	2.86	2.57	3.56
Count	460	460	460	460

5.   Use of geological evidence

The long period for which the performance of a geologic repository is to be assessed is unique and without precedent for engineering projects. While it is not feasible to conduct controlled experiments at the space- and time-scales of the repository, observation of natural systems may provide corroborative data to garner greater confidence in the performance assessment. Perhaps the best use of natural analogues is to enhance understanding of processes rather than obtaining data that can be input directly into the performance assessment. The latter is generally not possible because even the best analog is only an analog and not the site, and there always will remain questions about whether the interpreted parameters from an analog are appropriate for site-specific calculations.

However, as stated, a safety case should include multiple lines of evidence for safety. That means that the safety case should include, in addition to the main line of arguments, confidence-building qualitative and quantitative analyses that would add to the understanding of uncertainties inherent in long-term performance assessment. Studies of natural analogues have the potential of contributing to such understanding.

The reader is referred to papers on observations of retention processes in nature included in this set of workshop proceedings. From these papers and others in the literature, it can be concluded that retention processes play a significant role in the migration of contaminants in the subsurface environment. What is not as clear is whether from natural analog studies, one could deduce reasonable and unique correlations between the rates of these retention processes and the geochemical conditions. It is apparent that a combination of natural evidence together with laboratory data may lead to better confidence-building arguments than either one of these alone.

6.   Adequacy of simplifications

Regulators realise that performance assessment requires integration of all components of the waste isolation system, both natural and engineered. Various processes that will be incorporated in a performance assessment operate at different time- and space-scales necessitating simplifications during this integration process. However, the regulator expects every assumption made to simplify or abstract a complex process(es) to be justified. The justification can be based on detailed analyses, laboratory experiments, and evidence from natural analogues. Generally, simplifications that could lead to optimistic results should not be made without strong justification. Although a simplified conservative approach will probably be necessary for the system-level analysis, more realistic models and calculations may be needed to demonstrate detailed process knowledge and to provide reasonable confidence in the safety case.

7.   Future trends

In all the national programs, there is a significant period (tens to hundreds of years) of time lapse between beginning waste emplacement operations and closure of the repository. The regulators require (e.g., in the NRC-proposed regulations in 10 CFR Part 63) that the applicant continue investigations during the operations period to (i) resolve any safety-related issues identified at the time of construction authorisation or other licensing stages and (ii) confirm the assumptions and analyses included in the safety report. We envision that, consistent with the importance of the retention processes in the applicant's safety case, the applicant will continue to conduct both *in situ* and laboratory experiments to improve understanding of processes and obtain better values of the parameters including better estimates of the uncertainties in the models and the data. With the expected advance in computational power, it may be possible to include the more complex process level models directly into the performance assessment models and thus reduce the uncertainty due to

model simplification. Better geophysical and remote sensing techniques to characterise the structure of fractures, and full-scale, *in situ* experiments would also lead to better understanding of matrix diffusion. Reviews of existing performance assessment studies indicate significant room for improvement in the justification of radionuclide transport models (e.g., [21]).

Acknowledgements

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The Consideration and Representation of Retention Processes in the WIPP Performance Assessment: Justification of Adopted Approaches and Interaction with the Regulator

Part I: Chemical Retardation of Dissolved Actinides

Laurence H. Brush, Charles R. Bryan, Lucy C. Meigs, Hans W. Papenguth and Palmer Vaughn
Sandia National Laboratories, United States of America

1. Introduction

The Waste Isolation Pilot Plant (WIPP) is a United States (U.S.) Department of Energy (DOE) repository in Southeast New Mexico for defence-related transuranic (TRU) waste. The repository, which opened in March 1999, is located at a subsurface depth of 655 m in the Salado Formation, a Permian bedded-salt formation. The repository will eventually contain the equivalent of about 844 000 208-L drums of TRU waste in 56 disposal rooms arranged in eight seven-room panels, and in the access drifts.

The TRU waste to be emplaced in the WIPP will contain a wide variety of materials such as clothing, glassware, paper, rags, tools, wood, and solidified process sludges. These materials are contaminated with about 11 g of Th, 187 g of U, 17 g of Pu, and lesser quantities of other actinide elements per drum [1]. TRU waste also contains organic compounds such as acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate used for actinide separation and decontamination [1]. DOE suspected that these organics could form complexes with the actinides in TRU waste, and could decrease the extent to which they are retarded after release from WIPP disposal rooms. About 96 vol. % of the waste will be contact-handled (CH) TRU waste in mild-steel drums and boxes stacked three layers high in the 90-m-long by 9-m-wide by 4-m-high disposal rooms, and in the access drifts. The other 4% will be remote-handled (RH) TRU waste in shielded steel canisters in the ribs (sides) of the disposal rooms. RH TRU waste is similar to CH TRU waste, except that RH TRU waste contains enough ^{137}Cs and ^{90}Sr to require shielding and remote handling. The WIPP will contain an MgO backfill to decrease the solubilities of actinide elements by consuming essentially all of the CO_2 produced by (possible) microbial degradation of the cellulosics, plastics, and rubbers in TRU waste. This backfill will reduce the concentration of CO_3^{2-} and buffer the pH of any brine present between about 8.5 and 10. After filling and sealing, creep closure of the salt will crush the drums, boxes, and canisters, and encapsulate the waste.

DOE submitted the WIPP Compliance Certification Application (CCA) to the U.S. Environmental Protection Agency (EPA) in October 1996 to demonstrate compliance with EPA regulations for the radioactive constituents of TRU waste [2]. Performance-assessment (PA) calculations carried out for the WIPP CCA demonstrated that, in the absence of human intrusion, no radionuclides would escape from the repository to the accessible environment during the 10 000-year regulatory period. In the event of inadvertent human intrusion during drilling for oil, gas, potash, or other resources, small quantities of radionuclides could escape up the borehole, either: (1) directly from the repository to the surface; or, (2) from the repository to the Culebra Member of the Rustler Formation (which overlies

the Salado), through the Culebra, and up a water well to the surface. Of these direct releases, cuttings, cavings, and spallings (blowouts caused by pressurisation resulting from anoxic corrosion of mild-steel waste drums and boxes, Fe- and Al-base metals in TRU waste, and possible microbial degradation of the cellulosics, plastics, and rubbers) would be far more significant than direct brine releases, the only type of direct release affected by actinide solubilities. Nevertheless, all four types of direct releases would still be small enough to comply with the EPA regulations for TRU waste.

DOE suspected that transport of radionuclides through the Culebra, a fractured, microcrystalline dolomite and the most transmissive unit above the Salado, might be significant in the event of human intrusion. Therefore, DOE carried out thorough investigations of this potential release pathway, including Culebra hydrology, and physical and chemical retardation of actinides and other elements by samples of dolomite from the Culebra. However, the WIPP CCA PA calculations demonstrated that this release pathway is insignificant relative to direct releases from the repository to the surface following human intrusion.

The EPA certified that the WIPP complies with its regulations for the radioactive constituents of TRU waste in May 1998 [3]. DOE emplaced the first TRU waste in the WIPP in March 1999. The EPA must re-certify that the WIPP continues to comply with the regulations every five years after the first receipt of waste until the WIPP is filled in 2033.

2. Studies of chemical retardation of dissolved actinides

The PA calculations for the WIPP CCA in 1996 required linear, reversible, sorption isotherms (K_ds) for isotopes of Th, U, Pu, and Am. DOE also included Np in its studies. From the standpoint of their potential effects on the long-term performance of the WIPP, the order of importance of these actinides is Pu > Am >> U > Th >> Np. Because of the large quantities of reductants to be emplaced in the repository (Fe- and Al-base metals, and cellulosics, plastics, and rubbers), conditions will be reducing, both in the repository and the Culebra. Under these conditions, these actinides will speciate as Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III). However, DOE used Th(IV), U(VI), Np(V), Pu(V), and Am(III) under oxic conditions for all of its studies to avoid the experimental difficulties involved in maintaining U, Np, and Pu in the +III and/or +IV oxidation states. This necessitated use of the oxidation-state analogy (see Section 3, Use of chemical retardation data for dissolved actinides in the WIPP CCA PA) to establish ranges and probability distributions of K_ds for U(IV), Np(IV), Pu(III), and Pu(IV).

DOE used results from three laboratory studies to predict the retardation of Th, U, Np, Pu, and Am in the Culebra [4]: (1) an empirical (batch) study of the sorption of these actinides from WIPP brines by crushed Culebra dolomite; (2) a mechanistic study of the sorption of these actinides from pure NaCl solutions by pure dolomite from a location other than the WIPP Site; (3) a column-transport study of the retardation of these actinides in WIPP brines pumped slowly through well-preserved, intact Culebra cores maintained under *in situ* conditions.

I. Triay and her group at Los Alamos National Laboratory (LANL) carried out an empirical study of the sorption of Th(IV), U(VI), and Np(V), Pu(V), and Am(III) by samples of dolomite-rich rock from the Culebra. These samples came from core segments adjacent to those used for the column-transport study (see below). X-ray-diffraction analysis of this rock failed to detect clay minerals in most cases. Because the detection limit of this technique is about 1%, the samples that yielded the K_ds for PA contained a lower concentration of clay minerals than the Culebra as a whole (about 1 to 5%). They also carried out a few experiments with dolomite from the H-19 Hydropad and clay-rich rock from the lower, unnamed member of the Rustler. (The clay minerals in the lower member are identical to those on fracture surfaces and dispersed in the matrix of the Culebra.) They

crushed the samples, selected the 75-to-500-μm size fraction, washed these sub-samples with dilute HCl to remove crystallographically strained surfaces, fine particles of dolomite, and Fe- and Mn-oxyhydroxides, and pre-treated them with the same type of brine to be used for the actual experiment for periods of time for the most part identical to those of the sorption and desorption runs. They used four synthetic fluids, Brine A, ERDA-6, AISinR and H-17, for these experiments. Brine A simulates intergranular Salado brines at or near the stratigraphic horizon of the repository [5]. These brines could accumulate in WIPP disposal rooms after filling and sealing, and flow from the repository into the Culebra in the event of human intrusion into the repository. ERDA-6 simulates brines that occur in isolated but occasionally large reservoirs in the underlying Castile Formation [6]. These brines could also flow through the repository and into the Culebra in the event of human intrusion. AISinR simulates brine sampled from the Culebra in the WIPP Air Intake Shaft (AIS). H-17 simulates Culebra brine from the H-17 Hydropad. They carried out the pre-treatments and the actual experiments with 20 ml of brine and 1 g of rock. During the runs that yielded the K_ds to be used by PA, they used one actinide element at a time. At the end of the runs, they separated the aqueous and solid phases by sequential filtration to 0.2 μm, analysed the solutions by liquid scintillation counting (LSC), and determined K_ds from the differences between the initial and the final radionuclide concentrations in the solutions. Triay and her group studied the effects of the partial pressure of CO_2 on sorption. They carried out experiments on the bench top (in contact with ambient air, which has a CO_2 partial pressure of $10^{-3.5}$ atm), and in glove boxes with CO_2 partial pressures of $10^{-2.73}$, $10^{-1.98}$, and $10^{-1.50}$ atm. They also studied the effects of dissolved actinide concentration on sorption. These experiments yielded sorption isotherms, plots of the quantity of radionuclide sorbed by the solid phase or phases *versus* the final dissolved radionuclide concentration. These plots in turn provided information on the nature of the reaction(s) responsible for removal of radionuclides from solution. Finally, they studied the effects of equilibration time (3 days and 1, 3, 6, or 8 weeks) and direction of reaction (sorption or desorption) on sorption. This study yielded a large number of K_ds for actual samples of nearly pure Culebra dolomite and actinide-bearing synthetic fluids closely resembling those that could flow through the Culebra after human intrusion.

P. V. Brady and his colleagues at Sandia National Laboratories (SNL) and LANL carried out a mechanistic study of the sorption of Nd(III) (a non-radioactive analogue of Pu(III) and Am(III)), Th(IV), U(VI), Np(V), Pu(V), and Am(III) from synthetic 0.05, 0.5 and 5 M NaCl solutions by samples of well characterised, pure dolomite from Norway [7]. They used a limited- residence-time (1-min.) reaction vessel to minimise the extent of dolomite dissolution, actinide precipitation, and other reactions unrelated to sorption. This allowed them to study the effects of pH (from about 3 or 4 to 9 or 10 in most cases), the CO_2 concentration of the headspace (atmospheric, 0.5, and 5%), and the concentrations of various dissolved species on sorption in the absence of complexities caused by other reactions. They crushed the samples, selected the < 106-μm size fraction, washed them with dilute HCl, and pre-treated them overnight in an NaCl solution with the same concentration to be used for the experiments, and a solution-to-solid ratio of 100 mL per gram of dolomite. They carried out experiments with several actinide elements at a time, and a solution-to-solid ratio of 200 mL/g. After the runs, they separated the aqueous and solid phases with a 0.22-μm filter, analysed the solutions by inductively coupled plasma/mass spectrometry, and determined K_ds from the differences between the initial and the final radionuclide concentrations in the solutions. Although this study did not yield K_ds for actual samples of Culebra rock or for synthetic Culebra fluids, it did yield results that have proven highly useful for interpreting the results of the empirical sorption study at LANL, and for extending the empirical data to the basic conditions (pH values of about 8.5 to 10) expected to result from use of an MgO backfill in WIPP disposal rooms.

D.A. Lucero and his colleagues at SNL carried out a column-transport study with intact, 14.5-cm-diameter cores obtained from the Culebra in the WIPP AIS [8]. They obtained the cores from

5-m-long horizontal boreholes aligned in the current direction of groundwater flow in the vicinity of the AIS and stored them under conditions that minimised evaporation of pore water. Prior to the experiments, they cut 10- to 50-cm sections from the original cores and encapsulated them in rubber sleeves. They then placed the core sections in Al core holders, mounted them vertically in a glove box, and pressurised them to about 50 atm, the *in situ* pressure at the depths from which these cores were obtained (218 and 220 m). They carried out spike injections or, in a few experiments, continuous injections of Th(IV), U(VI), Np(V), Pu(V), and/or Am(III) by introducing synthetic AISinR or, in a few runs, synthetic ERDA-6 with low concentrations of the radionuclide(s) into a cavity cut in the top of each core. They then pumped additional brine through these cores at low flow rates (0.05. 0.1, and 0.5 mL/min) for periods of up to 237 days (equivalent to pumping up to 34.2 pore volumes of brine through these cores). These flow rates are at or close to the upper limit of the range of *in-situ* fluid velocities. They collected the effluent and analysed it in 5-mL increments by α spectrometry or LSC. They also used scanning γ emission tomography to image the cores. By injecting different radionuclides at different times and, in some cases, by using different brines, they carried out multiple, sequential experiments with the same core. Because this study quantified actinide sorption from fluids flowing through intact samples of Culebra rock, it complemented the static empirical and mechanistic sorption studies with crushed Culebra rock and pure dolomite. However, this study did not yield K_ds directly. For U and Np, which were moderately retarded by sorption, the observed delays between the elution peaks of non-sorbing radionuclides (such as ^{3}H or [22]Na) and those of U and Np yielded discrete values for the retardation factors R, which were then used, along with porosities determined with the non-sorbing tracers, to calculate K_ds. For Th, Pu, and Am, which were strongly retarded by sorption, they did not observe breakthrough, even after pumping brine through these cores for 133, 146, and 237 days (Th), and 61, 118 and 211 days (Pu and Am), equivalent to 19.1, 21.0 and 34.2 pore volumes (Th), and 8.83, 17.0, and 30.4 pore volumes (Pu and Am). Therefore, they were only able to calculate minimum values of R and K_d.

3.   Use of chemical retardation data for dissolved actinides in the WIPP CCA PA

DOE established ranges and probability distributions of K_ds for Th(IV), U(IV) and U(VI), Pu(III) and Pu(IV), Np(IV) and Np(V), and Am(III) for the 1996 CCA PA calculations (see [9] for a detailed description of the methods used to establish these ranges and probability distributions.) DOE used experimentally obtained K_ds for Th(IV) and the oxidation-state analogy to predict K_ds for U(IV), Np(IV), and Pu(IV). DOE planned to use experimentally obtained K_ds for Am(III) and the oxidation-state analogy to predict K_ds for Pu(III). However, it could not use the K_ds for Am(III) because they were non-linear, and the far-field radionuclide-transport code SECO-TP requires linear sorption isotherms to predict retardation. Therefore, DOE used the experimentally obtained K_ds for Pu(V) for Pu(III) and Am(III). This is defensible because the K_ds for actinides in the +III oxidation state are similar to or higher than those for actinides in the +V oxidation state.

DOE used mainly the 6-week sorption data from the empirical (batch) study (see above) to establish ranges of K_ds for the CCA PA. This was the only study in which experiments were carried out with a wide range of dissolved actinide concentrations and, hence, the only study that yielded sorption isotherms that could be checked for linearity. DOE did not include the results of the six-week desorption runs from the empirical study because these data could be artificially higher than those from the sorption runs. Possible reasons for this include: (1) removal of a weakly sorbed actinide species concentrated in the aqueous phase by discarding the solution at the conclusion of a sorption experiment, thereby concentrating a strongly sorbed species prior to the start of a desorption run; (2) saturation of a sorption site with a high K_d followed by removal of the dissolved actinide after a sorption experiment, thereby resulting in sorption of a higher proportion of the actinide on the sorption site with a high K_d during the desorption run. DOE used the data obtained from the 6-week batch sorption runs with the deep brines (Brine A and ERDA-6) equilibrated with ambient air, which has a

partial pressure of $10^{-3.5}$ atm (the lowest CO_2 partial pressure used in this study). DOE did not use 6-week empirical sorption data from Brine A and ERDA-6 equilibrated with higher partial pressures of CO_2 because the MgO backfill will remove essentially all microbially produced CO_2. For the Culebra brines (AISinR and H-17), DOE used the 6-week batch sorption data obtained at CO_2 partial pressures of $10^{-3.5}$, $10^{-2.73}$, and $10^{-1.98}$ atm, the currently expected range for the Culebra.

DOE used data from the mechanistic sorption study to extend the empirical sorption data to the basic conditions expected to result from the use of an MgO backfill in WIPP disposal rooms.

Lucero *et al.* [8] did not observe breakthrough of Th(IV), Pu(V), or Am(III) during the column-transport study. Therefore, it was only possible to determine minimum values of K_d for these actinides. These minimum K_ds are within the ranges obtained from the empirical and mechanistic sorption studies. However, they did observe breakthrough of U(VI) and Np(V) and, in most cases, the U(VI) and Np(V) K_ds from the column-transport study were less than the lower limits of the ranges obtained for these elements from the empirical and mechanistic sorption studies. Therefore, DOE used the data from the column transport study to extend most of the ranges for U(VI) and Np(V) to lower values.

Thus, DOE established ranges of K_ds of $2 \cdot 10^1$ to $5 \cdot 10^2$ mL/g for Pu(III) and Am(III); $9 \cdot 10^2$ to $2 \cdot 10^4$ mL/g for Th(IV), U(IV), Np(IV), and Pu(IV); $1 \cdot 10^0$ to $2 \cdot 10^2$ mL/g for Np(V); and $3 \cdot 10^{-2}$ to $3 \cdot 10^1$ mL/g for U(VI). DOE used a uniform probability distribution for all of these ranges. Currently, DOE uses ranges of K_ds of $2 \cdot 10^1$ to $4 \cdot 10^2$ mL/g for Pu(III) and Am(III); $7 \cdot 10^2$ to $1 \cdot 10^4$ mL/g for Th(IV), U(IV), Np(IV), and Pu(IV); $1 \cdot 10^0$ to $2 \cdot 10^2$ mL/g for Np(V); and $3 \cdot 10^{-2}$ to $2 \cdot 10^1$ mL/g for U(VI) [10], and a log-uniform probability distribution for all of these ranges.

4. Major issues pertaining to the use of actinide K_ds in the WIPP CCA PA

The EPA raised issues pertaining to the ranges and probability distributions of K_ds used for the PA calculations during its review of the WIPP CCA. The New Mexico Environmental Evaluation Group (EEG), an independent, full-time, WIPP review panel, and the U.S. National Academy of Sciences (NAS) Committee on the WIPP also raised issues relevant to these K_ds. The discussion below presents the major issues raised by the EPA, EEG, and NAS, but does not attempt to prioritise them.

4.1 Use of the empirical sorption study as the main source of data for the ranges and probability distributions of K_ds for the WIPP CCA PA

Several reviewers expressed concerns such as: (1) crushing Culebra samples created new surfaces that will not be present in the Culebra; (2) the empirical study did not include the conditions that will be produced by brine-backfill reactions (DOE decided to use MgO too late to include these conditions in this study); (3) in most cases, the U(VI) and Np(V) K_ds from the column-transport study were less than the lower limits of the ranges obtained for these elements from the empirical and mechanistic studies.

DOE responded by quantifying the specific surface areas of numerous Culebra samples before and after crushing, which demonstrated that crushing did not increase the surface areas of these samples significantly. This is because the 75-to-500-μm particles used for this study were significantly larger than the mean dolomite grain diameter of about 2 μm. Furthermore, the EPA determined that, although the empirical study did not include the conditions that will be produced by MgO, the mechanistic study provided adequate data to address these conditions [11, this volume]. Finally, application of a multiple-rate, double-porosity transport model to the Culebra by Holt [12], and post-test analysis of the column-transport experiments by Perkins *et al*. [13] demonstrated that, because of the short spatial and temporal scales of the column-transport study, there was not significant diffusion of U(VI) and Np(V) from the zones in which transport is dominated by advection into zones

dominated by diffusion. Therefore, the retardation factors for U(VI) and Np(V) reflected mainly sorption in the advective zones. However, field tracer tests [14-17] demonstrated that at larger scales, such as those relevant to PA, there will be significant diffusion from the advective zones into the diffusive zones. Sorption of Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III) by the large surface areas within the diffusive zones will then retard these radioelements effectively.

4.2 Use of data for other actinides and the oxidation-state analogy to establish ranges and probability distributions of K_ds for Pu(III) and Pu(IV)

Several reviewers also expressed concern that DOE used experimentally obtained K_ds for Th(IV) and the oxidation-state analogy to predict K_ds for U(IV), Np(IV), and, especially, Pu(IV); and experimentally obtained K_ds for Pu(V) for Pu(III) and Am(III). This was – and continues to be – an issue pertinent to actinide solubilities in the WIPP, for which DOE used solubilities of Am(III) obtained from experimental and modelling studies and the oxidation-state analogy to predict solubilities of Pu(III), and similarly obtained solubilities of Th(IV) and the oxidation-state analogy to predict solubilities of U(IV), Np(IV), and, especially, Pu(IV).

DOE asserted – and continues to assert – that its use of the oxidation-state analogy is defensible (K_ds for Th(IV) are similar to those for U(IV), Np(IV), and Pu(IV); K_ds for Pu(V) are similar to or higher than those for Pu(III) and Am(III); solubilities of Am(III) are similar to those of Pu(III); and solubilities of Th(IV) are higher than those of U(IV), Np(IV), and Pu(IV)). The EPA compared the K_ds used for the WIPP CCA to those reported for a variety of geologic media and found that the WIPP K_ds generally corresponded to the lower ends of the ranges from other sources [11, this volume]. Furthermore, the insignificance of the Culebra release pathway relative to direct releases (see Section 1, Introduction) also helped eliminate this issue. However, because the long-term performance or the WIPP is somewhat more sensitive to actinide solubilities than to actinide K_ds, DOE's use of the oxidation-state analogy to predict Pu(III) and Pu(IV) solubilities is still an issue.

4.3 Effects of organics in TRU waste on actinide K_ds

Various reviewers contended that the acetate, citrate, EDTA, and oxalate in TRU waste will decrease actinide K_ds significantly. This also was – and continues to be – an issue for actinide solubilities in the WIPP, which these reviewers have contended could increase significantly in the presence of these organics.

DOE asserted – and continues to assert – that the acetate, citrate, EDTA, and oxalate in TRU waste will not decrease actinide K_ds, nor increase actinide solubilities, significantly. Based on preliminary calculations using stability constants for organo-actinide complexes in aqueous solutions with ionic strengths lower than those of WIPP brines, US DOE [2, Appendix SOTERM] asserted that, under expected WIPP conditions, Ni would complex 99.8% of the EDTA, thus rendering EDTA unavailable for complexation with the actinides. This conclusion was conservative because the calculation did not include numerous other metals that will be present. Since the CCA PA, DOE has carried out extensive experimental and modelling studies of the complexation of Nd(III), Eu(III), Th(IV), U(IV), U(VI), Np(V), and Am(III) by acetate, citrate, EDTA, and oxalate. The results demonstrated that divalent metals initially present in WIPP brines, especially Mg, or divalent metals dissolved from TRU waste, such as Fe, Ni, or Pb, will prevent significant complexation of Th(IV) and Am(III) and, by analogy, complexation of U(IV), Np(IV), Pu(III), and Pu(IV) by these organics. Therefore, these organics will not increase actinide K_ds, nor increase actinide solubilities significantly. Moreover, the insignificance of the Culebra release pathway (see Section 1, Introduction) also helped defuse this issue. However, because the long-term performance or the WIPP is somewhat more sensitive to actinide solubilities, the effect of organics on solubilities is still an issue.

5. Studies of chemical retardation for WIPP recertification

Since the CCA PA, DOE has carried out very few additional studies of the chemical retardation of dissolved actinides in the Culebra. However, DOE has conducted extensive studies of actinide solubilities in WIPP disposal rooms. This is because the long-term performance of the WIPP is very insensitive to releases through the Culebra, but is somewhat more sensitive to direct brine releases (see Section 1, Introduction). In the post-CCA studies of actinide solubilities, DOE has continued to address issues such as the oxidation-state analogy and the effects of organics on actinide speciation and solubilities.

DOE expects to make very few changes in its use of chemical-retardation data for dissolved actinides for the first re-certification. DOE will use ranges and probability distributions of K_ds for Th(IV), U(IV) and U(VI), Pu(III) and Pu(IV), Np(IV) and Np(V), and Am(III) very similar to those established by Brush [9] for any PA calculations carried out for this recertification. However, it will modify these ranges slightly [10], and use a log-uniform probability distribution for all of these ranges [11, this volume] instead of the uniform distribution used in the CCA PA. These changes will probably not affect the conclusion that the Culebra will effectively retard essentially all of the small quantities of radionuclides that could be released into this unit following human intrusion.

Acknowledgements

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The Consideration and Representation of Retention Processes in the WIPP Performance Assessment: Justification of Adopted Approaches and Interaction with the Regulator

Part II: EPA Review Process and Approval Justification

Charles Byrum and R. Thomas Peake
United States Environmental Protection Agency, United States

1.   Introduction

The Environmental Protection Agency (EPA) was directed by Congress to review whether the Waste Isolation Pilot Plant (WIPP) would comply with EPA regulations on radioactive waste disposal. The review of the effectiveness of retardation in the Culebra Dolomite Member of the Rustler Formation was a major focus of the Agency's review since the Culebra is postulated to be the major long-term pathway for the movement of radionuclides. EPA review consisted of reviewing the Department of Energy's (DOE) data as well as conducting separate evaluations and modelling. EPA independent evaluation identified several issues of concern: First, steady-state conditions did not appear to be reached in some experiments. Second, the effect of actinide concentration did not appear to be addressed. Third, the effect of magnesium oxide backfill in the repository for creating alkaline pH conditions in the brines passing through was not considered. Fourth, the experiments for Am(III) failed for various reasons and Pu(V) was used to represent Am(III). EPA also considered other concerns voiced by different reviewers in its review. After receipt of information supplemental to DOE's Compliance Certification Application (CCA), EPA was able to determine that the experimental foundation supported the retardation conceptual model in the Culebra and the parameters used were adequate. EPA independent modelling confirmed DOE's modelling that indicated radionuclide releases through the Culebra would be greatly reduced by even low K_d values. However, EPA did determine that DOE should have used a log-uniform probability distribution for the retardation distribution coefficients (K_ds)instead of the uniform probability distribution used in DOE's compliance calculations. EPA required an additional Performance Assessment (PA), called the Performance Assessment Verification Test (PAVT). The change in the K_d distribution from uniform to log-uniform was incorporated for the K_d values used in the PAVT. The use of a log-uniform instead of a uniform distribution resulted in lower K_d values being sampled in the PAVT. This resulted in a greater number of realisations where ^{234}U was discharged across the WIPP compliance boundary in the Culebra. Although releases through the Culebra across the WIPP boundary were higher in the PAVT than in the CCA PA, the cumulative releases from the Culebra under the PAVT were still insignificant relative to the total releases and were well below the EPA regulatory limits.

2.   EPA review of retention processes in the Culebra

EPA review of all technical aspects of the WIPP project was guided by two regulations, concerns of the public, sound science, and the need for the review to be legally defensible. This involved reviewing DOE's experimental and field work for technical adequacy and completeness,

providing opportunity for public input and responding to the public's issues, and ensuring that DOE provided appropriate documentation. In addition, the issue of transport and retention processes in the Culebra had to be placed in the context of the entire performance of the disposal system, such as the site conceptual model and the need for an artificial pathway (the borehole) before any radionuclides could be realistically transported into the Culebra.

Figure 1 is a graphic used to illustrate the major considerations in developing repositories in the United States, which could be generally applicable globally. All repositories need to be able to contain radionuclides and demonstrate that they will do so; public concerns need to be identified and addressed; and the process needs to pass legal muster in the applicable legal and regulatory framework being applied. We had to consider all of these issues in the review of DOE's treatment of retention processes and all disposal system issues.

Figure 1. **The major influences EPA considered in certifying the WIPP.**
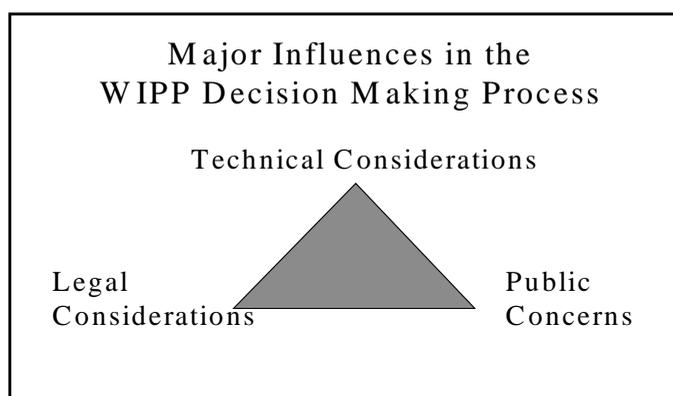
2.1   *EPA regulatory framework*

EPA review of the WIPP project was guided by two regulations: the general radioactive waste disposal requirements and standards (40 CFR Part 191, hereafter "191") and the WIPP-specific compliance criteria (40 CFR Part 194, hereafter "194" or "the Compliance Criteria") that implement the general radioactive waste disposal standards, 191. The disposal requirements set the allowable releases from a radioactive waste disposal system, establish qualitative requirements, and the method (probabilistic performance assessment) by which the releases are to be assessed. EPA proposed the disposal requirements in 1985 and completed them in 1993.

The regulation at 191.13(b) also establishes the concept of "reasonable expectation" that EPA used in its technical review. The reasonable expectation criterion acknowledges that uncertainties exist and that "proof of the future performance of a disposal system is not to be had in the ordinary sense of the word". The 191 regulation provides specific numerical requirements required for the disposal system. However, the regulation does not address additional specifics because the original intent of the 1985 regulation was to be generic and applicable to all transuranic and high-level radioactive waste sites. One quantitative example of the reasonable expectation concept was the use of parameter probability distributions for uncertain parameters instead of using parameters set at only high or low values. A qualitative example at WIPP involves our decision-making: we, as the regulator, had to determine adequacy. We were not tasked with identifying if DOE's approach was the "best", but whether it was "adequate". This was important when there were multiple technical choices that could be made, such as with the selection of alternative computer models.

In 1992, Congress limited the scope of 191 to WIPP and gave EPA the authority to develop WIPP-specific criteria for the implementation of 191, hence the 194 Compliance Criteria. The Compliance Criteria were developed in the mid-1990s and were designed to control the process used to show compliance with the disposal standards specifically at WIPP. Examples of the types of PA-related information in the Compliance Criteria are requirements for the development of computer codes, scope of performance assessment, and site-characterisation requirements. The specific compliance criteria were especially important in the consideration of retention processes in the Culebra. The Compliance Criteria defined the Delaware Basin based on its consistent geology. This was then used by DOE in determining geologic formations to be considered in the development of the PA, such as consideration of the Culebra as the most transmissive unit and the evaluation of retention processes such as chemical and physical retardation as characteristics of the Culebra.

The combination of the general guidelines in 191, the specific numerical requirements in 191, and the site-specific criteria provided in the Compliance Criteria thus provided the framework for DOE's CCA development and EPA review of DOE's CCA.

2.2 Public involvement

The certification of WIPP was performed using what is known in the United States as an informal rulemaking, much like a licensing process in other countries. In such a rulemaking, the public and other interested groups are asked to comment on any concerns they may have. For the WIPP compliance certification, public comments were very important. In the United States, it is a federal requirement in a rulemaking that public concerns be documented and a written response be given.

The public process used in EPA review of DOE's WIPP CCA consists of multiple steps. Once DOE submitted the CCA, EPA reviewed the documentation for completeness, began the formal EPA review in the year allotted by Congress, developed a draft proposed regulation of our certification decision, allowed the public to comment, and then finalised our decision and responded to comments on the proposed regulation. The response to comments included analyses that EPA conducted on its own in addition to those EPA required of DOE. Prior to DOE's submission of the CCA, EPA and DOE held periodic technical exchange meetings that were open to the public and the public had an opportunity to ask questions.

EPA received hundreds of public comments related to many issues, some technical, some procedural, and many legal. Twenty-six comments were received related to retention in the Culebra focusing on eight specific topics (Table 1). EPA catalogued each of the comments and provided a written response [1].

Table 1. **Public concerns received By EPA related to Culebra retardation.**

1.	Should sorbing tracer tests be used to derive K_ds?
2.	Is the use of actinide analogues, such as using Pu(V) for Am(III) and Pu(III), appropriate?
3	Are batch and column scale sorption experiments representative?
4.	Do the use of homogeneous and non-linear isotherms based K_ds represent complex reactive chemistry?
5.	Will organic ligands affect K_ds?
6.	Does shallow resource mining change K_ds?
7.	Should actinide colloids be considered when considering retardation?
8.	Should a zero K_d be considered for U(VI)?

Comments and concerns voiced by the public and other interested parties were evaluated, considered by the EPA, and incorporated into our review. Based on the many public comments, as well as EPA concerns, we requested more information in particular on subjects related to the sensitivity of retardation in the Culebra and the results of (then) recent field tracer tests and their relationship to Culebra transport parameters.

3.   EPA review process

EPA review process consisted of many steps including:

- Reviewing the CCA documentation to determine if the CCA provided complete enough information for EPA to review and make a decision.

- Requesting and receiving additional information from DOE concerning specific questions that the public or we had.

- Conducting multiple analyses as part of a comprehensive evaluation of the CCA and supplemental information.

- EPA required DOE to execute the PAVT to evaluate the changes to the WIPP release because of changes in software and parameters. In the case of the K_ds, changing the probability distribution from uniform to log-uniform.

EPA used all of this information to make its final decisions about retardation in the Culebra.

3.1   *EPA review of the original certification application*

In the original CCA, DOE submitted a great deal of documentation about retention of actinides in the Culebra dolomite. DOE provided a general description of dissolved actinide transport including retardation in the Culebra. ([2 (Section 6.4.6.2.1 of Volume I and CCA Appendix MASS, Section MASS 15.2)] contains a detailed description of studies done to support Culebra transport retardation.) This documentation included evidence that retarded transport in the Culebra will occur and will attenuate the cumulative radionuclide releases [2 (Volume X, Appendix Mass. p. MASS-81-83)]. However, the information was not definitive enough for EPA to agree with DOE. After review of the CCA documentation and other referenced work, the EPA requested more information.

3.2   *EPA request for more information*

After EPA initial review of the CCA, the Agency did not feel that the sensitivity of Culebra transport to retardation had been adequately evaluated by DOE. Therefore, in a letter to DOE dated December 19, 1996, EPA requested that a sensitivity analysis be done by DOE. Also, EPA requested that DOE report the results of tracer tests completed shortly before submission of the CCA. EPA believed that the Agency could not complete its technical review without this new information. Additionally, the EPA stated that the uniform probability distribution for K_ds used in the PA calculations did not seem appropriate based on DOE's own guidance and requested that DOE justify its usage.

3.3   *Additional information submitted by DOE*

In January of 1997, DOE began to respond to EPA request in a series of letter responses. EPA combined this information with the original CCA documentation related to Culebra retardation as part of its review.

4.   EPA final review of the combined information

4.1   Sources of K_d data used by DOE in the CCA

Ranges of K_d values were developed by DOE for specific actinides modelled in the CCA PA. These ranges were based on experimental studies performed by DOE (and its contractors) and applicable literature. This section presents a summary of the primary sources of data used to derive the K_d ranges.

DOE derived K_d values for four actinides, representing six oxidation states: Pu-239 (Pu III and IV), Am-241 (Am III), U-234 (U IV and U VI), and Th-230 (Th IV). The strategy implemented by DOE to develop K_d ranges for these actinides was to first establish experimentally obtained K_d ranges for Am(III), U(VI), Th(IV), and Np(V), and then to use an oxidation-state analogy (see Section 4.2) to extrapolate this range to represent Pu(III), Pu(IV), U(IV), and Np(IV) [3, 4]. From this work, DOE derived the K_d values for the Am(III), Th(IV), Np(IV and V), Pu(III and IV), and U(IV and VI) used in PA [2 (Appendix PAR, Parameters 52 to 57)]. A uniform probability distribution was recommended by Brush [3,4] as appropriate for use in the PA based on the narrow range of values (less than three orders of magnitude) and the uncertainty associated with possible conditions in the Culebra (brine type, partial pressure of CO_2(g) and resulting pH).

According to Brush [3,4], the primary source of actinide K_d measurements was the experimental work by Triay and co-workers at Los Alamos National Laboratory. Triay conducted experiments on sorption of Pu(V), Am(III), U(VI), Th(IV), and Np(V) on crushed dolomite rocks from the Culebra using different brine compositions, various CO_2(g) partial pressures and varying actinide concentrations.

Results of the 6-week Triay experiments using a CO_2(g) partial pressure of $10^{-3.5}$ atm for the deep brines and CO_2(g) partial pressures from $10^{-3.5}$ to $10^{-1.98}$ atm for the Culebra brines established the initial range of K_d values for Pu(V), U(VI), Th(IV), and Np(V) [3,4]. A K_d range for Am(III) was not developed from the Triay experimental data because of an observed relationship between K_ds and the final dissolved concentration of Am(III). This relationship indicated that processes other than sorption to the matrix were occurring within the Am(III) K_d experiments [3,4]. As a result of the failure of the Am(III) K_d experiments, DOE chose to use experimentally obtained ranges for Pu(V) K_ds to represent Am(III) K_ds in the CCA modelling [2 (Appendix MASS, Attachment 15-1,15-2)]. This decision by DOE was based on the assumption that K_ds for Am(III) are greater than or equal to those for Pu(V), therefore use of the Pu(V) value would be conservative. Furthermore, the K_d range established for Th(IV) in the deep brine was used for the K_d range of Th(IV) in the Culebra because the data from the Th(IV) Culebra brine experiments did not meet certain experimental control criteria. Some of the initial K_d ranges established from the Triay experiments were revised based on the results of additional experimental studies, as described below.

DOE conducted a mechanistic study on sorption of Am(III), U(VI), Th(IV), Pu(V), and Np(V) on a Norwegian dolomite under a variety of ionic strength solutions (0.05, 0.5, and 5.0 M NaCl). Although this study did not yield Culebra-specific K_d data, the results were used to extend some of the empirical data from the Triay deep brine experiments to the alkaline pH conditions anticipated from the use of an MgO backfill in WIPP disposal rooms. The lower end of the K_d range for U(VI) was decreased and the upper end of the K_d range for Np(V) was increased based on the results of the mechanistic study [2 (Appendix MASS, Attachments 15-1, 15-2)].

Brush [3,4] also reported the results of experimental studies of actinide transport through cores obtained from the Culebra in the WIPP Air Intake Shaft. These experiments included spike and, in a few cases, continuous injections of Am(III), Th(IV), Np(V), Pu(V), and U(VI) in synthetic Culebra and deep brines into the cores. DOE did not directly determine K_ds from these experimental

results. Instead, values of the retardation factor were calculated from the observed delay between the elution peaks of non-adsorbed radionuclides and those of U and Np. Values of K_ds were then back calculated from the retardation factor and the experiment-derived porosities. Breakthrough was not observed for Pu, Am, and Th [5]. Minimum K_ds were calculated for these strongly retarded actinides. The lower ends of the K_d ranges for U(VI) and Np(V) were decreased based on the results of the intact core study [2 (Appendix MASS, Attachment 15-1, 15-2), 3, 4].

The post-test cores used in the column experiments were examined to determine the distributions of Pu(V) and Am(III) as a function of distance from the influent ends. These results were presented to the New Mexico Environmental Evaluation Group (EEG) by Perkins and Lucero, July 30, 1997, Albuquerque, New Mexico [5]. Nearly all of the Am(III) was found to be present in the top 1 mm of the core. Depending on the solubility of the Am(III) solid precipitated, the solution concentration would have been decreased, but some amount of Am(III) would have been left in solution and available for transport through the column, as suggested by the low concentrations in the solid phase beyond 1 mm from the influent end. However, no Am(III) was detected in the effluent solution, indicating that all of the Am(III) was effectively attenuated.

The concentration profile for Pu(V) showed a more smeared out concentration gradient from the influent end that was suggestive of sorption attenuation processes. Based on these results, Perkins and Lucero calculated minimum K_ds in the range of 175 to 282 mL/g for Pu(V) and 190 to 327 mL/g for Am(III). These K_d values are within the range of 20 to 500 mL/g determined for Pu(V) in batch experiments as reported by Brush [3,4].

4.1.1   EPA assessment of DOE experiments

In addition to the experimental work by Triay and co-workers at Los Alamos National Laboratory, experimental work by Brady and Lucero [3,4] at Sandia National Laboratories was used to augment the results of Triay, where appropriate. EPA noted that Triay's work, for the most part, appeared to be the primary study used to define K_d values representative of actinide retention by the Culebra dolomite. Triay conducted experiments with different brine compositions covering the range of possibilities expected in the event of a release from WIPP under different scenarios. DOE believed, and EPA concurred, that the compositions of the electrolyte solutions can be expected to be the most important factor affecting the variability of K_ds [6,7]. Also, Triay used crushed dolomite rock from the Culebra Member of the Rustler Formation so that site-specific material was used.

EPA determined that the initial actinide concentrations in experimental brine effluent appeared to be about an order of magnitude less than the solubilities of any actinide solids that might be expected to form under the experimental conditions, although the results of such calculations are not presented by Brush [3,4]. That is, the experimental brines were undersaturated with respect to potential actinide solids. EPA believed that this check was important to ensure that losses of actinide from solution are caused by adsorption processes rather than precipitation reactions. As a result, EPA concluded that changes in actinide concentrations observed were most likely a result of adsorption reactions rather than precipitation of actinide solids.

4.2 K_d ranges derived from oxidation state analogies

DOE used oxidation state analogies to define the K_d ranges for Pu(IV), U(IV), and Np (IV). The analogies are based on the assumption that actinides in the same oxidation state exhibit similar trends and behaviours and that these trends allow the behaviour of one actinide in a particular oxidation state to be estimated from or bounded by the behaviour of another actinide in the same oxidation state ([8], presentation summarised in [5]). Based on this analogy, predicted adsorption of an early (lower atomic

number) actinide series element was used as a lower bounding estimate for adsorption of a late (higher atomic number) actinide series element in the same oxidation state. For example, the K_d range for Th, which is the first actinide series element, should have the lowest K_d values among the actinides in the (IV) oxidation state. Therefore, the experimentally derived K_d range for Th(IV) was used as the K_d range for Pu(IV), U(IV), and Np(IV) [3,4]. Nowak [8] cited work by Silva [9] that showed the following relationship between oxidation state and average K_d for a number of actinides on an assortment of minerals:

$$(IV) > (III) > (VI) > (V).$$

These results and other empirical data support the use of the K_d range developed for Pu(V) as a lower bound for Am(III). By the oxidation state analogy, Am(III) chemical behaviour is quantitatively similar to Pu(III) chemical behaviour and, therefore, the K_d range developed for Pu(V) was also extrapolated to Pu(III) as a conservative lower bound [8].

DOE conducted laboratory studies under expected WIPP conditions to predict oxidation state distributions of Pu, U, and Np in deep Castile and Salado brines. The results of the study, as well as other previously published results regarding projects other than the WIPP Project, predicted that Pu will be present predominantly as Pu(III) and Pu(IV) but not as Pu(V) or Pu(VI), U will be present as U(IV) and U(VI), and Np will be present as Np(IV) and Np(V) under expected repository conditions.

In June and July of 1996, DOE repeated the procedures used to establish K_d ranges described in Brush [3] using revised empirical sorption, revised mechanistic sorption, and original transport data [4]. This reassessment [4] indicated that revised K_d ranges were in order, but DOE concluded that although it was "too late for performance assessment (PA) personnel to rerun their transport calculations with the revised ranges ... PA can still use these K_ds to assess the impact of the erroneous values on their calculations. Based on our discussions with them, we do not expect any significant impact" [4]. The ranges recommended by Brush [3] for use in the PA are presented in Table 2. The PA was conducted using the initial K_d ranges noted on this table because the revised ranges in parentheses were not received in time to be implemented prior to the October 1996 PA submission.

Table 2. **Ranges of matrix K_ds (mL/g) for actinides recommended by Brush [3] and used in PA. Values in parentheses are the revised K_d values recommended in Brush [4], but not used in PA.**

Oxidation state	Am	Pu	U	Th	Np
III	20-500 (20-400)	20-500 (20-400)			
IV			900-20 000 (700-10 000)	900-20 000 (700-10 000)	900-20 000 (700-10 000)
V					1-200
VI			0.03-30 (0.03-20)		

4.3   *Four areas incompletely addressed*

EPA concluded that there were four areas that were not completely addressed by Brush [3,4] in his descriptions of Triay's work.

First was the question as to whether steady-state conditions were reached in the K_d experiments. Triay collected samples after variable equilibration times (e.g., three days, one week, two weeks, three weeks, six weeks, and eight weeks). Only the 6-week results were used to define K_ds without any discussion of the time-series experiments. Although no discussion was provided regarding

time trend data, EPA believed it was likely that steady-state conditions were achieved given the relatively long equilibration times of the experiments (i.e., six weeks).

Second, the effects of actinide source term concentration on the K_ds were not addressed, making it difficult to determine whether the experiments were conducted under conditions where a linear relationship between retention and concentration would be expected. EPA notes that although evidence of linearity was not provided by DOE, under the experimental conditions of high pH, the adsorption densities of most aqueous cations, such as the actinides, tend to deviate from a linear dependence on concentration only with increases in their aqueous concentrations [10]. EPA concluded that the use of K_ds to represent the reversible partitioning of actinides between the solid and liquid phases was reasonable and conservative for the extremely low concentrations of actinides expected for the chemical conditions of the subsurface as dictated by the low solubilities of the actinide solids.

Third, the effect of the magnesium oxide backfill in the repository for creating alkaline pH conditions in brines passing through it was not considered in the experimental design of Triay. Reactions between magnesium oxide, water, and carbon dioxide are expected to produce pH from about 9 to 10, whereas the brines used by Triay had near-neutral pH. However, EPA concluded that the adsorption of cationic species, such as for the dissolved actinides, generally increases with increasing pH, hence the reported values might be considered conservative with respect to changes attributable to pH. For example, Pu(IV), Pu(V), and Np(V) adsorption to iron oxyhydroxide [FeOOH] increase substantially at pH > 5 to 6 [11,12]. Similar observations have been made for Am and Np adsorption to various silicic rock types as a function of pH [13].

Fourth, the K_d experiments for Am(III) failed for various reasons described by Brush [3,4]. Consequently, K_ds measured for Pu(V) were used to represent Am(III). Then, because Am(III) is the analogue for Pu(III), the K_ds measured for Pu(V) were also used to represent Pu(III). EPA concluded that this approach requires the extrapolation of one data set to represent two others, which increases the uncertainty of the results, but this was necessary given the constraints of the experimental program. Also, given the general trend in actinide K_ds for different oxidation states of (IV) > (III) > (VI) > (V), the use of a K_d determined for Pu(V) to represent Am(III) and Pu(III) was probably a conservative underestimate.

4.4 *Comparison of DOE K_d values with other sources*

The actinide K_ds described by Brush [3,4] were determined for brine solutions with Culebra dolomite rock for a range of $CO_2(g)$ partial pressures. The brines used in the experimental studies include Brine A, which represents the Salado formation water, ERDA6, which represents the Castile formation water, and AISinR and H-17, which both represent the Culebra formation water [3,4]. The conduct of K_d experiments in these different solutions produced a range of K_d values for each actinide. To provide a context for the ranges in actinide K_ds, EPA compared these to values reported for a range In most cases, EPA found that the actinide K_ds determined for the WIPP brines fell into the lower range of values reported for sands, loams, and clayey soils with the possible exception of Np(IV) (Table 3). Sheppard and Thibault [7] report a lower range of K_ds for Np than Brush [3,4], but they did not indicate an oxidation state, making a direct comparison impractical. The K_d range for Np(V) reported by Brush [3,4] was comparable to that reported by Sheppard and Thibault [7].

Table 3. **Actinide K_ds (mL/g) determined for Culebra dolomite under brine conditions compared to those measured for general soil types from Sheppard and Thibault [7].**

Element	DOE K_d	Sand K_d		Loam K_d		Clay K_d	
		Mean[a]	Range	Mean[a]	Range	Mean[a]	Range
Am(III)	20-500	1 900	8.2-300 000	9 600	400-48 309	8 400	25-400 000
Pu(III)	20-500	550[b]	27-36 000[b]	1 200[b]	100-5 933[b]	5 100[b]	316-190 000[b]
Pu(IV)	900-20 000	550[b]	27-36 000[b]	1 200[b]	100-5 933[b]	5 100[b]	316-190 000[b]
U(IV)	900-20 000	ND	ND	ND	ND	ND	ND
U(VI)	0.03-30	35[c]	0.03-2200[c]	15[c]	0.2-4 500[c]	1 600[c]	46-395 100[c]
Th(IV)	900-20 000	3 200	207-150 000	ND	ND	5 800	244-160 000
Np(IV)	900-20 000	5[d]	0.5-390[d]	25[d]	1.3-79[d]	55[d]	0.4-2 575[d]
Np(V)	1-200	5[d]	0.5-390[d]	25[d]	1.3-79[d]	55[d]	0.4-2 575[d]

a   Geometric mean
b   Oxidation state not specified by Sheppard and Thibault [7]; equivalent values assumed for both Pu(III) and Pu(IV).
c   Oxidation state not specified by Sheppard and Thibault [7]; assumed to be representative of U(VI) because of insolubility of U(IV) phases.
d   Oxidation state not specified by Sheppard and Thibault [7]; equivalent values assumed for both Np(IV) and Np(V).

4.5   *EPA assessment of K_d distribution*

Brush [3,4] recommends the use of a uniform distribution about an arithmetic average to represent the range of K_d values for the actinides, based on the observation that the measured minima and maxima are three orders of magnitude or less apart. EPA noted that this approach differs from observations of K_d distributions in the literature. Previous reviews found that K_ds for numerous metal solutes in different media, mostly different types of soils, are lognormally distributed [7, and 14,15 cited by [7]].

The experimental measurements of K_ds described by Brush [3,4] focused on only one type of material, the Culebra dolomite rock, hence these measurements might be expected to show uniform distributions in arithmetic space. However, the experiments were conducted for four different brine compositions and a range of $CO_2(g)$ partial pressures. These factors introduce variability in the results almost as great as those observed for different soils by Sheppard and Thibault [7].

Using examinations of probability plots for the different actinides and noting the deviation when using an arithmetic scale but approximating a straight line when plotted on a logarithmic scale, EPA concluded that these analyses indicate the actinide K_ds are loguniformly distributed and would be better represented by sampling from a log-transformed range rather than the arithmetic uniform range advocated by Brush [3,4].

5.   **Model application and effects of K_d on actinide transport**

The WIPP CCA included results of a performance assessment (PA) in which Complementary Cumulative Distribution Function (CCDF) curves for the normalised cumulative radionuclide release(s) to the accessible environment were computed. A component of this assessment included the simulation of groundwater flow and radionuclide transport in the Culebra Dolomite Member of the Rustler Formation.

5.1   Model application of K_d

Actinide transport in the Culebra was simulated using the codes SECOFL2D and SECOTP2D [16, 17]. SECOFL2D was used as a two-dimensional groundwater flow model capable of simulating transient and steady-state flow in porous media. SECOTP2D was used as a two-dimensional dual-porosity transport model capable of simulating transport of radionuclides through fractured porous media. Parallel plate type fracturing was assumed in the SECOTP2D code. Fluid flow was restricted to the advective continuum (fractures) and mass was transferred between the advective and diffusive continuum (matrix) via molecular diffusion. The SECOTP2D model was capable of simulating retardation of actinides in both the advective and diffusive continuum using linear equilibrium sorption isotherms. However, sorption was restricted to the matrix in the simulations. No credit was taken for actinide sorption in the advective porosity (along fracture linings) [3, 4].

The transport simulations were calculated using only a local flow field (grid). Only dissolved species were considered in the transport simulations and transport of four actinide isotopes with a total of six oxidation states was simulated including ^{241}Am, ^{239}Pu, ^{234}U, and ^{230}Th. A key assumption applied to the transport model was that spatially averaged, constant transport parameters can be used to describe the behaviour of a heterogeneous fractured porous medium. However, the transport parameters were varied from one run to the next through sampling to account for the uncertainty due to heterogeneity. An actinide source, representing discharge from an intrusion borehole penetrating the repository, was injected into the Culebra as part of the model. A mass flux rate was specified in the model such that 1 kg of each isotope was injected over a fifty-year period. The results of the transport simulations predict the movement of radioisotopes for scenarios.

In addition to the PA transport model used in the CCA, DOE performed bounding estimates using the minimum K_ds necessary to achieve compliance with EPA limits [18]. The bounding estimates were made for ^{239}Pu and ^{241}Am, which are considered the critical actinides with respect to releases to the accessible environment. Results of DOE's bounding assumptions (whereby all other factors are set to the least favourable value) indicated that a K_d of 3 mL/g was sufficient for compliance for ^{239}Pu and ^{241}Am. Estimates based on typical CCA sample sets indicated that K_ds greater than 1 mL/g are sufficient for compliance [18]. The K_d ranges determined from DOE experiments and literature for ^{239}Pu and ^{241}Am are typically greater than 100 mL/g, thus implying that K_d values used in PA are more than sufficient to ensure compliance with EPA limits with respect to accessible environment release through the Culebra.

5.2   Results of the PA verification test

EPA identified concerns with some parameter values (~1.5% of DOE's parameters) and computer codes. As a result of these concerns, EPA required DOE to make changes to the parameters and the codes and then conduct additional calculations in a Performance Assessment Verification Test (PAVT). The PAVT was a set of 300 additional PA realisations (calculations) that tested the cumulative impact of parameter value changes identified by EPA. In addition, the PAVT addressed whether software problems identified by DOE would affect the results of the calculations. EPA goal with the additional PAVT calculations was to verify that the cumulative impact of the changes to computer codes and parameters did not violate the radioactive waste disposal standards.

The primary difference in the use of K_ds between the PAVT and the CCA was that K_ds were represented in the PAVT using a log-uniform distribution rather than a uniform distribution [19]. The same ranges of K_d values used in the CCA for each probability distribution were also used in the PAVT. The use of a log-uniform instead of a uniform distribution resulted in lower K_d values being sampled in the PAVT. This resulted in a greater number of realisations where ^{234}U was discharged across the WIPP site boundary. In the CCA, only two realisations resulted in conditional releases across the site boundary.

In the PAVT, 42 realisations produced conditional releases of ^{234}U across the site boundary in excess of 10^{-10} kg. Of these, 15 realisations produced a conditional release greater than 0.1 kg. (This assumed that the amount injected into the Culebra was 1.0 kg).[1] All of the conditional releases greater than 10^{-10} kg had a ^{234}U oxidation state of (VI), which has the lowest distribution coefficient.

Although releases through the Culebra across the site boundary were higher in the PAVT than in the CCA (because of the greater proportion of sampled low K_d values), the cumulative releases from the Culebra under the PAVT were still insignificant relative to the total releases [19]. The total PAVT releases were dominated by cuttings and spallings releases with a smaller contribution from direct brine release. Table 4 lists the releases from each of the individual release mechanisms. The long-term releases from the Culebra are zero for the 0.1 probability of release for both the PAVT and CCA. The long-term release from the Culebra is zero for the 0.001 probability of release for the CCA and only 0.0007 for the PAVT.

The PAVT mean CCDF for total normalised releases to the accessible environment still did not exceed or come within an order of magnitude of the EPA Limit. EPA concluded that although releases to the accessible environment through the Culebra appear to be highly sensitive to K_ds, total releases to the accessible environment are relatively insensitive to the results of the Culebra flow and transport model.

Table 4. **CCA and PAVT Normalised Releases (EPA Units) for Probabilities of 0.1 and 0.001**

	EPA Units Released @ 0.1 Probability[a]		EPA Units Released @ 0.001 Probability[a]	
Release Mechanism	**PAVT**	**CCA**	**PAVT**	**CCA**
Cutting and cavings	0.0732	0.0326	0.2754	0.1451
Spallings	0.0756	0.0310	0.2149	0.1750
Direct Brine Release	0.0003	0	0.1545	0.0452
Long-term brine release in the Culebra	0	0	0.0007	0
Total[b]	0.1297	0.0576	0.3818	0.2219

a Releases of 10^{-6} or less are considered to be zero.

b The compliance standard at probability = 0.1 is 1 EPA Unit, and for the probability = 0.001 the standard is 10 EPA Units.

5.3   *Results of additional EPA modelling*

Additional modelling was performed by the EPA [20] to evaluate the effect of K_d on groundwater flow and transport in the Culebra. Low-end K_d values were simulated for U (3.0×10^{-5} m^3/kg) and Am and Pu (0.02 m^3/kg) using the transport code STAFF3D and the mean transmissivity field from the 1992 PA. Radioactive decay of the solute was not simulated. Assuming a network of 10 fractures, breakthrough occurs at the downgradient edge of the land withdrawal boundary at about 3 000 years for uranium. Breakthrough does not occur at relative concentrations greater than 1×10^{-5} during the 10 000-year simulation for Am or Pu. For a scenario in which

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1.   In the CCA modeling, DOE assumed that a unit release of 1 kg mass of an actinide was injected into the Culebra. DOE modeled the transport of this unit mass through the Culebra. For the fraction of the 1kg that reaches the boundary, DOE multiplied the fraction by the actinide that is injected to the Culebra via the BRAGFLO calculations.

100 fractures are simulated, no breakthrough was observed at relative concentrations greater than $1x10^{-5}$ during the 10 000-year simulation for U, Am, or Pu. The results of these model simulations are in reasonable agreement with the results of the CCA and the PAVT. These results support the conclusions previously stated that releases across the WIPP site boundary through the Culebra are relatively insignificant compared to total releases from all mechanisms.

6. EPA final conclusions

In the review of DOE's approach to retention processes in the WIPP performance assessment, EPA considered technical issues, public concerns, and legal issues. EPA requested and responded to numerous comments on DOE's WIPP compliance application that involved retardation in the WIPP disposal system. EPA considered public concerns and included them in the review of retardation. Ultimately, EPA concluded that DOE's experiments provide reasonable actinide K_d values that are appropriate for use in PA. Also, EPA concluded that DOE methodologies regarding oxidation state analogies and distributions, as well as the brine compositions used in PA and application of K_ds in PA, are reasonable. Further, EPA concluded that the values and ranges of actinide K_ds used by DOE in the PA are reasonable for use in modelling actinide transport in the Culebra.

However, EPA also concluded that K_d values derived from DOE experiments appear to be log-uniformly distributed, contrary to the DOE position that a linear uniform distribution was appropriate. A log-uniform distribution was consistent with trends reported in the literature for retention of solutes by various geologic media. Representation of the actinide K_ds as a log-uniform distribution in the PAVT resulted in a significant increase in the number of simulations in which releases occurred at the WIPP site boundary.

[For details of EPA review see [21], Requested from the EPA Docket – webmaster.oria@epa.gov. In addition, many EPA WIPP documents can be found at: www.epa.gov/radiation/wipp/regulations.htm.]

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Part C

Poster Session

Effects of Heterogeneous Porosity on Retention: Results from the TRUE Laboratory Experiments

Johan Byegård, Mats Skålberg and Henrik Widestrand
GEOSIGMA AB, Sweden

Eva-Lena Tullborg
Terralogica AB, Sweden

Abstract

This paper presents some results of investigations of porosity distributions and the effects of heterogeneous porosity on retention in crystalline rock. The materials used were host rock diorite, altered diorite and mylonite from the Äspö Hard Rock Laboratory, Sweden. The porosities have been investigated with the ^{14}C-labelled methamethylacrylate impregnation (^{14}C-PMMA) method. The ^{14}C-PMMA analysis shows that the porosity is strongly heterogeneously distributed in all materials, where high porosity often can be correlated to cracks and micro fractures, which is even more pronounced in mylonite. An increase in porosity towards the fracture surfaces was observed. Experimentally obtained heterogeneous porosity distributions could be used to explain the shape of breakthrough curves and penetration profiles better than a model assuming homogeneous porosity. General porosity profiles are outlined and discussed for altered and fresh rock. The combined effect of a porosity gradient and increased pore connectivity near the fracture surfaces may lead to markedly increased diffusivity and sorption capacity near the fracture surface, compared to further into the wall rock. This may be an important factor for the interpretation and modelling of experiments performed at different time and size scales, such as laboratory experiments and field tracer tests where penetrations depths may differ.

1.   Introduction

Diffusion of radionuclides from flowing groundwater into stagnant water in pores within the rock (matrix diffusion) is often considered in performance assessment as the most important process for retention of radionuclides in water-conducting rock fractures. The accessible pore volume of stagnant water is therefore of high importance for the barrier functions of the bedrock surrounding a geologic repository. A parameter that has focused some interest during recent years is the heterogeneity of the porosity. It has been shown using the ^{14}C-polymethylmethacrylate (^{14}C-PMMA) method that the porosity is strongly heterogeneously distributed in crystalline rock [1, 2]. There are also indications that heterogeneous porosity may be of importance for interpretation of diffusion and sorption properties in short term experiments in both laboratory [3] and field scales [4, 5].

In the TRUE-1 project [6], sorption and diffusion of weakly to moderately sorbing radionuclides has been studied on fresh and altered site-specific materials [7]. Studies of porosity distributions have been done and these have recently been implemented in the evaluation of diffusion experiments [8]. The aim of this paper is to summarise some old and new laboratory results indicating heterogeneous porosities and to discuss what possible implications the observed heterogeneity will cause on the retention capacity when extrapolated to the field scale.

2.   Porosity distributions, profiles, and mineralogy in altered rock

It has previously been shown using the ^{14}C-PMMA method that porosity frequency distributions of approximately lognormal shape exist in fresh Äspö diorite collected at the Äspö Hard Rock Laboratory (Äspö HRL) [3]. Äspö diorite is a medium-grained porphyritic quartz-monzodiorite with K-feldspar megacrysts.

In recent work, a drill core of a borehole intersection (KXTT3 14.10m) with Feature A was investigated using the ^{14}C-PMMA method. Feature A, which is a reactivated mylonite located in Äspö diorite host rock, is a single fracture system that was used for sorbing tracer tests in the TRUE-1 project. The sample used had natural fracture surfaces on both sides of the core. One of the surfaces is interpreted as the Feature A surface. A porosity histogram obtained by ^{14}C-PMMA on a surface sawed parallel at a depth of 8 mm from the other fracture is shown in Figure 1.

Figure 1. **Porosity histogram (left) obtained after a digital imaging of a selected part of the autoradiograph of the KXTT3 sample. A lognormal distribution fitted to the experimental results is also given in the histogram.**

Photo

Autoradiograph
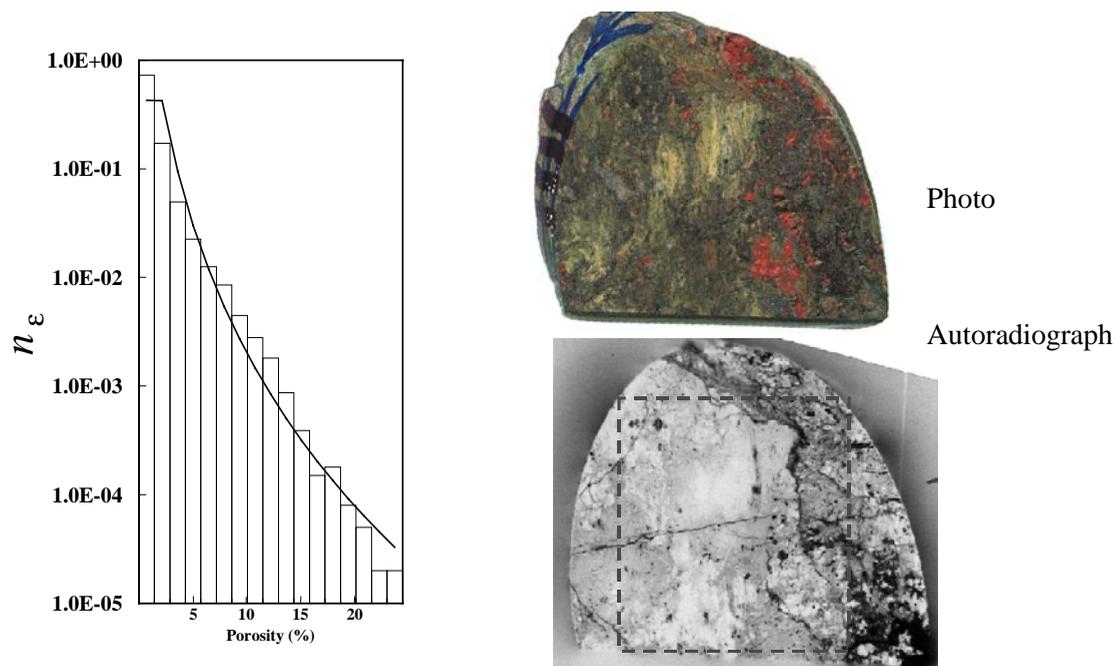
Indications of lognormal porosity distributions were found in samples consisting of altered diorite and mylonite, see e.g., Figure 1 [8]. The porosity distribution varied from 0.5% to 20% porosity. The light green, highly chloritised layers were not infiltrated and thus of very low porosity. Very low porosities and transsecting intragranular fissures were observed in potassium feldspar grains. The second natural fracture showed an increased porosity zone to a depth of 20 mm from the surface. Plenty of micro fissures and highly porous mineral areas with up to 20% porosity were found (see Figure 1).

In Figure 2 a porosity profile perpendicular to the Feature A surface is shown. The increased porosity zone reached depths of 3-6 mm from the Feature A fracture surface. The increased porosity was mainly found to consist of micro fissures parallel to the natural surface. Porosity profiles near fractures have been reported in several other studies [9-11].

Figure 2. **Porosity profile measurement determined from selected parts of the KXTT3 sample perpendicular to the natural Feature A surface.**
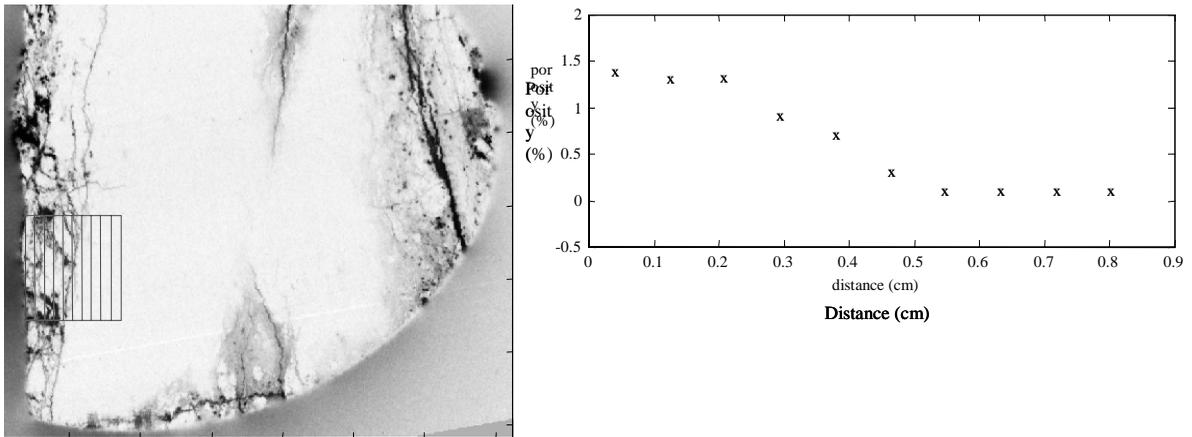
A ^{14}C-PMMA autoradiograph of a wall rock sample from the TRUE Block Scale project is shown in Figure 3. In contrast to the often-observed higher porosity near fracture surfaces, very dense mylonite areas of extremely low porosity are adjacent to the fracture surface (left) and in the middle of this sample. The parts of altered diorite are porous and the micro fissure or crack in the middle of the sample may act as a connector between the fracture and deeper lying parts of the altered zones.

Figure 3. **[14]C-PMMA autoradiograph of a wall rock sample from the TRUE Block Scale project (#20 KA256 188.7 m). The natural fracture surface is to the left.**
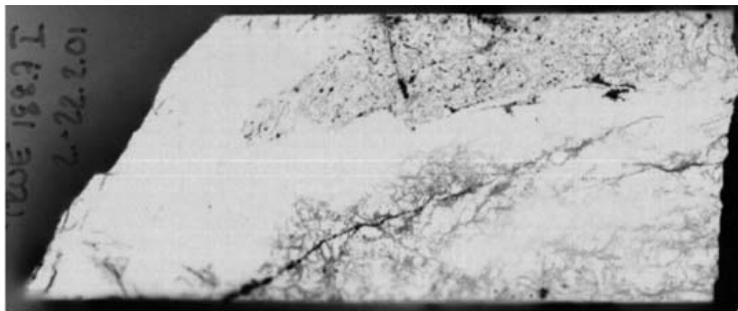
The generalised picture of the wall rock porosity at Äspö HRL is that the porosity distributions show the complexity and heterogeneity of the mylonite and altered diorite. Areas of high porosity can often be correlated to cracks and micro fractures in the mylonites. Micro fractures are also important as connectors through the very dense mylonite. An increase in porosity (maximum of approx. 1 to 2%) near the fracture surfaces is often observed, extending from a few millimetres in some parts to a few centimetres in other parts.

3.   The effect of heterogeneous porosity in laboratory experiments

An example of evaluation of penetration profiles of sorbing tracers in a wall rock sample consisting of mylonite and altered diorite is shown in Figure 4. By using the experimentally obtained porosity distribution from Figure 1 a significant improvement of the fitting is obtained compared to the homogeneous model (without increasing the number of fitting parameters).

Sorption distribution coefficients determined in diffusion experiments on Äspö materials are generally lower than using crushed material. The sorption distribution coefficients calculated from the heterogeneous model tends to be higher than those obtained from the homogeneous model. Thus, a somewhat better consistency between sorption coefficients determined in batch experiments using mm-sized crushed rock material and diffusion experiments is obtained.

Similar results as those mentioned above have been obtained earlier for evaluation of penetration profiles in fresh Äspö diorite. A heterogeneous porosity model has also been shown to improve the modelling of the early part of breakthrough curves from through-diffusion experiments in fresh rock [3].

Figure 4. **Evaluation of penetration profiles
in a mylonite/altered diorite wall rock sample used in a laboratory diffusion experiment.
In the *left* figure, the fit of the ordinary diffusion equation
assuming a homogeneously distributed porosity is plotted as dashed lines.
In the *right* figure, a porosity distribution according to the measured 2D distribution (Figure 1)
was used for the model calculations showed as dashed lines.
In both cases, the pore diffusivity and sorption distribution coefficient were fitted for each tracer [8].**
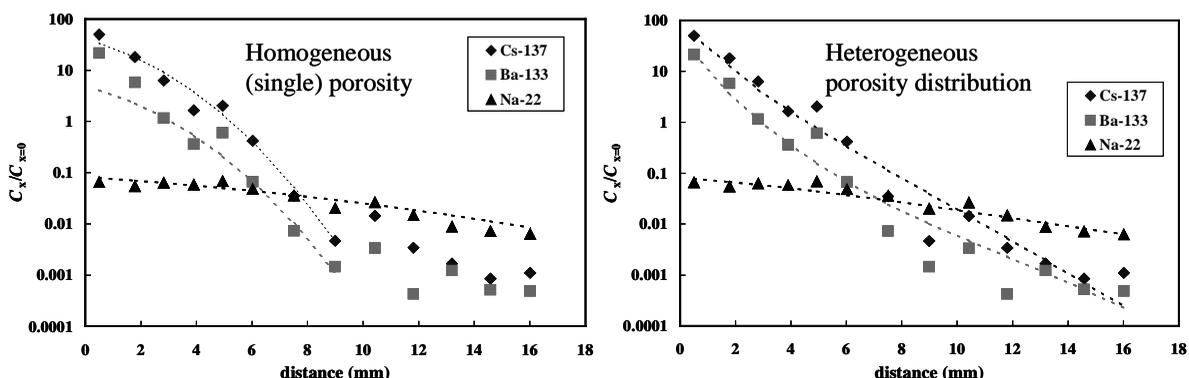
It is not clear if heterogeneity will be of importance for diffusion over longer distances than some centimetres. At larger scales, the rock properties may become macroscopically homogeneous which would smooth out the heterogeneities seen at smaller scales. On the other hand, at larger diffusion distances the main question is to what extent pore connectivity exists in a low-porosity medium. However, even if the porosity heterogeneity may have little effect for performance assessment, it will be of importance for making a correct interpretation of laboratory results. It could also be of importance for interpreting short-term in situ experiments since these results may be influenced by diffusion with short penetration depths.

The results of some effective diffusivity measurements by through-diffusion experiments in fresh Äspö diorite samples of varying thickness are shown in Figure 5. There is a tendency towards a decreasing effective diffusivity with increasing sample thickness, with a significant decrease below ~10 mm. This has been interpreted as an effect of increasing pore connectivity and decreased tortuosity for shorter sample dimensions [12]. Increased pore connectivity leads to an increased transport porosity, which consequently gives a higher effective diffusivity. An influence of the sample length on the effective diffusivity (or formation factor) has also been observed in other studies of through-diffusion in crystalline rocks [10, 13]. By using electrical conductivity methods, decreasing conductivity (corresponding to formation factor, [15]) to about 2 to 5 cm length followed by a stabilisation of conductivity at a certain level up to several decimetres has been observed in several studies [14-16] although this is not always the case [17].

Figure 5. **Effective diffusivity, D_e, _versus_ sample thickness for iodide (4 and 6 mm samples [19])
and HTO (1, 2 and 4 cm samples [18]) through-diffusion experiments in Äspö diorite.
The arrows indicate that the range of measured diffusivities continues out of scale
for the 4- and 6- mm sample sizes.**
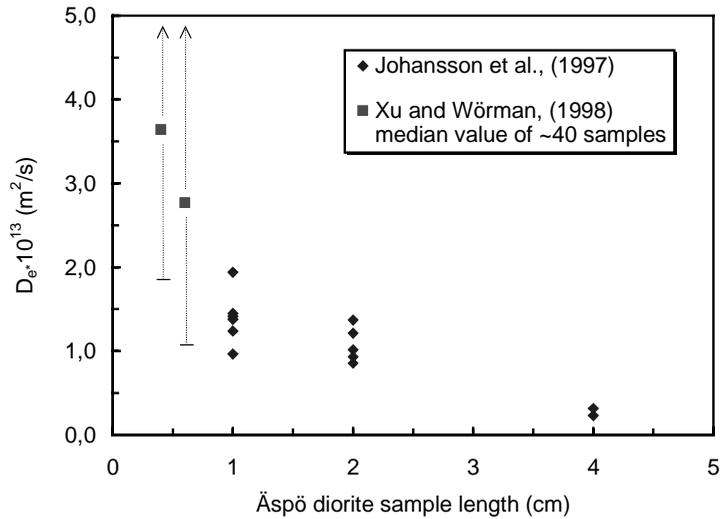
4.   Generalised pictures of wall rock porosity patterns

In order to discuss the effects of porosity on diffusion and sorption properties from a more general point of view, generalised porosity profiles are outlined for two fracture types in low porosity crystalline rocks: altered wall rock with a total porosity gradient (Figure 6) and a newly opened fracture in fresh rock where there is a constant porosity from the fracture surface (Figure 7). In both cases, all porosity in direct contact with the fracture will be available for diffusion. Moving further into the rock, the path becomes tortuous when grain boundary pores change directions. Furthermore, pores will sometimes end and the connected porosity and effective diffusivity will therefore decrease with diffusion distance into the rock. This decrease will be more pronounced for the altered rock where porosity is higher at the fracture surface. Whether the connected porosity reaches a constant value or continues to decrease with distance into the rock is still an open question. The decrease in e.g., effective diffusivity in fresh rock (as shown in Figure 5) is most likely an effect of such an increase in tortuosity and decrease in pore connectivity with increasing sample thickness (as sketched in Figure 7). Thus, the transport porosity at a certain depth from the fracture surface, used by a diffusing substance, is only a fraction of the total porosity of the rock.

As an example, the decrease in effective diffusivity over the first centimetre of Äspö diorite can be estimated from the ratio of the known value of the formation factor at 1 cm depth ($F \sim 7 \cdot 10^{-5}$) and the estimated maximum value at the fracture surface. Very close to the fracture surface the formation factor can be estimated to be less than or equal to one third of the total porosity ($\sim 5 \cdot 10^{-3}/3$). One third comes from the fact that one-dimensional diffusion is considered; therefore one third of the connected porosity will lead the diffusion in the desired direction (assuming no preferred orientation of the micro fractures). The decrease in effective diffusivity over the first centimetre may thus be one to two orders of magnitude (in this case a factor of ~25).

Figure 6. **Generalised schematic picture of porosity in altered wall rock with an increasing total porosity towards the fracture surface. Connected porosity is drawn in lines and non-connected porosity in dashed lines.**
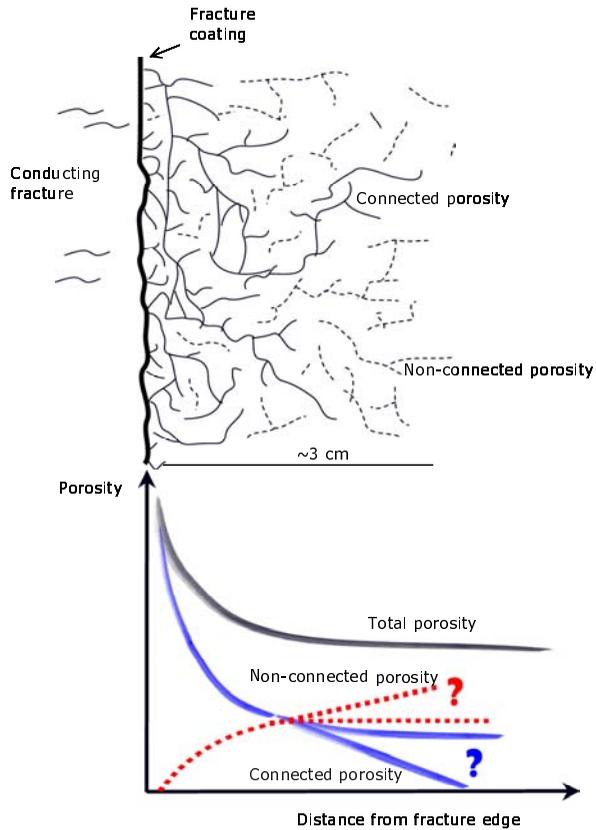
Figure 7. **Schematic porosity profiles in fresh rock where the total porosity is constant as a function of diffusion length.**
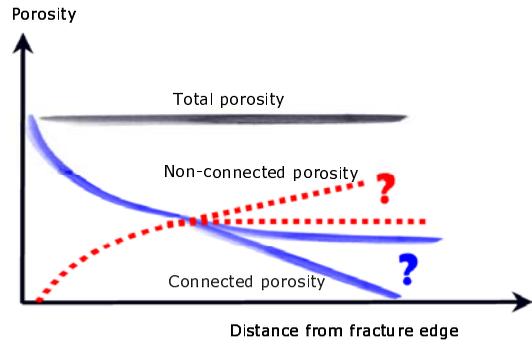
Figure 8. **Schematic profiles of several physical properties as a function of diffusion distance from a fracture surface.**
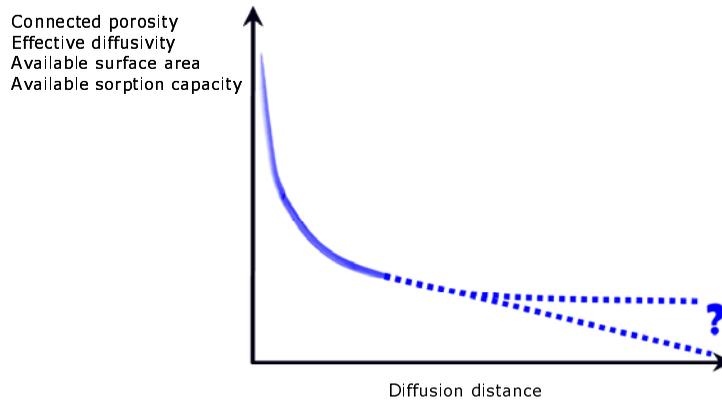
The available surface areas depend on the structure and amount of pore space. The greater the number of pores that are connected within a volume, the greater the available surface area will be. Thus, it is likely that the available surface area and thereby the available sorption capacity show a similar gradient as the effective diffusivity, as is sketched in Figure 8. The combined effect of the individual processes will be a distance dependent retardation capacity over at least the first few cm of rock in contact with groundwater. It means that stronger retardation is expected in experiments with short penetration depths, than in experiments with larger penetration depths. This may be of great importance when interpreting experiments performed over different time and size scales and should therefore be recognised when comparing results from e.g., laboratory experiments and *in situ* experiments.

5. Concluding remarks

The introduction of heterogeneity can be regarded as a first attempt to obtain better understanding and consistency between results of rock-water interaction experiments in crystalline rock performed at different scales, e.g., batch sorption experiments, different types of diffusion experiments and *in situ* transport experiments.

Experimentally observed porosity and diffusivity gradients near fracture surfaces indicate that the combined effect of individual processes leads to a distance dependent retardation capacity over the first few cm of rock in contact with groundwater. This means that stronger retardation is expected in experiments with short experimental time and short penetration depth, than in experiments with longer time/penetration depth. It seems therefore important to consider the scale and time effects of diffusion and retardation in heterogeneous rock, especially when experimental results are extrapolated to other time or space scales than they were obtained in.

For diffusion over longer distances than some centimetres, the rock properties may become macroscopically homogeneous which would smooth out the heterogeneities seen at smaller scales. However, for longer diffusion distances or time scales the important issue is likely if the pore connectivity is limited or unlimited.

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Immobilisation and Retention Processes of Uranium in Tertiary Argillaceous Sediments (Czech Republic)

Aleš Laciok and Mirek Hercik
Nuclear Research Institute (NRI) Rez, Czech Republic

Ulrich Noseck and Thomas Brasser
Gesellschaft für Anlagen- und Reaktorsicherheit (GRS), Germany

Abstract

Natural analogues can provide valuable information on timescales that are important for performance/safety assessment of deep geological repositories, specifically in the fields of process understanding and model validation. The Ruprechtov natural analogue study is focused on understanding and quantification of relevant geochemical and hydraulic processes related to uranium (U) mobilisation and behaviour in argillaceous sediments. The Ruprechtov site is situated in the western part of the Czech Republic where Tertiary basins with clay and organic material (coal, lignite) commonly occur, in some cases with high concentrations of U.

U accumulation was identified in two separated horizons at the depths of 12-15 and 30-40 m in argillitised volcanodetritic layers with kaolin and granite forming the underlying rocks. It is supposed that granite was the source of the U. The volcanodetritic sediment is highly heterogeneous in mineralogical content even at a small scale. U in sediment is present in the form of secondary phosphorous minerals (ningyoite) and also associated with organo-clay complexes and Fe hydrous oxides. There is an indication that U accumulation can also be present in the underlying kaolin.

Two borehole monitoring systems with bladder pumps were established to allow sampling of undisturbed groundwater. Interpreting acquired data, it is supposed that U was mobilised under near-surface oxidising conditions with subsequent immobilisation in downgradient reduced conditions. Minor supply due to *in situ* dissolution of U-bearing minerals or from discrete tectonic zones in underlying granite could also contribute to the accumulation of U.

Future investigations will be focused on site-scale characterisation (connectivity of permeable horizons) integrated with a laboratory migration/retention experimental programme and transport/ geochemical modelling.

1.   Introduction

Clay-based materials will play an important role in deep geological repositories due to their physical (swelling, low hydraulic and gas conductivity) and chemical properties (ion exchange capacity, sorption, buffering). Clays are suitable buffer and backfill materials and/or can form overlying strata of granitic (Czech concept) or salt host rocks (German concept of deep repository). In performance assessment, all relevant processes are evaluated, transport of radionuclides through the multibarrier system is quantified, and the impact to human health and biosphere is assessed and compared with regulatory criteria. The models and data used are mostly derived from laboratory and *in situ* experiments, containing, therefore, uncertainty connected with extrapolation of these data to

real time and space conditions. The study of long-term behaviour of the natural occurrence of U, Th, and Ra at the Ruprechtov site can help to overcome this gap and should contribute to better understanding of mobilisation/deposition processes and validate models used in performance assessment.

2. Geological setting

The Ruprechtov site is situated in the Northwest part of the Czech Republic (Figure 1) where three large Tertiary basins (Cheb, Sokolov, and North Bohemian basins) are situated with coal deposits that are intensively exploited.

Figure 1. **Localisation of the Ruprechtov site.**

The Ruprechtov study site is localised in the Hroznetin part of the Sokolov basin (Figure 2) that is filled with ***Oligocene and Miocene sediments*** represented mainly by argillitised pyroclastical complex (volcanodetritic formation) with thickness of 0-100 m. Low-grade U accumulation is unevenly distributed within some volcanodetritic layers in the depth of 10-40 m. In the past, kaolin was excavated at sites around Ruprechtov. In the 1970s, tests with U *in situ* leaching were performed there with unsuccessful results.

In a broader area of the Hroznetin sub-basin and also directly beneath the sedimentary layers at Rupechtov, ***granitic rocks of Carboniferous age*** form the massive Karlovy Vary. Granites underwent intensive kaolinisation in the Mesozoic and Paleocene.

These granitic bodies are elongated roughly in the NW–SE direction. The current classification of granitoids in this region discriminates between two intrusive complexes: Older Intrusive Complex (Mountain granite, 325-310 Ma) and Younger Intrusive Complex (Erzgebirge granite < 305 Ma).

Mountain granite is a medium-grained, rarely porphyritic biotite to two-mica monzogranite–granodiorite, often with a strong planar fabric [1]. The typical accessory minerals are allanite, anatase, andalusite, apatite, ilmenite, magnetite, rutile, titanite, tourmaline and zircon. The Mountain granites are characterised by high contents of high field strength elements (HFSE) (Ti, Zr, Nb), light rare earth elements (LREE) and Eu, as well as some large ion lithophile elements (LILE) (Ba, Rb, Cs). They show high average contents of Th (23 ppm, up to 42 ppm) at low U (median 5.3 ppm, total range 3.4-13.4 ppm) and Th/U > 1 (1.2-8.7, on average 4.0).

Figure 2. **Simplified geological map of the Sokolov basin.**
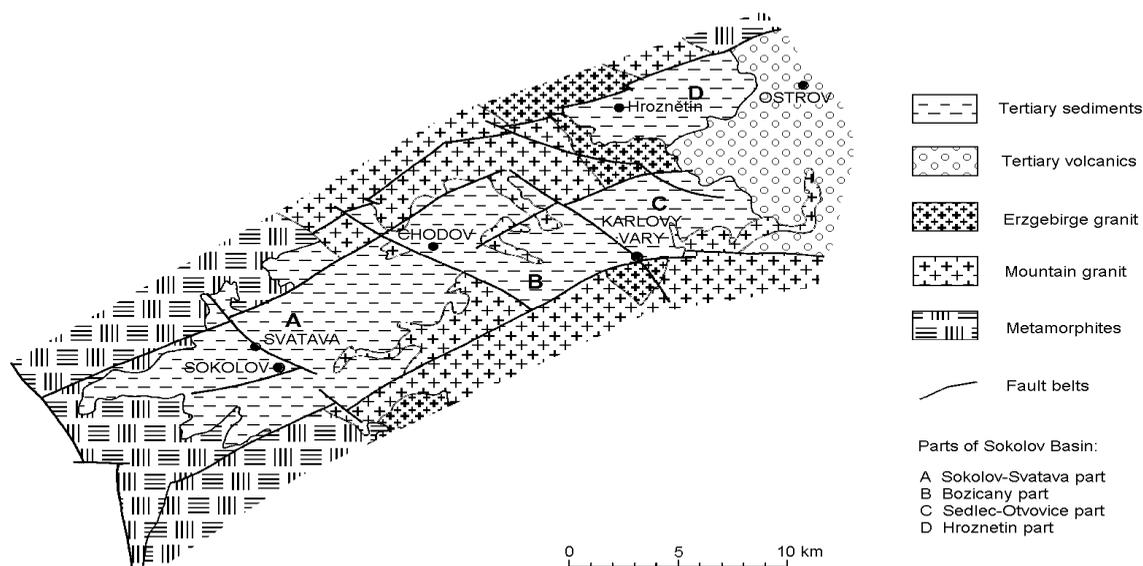
Erzgebirge granite is extremely structurally variable; typically these are porphyritic biotite granites, with subordinate medium-grained muscovite–biotite and fine-grained biotite granites, commonly topaz bearing [1]. Apart from topaz, the common accessories are apatite, fluorite, opaque minerals, monazite, rutile, tourmaline and zircon. For this group are typical higher concentrations of transition metals (Cr, Ni), higher heavy rare earth element (HREE) and U (median 11, maximum 28 ppm) concentrations coupled with relatively low Th contents (median 17 ppm) and significantly lower Th/U (0.5-4.8, mean 1.7)

In the Doupovskéhory Mountains situated eastwards of the Ruprechtov/Hroznetin site (Figure 2), by far the most abundant rocks are ***basic neovolcanites*** (alkaline basalts, basanites, and olivine nephelinites), with acid volcanites (mainly phonolites and trachytes) being subordinate. The age of all volcanic rocks is roughly the same (22-28 Ma). Neovolcanites have low Th concentrations accompanied also by relatively low U contents.

4.   Research activities and results

In 1996 and 1997, three boreholes were drilled (NA1 to NA3) to verify information about the depth and grade of U mineralisation indicated from previous kaolin and uranium surveys and to better characterise sediments and U accumulation. The mineralogical analysis showed that the sediment is mainly composed of quartz kaolinite, montmorillonite, pyrite, anatase, and siderite. Very high heterogeneity in mineralogical content was found even at small scale. Unevenly distributed U-mineralisation was found at depths between 33 and 39 m and a small peak was also detected at the depth of approximately 12-13 m.

Based on these preliminary results, two additional boreholes (NA4 and NA5) were drilled in 1999 with the purpose of detailed characterisation of U mineralisation and to obtain hydrogeochemical data. Geophysical logging identified more permeable horizons (at depths of 20 and 35 m) within very impermeable clay sequences along with the strata with higher radioactivity. In order to obtain undisturbed groundwater samples, these two permeable sections were packed-off (34.5-36.5 m in NA4 and 19-21 m in NA5) and bladder pumps were installed (Figure 3) that allow pumping of groundwater to the surface without contact with air.

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Figure 3. **Geological profile of NA4 borehole with schematic picture of borehole equipment for long-term groundwater monitoring.**
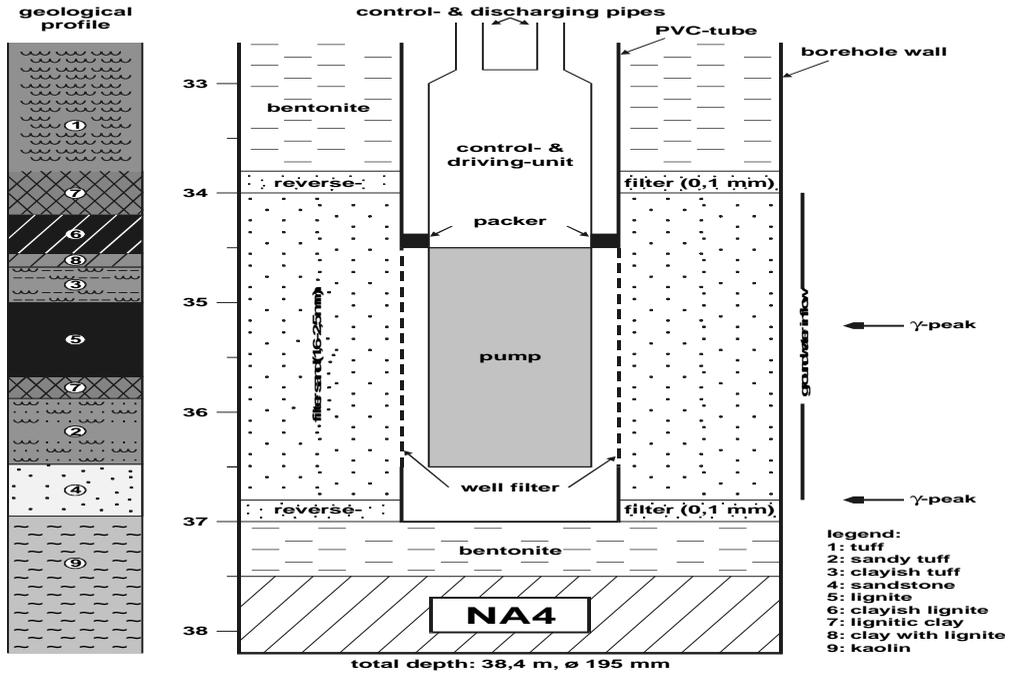
All five boreholes (NA1 to NA5), drilled within the framework of bilateral NRI-GRS co-operation, were situated due to practical reasons with separations of only a few metres from each other (Figure 6). From the regional point of view, we have acquired relatively point information so far.

Hydraulic conductivity measured on core samples and by *in situ* tests showed high differences between two detected permeable features (10^{-6}-10^{-7} m/s) and impermeable sediments (10^{-11} m/s). The local groundwater flow from south to north in Tertiary volcanodetritic sediments is driven mainly by morphology (Figure 4).

Figure 4. **Local geomorphology.**
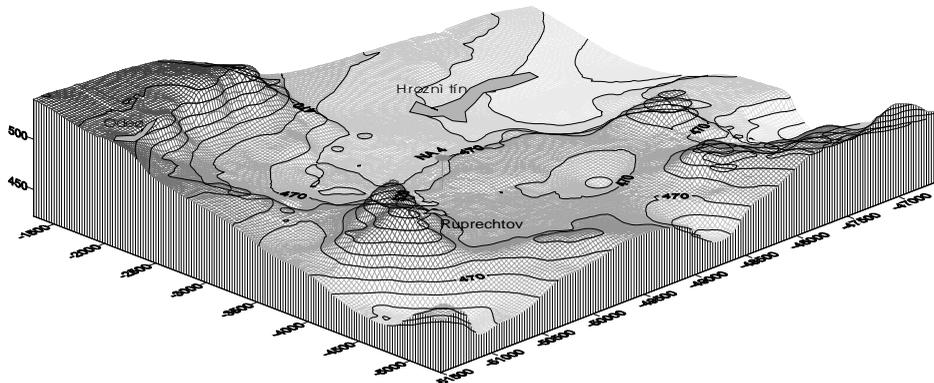
The U-bearing layer in the depth of 35-36 m identified in all drilled boreholes (Figure 5) was characterised in detail.

Figure 5. **Activity profile of boreholes NA1, NA3 and NA5.**
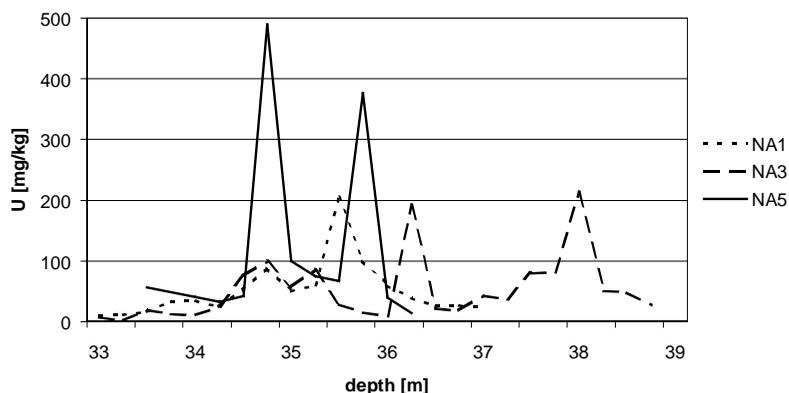
The higher groundwater permeability, high content of organic matter (lignite) and occurrence of pyrite are features of primary importance of this layer. Ningyoite (hydrated phosphate of U^{4+} and Ca) was identified as a main U mineral with subordinate (and inconclusive) occurrence of other phases (uraninite, zippeit, schoepite). The occurrence of ningyoite is documented from many sedimentary U deposits from the north and Northwest parts of the Czech Republic [2].

Selected core samples have been analysed by a slightly modified sequential extraction method used by Percival at Cigar Lake [3] in order to determine the U and Th forms in the U-bearing section. The following Table 1 shows the main characteristics of the method applied. The fraction B contains the highest U content in all analysed samples, 30-70% of the totally extracted U. In contrast, only a very small part of Th is extracted in the first two steps (A and B), which means, as expected, that this element is significantly less mobile than U.

Table 1. **Steps in sequential extraction of uranium.**

Step A	Exchangeable carbonates	1M NaOAc, pH = 5, laboratory temperature
Step B	Uraninite, organic-bound uranium	30% H_2O_2 (laboratory temperature), then 2.5% Na_2CO_3 (90^0C)
Step C	Amorphous iron oxides	0.25 M $NH_2OH.HCl$ in 0.25 M HCl (50^0C)
Step D	Crystalline iron oxides	Mixture of Na dithionate and Na citrate in 0.05M citric acid
Step E	Residuum	Mixture of HF and $HClO_4$

Measurement of isotopic ratios (alpha and gamma spectrometry) in the U decay chain shows significant non-equilibrium states in the U-bearing section. In Figure 6, the ratio of $^{234}U / ^{238}U$ *versus* $^{230}Th / ^{238}U$ is plotted for U peaks obtained in four boreholes. On the right, the corresponding co-ordinates of the boreholes are shown. This figure indicates that the $^{230}Th / ^{238}U$ ratio is significantly different from unity and changes along the path of the expected flow direction (South-North). Considering the analytical uncertainty, the $^{234}U / ^{238}U$ ratio is indistinguishable from unity. These results clearly show that U removal as well as U deposition processes occurred during the last 10^6 years.

Figure 6. **Non-equilibrium state of $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios in different borehole samples (*left*). The correlation with the co-ordinates of the respective boreholes (*right*) gives indications for uranium transport from NA5 (uranium removal) to NA2 (uranium deposition).**
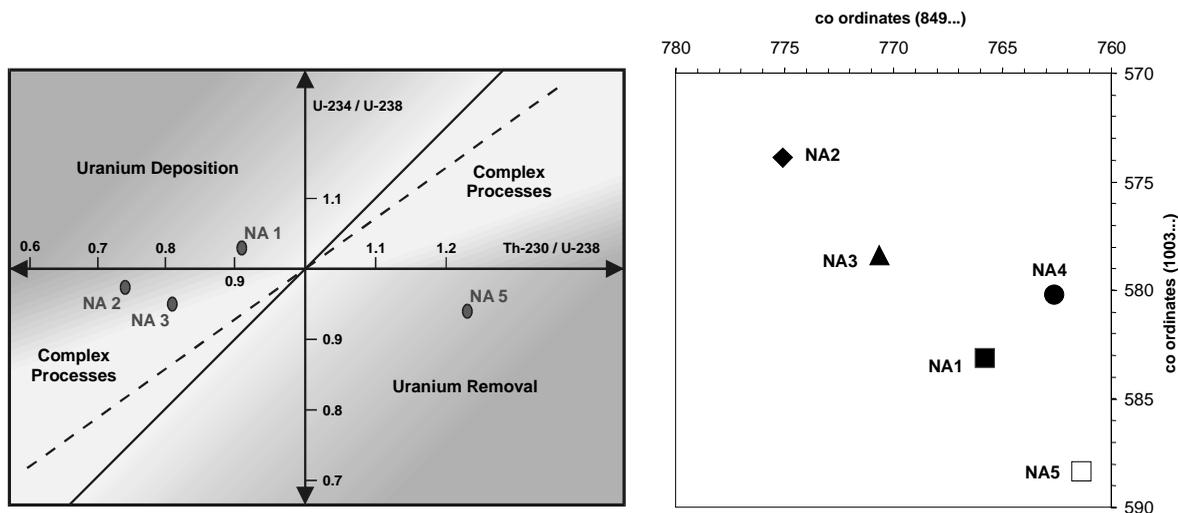
The analyses of groundwater samples have shown the water is of a Ca-Na-HCO$_3$ type, with around neutral pH values. Concentrations of sulphate are relatively low (about 30 mg/L or less) and they decrease with depth. The high alkalinity (above 300 mg CaCO$_3$/L) is a consequence of decomposition of primary silicates and production of dissolved inorganic carbon in redox processes. Significant concentrations of phosphate (about 1.0 mg/L) are probably a consequence of apatite dissolution and decomposition of organic matter. The source of F$^-$ with concentrations close to 1.0 mg/L is probably fluorapatite in granites. Concentrations of Cl$^-$ are low (about 6.0 mg/L) and they show no trend with depth. The Cl/SO$_4$ ratio on a molar basis increases with depth from 0.63 in the shallow permeable horizon to 1.09 in the deep permeable horizon. This is consistent with expected sulphate reduction. Tritium has not been detected, proving the lack of contact of groundwater with surface waters and at least pre-bomb infiltration time. Stable isotope composition of H and O confirms the meteoritic origin of groundwater ($\delta^{18}O$ approx. –8.9 to –9.8, δ^2H approx. –62 to –68, both in $^0/_{00}$ SMOW). The samples from both permeable horizons are positioned close to the Global Meteoric Water Line. Preliminary measurement of ^{14}C (by liquid scintillation) indicates its very low concentration (high radiocarbon age), suggesting a glacial age origin of water (20-30 ka).

The differences in groundwater from the two distinct permeable features are shown in Table 2.

Table 2. **Comparison of properties of two permeable horizons.**

	NA4 (34.5-36.6 m)	**NA5 (19-21 m)**
Conductivity (μS/cm)	450-480	560-640
pH	6.9	7.2-7.3
Eh	Generally reducing	Trend to oxidising
Bacteria	Lower content of viable bacteria Lower content of aerobic bacteria	Higher content of viable bacteria Higher content of aerobic bacteria
$\delta^{18}O$, δ^2H	Isotopically heavier	Isotopically lighter
Concentration of U (μg/L)	0.X-0.0X	X-0.X
Processes controlling U behaviour	Precipitation/dissolution ($\pm$ surface processes)	Surface processes

The pore water was also extracted in samples from the U-bearing horizon by the squeezing method (BGS) and analysed. Higher pH and salinity in comparison with groundwater and concentrations of U at the level of µg/L were found.

Geochemical modelling was focused on calculation of speciation of elements and sensitivity analysis with respect to factors that could control the concentrations of dissolved species, and also served for checking of consistency of laboratory analyses. Groundwater is in equilibrium with kaolinite, but not with montmorillonite, despite this mineral being identified by X-ray diffraction. This is probably related to infiltration of a significant portion of water recharge through macropores. In the matrix between macropores, concentrations of dissolved cations and silica are higher. Under these conditions, the clays of the smectite group can be persistent [4]. Calculated saturation indices for selected minerals are shown in Table 3.

Table 3. **Calculated saturation indices for selected minerals.**

	Uraninite	**Ningyoite**	**Coffinite**	**CaCO$_3$**	**FeCO$_3$**	**Vivianite**	**Kaolinite**	**SiO$_2$(am)**
NA4	1.794	− 2.433	2.882	− 0.616	− 0.219	− 1.635	3.767	− 0.111
NA5	− 0.217	− 3.311	− 0.540	− 0.214	− 0.167	− 0.130	5.92	− 0.209

Redox calculations were performed using PHREEQC [5] because it was necessary to correct concentrations of redox-couple members for complexes. Results of redox calculations including field Eh measurements are shown in Table 4.

Table 4. **Results of redox couples calculations.**

	Eh	**O$_2$/H$_2$O**	**NH$_4^+$/NO$_3^-$**	**Fe^{2+}/Fe^{3+}**	**H$_2$S/SO$_4^{2-}$**
NA4	− 0.155	0.773	< 0.415	< 0.219	> − 0.156
NA5	− 0.055	0.782	< 0.387	< 0.194	> − 0.194

A conceptual model of U origin and migration based on currently available data was formulated (Figure 7). It is likely that U has been mobilised under oxidising conditions and transported through the Tertiary aquifer of 1-2 m thickness. Especially in the surrounding lignite seams or lenses, reducing conditions have led to reduction and subsequent precipitation and/or sorption of U (similar to roll-front U deposits). Minor supply due to *in situ* dissolution of U-bearing minerals or from discrete tectonic zones in underlying granite could also contribute to the formation of the observed U accumulation.

Figure 7. **Scenario of U mobilisation and retardation processes at the Ruprechtov site.**
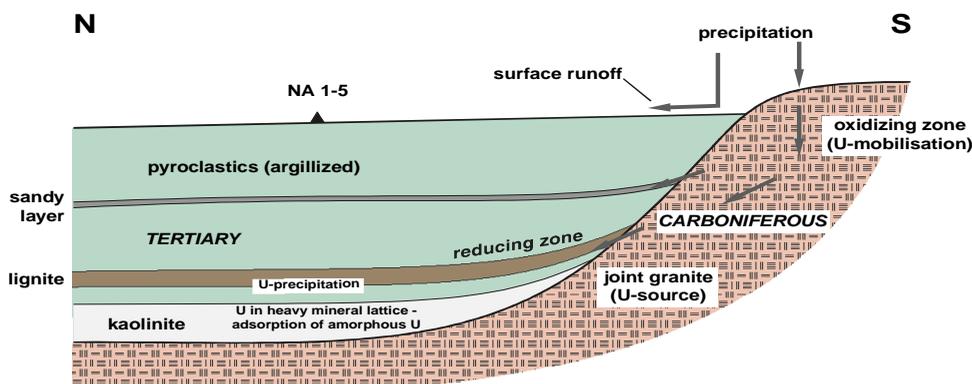
## 5.	Future activities

Future investigations will be focused on proving the preliminary formulated conceptual model of U migration at the Ruprechtov site (Figure 7). Drilling activities will be focused on characterisation of the underlying kaolin (U content, permeability) and granitic basement (fracturing, weathering profile) along with the spatial extent of U accumulation and permeable zones.

An extensive laboratory programme is planned for better understanding and quantification of the main geochemical processes controlling the behaviour of U. The role of dissolution/ (co)precipitation in comparison with surface-controlled processes (clay, organic matter, hydrous oxides) will be studied in the different geochemical conditions observed at the Ruprechtov site. Diffusion cells and columns were prepared and tested for the purpose of quantification of migration processes. The activities will also be focused on quantification of colloids and bacteria and evaluation of their role under local geochemical conditions, specifically on the behaviour of U.

The final goal is transfer of results to performance assessment (repository conditions), mainly through testing of transport and geochemical codes.

## 6.	Conclusions

Current results proved that the Ruprechtov site is a suitable analogue for investigation of U behaviour and migration in plastic argillaceous sediments. Comparing expected repository conditions with the situation at the Ruprechtov site, the following aspects are of primary importance that justify studying the migration, immobilisation, and retention processes of U there:

- Similarity in timescales of processes of U migration – at the level of Ma.
- Similarity in geological conditions – mixture of clay minerals with clastic components and content of organic matter (far-field of deep repositories).
- Similarity in geochemical conditions – low Eh, near neutral pH, corresponding low concentration of uranium in groundwater.
- Similarity in hydraulic conditions – generally low hydraulic conductivity.

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Colloid Retention in Äspö Crystalline Rock:
A Generic Computational Assessment

Georg A. Lindgren and Vladimir Cvetkovic

Division of Water Resources Engineering, Royal Institute of Technology, Stockholm, Sweden

1. Introduction

To assess the impact of colloid-facilitated transport of radionuclides (RN) through the fracture network of the Äspö crystalline rock we have modelled the following scenario:

RNs are injected into the fracture system irreversibly bound to colloids and are transported downstream as a particulate phase. The colloids are retarded due to reversible attachment on the fracture walls and weak limited diffusion into the rock matrix. Since the detachment of the colloids is expected to be significantly slower than the attachment, we account for the kinetics of the process.

Based on the zero-th temporal moment of radionuclide discharge, (i.e., the fraction of mass recovered at the control plane) a dimensionless indicator, the "containment index", is proposed for assessing the potential impact of colloids on the field-scale (or performance assessment (PA) scale). This indicator is also suited for setting further constraints on relevant parameters which need to be estimated in the field.

As advective transport parameters we use the groundwater residence time τ, and a flow/geometry dependent retention parameter β. Complementary cumulative density functions (CCDF) for τ and β were obtained using site specific flow and particle transport simulations in a three-dimensional discrete fracture network of Outters and Shuttle [1].

We account for the kinetics of colloid retention based on a model recently used by Knapp *et al.* [2] for interpreting their laboratory experiments of colloid transport in a single fracture. Specifically, their model includes sorption coefficients for colloids onto fracture walls and the rock matrix, as well as a colloid diffusion coefficient within the rock matrix.

As our computations are based on simplifying assumptions and a limited set of experimental data, the results provide only a first assessment of the potential effects of colloid facilitated transport of RNs, and the relative importance of a few key transport parameters.

2. Transport model and assumptions

We model the transport of colloids through a fracture network according to following assumptions:

- Colloids are injected into the system carrying radionuclides that are irreversibly bound to them. This assumption is relevant if, e.g., colloids detach from the bentonite barrier.

- The colloids are transported downstream with the advective velocity of the flow. Size exclusion effects, leading to somewhat higher velocities of the colloids, are neglected.

- The colloids do not aggregate, i.e., they are stable over the considered PA transport times.

- The colloids interfere with the fractured rock in the following ways: They attach to, and detach from the fracture surfaces, they diffuse into the rock matrix, and they reversibly attach within the rock matrix.

The colloid transport model applied in this assessment captures the uncertainty of the flow parameters of the system through applying a stochatic approach based on the CCDFs of the travel time τ and the flow/geometry dependent retention parameter β.

The attachment/detachment of the colloids to the fracture walls is modelled as equilibrium "sorption", as well as the corresponding processes within the rock matrix [2]. The diffusion of the colloids into the rock matrix is accounted for as a kinetic process.

Considering the processes as described above we can express the Laplace transform (denoted by a hat) of colloid-bound RN discharge for a unit pulse as:

$$\hat{\gamma}(s) = \exp\left[-(\tau + \beta K_a)(\lambda + s) - \beta\kappa(s + \lambda)^{1/2} \right] \qquad \text{Equation 1}$$

$$\mu = \hat{\gamma}\big|_{s=0} = \exp(-\tau\lambda - \beta\varepsilon) \qquad \text{Equation 2}$$

where

$$\tau = \sum \frac{l_i}{V_i} \qquad \beta = \sum \frac{l_i}{V_i b_i} \qquad \text{Equation 3}$$

$$\varepsilon = K_a\lambda + \kappa\lambda^{1/2} \qquad \kappa = \left[\theta F D_w \left(1 + \frac{\rho K_d^m}{\theta} \right) \right]^{1/2} \qquad \text{Equation 4}$$

The key parameters are the groundwater residence time τ, the radioactive decay rate λ, the diffusion coefficient of colloids in water D_w, the formation factor F, the flow/geometry dependent parameter β, the surface "sorption" coefficient for colloids onto the fracture walls K_a, and the sorption coefficient for colloids between matrix water and rock K_d^m.

Since the colloid-bound radionuclide mass released from bentonite is unknown, we consider a *relative* transport measure, the *containment index* ψ, defined as:

$$\psi = \frac{m_0 - m}{m_0} = 1 - \hat{\gamma}\big|_{s=0} \equiv 1 - \mu \qquad \text{Equation 5}$$

where m_0 is the total colloid-bound radionuclide mass released into the rock from bentonite, and m is the total colloid-bound radionuclide mass released from the crystalline rock into the biosphere.

3.   Parameter estimation

For the estimation of the model parameters, we use data from the Äspö site, and if such are not available, we derive values based on the measurements of Knapp *et al*. [2]. As mentioned above, the CCDFs for the residence time τ and the flow/geometry parameter β are derived from simulation results of Outters and Shuttle [1].

The diffusion coefficient of colloids in water is calculated using the Stokes-Einstein equation for colloids of diameter $d_s = 1\mu m$:

$$D_w = \frac{kT}{3\pi\eta d_s} = 1.54\times10^{-9}\,\mathrm{m^2h^{-1}}$$

Equation 6

The effective diffusion in the rock matrix can be described as: $D_e = FD_w$, where F is the formation factor, estimated by Archie's Law:

$$F = a\theta^p = 0.00044$$

Equation 7

where $\theta = 0.01$ is the matrix porosity at Äspö. We assume that $a = 0.7$ and $p = 1.6$ [3].

For measurements in tuff ($F = 0.0123$, $\rho = 2\,600\ kg\ m^{-3}$ and $\theta = 0.08$) Knapp *et al.* [2] obtained $\kappa = 10^{-5}\ mh^{-1/2}$. We use this to infer the "sorption" coefficient in the rock matrix as $K_d^m = 0.0022\ m^3kg^{-1}$. The "surface sorption" coefficient for the tuff is $K_a = 7\times10^{-5}\ m$ [2].

Using above values and a rock density of $\rho = 2\,700\ kg\ m^{-3}$ for the rock at Äspö, we get:

$$\kappa = \left[\theta FD_w\left(1+\frac{\rho K_d^m}{\theta}\right)\right]^{1/2} = 1.9\times10^{-6}\,\mathrm{mh^{-1/2}}$$

Equation 8

The modelling is performed for several radionuclides, having a large range of half lives:

Table 1. **Modelled radionuclides and their half-lives.**

Radionuclide	^{227}Ac	^{234}Am	^{239}Pu	^{226}Ra	^{90}Sr	^{99}Tc
Half-life (a)	2.18	7370	24 000	1 602	29	64 000

4. Probabilistic computations

The containment index $\psi = 1-\mu$ is a random variable due to the randomness of the residence time τ and the parameter β, which is related to the aperture of the fracture. We therefore require a joint pdf $f(\tau,\beta)$ to describe the relation between ψ and τ,β.

$$\beta = k\tau$$

Equation 9

where k is obtained from simulations and assumed constant. We compute the complementary cumulative distribution function (CCDF) as:

$$\mathrm{Pr}\,ob\{\psi > \psi^*\} = CCDF(\psi) = 1-\int_0^{\psi^*} f(\psi)\ d\psi$$

Equation 10

where $f(\psi)$ can be related to $f(\tau)$ using a standard formula of probability. We derive $f(\tau)$ from site-specific simulations of Outters and Shuttle [1].

5. Results

The results of the modelling are shown in Figure 1. For the six RNs named above, the CCDFs are plotted against the containment index ψ. For a given ψ, the points on the curves provide the probability that in a given realisation of the rock formation, ψ will attain a larger value. It can be seen that the larger the containment index, the smaller the probability that it is exceeded, which of course is a property of a CCDF.

Figure 1. **CCDFs of ψ for different RNs.**
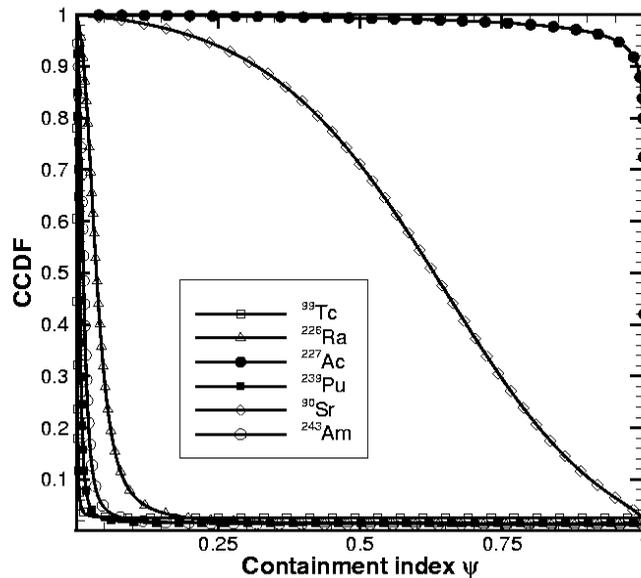
The graph shows large differences for the CCDFs depending on the half lives of the RNs. The probability that the long-lived RNs (^{99}Tc, ^{239}Pu, ^{234}Am, ^{226}Ra) have containment indices larger than 0.2 is very small; the colloids pass the fracture system with only small retention. The short-lived ^{227}Ac shows the opposite behaviour, the probability for a large containment index is high. ^{90}Sr having a half life of 29 years is somewhat retarded, e.g., the probability for ψ being larger than 0.5 is 70%.

6. Conclusions

- Colloids are subject to comparatively weak retention, relative to tracers; nevertheless the retention is a mechanism that may be important, in particular for shorter lived radionuclides.

- This analysis is based on the combination of "first principles" with data from Knapp *et al.* [2] for tuff. No site-specific experimental data on colloidal transport at Äspö are available. The *in situ* retention of colloids may be larger than assumed here.

- One potentially important neglected mechanism is irreversible removal of colloids. The "sorption" (attachment/detachment) coefficient for crystalline rocks could be significantly larger than for tuff (assumed here). Site-specific data are required for a more accurate assessment of colloidal transport.

For a full assessment of potential impact of colloid-facilitated RN transport, we need field parameters. But even more importantly, we need to characterise the source term, i.e., how colloids can be generated from bentonite and to which colloid concentrations this could lead in a field situation. Research is going in this field.

Notation

- b_i [L]   fracture aperture
- $d_s = 1\ \mu m$ (colloid diameter, constant)
- D_w [L^{2}T^{-1}]   diffusion coefficient of colloids in water
- F [-]   formation factor
- $K = 1.38066 \times 10^{-23}$ JK^{-1} (Boltzman constant)
- K_a [L]   "surface sorption" coefficient for colloids onto fracture walls
- K_d^m [L^{3}M^{-1}]   sorption coefficient between matrix water and rock
- l_i [L]   discretised flow path length
- s [T^{-1}]   Laplace transform variable
- T = 293 K   (temperature, constant)
- V_i [LT^{-1}]   advective velocity
- β [TL^{-1}]   flow/geometry dependent retention parameter defined in (equation 3)
- γ (s) [-]   Laplace transform of RN discharge
- $\eta = 10^{-3}$ Nsm^{-2} (dynamic viscosity, constant)
- θ [-]   matrix porosity
- κ [LT^{-1}]   parameter group defined in (equation 4)
- λ [T^{-1}]   radioactive decay rate
- ρ [ML^{-3}]   rock density
- τ [T]   groundwater residence time

- CCDF   Complementary cumulative distribution function
- DFN   Discrete fracture network
- PA   Performance assessment
- RN   Radionuclide

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Comparison of Formation Factor Logs Obtained
by Electrical Methods *In Situ* and at Laboratory

Martin Löfgren, Yvonne Ohlsson and Ivars Neretnieks

Department of Chemical Engineering and Technology, Royal Institute of Technology,
Stockholm, Sweden

1.   Background and theory

When making a safety assessment for a nuclear waste repository, radionuclide transport through rock is of great importance. Matrix diffusion has been identified as one of the most important mechanisms governing the retardation of radionuclide transport in rock. Radionuclides that have escaped from a repository will mainly be transported in water-bearing fractures through the rock. The surrounding rock is porous and the radionuclides will diffuse into the water-filled micropores and thus be withdrawn from the water flow that could otherwise carry them to the biosphere. The surface area of the micropores will also be much larger than the surface area of the fractures and thus the sorption will increase.

The matrix diffusivity of a non-sorbing specie in rock, D_r, is its diffusivity in free fluid, D_w, times the formation factor, F_f:

$$D_r = F_f \cdot D_w$$

Equation 1

If the size of the diffusing specie is much smaller than the characteristic pore size, the formation factor depends only on the geometry of the micropore system and is independent of the identity of the diffusing specie. Therefore, species occurring naturally in groundwater can be used to obtain the formation factor which later can be used to obtain matrix diffusivities for radionuclides. The formation factor is defined as the transport porosity, ε_t, times the constrictivity, δ, divided by the tortuosity, τ^2.

$$F_f = \varepsilon_t \cdot \frac{\delta}{\tau^2}$$

Equation 2

The formation factor has traditionally been studied by liquid diffusion experiments in the laboratory, which are very time consuming and have a limited sampling volume. Ohlsson [1], among others, has shown that electrical methods could be used as a complement to liquid diffusion experiments. Here the electrical conductivity of the rock, κ_r, and free pore water, κ_w, is measured and the formation factor is calculated from:

$$\kappa_r = F_f \cdot \kappa_w$$

Equation 3

In order to obtain accurate values of the pore-water conductivity, the original pore water is exchanged for pore water of a known chemical composition. If the ionic strength of the pore water is high enough, no corrections have to be made for surface conduction. When comparing traditional through-diffusion experiments with electrical conductivity experiments performed on the same diorite samples, it

was found that the formation factors obtain from the latter method were about twice as great as those obtained by the former [1]. As no explanation yet has been given, this issue deserves further attention.

2.   *In situ* methods

Even if the workload is significantly reduced by measuring the formation factor in the laboratory with electrical methods instead of liquid diffusion methods, it is still quite a task to log a bore core from, say, a 1 000-m-deep borehole. In addition, the micropore network in the core may have been altered during the drilling and cutting and also as a result of relaxation. Therefore, it would be valuable to develop a fast *in situ* method based on electrical methods. The same entities are required when measuring the formation factor *in situ* as in the laboratory: the rock resistivity and the pore-water resistivity.

In a prior campaign performed in the borehole KAS02 in Äspö, Sweden, the rock resistivity was obtained by the normal resistivity log and the pore-water resistivity was obtained by measuring the borehole-fluid resistivity [2]. Both these methods proved to be unsatisfactory and new tools had to be tested. Soon, it became clear that a focused rock resistivity tool had to be used and that the pore-water conductivity had to be measured on free groundwater withdrawn from local water-bearing fractures in the rock.

After an extensive search on the market for rock resistivity tools, we became aware of the Antares slimhole Dual-Laterolog. The tool, which is based on a focused technique, is specially designed for quantitative resistivity measurements in highly resistive rock. A principal sketch of a focused rock resistivity tool is shown in Figure 1. In addition to the common main current electrode, two guard electrodes are also emitting current. The field from the guard electrodes forces the current from the main electrode to leave in the form of a plane. No part of the main electrode current could leave vertically as the tool assures that the vertical potential gradient is zero. This is achieved by a potential electrode pair on each side of the main electrode and adjusting the electric field from the guard electrode before measuring.

Figure 1. **Principal sketch of a focused rock resistivity tool.**

Winch.

Current line from a guard electrode.

Guard electrode.

Main current electrode.

Current line from the main current electrode.

Potential electrodes pair, ensuring that no current passes vertically in the borehole fluid.
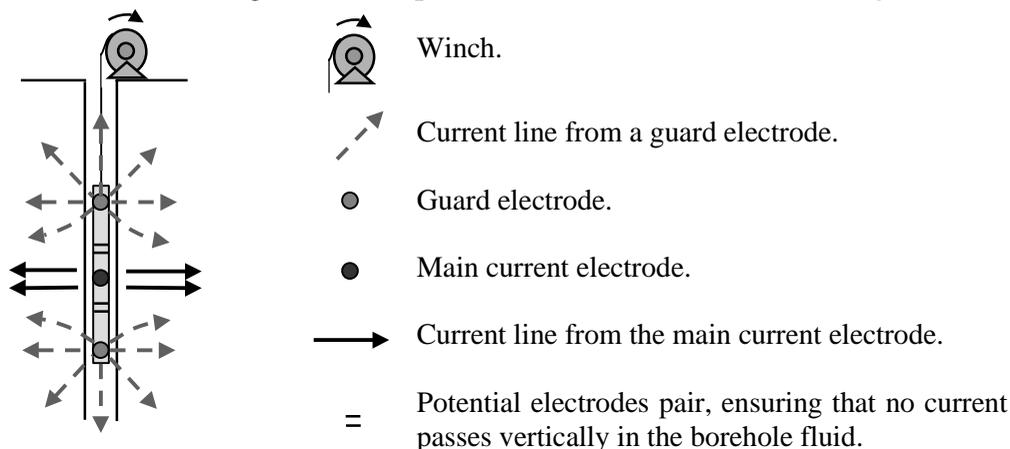
The Antares slimhole Dual-Laterolog could be acquired with a tool diameter of 38 mm and a quantitative measuring range of 0.1-600 000 ohm·m. According to the manufacturer, the measurement error should not exceed 3% and the vertical resolution should be only 0.1 m.

Obtaining the pore-water conductivity was found to be the most difficult part of *in situ* formation factor logging by electrical methods. At present, there is no way of directly obtaining this entity *in situ*. Therefore, the assumption has to be made that the pore water has the same conductivity

as natural free groundwater in fractures at a corresponding depth. There are, however, concerns about this assumption. It is likely that it is valid before drilling the borehole, as the groundwater at depth typically only flows a few metres per year and should be in equilibrium with surrounding rock. However, when a borehole is drilled, the groundwater situation is disturbed. The longer time that passes between the drilling and the measurements, the poorer this assumption may be.

The Posiva Difference Flow Meter measures the groundwater conductivity in fracture-specific groundwater. By using rubber disks, a 0.5-m section of the borehole is packed off. If the section contains a water-bearing fracture, groundwater is withdrawn and the flow is measured. The withdrawal is achieved by pumping at the surface, which creates an under-pressure in the borehole. A thermal pulse or a thermal dilution detector measures the water flow. A principal sketch of the tool is shown in Figure 2.

Figure 2. **Principal sketch of the Posiva Difference Flow Meter.**

Pumping on the surface.

Tool with rubber disks packing off a 0.5-m section of the borehole. The detector on top measures groundwater flow and electrical conductivity.

Water-bearing fracture from where water is withdrawn.

General groundwater flow.
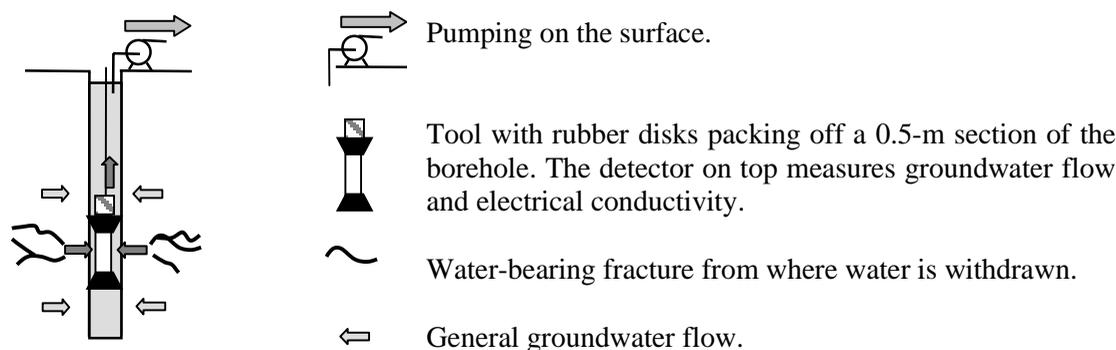
After determining the water flow rate, the time that has to elapse in order to fill up the section volume three times is calculated. If the time is acceptable, the tool is halted and the electrical conductivity (called EC in order to avoid confusion with hydraulic conductivity) of the fracture-specific groundwater (fracture-specific EC) is measured. While the tool is halted, the electrical conductivity is measured continually. Ideally this EC, called the transient EC, should approach the fracture-specific EC along a smooth curve. By examining the transient EC, one gets an indication if the measurement is successful or if it has been disturbed by leakage or gas formation. Once the fracture-specific EC of the section is measured, the tool moves to another water-bearing fracture. During this time, the EC is also measured. However, due to leakage when moving the tool, this EC, called background EC, is strongly affected by the borehole fluid.

3. The borehole

At the time when the Antares slimhole Dual-Laterolog was found on the market and it was agreed that a demonstration log should be performed, the Posiva Difference Flow Meter was tested in the borehole KLX02 in Laxemar, Sweden. Therefore, it was decided that the case study would be performed in this borehole, even if its history and water chemistry were not that suitable for testing the *in situ* formation factor method.

The borehole is 1 700 m deep and was core drilled in 1992. The core log divides the surrounding rock into granite, granodiorite, mafic volcanite, and aplite. Without pumping, non-saline surface water infiltrates the borehole down to 1 100-1 200 m. Below this depth, the groundwater has a high salinity (conductivity around 7 S/m). Between the non-saline surface layer and the saline lower layer, brackish water and non-saline water have infiltrated naturally before drilling the borehole. The geochemistry of the Äspö area (including Laxemar) is described in Gascoyne and Wikberg [3].

4.   Results

The rock resistivity was measured with the Antares slimhole Dual-Laterolog in the region from 200-1 400 m. The logging took about two hours. Figure 3 shows the rock resistivity in the section from 350-400 m of the borehole. The black squares show the location of natural fractures detected in the core log. Individual fractures could easily be detected in the resistivity log as dips and, due to the high vertical resolution of the tool, it was possible to measure the undisturbed rock resistivity between two nearby fractures. This is clearly shown at, for example, 365 m in Figure 3. The rock in the section 350-400 m is granite except at 356-358 m and 384-389 m, where the core log has designated the rock as mafic volcanite. The rock in these regions has a higher resistivity which is clearly shown at 356-358 m. Much of the rock at 384-389 m is fractured wherefore this feature is partly disguised.

Figure 3. **The rock resistivity in the section 350-400 m in KLX02 in Laxemar, Sweden.**
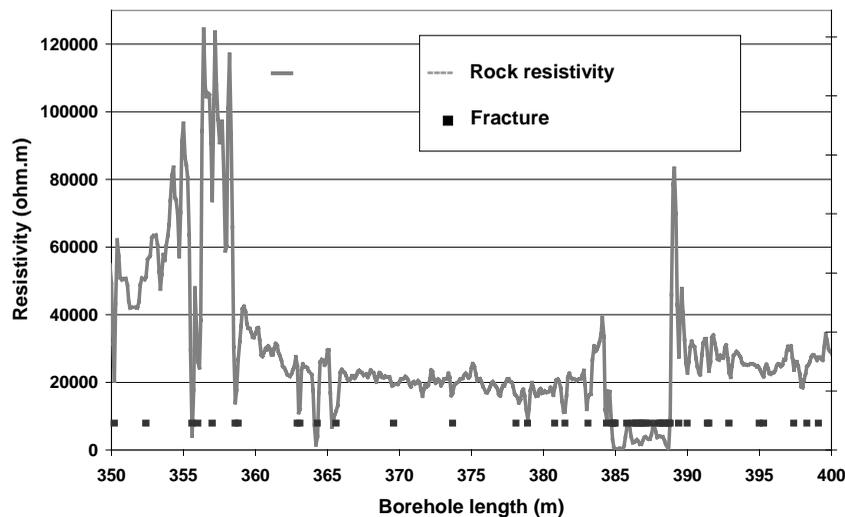
By dismissing all the rock resistivity values obtained from points closer than 4 dm from a natural fracture, an "undisturbed" rock resistivity log, free from fracture anomalies, was obtained.

The groundwater conductivity was measured with the Posiva Difference Flow Meter. The black diamonds in Figure 4 represent fracture-specific EC while the grey diamonds represent background and transient EC. Due to the fact that water was pumped up and out of the borehole, saline groundwater from deeper rock affected the borehole fluid which became more conductive that the groundwater in the rock at a corresponding depth. This is seen in Figure 4, where the background EC, which is strongly affected by the borehole fluid due to leakage, has a higher conductivity than the fracture-specific groundwater at a corresponding depth. No values of the fracture-specific EC were obtained in the section from 350-400 m. At 385 m, an attempt was made to measure fracture-specific EC, but due to leakage the value had to be dismissed. However, the fracture-specific EC at 385 m should be around or below 0.6 S/m as the transient EC in this case is due to mixing of saline borehole fluid and non-saline fracture-specific groundwater. As no fracture-specific EC was obtained in the section from 350-400 m, a linear fitting was made between the nearest values on each side of the section, crossing 0.6 S/m at 385 m. This is represented by the broken line in Figure 4. The values of the fitting were used as an approximation of the pore-water conductivity in the section. It is recommended to perform a greater number of fracture-specific EC measurements in the future in order to obtain a clearer picture of how the groundwater chemistry varies with depth. This was done in the section from 200-300 m with satisfactory results and maybe we should have focused on this section instead of the section from 350-400 m.

Figure 4. **The groundwater conductivity in the section 200-1 100 m in KLX02 in Laxemar, Sweden.**
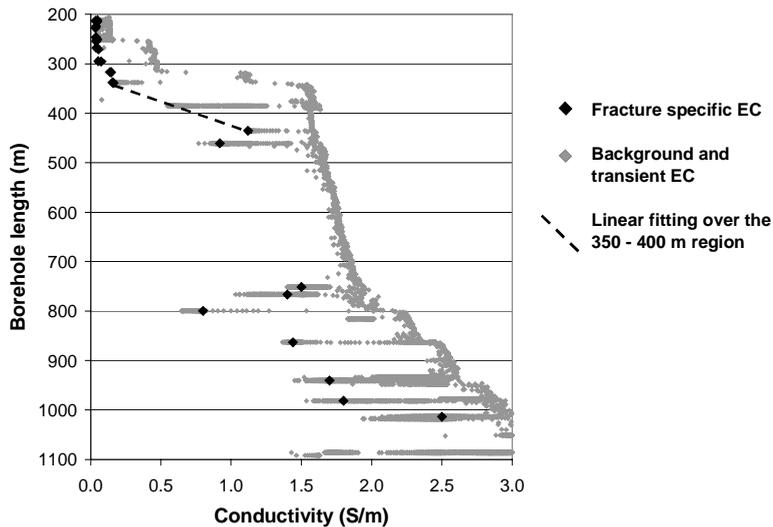
An *in situ* formation factor log was obtained from the groundwater conductivity log and the "undisturbed" rock resistivity log in the section from 350-400 m. In order to validate the results, a great number of rock pieces was taken from the core for laboratory measurements.

From each piece, one or two samples, with the diameter of 4.6 cm and a length of around 1.5 cm, were cut. From one 40-cm piece at 355 m, where a rock type change occurred, 21 samples were cut. Over 70 samples were glued into PVC frames and then saturated with a 1 M NaCl solution. After equilibration with the NaCl solution, the formation factor was measured by using the laboratory electrical method [1]. Also, 20 samples of greater length were cut from the section from 720-800 m. These samples have not yet been evaluated.

Figure 5 shows both the *in situ* and the laboratory formation factor log. The two curves clearly follow each other and geological features, such as the rock type changes, are visible. Note that the two logs have different scales. On average, the *in situ* formation factors are around 35% of the laboratory formation factor values. This is consistent with the fact that the core samples are unstressed and possibly slightly altered by the drilling. Here it should, however, be remembered that the pore-fluid conductivity was obtained from a linear fitting and that the value 35% easily could change if choosing another way of fitting the data. If choosing the constant pore conductivity value of 0.16 S/m (the closest value obtained above the section), the *in situ* and laboratory formation factor logs would almost coincide. If choosing the constant value 1.12 S/m (the closest value obtained below the section), the *in situ* values would be around 20% of the laboratory values. However, using a constant value makes it impossible to fit the curves at both ends of the section.

The relatively high spread in the laboratory formation factor may be due to the fact that many core pieces were chosen because they where already parted in about 1 dm pieces by natural fractures. When cutting them into 1.5-cm samples, not enough care was taken to avoid rock which might have been naturally altered by flowing water. Therefore, there might be a slight overestimation of some formation factors obtained in the laboratory. For a future similar comparison, it would be recommended to use only undisturbed rock taken far from fractures.

Figure 5. *In situ* **and laboratory formation factor logs from KLX02 in Laxemar, Sweden.**
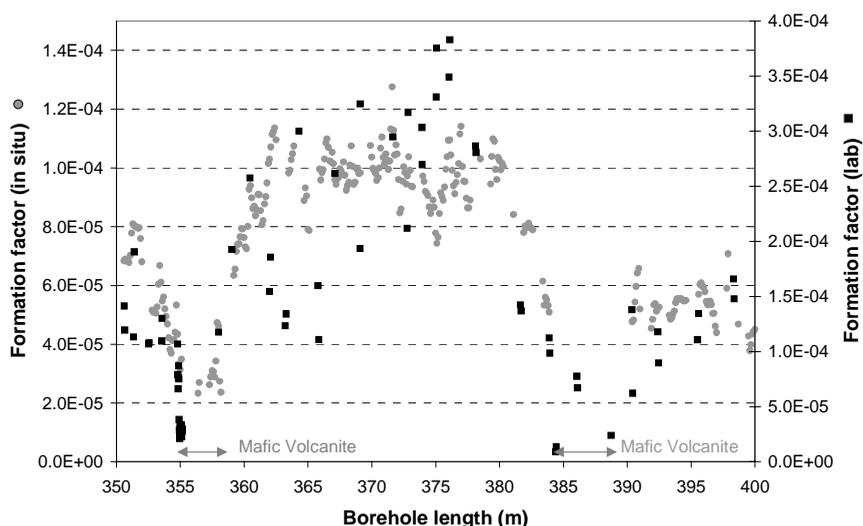
5.   Discussion

A fast way of obtaining quantitative formation factor logs *in situ* on a large scale in boreholes has been proposed and tested with very encouraging results.

The Antares slimhole Dual-Laterolog has been found to work in a satisfactory way. With the high vertical resolution, it was possible to filter out rock resistivity anomalies caused by water-bearing fractures without losing a substantial amount of data. In this work, the core log was useful.

The Posiva Difference flow log was also found to be an interesting tool for measuring groundwater conductivity. However, the tool and the logging technique may have to be slightly adjusted in order to fulfil the demand of a greater number of measuring points.

Before formation factor measurements by electrical methods could be generally accepted, it has to be proven that the formation factors obtained really characterise the pathways of diffusing species and not just charge, as electrically conducting minerals may interconnect otherwise dead end pores. However, the abundance of these conducting minerals is very low in, for example, granite and it would be surprising if they were shown to cause greater problems. Using direct current instead of alternating current and driving charged species though the rock by electromigration could be a possible way of testing the electrical method.

To conclude, it seems that the step from obtaining formation factors by electrical methods in laboratory to obtaining them *in situ* has already been taken and is no longer a speculative future project.

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Modelling of Colloid-facilitated Contaminant Transport with the Computer Code TRAPIC: Theoretical Basis and Application

Ulrich Noseck

Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Germany

Dietmar Klotz

Gesellschaft für Umwelt und Gesundheit (GSF) mbH, Germany

1.   Introduction

Organic and inorganic colloids are present in various concentrations in natural groundwaters. From field studies, it is known that colloids can have a strong impact on the transport of pollutants, since they migrate at velocities similar to the groundwater velocity and act as a carrier by sorbing a significant amount of contaminants [1]. This process can be of importance for the long-term safety of underground repositories. In order to describe colloid-facilitated transport in performance assessment, the computer code TRAPIC was developed [2].

Several column experiments with DOC-rich water have been performed up to now to investigate the impact of humic colloids on actinide transport (e.g., [3]). Emphasis was put on the investigation of the influence of flow velocity, column length, and different sediments. The results indicate that kinetic-controlled sorption processes play an essential role.

The aim of this study is to show the use of the code TRAPIC to model colloid-facilitated transport in column experiments. A number of new europium-humate migration experiments in different sandy sediments were performed [4] and are simulated. The relevant kinetic-controlled sorption mechanisms can be identified and values for the sorption rates are estimated. The results are compared with those of previous investigations.

2.   Description of the Eu migration experiment

The migration of Eu(III) through columns filled with five different sandy sediments was investigated [4]. In all experiments, the same humic-rich groundwater with a concentration of 80 mg DOC/L was used. Before injection into the column, the water was equilibrated with Eu(III). After equilibration, an amount of 98% Eu was bound to colloidal humic particles. Typical colloid sizes are in the range of 1 to 200 nm.

In order to investigate the influence of groundwater flow, the experiment with each sediment was performed at three different Darcy velocities. The column length is 0.5 m with a diameter of 0.05 m. The hydraulic properties of the columns were determined by experiments with ^{3}HHO tracers. The sediment properties and information on hydraulic conditions are listed in Table 1.

Table 1. **Description of sediment and hydraulic properties.**

Sediment	1	2	3	4	5
Description	Coarse sand	Fine sand	Fine sand	Medium sand	Coarse sand
Effective porosity Θ	0.05	0.29	0.290	0.261	0.283
Dispersion length [10^{-3} m]	120-220	1.2-1.5	1.4-2.2	2.5–2.9	3.1-3.4
Darcy velocity [10^{-3} m/h]					
– High	36.7	35.2	37.1	37.1	37.1
– Medium	8.35	8.17	8.21	8.64	8.50
– Low	1.71	1.65	1.13	1.74	1.68
Sorption value R_d [mL/g] from batch experiment	3.3	6.0	3.9	0.8	0.4

The main characteristics of the experimental results can be summarised as follows:

- The Eu tracer is transported as fast as ^{3}HHO,

- The recoveries are between 0.6 and 0.95 and decrease with increasing travel time (see Figure 1),

- The breakthrough curves show significant tailing.

The simulation results for these new experiments will be compared with two previous work [2, 5]: *pE-0.5m* denotes a similar experiment performed in 0.5-m columns and *pE-10m* denotes an experiment with a 10-m-long column. In both of the experiments, sediment 2 was used.

Figure 1. **Recoveries *versus* travel time.**
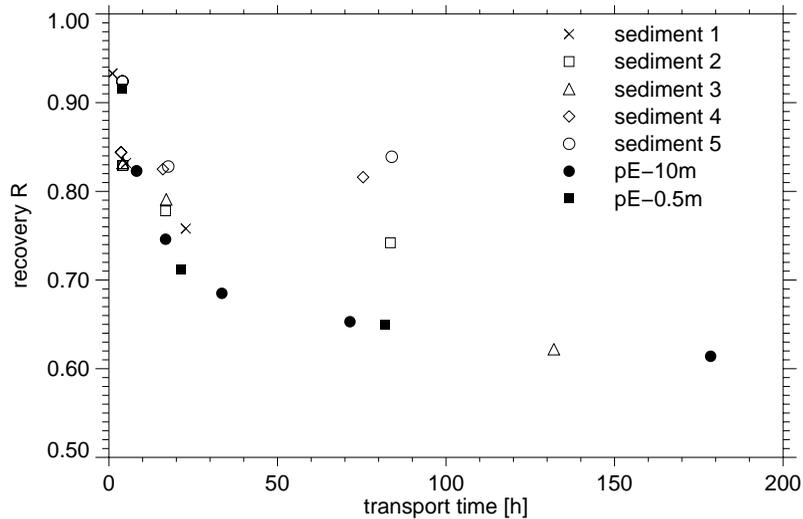
3. Description of the model

The computer code TRAPIC (**Tra**nsport of **P**ollutants **I**nfluenced by **C**olloids) considers one or two-dimensional colloid transport in porous media. The model is schematically shown in Figure 2. The colloids are considered to be dissolved in the aqueous phase or attached on retention sites of the sediment matrix. The contaminants are assumed to be mobile or immobile. TRAPIC has been described in previous publications [2, 6].

Figure 2. **Schematic representation of the model.**
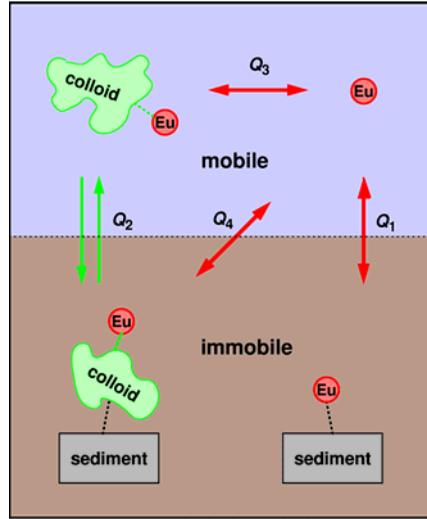
The mass-balance equations for the contaminants are written as:

$$\frac{\partial}{\partial t}\left(\Theta C_{Pf}\right) + \nabla \cdot \left[\bar{q}_p C_{Pf} - \Theta D_P \nabla C_{Pf}\right] = -Q_1^P - Q_3^P - Q_4^P$$

$$\frac{\partial}{\partial t}\left(\rho S_{Pf}\right) = Q_1^P \qquad\qquad \text{Equation 1}$$

$$\frac{\partial}{\partial t}\left(\Theta C_{Pb}\right) + \nabla \cdot \left[\bar{q}_C C_{Pf} - \Theta D_C \nabla C_{Pb}\right] = -Q_2^P + Q_3^P$$

$$\frac{\partial}{\partial t}\left(\rho S_{Pb}\right) = Q_2^P + Q_4^P$$

where C_{Pf} [ML^{-3}] denotes the dissolved contaminant concentration, C_{Pb} [ML^{-3}] and S_{Pb} [ML^{-3}] the concentration of contaminants sorbed to mobile and immobile colloids, respectively, and S_{Pf} [MM^{-1}] the contaminant concentration sorbed on the sediment. The tensors D_P and D_C [L^{2}T^{-1}] describe the diffusion and dispersion effects of the contaminants and colloids, whereas the vectors of the Darcy velocity are given by $\bar{q}_p$ and $\bar{q}_C$ [LT^{-1}]. Q_1^P [ML^{-3}T^{-1}] describes the contaminant sediment interaction, Q_3^P [ML^{-3}T^{-1}] and Q_4^P [ML^{-3}T^{-1}] determine the interaction of dissolved contaminants between mobile and immobile colloids, respectively. The source term Q_2^P [ML^{-3}T^{-1}] gives the change of contaminant concentration due to reversible interactions of the colloids with the sediment.

The sorption of contaminants on the colloids and on the sediment is described by Langmuir isotherms:

$$C_{Pb} = C_C f_3(C_{Pf}) = C_C \frac{\beta_3 \kappa_3 C_{Pf}}{1 + \beta_3 C_{Pf}}$$

$$S_{Pb} = C_C f_4(C_{Pf}) = S_C \frac{\beta_4 \kappa_4 C_{Pf}}{1 + \beta_4 C_{Pf}} \qquad \text{Equation 2}$$

$$S_{Pf} = f_1(C_{Pf}) = \frac{b_1 \kappa_1 C_{Pf}}{1 + b_1 C_{Pf}}.$$

where C_C [ML^{-3}] and S_C [ML^{-3}] denote the concentration of mobile and immobile colloids, S_{Pf} [ML^{-3}] denotes the concentration of immobile contaminants, β_3 and β_4 [L^{3}M^{-1}] are the complexing constants, κ_3 and κ_4 [MM^{-1}] are the sorption capacities of the colloids for contaminants, b_1 is the Langmuir coefficient, and κ_1 the sorption capacity of the sediment for contaminants. The interaction processes are governed by kinetic Langmuir reactions and are as follows:

$$Q_1^P = k_1 \rho \left[f_1(C_{Pf}) - S_{Pf} \right]$$

$$Q_3^P = k_3 \Theta \left[C_C f_3(C_{Pf}) - C_{Pb} \right] \qquad \text{Equation 3}$$

$$Q_4^P = k_4 \left[S_C f_4(C_{Pf}) - S_{Pb} \right]$$

The interaction of colloids with the sediment was assumed to be a first-order kinetic:

$$Q_2^C = K_2 \Theta = k_2 \rho_C S_C \qquad \text{Equation 4}$$

with the effective porosity Θ and the capture and release constants K_2 and k_2 [T^{-1}]. Consistent with this, the change of the contaminant concentration caused by colloid-sediment interactions is:

$$Q_2^P = K_2 \Theta C_{Pb} - k_2 \, S_{Pb} \qquad \text{Equation 5}$$

A common approach of the deep bed filtration neglecting the remobilisation of filtered colloids leads to:

$$K_2 \Theta = |q_C| \lambda_f \alpha \qquad \text{Equation 6}$$

The filter coefficient can be defined as [3]:

$$\lambda_f = \frac{3}{2} \frac{1 - n}{d_C} \eta \qquad \text{Equation 7}$$

where η denotes the collection efficiency and α the attachment factor describing the part of the colloid matrix collisions leading to binding. According to approaches of Tien *et al*. [7] and Yao *et al*. [8] the collection efficiency can be divided into diffusion, sedimentation, and mechanical filtration processes. Under the conditions of the experiments considered here, the filtration is dominated by the diffusion process. This can be described according to Yao *et al*. [8]:

$$\eta = 0.9 \left(\frac{kT}{\mu d_p d_C q_C} \right)^{2/3} \qquad \text{Equation 8}$$

with the diameter of the colloidal particles d_p, the pore diameter d_C, and the dynamic viscosity μ.

4. Application of the transport code

The simulation of the europium-humate experiments was performed in the same way as in earlier studies with sediment 2 [6, 6].

Sensitivity analyses show that recoveries < 100% are due to irreversible filtration and/or desorption of Eu from colloids followed by sorption on the sediment matrix [2]. Investigations of Schüßler *et al.* [9] indicate that the latter process plays the predominant role in column experiments with actinide-humate complexes. In that case, the desorption rate k_3 of the colloid-bound europium determines the Eu recovery. Accordingly, k_3 is obtained from simulation.

The observed tailing of the breakthrough curve indicates reversible interactions between sediment matrix and the colloids. The capture rate, describing the dynamics of the process of colloids getting into contact with the sediment, depends according to filtration theory on the porosity and the flow velocity of the colloids (cf. Equations 6 and 7). Therefore, varying rates K_2 for the different experiments are expected. The K_2 values are derived by fitting the tailing of the breakthrough curve. Then k_2 yields to $K_2\Theta(C_{C0}/\rho_C S_{C0})$. On the assumption of a constant mobile colloid concentration, the ratio K_2/k_2 determines the immobile colloid concentration. The value K_2/k_2 was obtained as best fit from the migration experiment with sediment 2 and was held constant for the simulation of all other experiments. Therewith, the fraction of immobile colloids is determined to about 20%.

For the simulation, hydraulic data listed in Table 1 are used. In some cases, the Darcy velocities were moderately corrected, since small differences between the arrival time of ^{3}HHO and Eu are observed, which are assumed to be due to heterogeneities in the column. Further input data are listed in Tables 2 and 3. These data stem from independent batch experiments and from literature, respectively. For details, see [6] and [5]. According to the R_d values measured in batch experiments (cf. Table 1) and on the assumption of a constant mobile colloid concentration, the Langmuir coefficients shown in Table 3 were estimated.

Table 2. **Parameter values for the simulation.**

Column length l	0.5 m
Column diameter d	0.05 m
Injected volume of Eu-tracer solution V_p	1 mL
Injected Eu concentration $C_{Pf,-}$	$0.045 \cdot 10^{-3}$ g L^{-1}
Injected Eu-humate concentration $C_{Pb,0}$	$2.205 \cdot 10^{-3}$ g L^{-1}
Density of the sediment ρ	2600 kg m^{-3}
Density of the colloids ρ_C	1200 kg m^{-3}
Diffusion coefficient of the colloids D_m^C	10^{-11} m^2 s^{-1}
Diffusion coefficient of the pollutants D_m^P	10^{-11} m^2 s^{-1}
Dynamic viscosity μ	0.086 g m^{-1} s^{-1}
pore diameter d_C	$2 \cdot 10^{-4}$ m
Langmuir coefficient b_1	s. Table 3
Sorption capacity κ_1	$3.3 \cdot 10^{-3}$ kg kg^{-1}
Complexation constant $\beta_3 = \beta_4$	$5.23 \cdot 10^{-4}$ L mol^{-1}
Loading capacity $\kappa_3 = \kappa_4$	1.787 mol kg^{-1}
Concentration of mobile colloid C_C	0.08 g L^{-1}
Concentration of immobile colloid $\rho_C S_C$	$3.84 \cdot 10^{-3}$ g L^{-1}
Sorption rate k_1	$>1.4 \cdot 10^{-4}$ s^{-1}

Table 3. **Langmuir coefficients used for simulation.**

	Langmuir coefficient b_1 [m^3/g]
Experiment 1	0.250
Experiment 2	0.496
Experiment 3	0.320
Experiment 4	0.066
Experiment 5	

5. Results and discussion

As described above for simulation of the column experiments, only the rates k_3 and K_2 were fitted. Examples of the breakthrough curves for sediment 3 are shown in Figure 3. All experiments with sediments 2, 3, 4, and 5 are in good agreement with the simulations. For sediment 1, some slight deviations in the tailing of the breakthrough curve between experiment and simulation occur, which have to be further investigated.

Figure 4 shows the desorption rates k_3 obtained by simulation plotted *versus* the travel time of Eu-humate. Besides the results of this work, the values obtained in earlier investigations for 0.5-m and 10-m columns are included. The desorption rates decrease exponentially with transport time. The values obtained in this study are in good agreement with those determined in previous investigations.

The mechanisms that are responsible for the decrease of the desorption rate with increasing travel time are still under investigation, e.g., by Schüßler *et al*. [9].

K_2 rates are derived by simulations of the tailing of the breakthrough curves. In Figure 5, the capture rates ΘK_2 obtained by best fits are plotted *versus* Darcy velocity and are compared with results obtained from filtration theory. The error bars represent the values for $q\lambda_f\alpha$ calculated by the approach of Yao *et al*. [8] (see Equations 7 and 8) considering an uncertainty of colloid size between 1 and 200 nm. An average porosity of 0.27 and an attachment factor of $2\cdot10^{-5}$ were assumed. The capture rates increase with increasing Darcy velocity and are in the order of magnitude as expected by filtration theory.

6. Conclusions

Column experiments with five different sediments are simulated with the transport code TRAPIC. The results confirm those obtained in previous investigations. Since the same groundwater was used in all experiments, the same input parameter were applied in all simulations with the exception of the sorption values for Eu on the sediment. Important conclusions from the simulations are:

- The observed migration behaviour cannot be described by equilibrium models. Kinetically controlled sorption mechanisms for the contaminants have to be considered.

- The main fraction of europium exists as Eu-humate and migrates through the column without retardation.

- Recoveries of less than 100% are due to desorption of Eu from the colloids followed by sorption to the sediment matrix. A contribution of irreversible colloid filtration cannot be ruled out.

- The rates for desorption of europium from the colloids decrease exponentially with increasing transport time.

Figure 3. **Best-fit and experimentally observed curves for sediment 3 in linear (left) and logarithmic (right) presentation. C_p/C_{p0} represents the normalised concentration.** *Top*: **Darcy velocity $q = 37 \cdot 10^{-3}$ m/h,** *middle*: **$q = 8.2 \cdot 10^{-3}$ m/h,** *bottom*: **$q = 1.1 \cdot 10^{-3}$ m/h.**
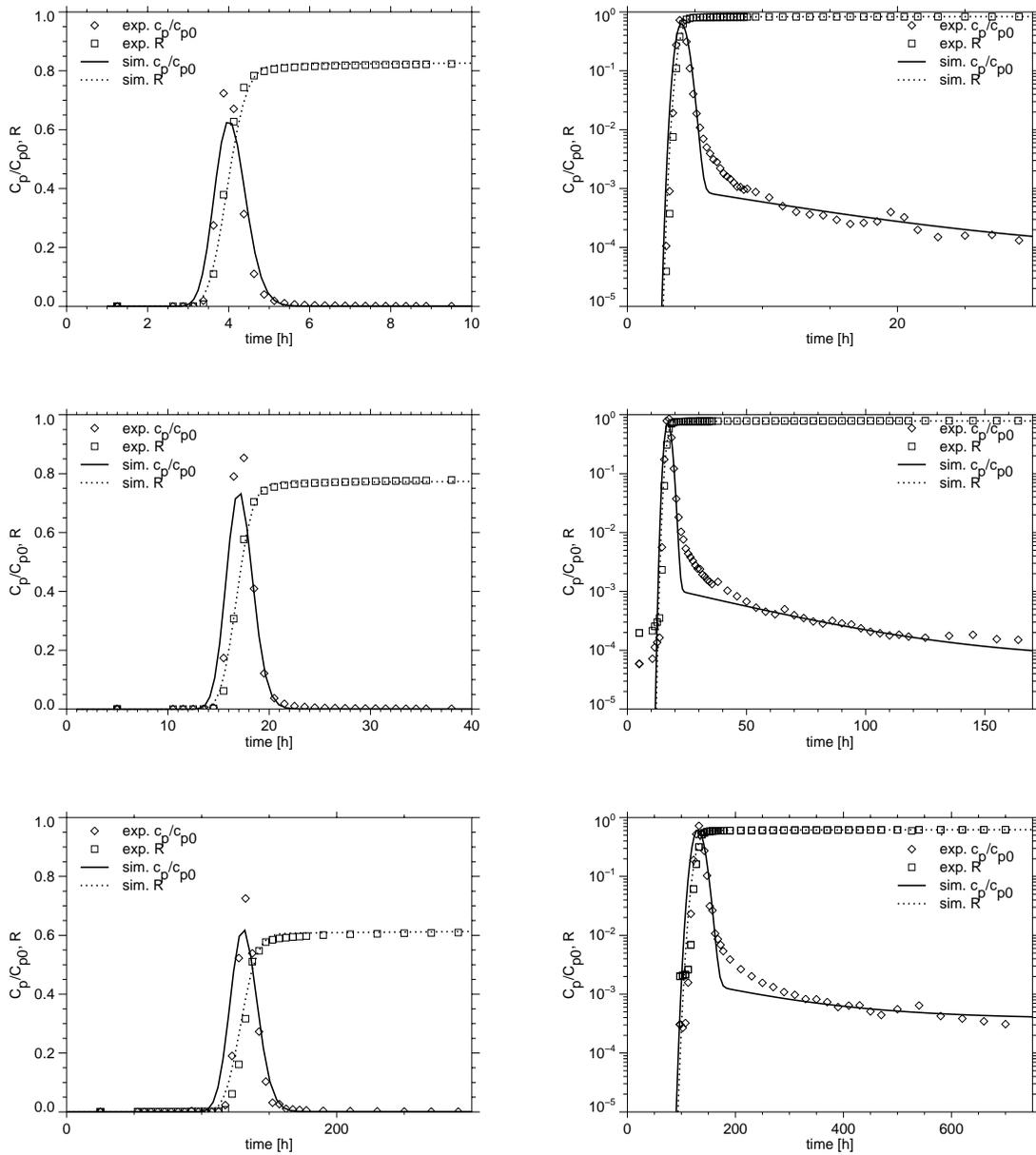
Figure 4. **Desorption rates k_3 as a function of transport time for all experiments.**
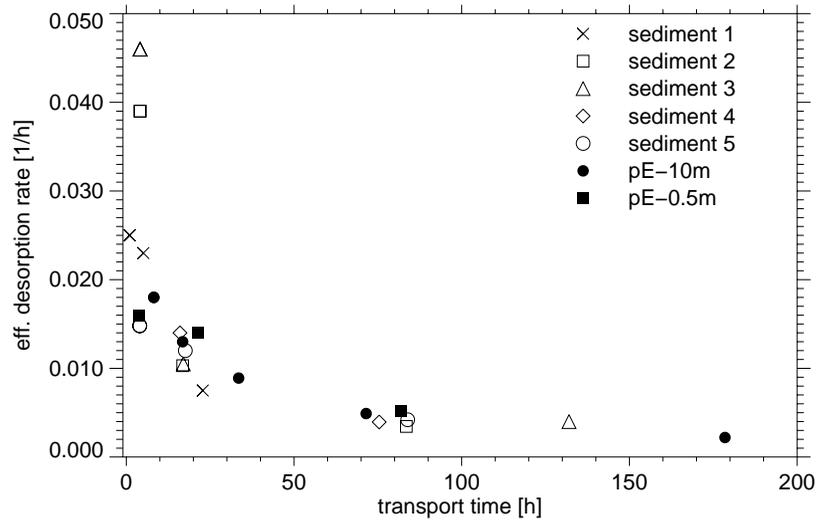

Figure 5. **Sorption rates from simulation ($K_2\Theta$) and theory ($\Theta = 0.27$, $\alpha = 2\cdot10^{-5}$). The error bars represent the values for $q\lambda_f\alpha$ considering an uncertainty of colloid size from 1 to 200 nm.**
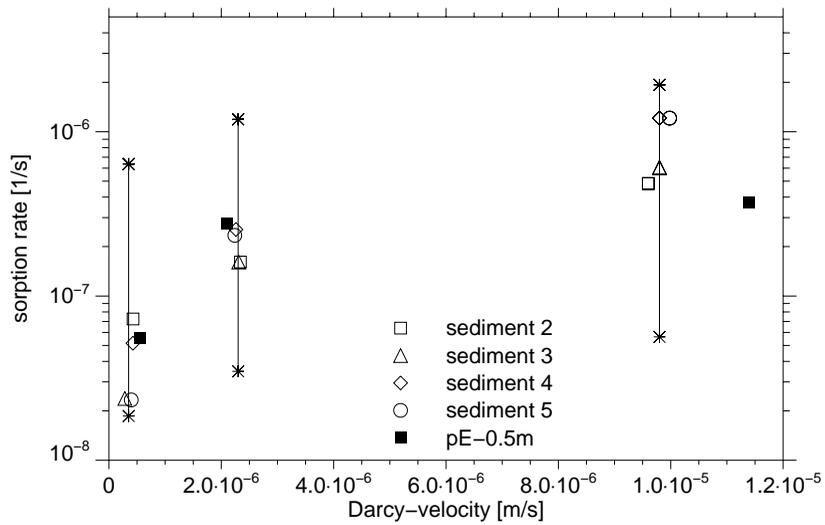
Reversible colloid-sediment interactions explain the tailing of the breakthrough curves. Assuming a constant ratio between mobile and immobile colloids, good agreement between simulated and experimentally obtained breakthrough curve is reached. The capture rates of the colloids obtained by best fits increase with increasing Darcy velocity. The values are in the same order of magnitude as calculated by filtration theory.

With regard to performance assessment, the mechanism of Eu desorption from the colloids has to be further investigated. This is a basis for scaling up desorption rates obtained from experiments of a few days duration to time periods of years.

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Matrix Diffusion:
Through-Diffusion *Versus* Electrical Conductivity Measurements

Yvonne Ohlsson
SWECO VBB VIAK, Sweden

Martin Löfgren and Ivars Neretnieks
Royal Institute of Technology, Sweden

Abstract

Laboratory experiments of matrix diffusion in dense porous rock ($\leq$ 1% porosity) are generally very time consuming and one is limited to rather short diffusion lengths, as well as to a small number of samples. Electrical conductivity measurements, on the other hand, are much quicker. Also, more and larger samples can be used. In addition, surface phenomena may be studied to some extent with this method.

In this study, traditional through-diffusion experiments as well as electrical conductivity measurements are carried out on the same rock samples. The formation factor is determined by both methods, and the methods are compared and discussed.

The surface conductivity is studied by exchanging the surface sites and the pore solution with different ions. After leaching out the free pore ions, the surface conductivity can be measured.

The formation factor differed by a factor of 2 between the two methods. There may be several explanations for this discrepancy, and there is a need for further investigation of this.

The surface conductivity measurements with Na^+, Sr^{2+}, or Cs^+ as surface specie, showed that Na^+-covered surfaces generally gave the higher conductivities. Cs^+ and Sr^{2+} both gave lower conductivities than Na^+ by approximately the same factor. For Sr^{2+}, the factor is the same as the difference in ionic mobility. Cs^+-covered surfaces have a lower conductivity, in proportion, than Na^+ and Sr^{2+}, which was contrary to expectations.

1.   Introduction and background

Matrix diffusion is considered to be of great importance in retarding radionuclides on their way from a repository to the biosphere. In addition to the delay by diffusion into the matrix, some nuclides are adsorbed to the pore surfaces either chemically to specific sites, or electrostatically to the negatively charged pore surfaces.

Determining matrix diffusivity by electrical conductivity measurements is a faster method than ordinary through-diffusion experiments, and may also be possible to carry out *in situ* [1]. The method has been used earlier for rock matrix diffusivity measurements, e.g., [2,3]. In this paper, however, the method is used on samples that were later used in traditional diffusion experiments, wherefore a comparison between the two methods is possible. Measurements of residual conductivity after leaching the samples of their free pore ions are also carried out to assess the importance and influence of conductivity of ions associated to the pore surfaces.

2. Theory

2.1 Liquid diffusion in porous material

The effective diffusivity of a non-charged molecule that migrates through the pore system of a rock sample deviates from the diffusivity of the molecule in a free solution by a *formation factor*, F_f. The formation factor takes into account the hindrance of the molecule by the solid rock material, and comprises the porosity (ε), the tortuosity (τ^2), and the constrictivity (δ_D) of the pores:

$$F_f = \varepsilon \frac{\delta_D}{\tau^2} \qquad \text{Equation 1}$$

The formation factor can be seen as a geometric constant for each piece of rock. Knowing the formation factor, the effective pore diffusivity, $D_p\varepsilon$ (m^2/s), of other molecules can be determined if their diffusivity in free liquid, D_w, is known:

$$D_p\varepsilon = F_f D_w \qquad \text{Equation 2}$$

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

$$J = -D\frac{dC}{dx} \qquad \text{Equation 3}$$

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

When the transport is transient and the solute accumulates or is depleted from the system, Fick's second law and the law of conservation of mass describe transport and accumulation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{Equation 4}$$

The solutions to problems described by Fick's second law may often be found in [4] and [5]. For diffusion through a porous medium with the boundary conditions constant concentration on the high-concentration side, C_1, and $C_2 << C_1$ throughout the experiment, the diffusion is described by Equation 5:

$$C_r = \frac{C_2 V_2}{C_1 Al} = D_e \frac{t}{l^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left\{-\frac{D_e n^2 \pi^2 t}{l^2 \alpha}\right\} \qquad \text{Equation 5}$$

where $\alpha = \varepsilon + \rho K_d$ and ρ is the dry density of the rock (m^3/kg), K_d the sorption coefficient (kg/m^3), t is the time (s), and l is the sample length (m). For large t values, the system is at steady state and the equation reduces to:

$$C_r = \frac{C_2 V_2}{C_1 Al} = D_e \frac{t}{l^2} - \frac{\alpha}{6} \qquad \text{Equation 6}$$

Plotting the reduced concentration, C_r, *versus* $\frac{t}{l^2}$ in a through-diffusion experiment results in a breakthrough curve, from which the effective diffusivity and the porosity can be determined from the steady-state part of the curve.

2.2 Electrical conductivity

The formation factor can also be determined from electrical conductivity measurements. The electrical conductivity through the electrolyte-filled pores of a rock sample (κ_p) is related to the formation factor and the conductivity of the free liquid solution (κ_w):

$$F_f = \frac{\kappa_p}{\kappa_w}$$

Equation 7

At low ionic pore liquid concentrations, the contribution to ionic transport from the surface-associated ions becomes significant. Therefore, the rock conductivity, κ_r, consists of a pore conductivity and a contribution from the surface conductivity, κ_s:

$$\kappa_r = \kappa_p + \kappa_s$$

Equation 8

3. Experimental

3.1 Sample description

All rock samples in this study were of the type "Äspö diorite". They are reddish grey to greyish red, finely medium-grained to medium-grained granitoids (granite, granodiorite, and quartz monzodiorites). One set of samples had the square cross-sectional area 3.5×3.5 cm^2 whereas the second set of samples were cylindrical with the diameter 4.1 cm. The lengths of the samples were 0.5-1 cm. The samples were fixed in plastic frames, and for the diffusion experiments the plastic frame was assembled between two containers with a sampling hole in each (Figure 1).

The porosities of the samples were determined by the wet/dry weighing method according to Archimedes principle [7]. Porosities ranged from 0.1-1% and the density of the rock material was around 2 700-2 800 kg/m^3, which agrees with other measurements on Äspö diorite [8].

Figure 1. **Rock sample: *a*) glued into plastic frame; *b*) assembled into diffusion cell.**

Sampling hole

a   b
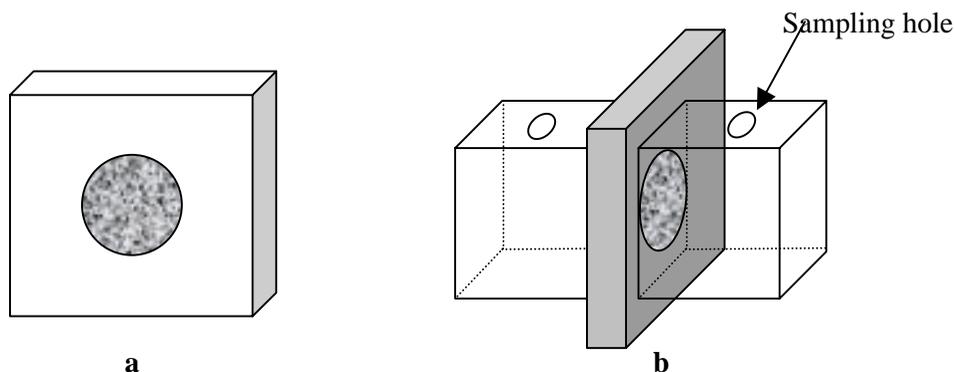
3.2 Through-diffusion experiments

The rock samples in the plastic frames were, after saturation and equilibration with a 1 M NaCl solution, fixed between two containers. One container was filled with 1 M NaCl solution (the low-concentration side) and the other (the high-concentration side) with 1 M NaCl and 10 g/L of uranine. pH was buffered to 8.0 with a NH$_3$/NH$_4$ buffer.

Samples (2.5 mL) were taken from a sampling hole on the low-concentration side. The sample volume was replaced with the same amount of 1 M NaCl solution. The samples were analysed with a spectrophotometer. It had earlier been found that the uranine solution was affected by light, wherefore the diffusion cells and the samples were kept dark by wrapping them in aluminium foil.

3.3 Electrical conductivity measurements

The electrical conductivity was measured by attaching copper electrodes to each side of the samples in the frames, and with a porous filter between rock surface and electrode. The filter was soaked in the same solution that the rock had previously been saturated with, and assured liquid contact between rock and electrodes. An AC current was applied and the electrical conductivity was measured. The samples had beforehand been vacuum-saturated with an electrolyte and kept in the solution. The temperature was in most experiments kept at 25 °C.

The frames that the samples were fixed in made 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. It also prevented evaporation of pore liquid from these surfaces during the measurements.

The rock conductivity was also measured directly in the diffusion cells through the two sampling holes, when the containers as well as the sample were filled with an electrolyte. Measuring directly in the cell gives no differences in results compared to if the copper electrodes were used.

Formation factor

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

The electrical conductivity is frequency dependent. At low frequencies (50-1 000 Hz), it is almost constant and the impedance is mainly resistive [3]. The rock conductivity for the determination of the formation factor was measured at 375 and 2 930 Hz. Not all samples could be measured at 94 Hz since the instrument measurement range limited measurements of high-conductance samples at this frequency. The difference in formation factor is generally small between the frequencies, but there is a trend of increase with increasing frequency (Table 1).

Table 1. **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

4. Results

4.1 Comparison between through-diffusion and electrical conductivity measurements

The through-diffusion experiments result in breakthrough curves from which the effective diffusivity can be determined. If the reduced concentration is plotted *versus* time over squared sample length, then the effective diffusivity can be read directly as the slope of the steady-state part (Equation 6). A breakthrough curve is shown below (Figure 2) for uranine diffusion through a 0.67-cm-long sample.

Figure 2. **Breakthrough curve for diffusion of uranine through a 0.67-cm-long Äspö diorite sample with the porosity 0.33%.**

$C_r = 3,63E-14*t/l^2 - 5,32E-04$
$R^2 = 9,96E-01$
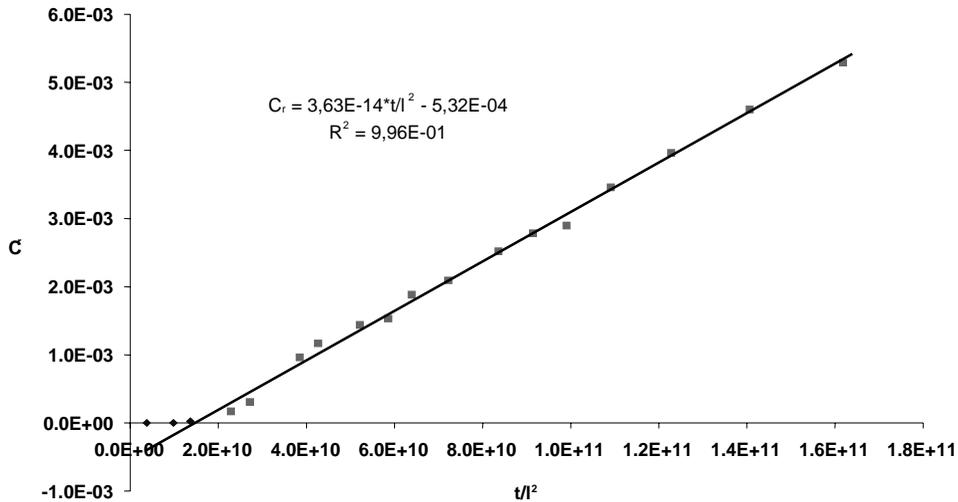
Formation factors from electrical and through-diffusion measurements are shown below in Table 2.

Table 2. **Formation factors determined by the two methods studied and with the ionic strength 1M in the pore solutions.**

Rock	$F_{f, el}$	$F_{f,diff}$	$F_{f,el}/F_{f,diff}$	Rock	$F_{f, el}$	$F_{f,diff}$	$F_{f,el}/F_{f,diff}$
20	1.4E-4	1.2E-4	1.2	48	1.6E-4	8.1E-5	2.0
24	1.3E-4	5.8E-5	2.2	69	9.7E-5	5.5E-5	1.8
26	9.2E-5	5.1E-5	1.8	70	7.5E-5	4.0E-5	1.8
34	1.0E-4	6.6E-5	1.6	71	5.7E-5	4.0E-5	1.4
38	6.3E-5	2.4E-5	2.6	72	8.2E-5	4.4E-5	1.9

4.2   *Ion-specific surface conductivity*

In Table 3, the surface conductivities measured on samples when pore surfaces are exchanged with a specific ion or contain the original ions from the original groundwater are presented.

Table 3. **Surface conductivity (μS/cm) for samples ion exchanged for specific surface ions. Surface conductivities for a few samples were also measured with the original surface ions from the groundwater. The temperature was 25°C in all measurements.**

Sample	55	60	62	63	12	23	28	65	66	67	68
Original	–	–	–	–	0.22	0.16	0.23	–	–	–	–
Na^+	0.34	0.50	0.37	0.43	0.30	0.21	0.25	0.30	0.35	0.30	0.30
Sr^{2+}	–	–	–	–	–	–	–	0.20	0.23	0.23	0.20
Cs^+	0.16	0.21	0.16	0.17	0.17	0.16	0.16	–	–	–	–
Sr/Na	–	–	–	–	–	–	–	0.67	0.66	0.77	0.67
Cs/Na	0.47	0.42	0.43	0.40	0.57	0.76	0.64	–	–	–	–

Na^+-covered surfaces generally give larger surface conductivities than Sr^{2+}- and Cs^+-covered ones.

5. Discussion

The electrical formation factor is higher than the diffusion formation factor on the average by a factor of 2. We have so far not found an acceptable explanation for this discrepancy. One possibility is that the diffusion is sterically hindered in the smaller pores, since the diffusing uranine molecule is a quite large anion. Another (not yet published) study with tritiated water showed similar behaviour, though.

A highly speculative reason for the higher electrical formation factor may be electrically conducting minerals blocking some of the pores (e.g., precipitated hematite). Conducting material in the pores could hinder diffusion of molecules, but add to the conductivity in the electrical measurements. Conductive minerals blocking the pores would result in an apparently higher connectivity in the pore system by, for example, connecting otherwise dead-end pores in the electrical conductivity measurements. The same would apply if conductive minerals were distributed in the matrix. However, the abundance of such minerals is very small in magmatic rock.

If the factor of 2 discrepancy were due to conductive minerals, it might increase with length of sample. One way of examining this would be to measure the rock conductivity by using both AC and DC current.

The surface conductivity measurements showed a clear trend of decrease when exchanging the sodium-covered surfaces for strontium or caesium ions. The decrease was larger for Cs than for Sr. One reason could be that the innermost surface caesium ions are more tightly bound to the surface than are the sodium ions. The activation energy for moving these ions may not be exceeded, wherefore part of the ions may remain immobile at the surface.

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Discordance in Understanding of Isotope Solute Diffusion and Elements for Resolution

Claudio Pescatore
OECD/NEA, France

Introduction

The NEA GEOTRAP project provides a unique technical forum where individuals playing different roles in repository programmes and experts from academia and the wider scientific community can have authoritative interactions on all topics relating to radionuclide migration in the geologic media presently considered by waste-disposal projects world-wide.

The lack of a common terminology has been identified, within GEOTRAP, as a hindrance to correct communication. In particular, specialists with different backgrounds tend to have their own jargons, and the meaning of concepts and words is not necessarily the same amongst disciplines. Another finding is that, often times, specialists in one discipline tend to think that other disciplines are more advanced than they actually are, or that some issues are fully understood when, perhaps, they are not.

Solute diffusion is one concept and mechanism on which there ought to be ample common understanding and agreement, the prediction of isotope migration as solutes being the ultimate goal of waste disposal assessment studies for safety purposes. A look at the literature as reviewed by Crank [1], Cussler [2], and Bird [3] shows, however, considerable lack of both experimental basis and unanimity when co-diffusion of isotopes of the same chemical element is concerned. In particular, the relevant technical papers are not very numerous, there are almost as many approaches as there are papers, and no approach is recognised to be entirely satisfactory. One possible reason, in this author's mind, is that all approaches tend to be based on the theory of diffusion of chemically distinct species, although Cussler [2] suggests that things should be different when chemically indistinguishable species are involved.

Cussler [2] reports some dramatic examples of discordance between predictions and experiments in diffusion of isotopic molecules, and suggests that the issue of solute-solute interaction is important to solve the problem. Crank [1] provides a wider review of the theoretical approaches and the difficulties they encountered. From Crank's review, this author notes one observation, made originally by Seitz, that molecules may not jump at the same rate in one direction or another in the presence of a composition gradient. The concepts of solute-solute interaction and that of uneven jumping probability within a concentration gradient seemed not to be common background to those who model radionuclide migration. Also, these concepts imply notions that are not shared by all disciplines that are involved. Given this uncertain background, the existing degree of commonality of understanding and agreement on what solute diffusion is and how it applies for isotopic diffusion was explored through a survey based on a questionnaire.

In Part 1, we give the results of the survey. These confirm the indeterminacy noted in the literature and show further that there exists professional bias in the interpretation of what diffusion is and/or implies for isotopic solutes. In particular, specialists working in the same broad field of radionuclide migration propose quite distinct predictions of radionuclide movement. Further debate of this issue and experimental work appear to be called for. In Part 2, we take the debate forward by taking side for one interpretation and proposing new insight and a modelling tool.

Part 1

The Questionnaire

A "simple" situation involving isotopic solute migration was described and four questions were asked to an audience of experts involved in GEOTRAP and in the NEA Thermodynamic Data Base project. A few outside experts in the same general field were also contacted. Thus all disciplines relevant to predicting radionuclide migration in geologic media, e.g., chemists, geochemists, geologists, physicists, performance assessors, etc. were involved.

Consider the situation of Figure 1 where the concentration gradient of an isotopically pure and non-radioactive solute, ^1A, is maintained steadily across an aqueous medium, Δx, by keeping C_0 and C_1 constant. In particular, C_0 is kept constant by maintaining it in equilibrium with a solid phase. C_1 may be considered equal to zero.

Question 1: *Starting at a given time, will the ^1A solute molecules at $\Delta x/2$ elute?* **A**. Equally to the left and right. **B**. Mostly to the left. **C**. Mostly to the right. **D**. It's difficult to say. **E.** Ill-posed question.

Question 2: *Consider we replaced instantly, and only at $\Delta x/2$, part of the ^1A isotopes with metastable but very-long-lived ^{1m}A isotopes, in a way that the concentration gradient in the chemical element, A, is not changed. Will the ^{1m}A solute molecules elute?* **A**. Equally to the left and right. **B**. Mostly to the left. **C**. Mostly to the right. **D**. It's difficult to say. **E.** Ill-posed question.

Figure 1. **Concentration gradient for solute ^1A.**
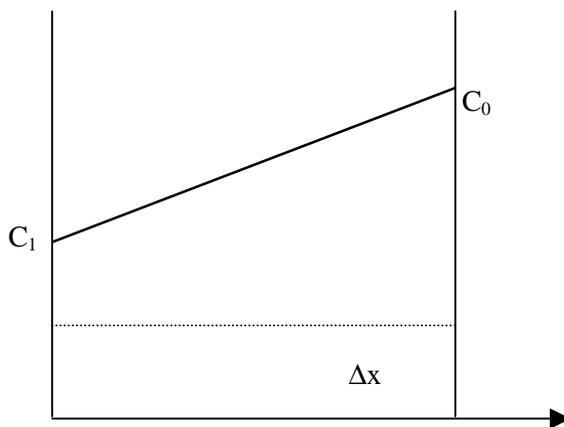
Question 3: *If, instead of ^{1m}A, we used a stable ^2A isotope, will the ^2A solute molecules elute?* **A**. Equally to the left and right. **B**. Mostly to the left. **C**. Mostly to the right. **D**. It's difficult to say. **E.** Ill-posed question.

Question 4: *Do you feel your mindset is closer to* **A**. a chemist's. **B**. a physicist's. **C**. It's difficult to say, I am a …

The results of the survey

Fifty-one responses were received from:

– 23 specialists with a chemist's mindset ("chemists", hereafter).

– 15 specialists with a physicist's mindset ("physicists", hereafter).

– 13 specialists with an "other" mindset ("other specialists", hereafter).

Table 1 summarises all the responses that were received regardless of the speciality domain of the respondent. Table 2 reports, for each set of respondents, the responses that were given to questions 2 and 3 together.

Table 1. **Total tally of responses.**

	A. **Equally to left and right**	**B.** **Mostly to the left**	**C.** **Mostly to the right**	**D.** **Difficult to say**	**E.** **Ill-posed question**
Question 1	23.5%	70.5%	0	1.9%	3.9%
Question 2	43.1%	35.2%	3.9%	13.7%	3.9%
Question 3	47.1%	33.3%	2%	13.7%	3.9%

Table 2. **Combined response to Questions 2 and 3 for each set of respondents.**

	Chemists	**Physicists**	**Others**
AA	43.4%	53.3%	30.8%
BA		6.7%	
BB	43.5%	13.3%	30.8%
BD		6.7%	
CB			7.7%
CC		6.7%	
DA			7.7%
DD	8.7%	6.7%	20.1%
EE	4.3%	6.7%	

Analysis of responses

While the responses cluster around the answers A and B, all together they show significant discordance (Table 1). In particular, the respondents are split on all three technical questions.

Also, a professional bias is evident from Table 2, where the BB response is preferred by 43.5% of the chemists but by only 13.3% of the physicists. Vice versa, 53.3% of the physicists give an AA response *versus* 43.5% of the chemists. The other specialists are split evenly on this: 30.8% for either AA or BB. These specialists also show significant indecision, unlike the chemists and physicists who showed very little doubt (D answers in Table 2).

The reason for the discrepancy seems to be as follows: chemists tend to consider solute diffusion as a "chemical" phenomenon, in the same class as osmosis, say. Also, chemists accept that coupling (and, therefore, correlation) amongst isotopic molecules of the same chemical element exists due to their chemical affinity and their sharing the chemical potential of the common element. The physicists tend to consider diffusion as a "non-chemical" phenomenon, such as Brownian

motion, whereby each solute molecule is completely independent of other kin molecules, even at the solubility limit.

The above results show that a clarification is needed of what diffusion is and what it engenders once isotopes of the same chemical element are involved. A dialogue is also needed among chemists, physicists, and other specialists in order to come to a common view. Ultimately, this may require experimental work.

In order to nurture the debate, the following observations and insights are offered.

Part II

The author's response to the questionnaire

Any A molecule will be submitted to interactions both with the solvent molecules, B, and with the kin molecules, A.

The B molecules can be pictured as a uniform field of particles vibrating about their current positions in a random and isotropic fashion. The A-B interactions will thus result in pure Brownian motion whereby no net momentum is imparted in one direction or another to individual A molecules and there is no preferential movement of any A molecule in one direction or another. However, because there are, at any point in space, more A molecules on the right than on the left of that point, more molecules are likely to move to the left than to the right. Thus, there will still be, on the whole, and at any point and any time, an excess number of A molecules moving to the left.

The molecules originally at $\Delta x/2$ would tend to move equally in both directions due to the A-B interactions but their movement towards the right will be hindered by the interactions with the excess kin A molecules coming from the right. The latter interactions will also impart a net momentum towards the left. Thus, in this non-equilibrium situation, the A-A interactions will resolve the motion of the molecules originally at $\Delta x/2$ mostly to the left.

This author's response is then that, in all three cases, migration of the molecules originally at $\Delta x/2$ will take place mostly to the left. An additional observation needs to be made, however, regarding the Question 1 where only [1]A molecules are present. In this case, the A molecules are indistinguishable and, even if there is a net mass transfer to the left, it cannot be known which molecule does what. Question 1 can then also be said, correctly, to be an ill-posed problem.

Implications for the prediction of isotopic diffusion

If the above response is the correct one, then:

1. The classical Fick's Law of diffusion – which is based on only Brownian motion of independent particles not statistically related amongst themselves – is insufficient to describe the diffusion of isotopic molecules of the same chemical element

2. Before utilising transport codes that implement Fick's Law, there is a need to argue that the effects of A-A interactions can indeed be neglected for the problem that is being considered

3. Considering the ubiquitous use of Fick's Law in radionuclide transport codes, it is of the essence to find a correction to this law that incorporates A-A interactions in order to evaluate their significance.

In accordance with the intuitive discussion provided above for the three thought-experiments, it may be expected that the total flux, $J_i(x,t)$, of ^iA-molecules has two components representing the effects of A-B and A-A interactions in the presence of the given solvent molecules, B, respectively. Namely:

$$J_i(x, t) = J_{iA\text{-}B,B} (x,t) + J_{iA\text{-}A,B}(x, t) \qquad \text{Equation 1}$$

The expression for $J_{iA\text{-}B,B} (x, t)$ is very simply the classical Fick's Law. Namely:

$$J_{iA\text{-}B,B} (x, t) = - D_{iA\text{-}B,B} \, \partial C_i / \partial x \qquad \text{Equation 2}$$

where $D_{iA\text{-}B,B}$ is the diffusion coefficient based on Brownian motion and C_i the concentration of the ^iA molecules.

In the next section, it is shown that a first approximation for $J_{iA\text{-}A,B}(x, t)$ is:

$$J_{iA\text{-}A,B} (x,t) = - D_{iA\text{-}A,B} \, (C_i/C) \, \partial C/\partial x \qquad \text{Equation 3}$$

where C is the total concentration of A molecules and the coefficient $D_{iA\text{-}A,B}$ has dimensions of a diffusion coefficient and is a measure of the mobility of ^iA molecules within a population of kin A solute molecules within a solvent B.

Amendment of Fick's Law in order to account for A-A interactions

In order to obtain $J_{iA\text{-}A,B}(x, t)$, let us first consider a gas composed of two isotopic molecules of A, e.g., the situation of case 3, and let us think of it as an ideal gas. In this gas, the ^2A and the ^1A molecules will undergo random motion due to all molecules interacting amongst themselves.[1] Thus, the ideal gas model is a model of random motion based on A-A interactions. In particular, at any position in the gas, these interactions will produce a total pressure P which, to a first approximation, depends only on the number and not the mass of the interacting molecules.[2] Namely: $P = C*RT$.

Consider now a slab of thickness Δx. It will be acted upon from the left and from the right by the total pressure, P, in the gas. The net force per unit area acting on the slab is then:

$$f_{A\text{-}A} = P(x+\Delta x) - P(x)$$

The force acting globally on the molecules contained in a unit volume in the slab is:

$$F_{A\text{-}A} = f_{A\text{-}A}/\Delta x$$

and the average force per molecule (or per mole, depending on how concentration is measured):

$$\varphi_{A\text{-}A} = F_{A\text{-}A}/C$$

Hence, the force due to A-A interactions and acting globally on the ^iA molecules contained in a unit volume is:

$$\Phi_{i\,A\text{-}A} = C_i \, \varphi_{A\text{-}A}$$

1. In the ideal gas model, the particles have random walks because they interact with one another, otherwise they would move in straight non-interacting trajectories. In an ideal gas, the mean free path is very large with respect to molecular diameters, but the collision frequency can still be very significant. For instance, with reference to N_2 at STP, it can be calculated – based on the ideal gas model – that each molecule makes a collision every nanosecond even if it travels about 10^3 molecular diameters between collisions.

2. The effect of mass is a higher order correction to the perfect gas law $P = C*RT$. This effect is practically undetectable in gases at ordinary temperature and pressures [4]. In the same vein, mass correction is a negligible correction when considering the chemical properties of isotopes of the same element, which is why, for instance, with the potential exception of the very lightest elements, thermodynamic databases do not distinguish amongst isotopes of the same element.

If we consider that, to a first approximation, the flux of ^iA molecules, $J_{iA-A}(x,t)$, out a unit volume in the slab must be proportional to the force acting on the molecules contained in that volume, Φ_{iA-A}, and if we call D_{iA-A} this proportionality factor, we have that:

$$J_{iA-A}(x,t) = - D_{iA-A} (C_i/C) \, \partial C / \partial x \qquad \text{Equation 4}$$

Equation 4 thus represents, to a first approximation, the flux of ^iA molecules due to the A-A interactions. D_{iA-A} is a coefficient of mobility (diffusion) of the ^IA particles within a population of A particles.

To the extent that there is analogy between the pressure of an ideal gas and the osmotic pressure of a solute, Equation 4 applies also for the effect of the A-A interactions in solution, only the force from these interactions and the diffusion coefficient will vary from solvent to solvent. Hence, for the sake of clarity, we replace D_{iA-A}, in Equation 4, with the a new coefficient $D_{iA-A,B}$, which yields Equation 3. The latter equation is also derived in the Appendix from the point of view of chemical thermodynamics.

Combining terms, we get the following constitutive law for the diffusion of isotopic solutes ^iA in a solvent B:

$$J_i(x, t) = - D_{iA-B,B} \, \partial C_i / \partial x - D_{iA-A,B} (C_i/C) \, \partial C / \partial x \qquad \text{Equation 5}$$

With reference to the questionnaire questions, Equation 5 would, indeed, resolve the motion of the relevant molecules of cases 2 and 3 above "mostly to the left", and there would be net mass transfer to the left in case 1. Namely, while Fick's Law alone, Equation 2, would result in a Gaussian distribution of the relevant solute molecules, Equation 5 would predict a modified Gaussian skewed towards the left.

Importantly, the specialisation of Equation 5 for a single-isotope solute (Case 1) reduces to a Fick's Law expression where the diffusion coefficient is the sum of $D_{A-A,B}$ and $D_{A-B,B}$. Thus, once more, *Equation 5 does not contradict Fick's Law, but completes it*. Equation 5 reduces to a Fick's Law expression also in a situation of chemical equilibrium, i.e., when $C(x,t) = constant$. This will be commented upon further in the Appendix.

It can be observed now that, according to Equation 5, net diffusion of ^iA molecules within a population of kin A molecules can take place with or against their own concentration gradient, depending on the circumstances. In particular, the second term in Equation 5 adds a sensitivity to the whole concentration of A and the total concentration gradient, i.e., a correlation to the sum of all isotope concentrations and to the sum of the concentration gradients of the different isotopic molecules.

It would seem reasonable to assume, for solutes, that the coefficients $D_{iA-B,B}$ are practically the same for all isotopic molecules of the element A given that these have the same partial molar volume and the same electronic configurations. The same may be true also for the coefficients $D_{iA-A,B}$, especially for the heavier chemical elements.

Where could Equation 5 make a contribution?

The fractionation of isotopes as solutes is a subtle phenomenon that manifests itself widely in Nature. Diffusion-coupling of isotopic solutes may contribute significantly to the manifestation of this phenomenon over large time scales. Understanding potential effects arising from isotope co-diffusion might make a difference on how predictions based on evidence from isotope geology are used. Fractionation phenomena may become evident on much smaller time scales and with higher amplitude in the case of radioactive waste disposal because of the enhanced differences in the isotopic mix of the waste from the ones that exists in nature. Also, tracer diffusion is a technique that is applied

in numerous fields, but problems do exist, as shown in the review by Cussler [2], and this new contribution may help get better results or place results in perspective.

Because Equation 5 reduces to Fick's Law in the case of a single-isotope solute, it is not clear at present whether the diffusion coefficient that is measured classically is dominated by the term $D_{A-A,B}$ or $D_{A-B,B}$. If the former is the case, then there may be, in certain cases, important non-linear effects vis-à-vis the calculations that are done presently regarding the speciation and the residence time of radioisotopes in the near field of waste repositories, where the diffusion regime is created and elemental concentrations are highest.

A general observation is that, although it is not clear at this stage where the new term, Equation 3, may or may not make a difference, this term is paramount in some problems, such as Cases 2 and 3 above. It is also paramount when $D_{iA-B,B} = 0$, i.e., for cases of self-diffusion.[3] The issue of the relevance of this term is, thus, by itself, an important problem and needs to be assessed case by case.

Finally, the reasoning provided for the resolution of cases 1 to 3 and resulting in Equation 3 seems to be sufficiently general to apply to any non-equilibrium situation. Thus, Equation 5 has the potential to become the reference constitutive law for the diffusion of isotopic solutes.

Conclusions

The literature is inconclusive on the modelling of isotopic co-diffusion, and notes the lack of a wide-enough experimental basis. Further, there is discordance amongst technical specialists on what diffusion is and what it engenders once molecules involving different isotopes of the same chemical element are involved. A dialogue is needed among chemists, physicists, and other specialists in order to come to a common view. This will require, ultimately, experimental work.

In the field of radionuclide migration there is a view – captured in Fick's Law – according to which the individual molecules of any isotopic mix are to be considered as independent and uncorrelated with one another and that diffusion is simply a manifestation of Brownian motion (*A-B* interactions) and is a non-chemical phenomenon. Another view also exists that interactions amongst molecules of the same chemical solute (*A-A* interactions) are at the core of chemical behaviour - they are at the basis of such concepts as chemical potential, fugacity, chemical activity and solubility product - and these interactions should play a role also in diffusion of isotopic solutes. This contribution is codified, in mathematical terms, in models such as that expressed by the new Equation 3. It is suggested that the overall constitutive law for the diffusion of isotopic solutes should take account of *both* the *A-B* and *A-A* contributions. The proposed law, Equation 5, should help in the debate that is hoped will be opened on the topic of the diffusion of isotopic solutes and, eventually, in assessing the relevance of any correction for isotopic effects.

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3.   Meaning by this term the diffusion of a tagged solute in an untagged but otherwise chemically identical solvent.

Appendix: The Chemical Thermodynamics Viewpoint

Isotopic exchange reactions are the main cause of isotopic dilution, a phenomenon well known to occur in Nature. A distinguishing feature of these reactions is that the number and type of molecules participating in the reaction remains constant throughout the process and only the isotopic composition of the compound involved in the exchange is altered. Isotopic exchange reactions of the type:

$$^{1}AX + {}^{2}AY \leftrightarrow {}^{2}AX + {}^{1}AY \qquad \qquad \text{Equation A.1}$$

must then be occurring all the time and are a form of, and constitute evidence for, *A-A* interactions.

The equilibrium constant of these reactions is 1, at least for the heavier isotopes, i.e. those with mass number greater than approximately 80. To the extent that reactions such as Equation A.1 take place and their $K_{eq} = 1$, one can say that the relevant isotopes are chemically interchangeable and indistinguishable amongst themselves and have the same chemical activity. Same chemical activity means, in particular, that, once the total concentration of the reference chemical element is fixed, the activity does not change by changing the mix of its isotopes. Indeed, the fact that activity of any mix of sister isotopes can be considered to coincide with that of the element is a working standard in everyday chemistry whereby no account needs to be made for an isotopic contribution. Accordingly, to the extent that the chemical potential is expressed in terms of chemical activity, it will depend on the activity of the element and not on the relative mix of isotopes that contribute to the elemental concentration. Thus, to a first approximation and for heavy isotopes, we can make reference to the gradient potential of the chemical element, μ, for driving the migration process.[4] Finally, it is worth observing that the concepts of chemical potential and chemical activity are very much about interactions taking place amongst molecules of the same chemical element.

It is observed in textbooks that, if the chemical potential depends on position, then the difference in chemical potential between two locations represents the work needed to move one mole of material between these two locations. The process of moving mass will be spontaneous if *Δμ < 0*. An effective force that is the combination of all internal forces locally operational – including the electrostatic force – performs this spontaneous work. This force equals the gradient $\partial\mu/\partial x$ and is directed in the direction of decreasing chemical potential. No thermodynamic driving force exists when *∂μ/∂x = 0*. The force per mole of A, $\varphi_{A\text{-}A,B}$, that arises form internal *A-A* interactions in the presence of the solvent, *B*, is then:

$$\varphi_{A\text{-}A,B}(x,t) = -\partial\mu/\partial x = -(1/a_{A,B})\,\partial a_{A,B}/\partial x = -(1/C)\,\partial C/\partial x - (1/\gamma_{A\text{-}A,B})\,\partial\gamma_{A\text{-}A,B}/\partial x \qquad \text{Equation A.2a}$$

where $a_{A,B}(x,t)$ is the chemical activity of *A* in the presence of *B*, and $\gamma_{A\text{-}A,B}(x,t)$ the activity coefficient, defined as $\gamma_{A\text{-}A,B}(x,t) = a_{A,B}(x,t)/C(x,t)$. The activity coefficient is unity at infinite dilution; the fact that it is different than unity is attributed to the interactions amongst solute molecules.

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4. This is not to say that there are no differences in isotopic molecules, as the energies of the zero levels of isotopic molecules differ by the amount of the zero-point energies of the oscillations. These effects, if any, constitute higher order perturbations to the chemical potential and do not enter in the normal definition of chemical activity and chemical potential. Also, in chemistry one is interested in the gradient of the chemical potential rather than in the absolute value of it, which, again, supports the view that these zero levels energies should not play a meaningful role, if at all.

It can now be observed that any relative change of $\gamma_{A\text{-}A,B}$ in space will normally be much less than the relative change of C, even for ionic solutes. Thus, to a very good approximation, Equation A.2a can be simplified[5] to:

$$\varphi_{A\text{-}A,B}(x,t) = -(1/C)\,\partial C/\partial x \qquad\qquad \text{Equation A.2b}$$

Accordingly, the force acting on the ^IA isotopic molecules is:

$$\Phi_i = C_i\,\varphi_{A\text{-}A,B} \qquad\qquad \text{Equation A.3}$$

which leads to the same expression as was obtained earlier for the flux of these molecules. Namely:

$$J_{iA\text{-}A,B}(x,t) = -\alpha\,(C_i/C)\,\partial C/\partial x \qquad\qquad \text{Equation 3}$$

The proportionality constant, α, is very simply the coefficient $D_{iA\text{-}A,B}$. The thermodynamic approach that suggests that Equation 3 should be a good approximation for higher mass isotopic solutes, both neutral and ionic.

It is noteworthy to see that chemical thermodynamics yields Equation 3 and not Fick's Law. The latter arises from the theory of fluctuations around equilibrium states and/or Brownian motion [5] whereby A-A interactions are not taken into account. Thus, while Equation 3 is about A-A interactions and about a situation of chemical disequilibrium ($\Delta\mu < 0$), Fick's Law is about A-B interactions as they arise in a situation of where all the positions in space are equivalent at all times ($\Delta\mu = 0$), and a concentration gradient of A is not needed for motion to take place.

$\Delta\mu$-equal-zero processes dominate at chemical equilibrium (no entropy change; Brownian motion) and can very well coexist with $\Delta\mu$-less-than-zero processes (evolution towards maximum entropy). Hence, the observation that Equation 3 *completes* the Fick's Law, Brownian model by bringing into the picture the A-A interactions and the situation of non-equilibrium. The final constitutive law for isotopic diffusion should account for both contributions from Brownian motion and from the gradient in chemical potential, i.e., Equation 5.

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5. Note that no assumption needs to be made about A-A interactions not taking place, and these interactions need not be ignored.

Determination of Natural Uranium Concentration in Boom Clay: Effect of Different Extraction Techniques

Lian Wang, M. De Craen, N. Maes, P. De Cannière, and M. Put
SCK/CEN, Belgium

A. Dierckx
NIRAS/ONDRAF, Belgium

Abstract

Natural uranium concentration has been measured in the pore water of Boom Clay extracted by three different techniques: (1) batch leaching of clay suspensions; (2) squeezing of clay cores; (3) collection by piezometers. The results show that the batch and the squeezing techniques extract higher uranium concentrations (up to three orders of magnitudes) than measured in the pore water collected by piezometers. Batch techniques (leaching and squeezing) tend to remobilise natural uranium from clay surfaces as colloids into aqueous phase. As a consequence, the batch distribution coefficient (K_d) may underestimate the retention capability of the clay. The *in situ* retention mechanisms for natural uranium may involve colloid filtration and/or dissolution of uranium-bearing minerals.

Introduction

Boom Clay has been studied as a candidate host for a deep geological disposal of radioactive waste. In the past 20 years, a lot of laboratory and *in situ* migration experiments have demonstrated that Boom Clay is an effective barrier to retain most of the radionuclides of interest [1,2,3]. The underlying retention mechanisms are, however, not well understood. To build confidence for the geological disposal concept, it is important to identify the key retention processes that Boom Clay can depend on to delay the migration of radionuclides.

Radionuclide retention on Boom Clay has so far been conceptualised as a reversible, linear sorption phenomenon and quantified by the distribution coefficient K_d [1]. The sorption mechanisms were interpreted by cation exchange on clay [4] or the interaction with and the distribution between the solid and the aqueous natural organic matter (NOM) [5]. The solubility and colloid-related retention mechanisms were, however, not well studied. Due to the Boom Clay geochemical conditions, i.e., slightly alkaline *pH* (8.2) and reducing redox potential (–300 mV) [3,6], radionuclide immobilisation induced by precipitation or colloid-related retention likely play dominant roles. This paper attempts to understand the Boom Clay retention mechanisms by the study of the natural uranium distribution. The focus is given to the effect of water-extraction techniques on the aqueous uranium and NOM concentrations.

Experimental

Batch experiments were performed in glove boxes filled with N_2 or Ar gas to prevent clay oxidation. Leaching was carried out in $NaHCO_3$ solutions of 1 mM to 1 M concentration. The solid to solution ratio used was between 20 to 800 g clay/L solution. The leaching duration was generally two to three months. After the leaching, the supernatant was centrifuged at 21 255 g before the total uranium measurement. Some samples were ultra-filtered with 30 000 molecular weight cut off (MWCO) membranes.

Pore waters were also collected through squeezing of natural clay cores by a mechanical presser at 30 MPa.

Natural pore waters were collected through piezometers installed at different locations in the underground laboratory, which is about 220 m below the surface.

Total natural uranium concentration of all samples was measured by ICP-MS for ^{238}U. The content of dissolved NOM was measured by total dissolved organic carbon (TOC) while the solid NOM on clay was measured by the total loss of ignition (LOI).

Results and discussions

The natural uranium distribution at the Mol-1 borehole was measured and the results are given in Figure 1. A photograph of Boom Clay outcrop at Terhagen is also given to see the correlation between the uranium content and the NOM content in the organic-rich layers.

Figure 1. **Natural uranium distribution on samples collected at the Mol-1 borehole. The pore waters (liquid phase) were collected by squeezing of clay cores at 30 MPa.**
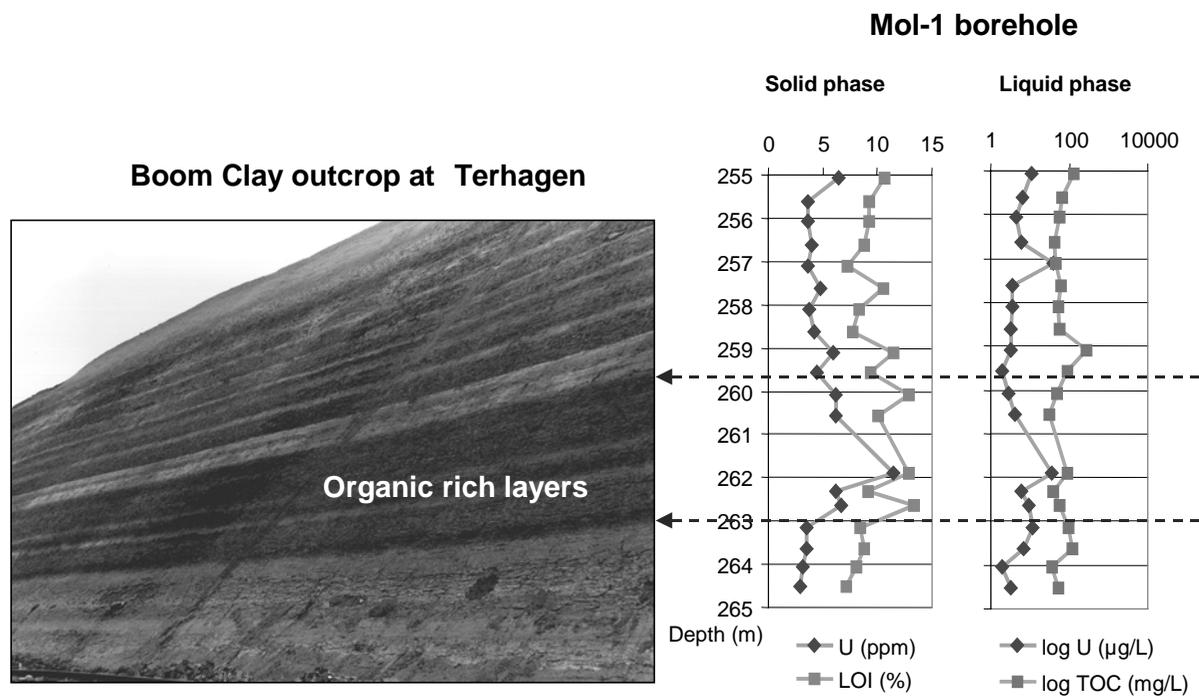
The results shown in Figure 1 indicate that the natural uranium concentration is highly correlated with the content of NOM. This finding, in term of retention mechanisms, may have different implications: (1) uranium is reduced in the organic-rich layers and hence mineralised to form uranium minerals; (2) uranium may form complexes with NOM on the clay surfaces; (3) uranium colloids are formed, either organic or inorganic in nature, and retained in the clay. The three hypothesised mechanisms may be related and occur simultaneously. The natural analogue study [7] has so far not detected any pure uranium minerals, possibly due to the very low uranium concentration (~ 4 ppm) being present in Boom Clay. The strong complex formation of uranyl with NOM has been measured [8], but the complex formation of tetravalent uranium species with NOM under reducing conditions are not well studied. The NOM colloids are known to be present in Boom Clay but their influence on the migration of radionuclides is not well understood.

Batch leaching tests were also performed to extract uranium and the results are shown in Figure 2.

Figure 2. **Total organic carbon and uranium concentrations extracted by 0.01 M NaHCO$_3$ as a function of solid to liquid ratio used in batch leaching experiments. Concentrations were measured in the supernatants after a 21 255-g centrifugation for 2 h.**
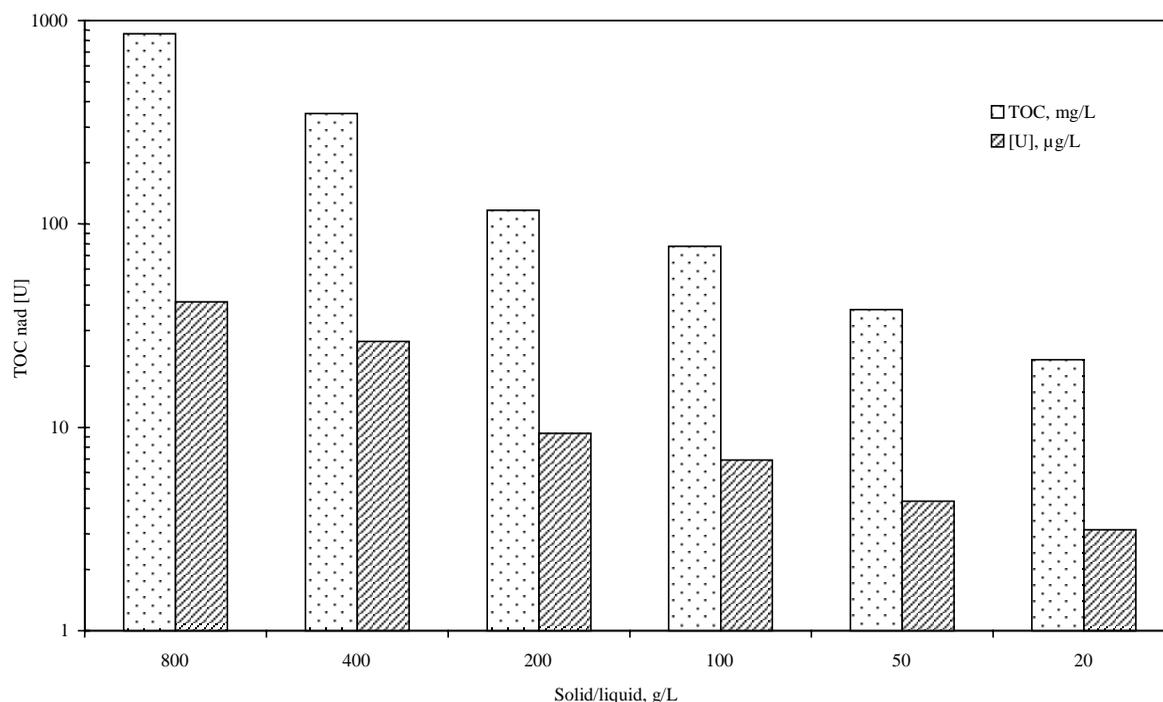
It is again clear from Figure 2 that uranium concentration is correlated with the content of NOM. Another interesting observation from Figure 2 is that the NOM and uranium concentrations increase as the solid to liquid ratio increases. This is in line with the observation made by Cremers and Henrion [5] for other radionuclides in their batch K_d experiment. The interpretation given by the same authors seems to stand for the present study as well: "the dissolution of sediment-originating organic matter appears to be the factor governing the solid-liquid distribution of the radionuclides" [5]. Further to this interpretation, as the organic matter was treated more like a complexing ligand, the NOM can also be considered as colloids so that the results shown in Figure 2 can be seen as the re-distribution of NOM colloids as a function of solid to liquid ratio. The increased colloids concentration (TOC content) is thus due to the increased amount of clay suspended and agitated. The colloid feature of the system was

further studied by ultra-filtration experiment. The ultra-filtration membrane of 30 000 MWCO was used to roughly separate the colloidal fraction from the soluble fraction of uranium (Figure 3). Increased concentrations of $NaHCO_3$ were then used to test the influence of complex formation of uranium with carbonate and the salt effect on the stability of colloids.

Figure 3. **Uranium concentration extracted by $NaHCO_3$ of different concentrations (1 mM to 1 M) after centrifugation and ultra-filtered by membrane of 30 000 MWCO.**
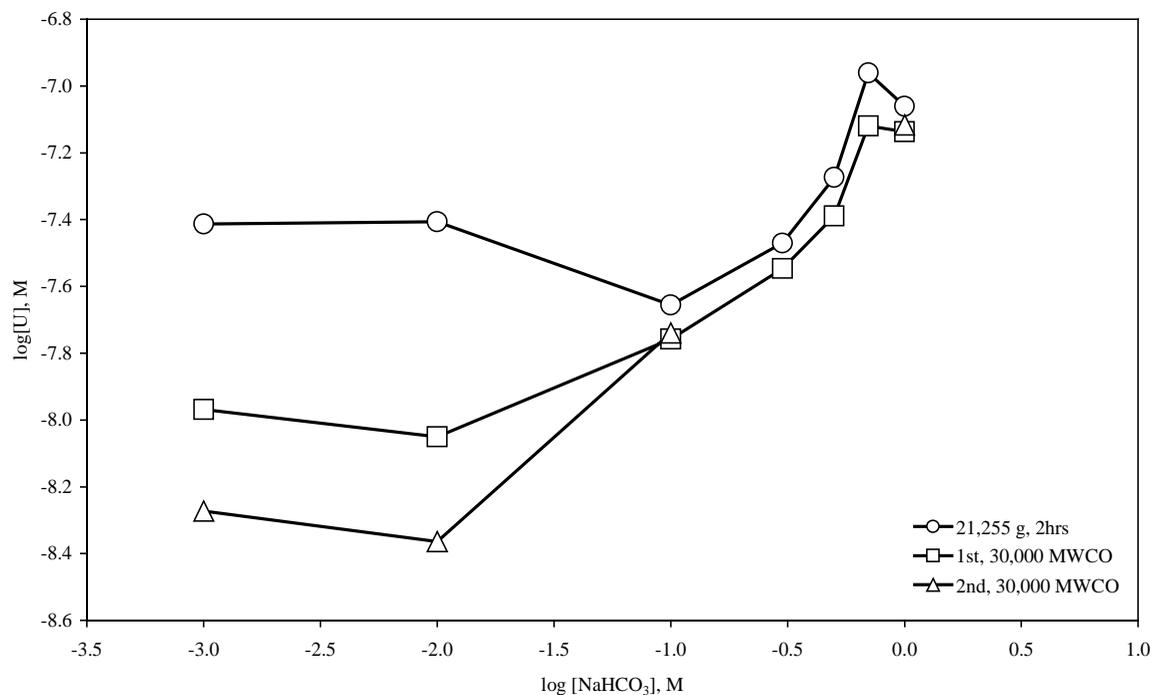

The results in Figure 3 show that the uranium can be removed by filtration membranes indicating the presence of colloids at low $NaHCO_3$ concentration level, e.g., in the concentration of Boom Clay pore water (~ 0.02 $NaHCO_3$). At high concentration of bicarbonate, uranium concentration increases and the speciation is present as a non-filterable form suggesting the formation of a uranium-carbonate complex.

The pore waters were also sampled from piezometers installed in the underground laboratory. The uranium and NOM concentrations were measured and the results are given in Figure 4 together with data from batch leaching and squeezing tests. The physical and chemical conditions prevailing in the neighbourhood of piezometers are considered as being disturbed the least compared to the laboratory systems. As a consequence, uranium concentration in the piezometer pore waters are much lower than the uranium concentrations extracted by the batch leaching and squeezing techniques. This can be explained as being due to the high compaction prevailing in Boom Clay surrounding the piezometers so that the colloids, either organic and/or uranium colloids, cannot be collected through the filters of the piezometers.

It is generally illustrated (Figure 4) that the uranium concentration is proportional to the NOM content in pore water at low TOC level, i.e., < 200 mg/L. At higher TOC level, mostly in the batch leaching tests, uranium concentration reached a plateau value indicating the maximum extractable uranium concentration under the given conditions.

Comparing the three data sets in Figure 4, it is interesting to note that at the same level of TOC, uranium concentration in the piezometer waters is about two to three orders of magnitudes lower than the concentration in the batch leaching and squeezed waters. This is not fully understood because we actually expect a similar level of uranium concentration at the same level of TOC if the uranium distribution is governed by the NOM distribution. This may instead indicate the presence of inorganic uranium colloids – uranium colloids or uranium-bearing clay colloids. In the batch and squeezed systems, inorganic uranium colloids are released from clay surfaces so that the apparent uranium concentration increased while under the *in situ* conditions surrounding the piezometer, inorganic uranium colloids may not be mobile so that the observed uranium concentration was much lower.

Figure 4. **Uranium and NOM concentrations extracted by three different techniques.**
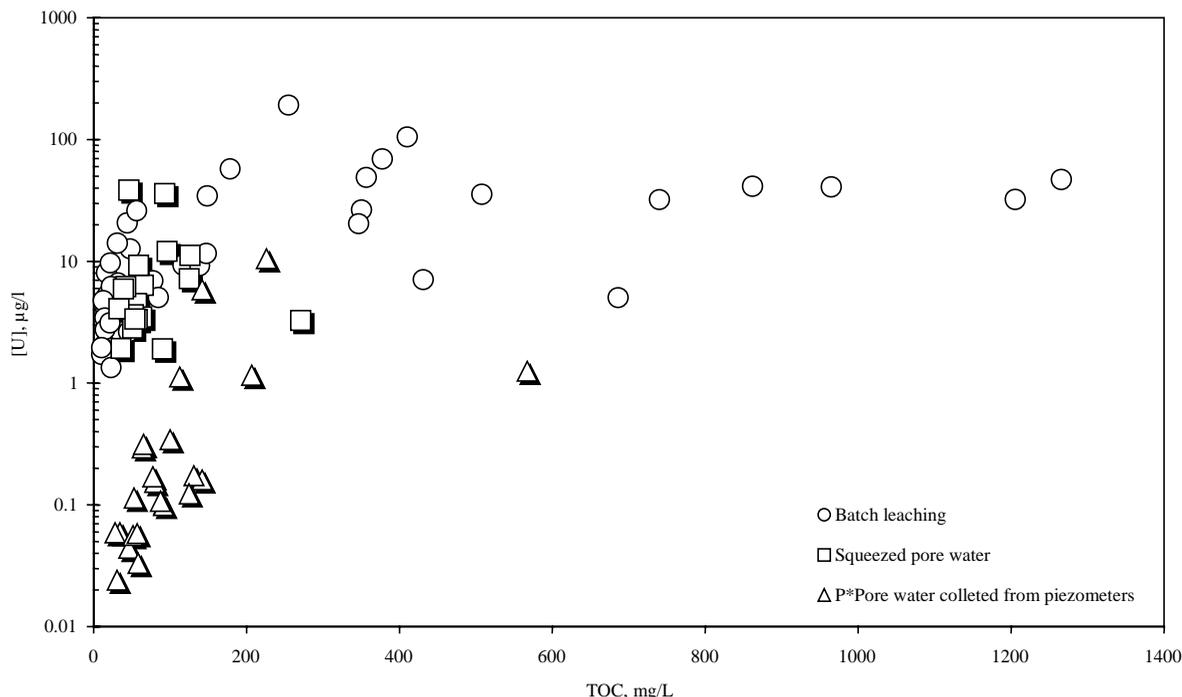
The uranium concentration in the piezometer waters is about 0.1 to 1 µg/L (10^{-10} to 10^{-9} M) at the TOC level of the Boom Clay pore water. This concentration is, interestingly, in line with the solubility of uraninite under the Boom Clay *pH* and redox conditions based on the data of Grenthe *et al.* [9]. Although we have not measured any detectable amount of pure uranium minerals in Boom Clay, it is not excluded that the *in situ* uranium concentration is controlled by the dissolution of some uranium minerals or by the uranium solid solution equilibrium.

Conclusions

Uranium concentration is generally very low (10^{-10} to 10^{-9} M) under the *in situ* compaction and the solid to water ratio of Boom Clay. The laboratory perturbations, i.e.*,* making clay slurry or squeezing pore water from clay cores, may free colloids and uranium from clay surfaces into the aqueous phase resulting in a much higher apparent uranium concentration. The attainable colloids in the batch and squeezed waters seem to be not mobile under the *in situ* Boom Clay conditions. Due to the presence of colloids, a laboratory-measured distribution coefficient (K_d) cannot be used for a predictive calculation under *in situ* conditions unless an appropriate extrapolation can be made based on well-established retention mechanisms.

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LIST OF PARTICIPANTS

BELGIUM

MAES, Norbert
SCK/CEN
Boeretang, 200
B-2400 Mol

Tel: +32 14 33 32 35
Fax: +32 14 33 35 53
Eml: nmaes@sckcen.be

WANG, Lian
SCK/CEN
Boeretang 200
B-2400 Mol

Tel: +32 14 33 32 36
Fax: +32 14 33 35 53
Eml: lwang@sckcen.be

CANADA

FLAVELLE, Peter
Wastes and Decommissioning Division
Canadian Nuclear Safety Commission
P.O. Box 1046, Station B,
280 Slater St.
Ottawa, Ontario, K1P 5S9

Tel: +1 613 995 3816
Fax: +1 613 995 5086
Eml: flavellep@cnsc-ccsn.gc.ca

JENSEN, Mark
Ontario Power Generation
700 University Ave, H16-E27
Toronto, Ontario, M5G 1X6

Tel: +1 416 592 8672
Fax: +1 416 592 7336
Eml: mark.jensen@opg.com

SUDICKY, Edward A.
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario, N2L 3G1

Tel: +1 519 888 4567 ext:6271
Fax: +1 519 746 7484
Eml: sudicky@sciborg.uwaterloo.ca

CZECH REPUBLIC

LACIOK, Aleš
Nuclear Research Institute - NRI
250 68 Rez

Tel: +420 2 661 724 05
Fax: +420 2 209 411 53
Eml: lac@ujv.cz

DENMARK

STIPP, Susan
Interface Geochemistry, Geological Inst.
University of Copenhagen
Øster Volgade 10
DK-1350 København K

Tel: +45 35 32 24 80
Fax: +45 33 14 83 22
Eml: stipp@geo.geol.ku.dk

FINLAND

HAUTOJÄRVI, Aimo
Posiva Oy
Toolonkatu 4
FIN-00100 Helsinki

Tel: +358 9 2280 3747
Fax: +358 9 2280 3719
Eml: aimo.hautojarvi@posiva.fi

JAKOBSSON, Kai
STUK
Radiation and Nuclear Safety Authority
P.O. Box 14
FIN-00881 Helsinki

Tel: +358 9 759 88 308
Fax: +358 9 759 88 670
Eml: kai.jakobsson@stuk.fi

SNELLMAN, Margit
Posiva Oy
Toolonkatu 4
FIN-00100 Helsinki

Tel: +358 9 2280 3742
Fax: +358 9 2280 3719
Eml: margit.snellman@posiva.fi

SUKSI, Juhani
University of Helsinki
A.I. Virtasen Aukio 1
P.O. Box 55
FIN-00014 HY

Tel: +358 9 1915 0129
Fax: +358 9 1915 0121
Eml: juhani.suksi@helsinki.fi

FRANCE

ALTMANN, Scott
ANDRA DS/HG
Parc de la Croix Blanche
1-7, rue Jean Monnet
F-92298 Chatenay-Malabry CEDEX

Tel: +33 1 46 11 84 81
Fax: +33 1 46 11 84 40
Eml: scott.altmann@andra.fr

GENTY, Alain
IPSN/DES/SESID - BP6
F-92265 Fontenay-aux-Roses CEDEX

Tel: +33 1 46 54 93 89
Fax: +33 1 46 54 77 27
Eml: alain.genty@ipsn.fr

LEBON, Patrick
ANDRA
1-7, rue Jean Monnet
F-92298 Chatenay-Malabry CEDEX

Tel: +33 1 46 11 80 82
Fax: +33 1 46 11 84 10
Eml: patrick.lebon@andra.fr

MOUCHE, Emmanuel
Commissariat à l'énergie atomique (CEA)
DM2S/SFME/MTMS
Centre d'études nucléaires de Saclay
F-91191 Gif-sur-Yvette CEDEX

Tel: +33 1 69 08 22 54
Fax: +33 1 69 08 82 29
Eml: emmanuel.mouche@cea.fr

GERMANY

BUCKAU, Gunnar
Institute for Nuclear Waste Management
Research Center Karlsruhe
P.O. Box 3640
D-76021 Karlsruhe

Tel: +49 7247 824 461
Fax: +49 7247 824 308
Eml: buckau@ine.fzk.de

FEIN, Eckhard
GRS
Theodor-Heuss Strasse 4
D-38122 Braunschweig

Tel: +49 531 8012 292
Fax: +49 531 8012 200
Eml: fei@grs.de

LARUE, Peter Jürgen
Gesellschaft für Anlagen- und
 Reaktorsicherheit (GRS) mbH
Schwertnergasse 1
D-50667 Köln

Tel: +49 221 2068 791
Fax: +49 221 2068 939
Eml: lar@grs.de

NOSECK, Ulrich
GRS
Theodor-Heuss Strasse 4
D-38122 Braunschweig

Tel: +49 531 8012 247
Fax: +49 531 8012 200
Eml: nos@grs.de

RÖHLIG, Klaus-Jürgen
Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH
Schwertnergasse 1
D-50667 Köln

Tel: +49 221 2068 796
Fax: +49 221 2068 939
Eml: rkj@grs.de

SCHELKES, Klaus
Bundesanstalt für Geowissenschaften
  und Rohstoffe (BGR)
Stilleweg 2
D-30655 Hannover

Tel: +49 511 643 2616
Fax: +49 511 643 2304
Eml: k.schelkes@bgr.de

WOLLRATH, Jürgen
Bundesamt für Strahlenschutz (BfS)
Postfach 10 01 49
D-38201 Salzgitter

Tel: +49 5341 885 642
Fax: +49 5341 885 605
Eml: JWollrath@BfS.de

JAPAN

SHIBATA, Masahiro
Waste Isolation Research Division
Japan Nuclear Cycle Development Institute (JNC)
4-33 Muramatsu, Tokai
Ibaraki 319-1194

Tel: +81 29 287 3695
Fax: +81 29 287 3258
Eml: shibata@tokai.jnc.go.jp

UMEKI, Hiroyuki
Nuclear Waste Management Organization of Japan (NUMO)
1-23, Shiba 4-Chome, Minato-ku
Tokyo 108-0014

Tel: +81 3 4513 1503
Fax: +81 3 4513 1599
Eml: humeki@numo.or.jp

SPAIN

BRUNO, Jordi
QuantiSci SL
Parc Tecnologic del Valles
E-08290 Cerdanyola

Tel: +34 93 582 4410
Fax: +34 93 582 44 12
Eml: jbruno@quantisci.es

GIL DE MINGO, Roberto
Nuclear Safety Council
Deputy Direction of Nuclear technology
C/Justo Dorado 11
E-28040 Madrid

Tel: +34 91 346 0649
Fax: +34 91 346 0588
Eml: rgm@csn.es

GIMENO, María J.
Dp. Ciencias de la Tierra, Facultad Ciencias
Universidad Zaragoza
Pza. S. Francisco, S/N
E-05009 Zaragoza

Tel: +34 976 762 482
Fax: +34 976 761 088
Eml: mjgimeno@posta.unizar.es

HERNÁN, Pedro
ENRESA
Emilio Vargas 7
E-28043 Madrid

Tel: +34 91 566 8192
Fax: +34 91 566 8165
Eml: pher@enresa.es

MISSANA, Tiziana
CIEMAT
Avnd. Complutense 22
E-28043 Madrid

Tel: +34 91 346 6185
Fax: +34 91 346 6005
Eml: tiziana.missana@ciemat.es

SWEDEN

ANDERSSON, Johan
JA Streamflow AB
Korta Gatan 7
S-171 54 Solna

Tel: +46 70 622 21 32
Fax: +46 8 562 00350
Eml: johan.andersson@streamflow.se

BYEGARD, Johan
Geosigma AB
Gymnasiegatan 6
S-442 34 Kungalv

Tel: +46 303 20 85 73
Fax: +46 303 20 85 79
Eml: johan.byegard@geosigma.se

CVETKOVIC, Vladimir
Dept. Civil and Env. Engineering
Royal Institute of Technology
AVAT, KTH, BV32
S-100 44 Stockholm

Tel: +46 8 790 62 90
Fax: +46 8 790 86 89
Eml: vdc@wre.kth.se

HEDIN, Allan
Swedish Nuclear Fuel and Waste Management Company (SKB)
Box 5864
S-102 40 Stockholm

Tel: +46 8 459 85 84
Fax: +46 8 661 57 19
Eml: allan.hedin@skb.se

LAAKSOHARJU, Marcus
GeoPoint
Frids hyddev. 15
S-191 36 Sollentuna

Tel: +46 8 92 77 14
Fax: +46 70 387 41 27
Eml: marcus@geopoint.se

LINDGREN, Georg
Dept. Civil and Env. Engineering
Royal Institute of Technology
AVAT, KTH, BV32
S-100 44 Stockholm

Tel: +46 8 790 87 25
Fax: +46 8 790 86 89
Eml: georg@aom.kth.se

LÖFGREN, Martin
Department of Chemical Engineering and Technology
Royal Institute of Technology
Kemisk Apparatteknik
Teknikringen 26
S-100 44 Stockholm

Tel: +46 8 790 82 36
Fax: +46 8 10 52 28
Eml: martinl@ket.kth.se

NERETNIEKS, Ivars
Royal Institute of Technology
Dept. of Chemical Engineering and Technology
S-100 44 Stockholm

Tel: +46 8 790 82 29
Fax: +46 8 10 52 28
Eml: niquel@ket.kth.se

OHLSSON, Yvonne
VBB VIAK
Box 34044
S-100 26 Stockholm

Tel: +46 8 695 62 85
Fax: +46 8 695 62 40
Eml: yvonne.ohlsson@sweco.se

SELROOS, Jan-Olof
Swedish Nuclear Fuel and Waste Management Company (SKB)
Box 5864
S-102 40 Stockholm

Tel: +46 8 459 84 25
Fax: +46 8 661 57 19
Eml: jan-olof.selroos@skb.se

SMELLIE, John
Conterra AB
Box 493
S-751 06 Uppsala

Tel: +46 18 12 32 41
Fax: +46 18 12 32 62
Eml: john.smellie@conterra.se

STRÖMBERG, Bo
Swedish Nuclear Power Inspectorate
SKI
S-106 58 Stockholm

Tel: +46 8 698 84 85
Fax: +46 8 661 90 86
Eml: bo.stromberg@ski.se

TULLBORG, Eva-Lena
Terralogica AB
Box 4140
S-443 14 Grabo

Tel: +46 302 42066
Fax: +46 302 42026
Eml: evalena@swipnet.se

WIDESTRAND, Henrik
Geosigma AB
Gymnasiegatan 6
S-442 34 Kungalv

Tel: +46 303 20 85 70
Fax: +46 303 20 85 79
Eml: henrik.widestrand@geosigma.se

WIKBERG, Peter
Swedish Nuclear Fuel and Waste Management Co. (SKB)
Box 5864
S-102 40 Stockholm

Tel: +46 8 459 85 63
Fax: +46 8 661 57 19
Eml: peter.wikberg@skb.se

WINBERG, Anders
Conterra AB
Ögärdesvägen 4
S-433 30 Partille

Tel: +46 31 44 32 90
Fax: +46 31 44 32 89
Eml: anders.winberg@conterra.se

SWITZERLAND

FRANK, Erik
HSK
Swiss Federal Nuclear Safety Inspectorate
CH-5232 Villigen-HSK

Tel: +41 56 310 39 45
Fax: +41 56 310 39 07
Eml: erik.frank@hsk.psi.ch

GAUTSCHI, Andreas
NAGRA
Hardstrasse 73
CH-5430 Wettingen

Tel: +41 56 437 12 38
Fax: +41 56 437 13 17
Eml: gautschi@nagra.ch

HADERMANN, Jörg
Paul Scherrer Institute
Waste Management Laboratory
CH-5232 Villigen PSI

Tel: +41 56 310 24 15
Fax: +41 56 310 28 21
Eml: joerg.hadermann@psi.ch

JAKOB, Andreas
Paul Scherrer Institute
OFLA/203
CH-5232 Villigen PSI

Tel: +41 56 310 24 20
Fax: +41 56 310 28 21
Eml: andreas.jakob@psi.ch

MAZUREK, Martin
Rock/Water Interaction Group
University of Bern
GGWW, Institutes of Geology
and of Mineralogy and Petrology
Baltzer-Str.1
CH-3012 Bern

Tel: +41 31 631 87 81
Fax: +41 31 631 48 43
Eml: mazurek@mpi.unibe.ch

UNITED KINGDOM

HEATH, Mike
Camborne School of Mines
University of Exeter
Pool, Redruth
Cornwall TR15 3SE

Tel: +44 01209 216647
Fax: +44 01209 216647
Eml: m.j.heath@exeter.ac.uk

HOOPER, Alan J.
Deputy Managing Director
United Kingdom Nirex Limited
Curie Avenue
Harwell, Didcot
Oxfordshire OX11 0RH

Tel: +44 1235 825 401
Fax: +44 1235 825 289
Eml: alan.hooper@nirex.co.uk

RANDALL, Matthew
British Nuclear Fuels plc
R&T
Rutherford House
Risley, Warrington, WA3 6AS

Tel: +44 1925 832922
Fax: +44 1925 833267
Eml: matthew.randall@bnfl.com

TRIVEDI, Divyesh
British Nuclear Fuels plc
R&T
Rutherford House
Risley, Warrington, WA3 6AS

Tel: +44 1925 833 405
Fax: +44 1925 832 922
Eml: dpt1@bnfl.com

UNITED STATES OF AMERICA

BRUSH, Laurence H.
Sandia National Laboratories
4100 National Parks Highway
Carlsbad, NM 88220

Tel: +1 505 234 0105
Fax: +1 505 234 0061
Eml: lhbrush@sandia.gov

BYRUM, Charles
U.S. Environmental Protection Agency
1445 Ross Avenue (6PD-N)
Dallas, TX 75202

Tel: +1 214 665 7555
Fax: +1 214 665 7263
Eml: byrum.charles@epa.gov

DAVIS, James A.
U.S. Geological Survey
M.S. 465
345 Middlefield Rd.
Menlo Park, CA 94025

Tel: +1 650 329 4484
Fax: +1 650 329 4327
Eml: jadavis@usgs.gov

HAGGERTY, Roy
Department of Geosciences
Oregon State University
104 Wilkinson Hall
Corvallis, OR 97331-5506

Tel: +1 541 737 1210
Fax: +1 541 737 1200
Eml: haggertr@geo.orst.edu

HONEYMAN, Bruce D.
Colorado School of Mines
Environmental Science and Engineering
Golden, CO 80401

Tel: +1 303 273 3420
Fax: +1 303 273 3413
Eml: honeyman@mines.edu

LINDEN, Ronald
U.S. DOE / Golder Associates, Inc.
1551 Hillshire Dr., Suite A
Las Vegas, NV 89134

Tel: +1 702 794 1404
Fax: +1 702 794 5040
Eml: ronald_linden@ymp.gov

MURPHY, William M.
California State University, Chico
Department of Geosciences
Chico, CA 95929-0205

Tel: +1 530 898 6269
Fax: +1 530 898 5234
Eml: wmurphy@csuchico.edu

SAGAR, Budhi
CNWRA-Southwest Research Institute
Post Office Drawer 28510
6220 Culebra Road
San Antonio, TX 78238

Tel: +1 210 522 5252
Fax: +1 210 522 5155
Eml: bsagar@swri.org

CONSULTANT TO OECD/NEA

SMITH, Paul
Safety Assessment Management Ltd.
20 Manor Place
West End
Edinburgh EH3 7DS

Tel: +44 131 226 6255
Fax: +44 131 226 1907
Eml: paul@sam-ltd.com

NEA SCIENTIFIC SECRETARIAT

BEAUHEIM, Richard
OECD Nuclear Energy Agency
Waste Management Division
Le Seine St-Germain
12, Boulevard des Îles
F-92130 Issy-les-Moulineaux
France

Tel: +33 1 45 24 10 47
Fax: +33 1 45 24 11 45
Eml: richard.beauheim@oecd.org

PESCATORE, Claudio
OECD Nuclear Energy Agency
Waste Management Division
Le Seine St-Germain
12, Boulevard des Îles
F-92130 Issy-les-Moulineaux
France

Tel: +33 1 45 24 10 48
Fax: +33 1 45 24 11 10
Eml: pescatore@nea.fr

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