

Using Thermodynamic Sorption Models for Guiding Radioelement Distribution Coefficient (K_d) Investigations

A Status Report



Radioactive Waste Management

**Using Thermodynamic Sorption Models
for Guiding Radioelement Distribution
Coefficient (K_d) Investigations**

A Status Report

NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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FOREWORD

Finding adequate solutions for ensuring the permanent, safe disposal of radioactive waste is a major preoccupation for all countries which make use of nuclear energy. At present, there is a world-wide consensus among technical experts that waste containing high levels of long half-life radionuclides can safely be disposed of in specifically engineered facilities located deep underground in an appropriate geological context. This concept includes siting a repository at a particular location in a geological formation selected for, *inter alia*, its capacity to act as a reliable, effective, long-term barrier to waste radionuclide (RN) movement towards the biosphere. The principal host formations under consideration at the present time are crystalline rock, clay, clayrock, tuff and salt.

Performance assessment (PA) studies are carried out to evaluate the overall capacity of a particular disposal site to confine waste and reduce radioactive releases to levels that are sufficiently low that they meet regulatory performance targets. Since the principal way in which radioactive elements might eventually reach the biosphere is by transport of dissolved RN species in groundwater, PA calculations must be able to estimate the rate of transfer of RN mass through each of the engineered and natural barriers of the repository and towards the biosphere. In order to be credible, PA calculations will need a clear method for selecting both the model and the corresponding parameter values to be used to account for each aspect's contribution to RN migration (i.e. within each barrier and for the entire range of conditions considered to be possible over the repository hasard time period).

It is well known that, for many radioelements, sorption reactions can lead to a reduction of the amount of radionuclides present in the solution phase. How best to take RN sorption reactions into account in PA models is the subject of this book.

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In October 1995, the NEA Performance Assessment Advisory Group decided to carry out a study to investigate the potential of mechanistic models for improving confidence in the representation of sorption in performance assessment. It proposed the creation of a Sorption Modelling Project, guided by a Sorption Forum with the following objectives:

1. to investigate how defensible sets of sorption data for PA can be developed and justified and what is the potential of mechanistic models for improving the confidence in these data;
2. to organise a workshop to gather new information and promote discussions with the scientific and waste management communities on the role of thermodynamic modelling in supporting selection of sorption data for PA;
3. to produce a comprehensive status report on these models.

The workshop was organised in Oxford in May 1997, with more than 50 participants from 14 countries, and included representatives of the PA community and both modellers and experimentalists in sorption research. In parallel with this activity, a comprehensive status report was commissioned to summarise the current knowledge in the field of sorption modelling.

Part 1 of this book, entitled “Performance Assessment Summary from the NEA Sorption Forum by Scott Altmann (BRGM), Jordi Bruno (QuantiSci) and Cherry Tweed (AEA Technology plc)”, is a summary that intends to fulfil objective 1 of the Sorption Forum by highlighting the main conclusions from the May 1997 Oxford Sorption Workshop and the Status Report.

Part 2 is the Status Report itself: “Using Thermodynamic Sorption Models for Guiding Radioelement Distribution Coefficient (Kd) Investigations for Performance Assessment – A Status Report by Scott Altmann (BRGM) and Jordi Bruno (QuantiSci)”. The purpose of this report is to demonstrate how a particular conceptual approach, *thermodynamic sorption models*, can serve as the framework for evaluating and predicting the contribution of sorption reactions to determining total radionuclide dissolved concentration. The report also includes a synthesis of the presentations and discussions at the Oxford Workshop, providing a review of the state of the art of sorption chemical modelling.

Summaries of the Workshop presentations are added for reference as Part 3: “International Meeting on Chemical Modelling of Sorption in the Field of Radioactive Waste Management, 6-8 May 1997, Oxford, UK – Summaries of Presentations”.

Considering that presentations at the Oxford workshop illustrated the advances that have been made in the field of sorption modelling, with many examples of the successful interpretation of sorption in natural samples, most participants agreed to launch a second phase of the Sorption Project. The Sorption Project, Phase II, is a benchmark exercise to interpret selected, well-characterised datasets for sorption in complex materials of interest to safety assessments of radioactive waste disposal systems, and to do so using several different modelling approaches applied at various organisations. This project was started in September 2000 with 12 organisations from 10 Member countries. Results of the Sorption Project, Phase II, will be published at the end of the exercise, probably at the beginning of 2002.

The opinions and conclusions expressed in this book are those of the authors only and do not necessarily reflect the views of the funding organisations or any OECD Member country.

ACKNOWLEDGEMENTS

The organisation of the “International Meeting on Chemical Modelling of Sorption in the Field of Radioactive Waste Management, 6-8 May 1997, Oxford, UK”, and the preparation of the Status Report and of the Summary have been jointly supported by the following organisations, in the framework of the NEA Sorption Modelling Project:

- ANDRA, France (National Radioactive Waste Management Agency).
- BNFL, United Kingdom (British Nuclear Fuels plc).
- ENRESA, Spain (National Agency for Radioactive Waste).
- IPSN, France (Institut de protection et de sûreté nucléaire).
- KAERI, Korea (Korea Atomic Energy Research Institute).
- NAGRA, Switzerland (National Co-operative for the Disposal of Radioactive Waste).
- NIREX, United Kingdom.
- ONDRAF/NIRAS, Belgium (National Organisation for Radioactive Waste and Enriched Fissile Materials).
- JNC, Japan (Nuclear Fuel Cycle Development Institute).
- POSIVA Oy, Finland.
- PSI, Switzerland (Paul Scherrer Institut).
- SKB, Sweden (Swedish Nuclear Fuel and Waste Management Company).
- SKI, Sweden (Swedish Nuclear Power Inspectorate); and
- RAWRA, Czech Republic (Radioactive Waste Repository Authority).

Furhermore, the US NRC (United States Nuclear Regulatory Commission) and the US DOE (United States Department of Energy) supported the project with in-kind contributions.

All these organisations are deeply thanked for their support and for their fruitful reviews and comments.

The NEA Secretariat wish to express its gratitude to the authors of this book: Scott Altmann (BRGM, now with ANDRA), as the main author of the Status Report, Jordi Bruno (QuantiSci) and Cherry Tweed (AEA Technology plc) who also agreed to chair the Sorption Forum during this first phase of the Sorption Project.

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PART 1

PERFORMANCE ASSESSMENT SUMMARY FROM THE NEA SORPTION FORUM

**Scott Altmann (BRGM, France), Jordi Bruno (QuantiSci, Spain)
and Cherry Tweed (AEA Technology plc, UK)**

Background and Objectives

In October 1995, the Performance Assessment Advisory Group (PAAG) decided to carry out a study to investigate the potential of mechanistic models for improving the confidence in the representation of sorption in Performance Assessment (PA). They proposed the creation of the NEA Sorption Forum with the following objectives:

1. to investigate how defensible sets of sorption data for PA can be developed and justified and what is the potential of mechanistic models for improving the confidence in these data;
2. to organise a workshop to gather new information and promote discussions with the scientific and waste management communities on the role of thermodynamic modelling in supporting selection of sorption data for PA;
3. to produce a comprehensive Status Report on these models.

The Sorption Forum held its inaugural meeting in September 1996 and organised a workshop in Oxford in May 1997. The workshop was attended by more than 50 participants from 14 countries and included representatives of the PA community and sorption research, both modellers and experimentalists. In parallel with this activity, a comprehensive status report was commissioned to summarise the current knowledge in the field of sorption modelling.

Purpose of this Summary

This summary intends to fulfil Objective 1 by highlighting the main conclusions from the NEA Sorption Workshop held in Oxford, May 1997, and the Status Report “*Using Thermodynamic Sorption Models for Guiding Radioelement Distribution Coefficient (Kd) Investigations for Performance Assessment*”. Summaries of the Workshop presentations are appended to this report for reference.

The Needs of Performance Assessment

At present, any Performance Assessment of a radwaste repository system, either deterministic or probabilistic, uses two main sets of chemical data:

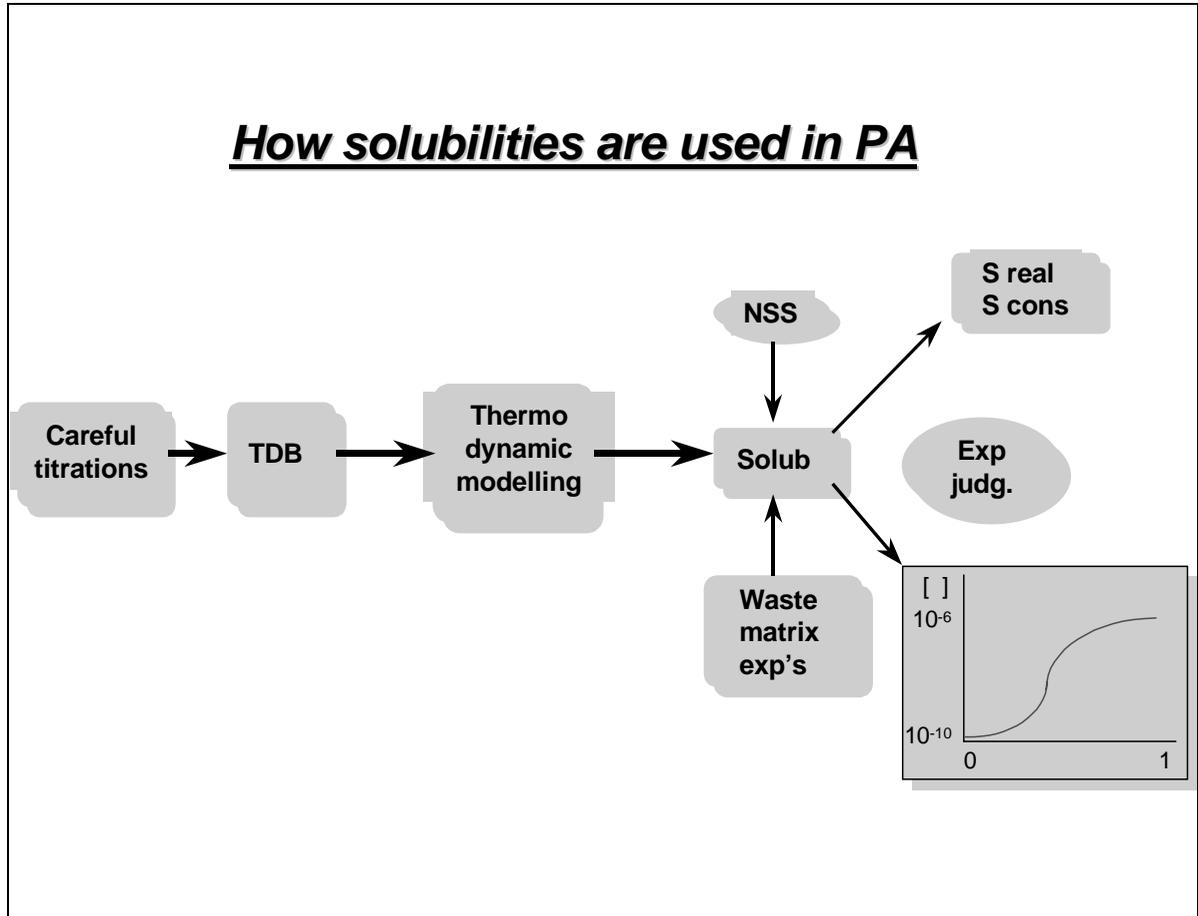
- Radionuclide solubilities to provide constraints on source term concentrations; and
- Radionuclide sorption coefficients to estimate radionuclide sorption in the various parts of the repository system (including the near field or engineered barrier). These are normally represented in the form of K_d or R_d parameters.

Other types of chemical information are used indirectly, e.g. to describe the geochemical evolution of the repository system under various scenarios. In addition, it is noted that several longer-timescale processes may also contribute to radionuclide retention over PA timescales, e.g. irreversible sorption and incorporation of radionuclide within the crystal structure of the “sorbing” mineral. The timescale of these processes is uncertain and therefore credit is not generally taken for these processes in PA. Therefore these processes were considered outside the scope of this review.

The various approaches used to estimate radionuclide solubilities and radionuclide K_d values are illustrated schematically in Figures 1a and 1b.

Figure 1a. **Schematic view of the process of deriving solubility values and estimates of the associated uncertainties for PA (Bruno, Oxford)**

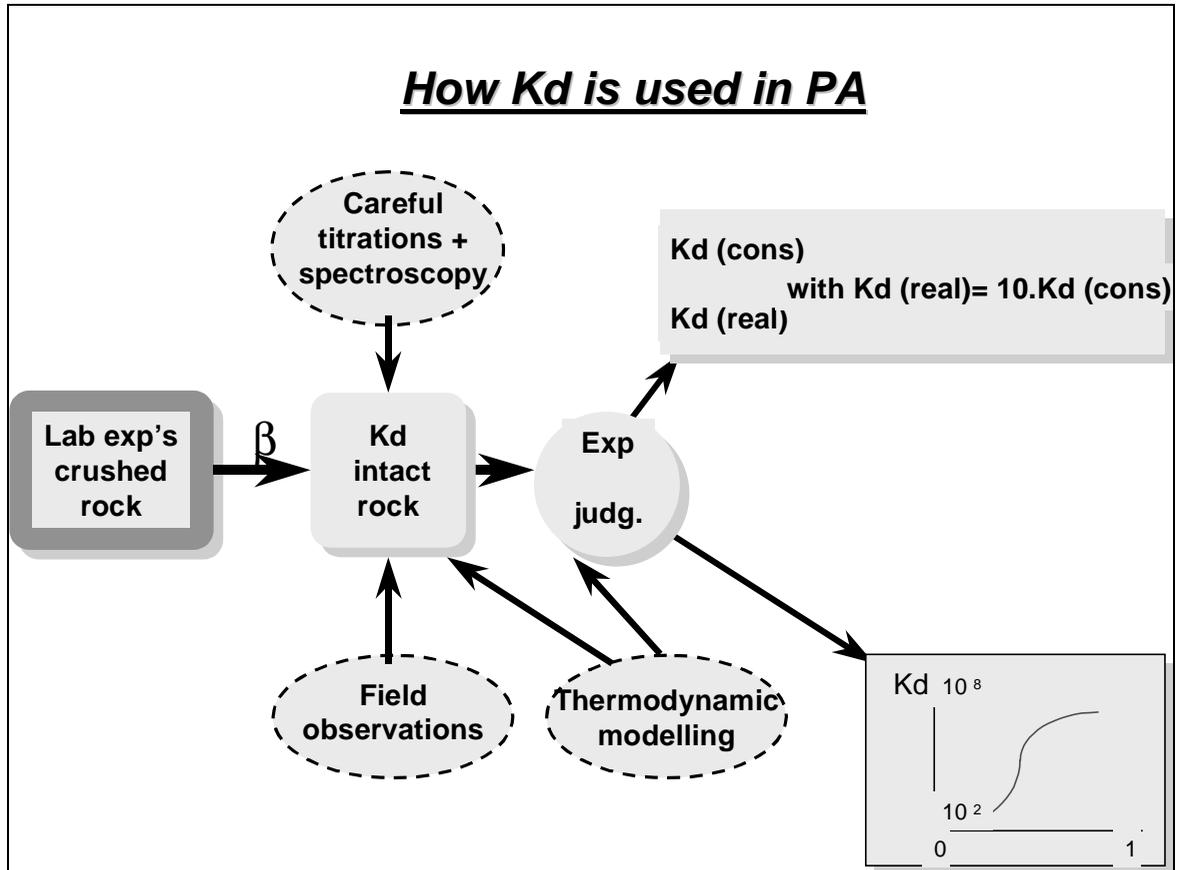
- TDB: Thermodynamic database
- NSS: Natural system studies
- S real: Solubility, realistic value
- S cons: Solubility, conservative value
- Graphic: Solubility probability function



The selection of radionuclide solubilities for PA exercises may draw support from waste matrix leaching experiments, laboratory solubility measurements and thermodynamic modelling. Information from relevant studies of natural systems, candidate sites, underground laboratories or natural analogues, is also used to some extent. Although the relative weights of laboratory data, field data and thermodynamic modelling may vary in the various programmes, chemical modelling is used throughout the process to support the selection of solubilities, as well as to estimate the associated uncertainties.

Figure 1b. Schematic view of the process of radionuclide K_d value selection and estimation of the associated uncertainties in PA (Bruno, Oxford)

K_d (cons): K_d , conservative value
 K_d (real): K_d , realistic value
 β : experimentally determined conversion factor
 Graphic: K_d probability function



The approach adopted for selecting solubility values can be contrasted with the estimation of radionuclide K_d values, which follows a more pragmatic pattern. As shown in Figure 1b, the most frequent approach is to base K_d values on data obtained at laboratory scale, normally with crushed materials. A correction procedure is then applied to upscale the K_d value to field conditions. In some cases, these empirical values are supported by surface chemical data and associated modelling but this is not universal.

The need for a modelling support for sorption data becomes greater as techniques for performance assessment of radioactive waste repositories become more advanced. The determination of the geochemical evolution of the entire repository system for the various time-dependent scenarios is often considered (particularly for time-dependent PA exercises). The variability of the geochemical composition of the system influences the sorption properties of the radionuclides along the migration path. Thermodynamic sorption models (TSMs) are able to integrate the geochemical variability of the system and its influence on the radionuclide sorption properties on a common framework. Therefore, these models have potential to support the selection of the values and estimated uncertainties of radionuclide K_d s.

The key parameters required to apply TSMs to radionuclide sorption, namely: flow wetted surface and detailed mineral characterisation (fracture fillings and coatings), are also needed for transport calculations in PA analyses. Most of the thermodynamic data required in a description of the surface interactions between the safety-relevant radionuclides and key mineral surfaces are considered to be available or estimable by applying chemical reasoning.

Advances in the Development and Application of Thermodynamic Sorption Models

In the last decade the main advances in the field of surface co-ordination chemistry can be grouped under three main areas:

- (i) development and application of unifying and consistent thermodynamic models for trace metal sorption onto metal oxides;
- (ii) development and application of thermodynamic models for radionuclide sorption onto bentonite type clays;
- (iii) application and testing of these models to interpret radionuclide sorption onto complex materials, even at field scale.

The main advances in each of these areas are summarised below. The numbers in parentheses refer to Presentation Numbers from the Oxford Workshop where the advance has been illustrated.

Sorption onto Metal Oxides

There have been two major advances in this field. The first was the development of an approach which allows the estimation of intrinsic surface complexation constants for cations where there are relatively few experimental data, for example, NpO_2^{2+} and UO_2^{2+} . The method uses Linear Free Energy Relationships (LFER) based on thermodynamic data for other similar cations. The same applies for other potentially important anions like SeO_4^{2-} , SeO_3^{2-} and MoO_4^{2-} . This approach has been successfully used to calculate the degree of U(VI) sorption on to Fe(III) oxyhydroxides at the Koongarra analogue site (3.6, 4.3) and has been applied in an assessment of drinking water contamination by Se in California.

The second significant advance was the publication of the book by Dzombak and Morel (1990): *Surface Complexation Modelling. Hydrous Ferric Oxide*. This publication defines a unified, consistent approach to quantify the surface chemical properties of hydrous ferric oxide, (HFO). HFO forms a surface phase in many geochemical systems considered in radioactive waste disposal.

Sorption onto Clays

Sorption of radionuclides onto clay is of importance to PA for three main reasons:

- (i) bentonite is the proposed backfill in several repository designs;
- (ii) clay formations are potential host rock for the disposal concepts in many countries;
- (iii) clay minerals are common as fracture infills in many crystalline host rock formations under consideration as potential repository sites.

A significant advance has been the recognition that the K_d behaviour of a given clay mineral results from the combined effect of the two broad classes of sorption site components: cation exchange (CE) sites and surface complexation (SC) sites. This conceptualisation has been used with varying degrees of success in many studies to construct TSMs for describing and predicting radionuclide

sorption for clay mineral-containing solids (most frequently, bentonite or montmorillonite). A number of examples are found in Marmier *et al.* (4.16) (Cs^+ , Ni^{2+} , Yb^{3+} on to kaolinite and montmorillonite). Bond *et al.* (4.7) also used a similar approach to model pH-dependent sorption of U(VI), Pu and Th onto muscovite and chlorite under oxic conditions. Baeyens and Bradbury (3.3) have carried out a very thorough study of Ni and Zn sorption on SWy-1 montmorillonite. Wang *et al.* (4.16) used a two site (ion exchange and pH dependent surface complexation) TSM to interpret experimental data for Eu^{3+} sorption onto illite, one of the most abundant minerals in Boom clay. Ochs and Wanner (4.15) have modelled bentonite sorption of Cs^+ , Sr^{2+} and Ra^{2+} using cation exchange reactions on a single IE site. Reactions with a second protolytic SC “edge” site (with electrostatic activity correction) were added in order to model sorption of Pb^{2+} .

Application to Natural Systems

The third milestone has been the demonstration of the application of thermodynamic sorption models to describe (and possibly predict) radionuclide sorption onto complex natural materials in both the laboratory and the field. The wide variety of the systems studied provides evidence of the general applicability of the approach, as demonstrated by the summary given below of the cases presented at the Oxford workshop.

- a) Application to complex solids, either by assuming that the mineral surface is composed of a mixture of several pure phases, or by assuming that the mineral sorption properties are dominated by oxyhydroxide and ion exchange sites, e.g. adsorption of U(VI) released from mine tailings onto phyllic materials (4.16), Ni(II) sorption onto St Bee’s sandstone (4.8), U(VI) sorption onto Koongarra materials (3.6, 4.3), and Cd(II) sorption onto a mixture of TiO_2 and Fe_2O_3 colloids (4.1).
- b) Application of a TSM approach to trace element migration over significant (5 km) distances in a groundwater system (3.8). The results of the *a priori* simulation of Zn(II) transport in the aquifer over a 54 year period showed encouraging agreement with the main observed features of the Zn contamination of the aquifer.

Conclusions and Recommendations

The significant advances in the field of thermodynamic modelling of sorption processes were clearly demonstrated by the presentations at the Workshop and by other recent literature publications. However, it was acknowledged that there is still some way to go in advancing sorption modelling to the level of solubility modelling. For this reason, the consensus from the experts present at the Oxford Workshop, as well as the information gathered in the Status Report, indicate that the experimental determination of radionuclide K_d will remain the main source to estimate sorption properties throughout the repository system and that this will continue for a timescale of at least the next five years. However, it was recognised that much confidence and transparency can be gained by using chemical reasoning and thermodynamic modelling to guide and support the experimental determinations in a similar fashion to the use of equilibrium calculations in radionuclide solubility estimations. This potential is not always recognised by those selecting parameters for PA.

Both the theoretical developments as well as the application cases, as presented at the Oxford Workshop, indicate the increasing scientific maturity of the field, as well as the possibilities of application of TSM to radionuclide sorption for PA purposes. There are significant areas of agreement in the types of TSM now being applied:

1. All the models describe the sorption in terms of Chemical Thermodynamics;

2. All use mass-action laws to describe the interaction between the solution species and the surface groups.

However, there is, at present, no clear consensus about the detail of a unified model that would integrate the sorption data in a self-consistent manner.

We make the following recommendations to the radwaste community from the Sorption Forum:

- a wider recognition of the value of TSM in supporting the selection of K_d values;
- a dedicated effort from the Radwaste Community to undertake a critical evaluation of the merits of the various sorption modelling approaches as the first step towards adopting a common and self-consistent TSM approach;
- rationalisation of the large amount of K_d data available in the various national programmes to identify similarities, differences and trends and so provide a summary of available information on sorption data.

PART 2

USING THERMODYNAMIC SORPTION MODELS FOR GUIDING RADIOELEMENT DISTRIBUTION COEFFICIENT (KD) INVESTIGATIONS FOR PERFORMANCE ASSESSMENT – A STATUS REPORT

Scott Altmann (BRGM, France) and Jordi Bruno (QuantiSci, Spain)

FOREWORD

In October 1991, a Workshop organised by NEA was held in Interlaken (Switzerland) concerning the Safety Assessment perspective on Sorption modelling. In this Workshop the potential for supporting sorption parameters in Performance Assessment (Kd) by mechanistic models was identified. The main conclusions of this Workshop were stated in a consensus position paper and were as follows:

- Sorption was identified as a key process contributing to repository safety.
- Sorption was defined as the uptake of a nuclide on a solid as a function of nuclide concentration in the aqueous phase, depending on a range of chemical conditions: master variables such as pH and Eh, radionuclide concentration and major ion composition, as well as apparently site specific parameters like the properties of the available reacting surfaces. The careful distinction between sorption and precipitation in PA models was also pointed out.
- The limitations of actual (91) sorption data bases were identified.
- The lack of sufficient justification of sorption data used in Performance Assessment was identified as a key problem. Quality control of these data in terms of peer review of selected parameters was judged unsatisfactory at that time.
- The heterogeneity of the reacting surfaces was identified as one of the key obstacles to generalised sorption models and site specific developments were recommended.
- Some of the main uncertainties related to sorption modelling were identified, such as definition of the redox condition, the effects of colloids and microbes and more importantly, the extrapolation of laboratory data to site conditions. A recommendation was made to reduce this uncertainty whenever possible.
- It was identified that the development of sorption databases would rely (ideally) to some extent on a mechanistic understanding, particularly in relating the changes in sorption characteristic with the evolving geochemistry of the system. The mechanistically supported models would allow the transportability (from lab to site) and predictability (for the evolving site) of sorption parameters. Therefore, the development of mechanistic models for sorption was strongly encouraged.
- It was stated that laboratory determination of key sorption parameters will always be required, in spite of future developments on mechanistic models. The different experimental approaches were discussed and the difficulties associated with these determinations were stated.
- Expert judgement was identified as being needed to complement laboratory determination and model development.
- NEA was identified as the general depository of sorption documentation as a means to ensure divulgence of the reports published in the various concerned laboratories. The Sorption Data Base (SDB) being the natural recipient of this information.

- The necessity and value of periodic inter-calibration exercises as well as exchange meetings were identified and encouraged. The role of NEA as co-ordinator of these activities was pointed out.

Following the recommendations of the Interlaken meeting, a small group of experts convened at Stanford University in April 1993. The main objective of this meeting was to debate the applicability of Surface Complexation Models (SCM) to serve as a framework for:

- defining experimental protocols for quantifying radionuclide sorption,
- interpreting currently available experimental data,
- organising information in a sorption database.

The main recommendations from this group of experts were:

- to undertake a collaborative effort to demonstrate the applicability of SCM by determining and interpreting the interactions between 2-3 critical radionuclides and 2-3 model surfaces.
- to develop and demonstrate the use of techniques to measure critical reacting surface characteristics to be applied in pertinent SCM.
- the establishment of the critical parameters required when applying SCM to radionuclide sorption data: set of components and species, associated thermodynamic data base, convention for surface activity corrections.
- to develop a non-electrostatic double layer data base for a series of reference solids (pure oxides, clays)
- to establish regular meetings (general or topical) to convey the various researchers active in applying SCM to natural system.

The main conclusion of the NEA resulting from the various recommendations from the Stanford meeting was that, because the experiences from the application of SCM in Natural Systems are promising but scarce, the main priority should be the establishment of a collaborative demonstration programme.

In October 1995, the Performance Assessment Advisory Group (PAAG) decided to start a study to investigate the potential of mechanistic models for improving the confidence in the representation of sorption in PA. They proposed the creation of a NEA Sorption Forum with the following objectives:

- to investigate how defensible sets of sorption data for PA can be developed and justified and what is the potential of mechanistic models for improving the confidence in these data;
- to organise a workshop to gather new information and promote discussions with the scientific and waste management communities on the role of thermodynamic modelling in supporting selection of sorption data for PA;
- to produce a comprehensive Status Report on these models.

The Sorption Forum held its inaugural meeting in September 1996 and organised a workshop in Oxford in May 1997. The workshop was attended by more than 50 participants from 14 countries and included representatives of both the PA community and sorption research, both modellers and experimentalists. In parallel with this activity, a comprehensive status report was commissioned to summarise the current knowledge in the field of sorption modelling.

The topics covered in the Oxford workshop (hereafter referred to as “Oxford”) were:

- the demonstration of the usefulness of sorption chemical models to performance assessment with examples to illustrate the success of the approach.
- a review of practical approaches to sorption chemical modelling, identifying key questions facing experimentalists and modellers.
- an overview of what has been done to date in the use of mechanistic chemical models to understand and model trace element retardation in Natural Systems.

The meeting was attended by participants from 13 countries covering a wide range of scientific expertise with representation from the major Nuclear Waste Management national organisations, as well as the NEA. *The programme of the meeting is given in Part 3.*

This report is in part a synthesis of the outcome of the presentations and discussions from the Workshop, providing a review of the state of the art of sorption chemical modelling.

1. Introduction

Finding adequate solutions for insuring the permanent, safe disposal of radioactive wastes (Radwaste) is a major preoccupation for all countries exploiting the benefits of nuclear energy. At present, there is a world-wide consensus that the most problematic Radwaste, high-level waste and long-lived intermediate level wastes, containing high levels of long half-life radionuclides, can best be disposed of in specifically engineered facilities located deep underground in an appropriate geological context. The disposal concept adopted in most international designs is a “multi-barrier” concept where the components of the engineered and natural system provide successive barriers to radionuclide release. This concept includes siting a repository facility at a particular location in a geologic formation selected for, *inter alia*, its capacity to act as a reliable, effective, long-term barrier to waste radionuclide (RN) movement towards the biosphere. In particular, since the principal way that radioactive elements might eventually reach the biosphere is by transport of dissolved RN species in groundwater, the host formation would ideally have characteristics insuring (i) a low rate of groundwater movement between the repository and the biosphere and (ii) delay, and spread (retardation) over time, of radionuclide migration towards host formation interfaces with transport pathways (generally over- or underlying aquifers) leading to the biosphere¹. The principal host formations under consideration at the present time are crystalline rock, clay and clayrock, tuff, and salt.

Performance Assessment (PA) studies are carried out to evaluate the overall capacity of a particular disposal site concept (repository and geological context) to confine Radwaste and reduce radioactive releases to levels that are sufficiently low that they meet regulatory performance targets in this respect. While there are presently several indicators being used in the safety assessment of Radioactive Waste Repositories, the principal information sought during a PA study is an estimation of the increase in radionuclide input to individuals and/or groups, presumed to be present at selected locations in the biosphere, resulting from the potential contribution from repository wastes. This input can only be calculated if it is possible to estimate the total amount of each radionuclide present at these locations as a function of time. To do this, PA calculations must be able to estimate the rate of transfer of RN mass through each of the engineered and natural barriers of the repository and towards the biosphere. For RN migrating as dissolved species in barrier groundwater, RN mass transfer through each barrier will depend (i) on the total RN concentration in barrier groundwater and (ii) on the nature and intensity of the physical phenomena governing RN transport through the barrier (diffusion, convection-dispersion, advection,...). In order to be credible, PA calculations will therefore need a clear method for selecting both the model, and the corresponding parameter values, to be used to account for the contribution of each of these aspects to RN migration, this within each barrier and for the entire range of conditions considered to be possible over the repository hazard time period.

It is well known that, for many radioelements, various chemical processes, in particular solubility limitation and **sorption** reactions, can lead to a reduction of the amount of radionuclide present in the solution phase. [Note that here the term “sorption” will be used to encompass both “surface complexation” and “ion exchange” representations of reactions with solids (see Chapter 3)].

1. The host formation also serves to protect the repository from changes in its hydrogeological boundary conditions caused by potential natural events (seismic, glaciation, desertification, etc.).

PA models generally attempt to account for the effect of both types of reactions. For example, the effect of solubility limitations on RN dissolved concentration is imposed by equilibrium with one or more specific RN-containing pure mineral phases. The solubility limitation of a certain solid is represented by a constant, the *thermodynamic solubility product*, the value of which, as well as the associated uncertainty, can generally be estimated with sufficient accuracy based on the results of appropriate experimental programs. In theory, once determined and validated a solubility product can be incorporated in a thermodynamic data base to estimate a solubility for any geological and chemical context. The use of these databases in PA varies from country to country. In some cases thermodynamic models of solubility are used directly to generate input data for PA. In other countries, the PA input data are based mainly on direct experimental measurement and the role of models is to assist in the interpretation of laboratory experimental data, to provide predictions of chemical aspects of radioelement behaviour under chemical conditions for which direct experimental data are unavailable and to provide support for the assumptions made in performance assessment calculations. This can be contrasted with the treatment of RN sorption. While there are certain similarities (cf. Figure 1), such a direct approach is generally not possible when studying the effect of RN sorption reactions on complex geological materials on RN dissolved concentration, and the results rarely if ever lead to universally applicable constants². How best to take RN sorption reactions into account in PA models is the subject of this document.

The purpose of the following chapters is to demonstrate how a particular conceptual approach, *thermodynamic sorption models*, can serve as the framework for evaluating and predicting the contribution of sorption reactions to determining total RN dissolved concentration. Since PA models generally use a so-called distribution coefficient, or K_d ³, to represent the effects of sorption, the objective here is to show how *Thermodynamic Sorption Models (TSM)* can aid PA in:

- defining migration field regions for use in PA models;
- estimating the most appropriate K_d value (or K_d model) for each region,
- deciding when the K_d value (or model) for a region should be changed to a new value (or when region limits should be redefined); and
- reducing the uncertainty associated with K_d value estimates by providing support for expert judgement determination of RN K_d values.

In focusing only on sorption phenomena, we are implicitly excluding consideration of other chemical processes (precipitation and co-precipitation, RN oxidation-reduction on solids, etc.) which may contribute, or under certain circumstances even dominate, RN retardation in certain cases. We are also obviously excluding the effect of purely physical processes such as matrix diffusion on RN retardation. The distinction between these processes, at least at the conceptual level, is essential if we are to make progress in reducing parameter uncertainty through improved understanding of underlying mechanisms. Therein, as we hope to clearly show, lies the principal advantage of a TSM-based approach; it is potentially capable of conceptually integrating the combined effect of all chemical processes, including sorption, within the thermodynamic framework. Sorption reactions are treated on a more-or-less equal footing along with all other reactions determining solution speciation and solid phase composition of natural “geochemical” and radioactive waste derived elements.

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2. Universal in the sense of being independent of the chemical model used for the interpretation of the experimental data.
 3. K_d is simply a normalised ratio describing the distribution of the total RN mass, present in a given migration field region (volume), between solid phase sorbed species and dissolved species. See annexe 1 for a more complete definition.

The discussion in the sections that follow relates principally to the treatment of sorption in the host rock formations surrounding a deep underground radioactive waste repository i.e. to sorption in the geosphere. Many of the principals described are equally applicable to the treatment of sorption onto components of the engineered system of the repository. Materials used in the engineered systems can include natural or engineered clay and cement.

It is important to point out that this separation of processes for study, in particular chemical reactions from mass transfer, in no way excludes their later “re-coupling”; the simultaneous consideration of both types of phenomena, whether experimentally or mathematically, remains the ultimate means of validating our understanding of the processes and critical parameters governing RN migration.

2. PA Requirements for Kd Values

2.1 Kd measurements and databases

Organisations responsible for carrying out PA calculations rely on a number of different sources of information when choosing the Kd value to be used for a particular RN in a given migration field region, the primary one being laboratory measurements of Kd values for radionuclide (or analogues) sorption on repository concept relevant solid materials in contact with solutions of varying composition. For practical purposes, these measurements are generally made directly in “batch” reactors (i.e. closed, completely mixed experimental systems) containing a known mass of solid material, a known volume of solution and a known total amount of radionuclide. Batch Kd values are frequently validated or supplemented, albeit indirectly, by interpretation of changes in the rate of RN mass transfer, relative to a non-sorbing tracer, in convection or diffusion experimental configurations. In certain cases mass transfer measurements constitute the principal source of Kd (actually retardation factor data: see Annex 1). The determination of the performance characteristics of the Boom clay formation is an excellent example (see Chapter 5). In addition, Kd values are accompanied by a variety of site specific supporting information regarding *in situ* groundwater composition, matrix and surface mineral phases, porosities and permeabilities, specific surface areas, etc.

The Kd measurement programme for any given repository site yields a set of site-specific Kd values (often known as a Kd database) which is the basis for deciding on the Kd values and uncertainty to be used as input to PA simulations. For various reasons, one of which being the search for reasonable reductions in the complexity of PA codes in order to allow repetitive modelling of larger, more complex systems over long periods of time, PA will generally prefer to use a single, constant Kd value for a given RN in each migration field region. This choice can be defended if it can be shown that either:

- the Kd value for a given RN is, in fact, relatively insensitive to migration field composition, an example being the “conservative” use of zero Kd values for RN present that may be predominantly in anionic forms ($^{36}\text{Cl}^-$, $^{99}\text{TcO}_4^-$, $^{79}\text{SeO}_4^{2-}$, ...), or;
- the groundwater and solid phase composition of the migration field region do not change significantly over the PA time period. This could be reasonable for trace RN migration in the geological host formation, outside the zone perturbed either by the repository or by climatic or geological events.

When either (or both) of these conditions can be shown to be met for a particular RN, PA requirements for Kd can be satisfied by direct experimental measurements under conditions as close as possible to those existing *in situ* (i.e. no chemical sorption model is needed for predicting Kd values). In this case, PA experts must decide how the measurements are to be made and/or which existing Kd values are to be used, and how Kd values obtained in the laboratory are to be scaled to *in situ* conditions.

In most cases however, a K_d measurement programme reveals significant variations in the K_d values obtained for samples taken from a given migration field region. In particular, three commonly observed results combine to make K_d selection particularly difficult and ambiguous:

- sorption observed to be kinetically slow, non-linear and partially irreversible;
- for a single solid material sample, K_d values measured for a given RN often vary significantly depending on the chemical composition of the solution phase. Figure 2 (Altmann and Chupeau, 1997) for example shows how the K_d value for trace Ni sorption on a sandy-clay aquifer material can vary as a function of pH and total Ca⁺⁺ concentration;
- for a given solution composition, measured K_d values can vary depending on how the sample is prepared (“intact” vs. ground, particle size distribution, separation of constituent solid phases, etc.), on how the measurement is made (length of equilibration time, solid-solution separation procedure,...), on where the sample was obtained within a given migration field region (spatial heterogeneity at various scales), etc.

As we shall see in Chapter 3, these results are not at all surprising given the types of chemical reactions responsible for RN sorption, the complexity of the chemical composition of natural material surfaces, the variety of solution reactions which can modify RN speciation, and the spatial variability of the chemical composition (mineral phases, groundwater) and physical characteristics of most geological systems. The important distinction that needs to be made regarding these different sources of K_d uncertainty is that, while certain sources of uncertainty cannot be reduced, i.e. spatial heterogeneity in natural system physical-chemical parameters, that due to other sources (solution composition, solid material mineral composition, particle dimensions, etc.) *can be potentially reduced by use of appropriate phenomenological models*. For example, when K_d is shown to depend on solution composition, a PA decision is required regarding the value and uncertainty of the K_d to be used for a particular migration field region over a given period of time. This decision can be significantly aided if a model exists that is capable of providing reasonable predictions of both the chemical composition (including uncertainty) of the region during this same time frame and the variation in RN K_d as a function of system composition.

It is important to note that K_d data obtained on site-specific material is not the only information available for making PA decisions. For example, an enormous amount of effort has been devoted over the last 2 decades to measuring K_d values for a large number of elements on a variety of engineered and natural materials pertinent to waste disposal. These data are contained in a variety of reports and databases (see reviews by McKinley and Scholtis, 1991; Higgo, 1988, Stenhouse, 1996), and critically selected values can be exploited, at least for comparative purposes, when reviewing site specific data. Much effort has also been devoted to improving our knowledge of radioelement dissolved phase chemistry as reflected in the extension and improved quality of databases of thermodynamic formation constants for solution species (Grenthe *et al.*, 1992; Silva *et al.*, 1995). Finally, there has been much progress in our understanding of the mechanisms and thermodynamic characteristics of adsorption and ion exchange reactions between dissolved species of both radioactive and non-radioactive elements and a variety of PA relevant natural and synthetic minerals (see Chapters 4 and 5).

2.2 K_d selection for PA

All K_d decision or review efforts have the same challenge and the same goal: based on a relatively small amount of site-specific K_d information (compared to migration field dimensions and physical-chemical complexity) obtained under conditions differing more or less significantly from those existing *in situ*, to select a set of K_d values and uncertainties representing as realistically as

possible the contribution of RN solid-solution partitioning reactions to RN mass transfer toward the biosphere. These decisions are made in different fashions by different PA organisations. For example, United Kingdom Nirex Limited, the organisation responsible for providing and managing facilities for the safe disposal of intermediate and certain low-level wastes (ILW and LLW), uses a structured elicitation procedure in which a panel of experts decides on the probability density functions used to represent Kd value uncertainty based on the site-specific Kd database and on a variety of supporting information including RN solution speciation, surface spectroscopic information, sorption behaviour on appropriate pure minerals, the results of Kd measurements on similar solid materials at other sites, etc. In some cases, a second expert elicitation is then carried out to select the correction factors to be used for scaling from laboratory Kd to *in situ* Kd values. For some materials, such as cement and some clays, this second correction factor can be set to 1.

A similar process has been used within the SKB SR'97 PA exercise, where the initially selected Kd values are reviewed by internal and external experts and the uncertainties in Kd parameters are assessed by independent teams.

Another example is the multi-step procedure used by the HSK, the Swiss Federal Nuclear Safety Inspectorate responsible for reviewing waste repository licence applications, for judging whether the Kd values used in PA calculations are “reasonable”. The principle criteria cited by Wanner (Oxford) include:

- Plausibility of selected values: Correlation with surface parameters (surface area, cation exchange capacity,)? Do elements and solids having similar characteristics give coherent Kd values?
- Transparency and correctness of data selection procedure: What has been done and why? Are solid and aqueous phases, redox conditions, etc. representative for the safety assessment case in question?
- Consistency with the state of the art: Has the relevant literature been considered? Has new evidence been reported from recent experiments and models?
- Consistency with transport parameters: Are the selected Kd values and transport parameters (e.g. diffusion coefficients) compatible with *in situ* data and migration experiments?
- Treatment of uncertainties: How have uncertainties been assessed, and how have they been considered in the safety analysis, for example, how have batch Kd values been “scaled” for *in situ* conditions?

In many cases, faced with a perceived lack of viable alternatives, PA has dealt with the large uncertainties in measured Kd values by choosing “conservative” values for PA model input parameters, values (and associated uncertainty function) shifted away from selected “realistic” values in the sense favouring RN mass transfer (i.e. maximising the calculated radionuclide mobility). For example, Kd values used in PA codes frequently differ by factors of 10 or more from the realistic value. While this is the PA equivalent of the design safety factors used in all fields of engineering, there is an important difference in repository PA: the uncertainties in the Kd and other parameters governing RN mass transfer through site geological formations can dwarf even an order-of-magnitude safety factor⁴. This being the case, and since any unreasonable increase in the safety factor can lead to unwarranted increased cost or rejection of a repository concept, building confidence in PA calculations

4. For example, in the Nirex '95 assessment, there were up to 4 orders of magnitude between the 10% and 90% confidence levels for the Kd values used, combined with 2 orders of magnitude between the 10% and 90% for the laboratory to-*in situ* correction factor.

becomes synonymous with using every practicable scientific means to reduce the uncertainty associated with *in situ* Kd values. As mentioned previously, thermodynamic sorption models offer this possibility.

All these illustrations demonstrate the important point there are two uncertainties to consider in selecting sorption values for PA:

- the uncertainty in the chemistry of the sorption process;
- the uncertainty in the scaling from Kd measurements, often made in the laboratory or in field experiments over scales of a few meters, to values representative of a rock formation.

This report seeks to demonstrate that TSM is a useful tool for addressing the first of these uncertainties. The importance of scaling is acknowledged here but will not be discussed further.

2.3 PA questions for proponents of thermodynamic sorption models approaches to Kd

Up until now, the PA community has relied only marginally on thermodynamic sorption models (TSM) based approaches for experimentally measuring and exploiting Kd data. There are various reasons for this, the more important being:

- PA began needing and collecting Kd values on natural materials during the same period as the research required to provide TSM sorption models with their theoretical and experimental underpinnings was being carried out. Therefore the theoretical framework was not developed at the start of the PA programme and the added value of the theoretical understanding has not yet been demonstrated. In contrast, the understanding of RN solubility was more advanced and the theoretical framework has been included in deriving or justifying PA inputs since the early days of research into radioactive waste disposal. Thus the improved understanding has been automatically carried through into PA.
- The chemical composition (and physical structure) of the solid materials (and groundwater solutions) present in geological repository migration field regions is generally much more complex than the composition and structure of the solid phases (and contacting solutions) which have been used for verifying and validating TSM models of sorption phenomena. i.e. lack of clear demonstrations of how to move TSM out of the laboratory and into real systems has made PA wary of using TSM.

While sorption is an important, and in some cases dominant, retarding process for certain radionuclides, it is only one of many phenomena and factors (including existing formation spatial heterogeneity and uncertainty in predicting future composition) contributing to the rate and uncertainty of RN mass transfer. At some point, further improvement in our ability to provide more realistic and more certain *in situ* Kd values for a particular migration field region will cease having a significant effect on the result of the overall safety calculation. i.e. PA needs to decide how much to invest in studying RN sorption, and when enough is enough.

These “realities” and what has been said before concerning the PA process lead more or less directly to the following key questions which should be answered, at least in part and hopefully in the form of an international consensus of TSM experts, to demonstrate to performance assessment community that TSM-based approaches to selecting or justifying *in situ* Kd values can provide added value in the PA process.

- What is a “TSM-based approach to determining *in situ* Kd values”?
 - Is there a consensus on the essential features of such an approach? If not, can such a consensus be reached? Why, or why not?
- Can a general TSM-based procedure for deriving Kd values be recommended? If so, what should be done and in what priority?
 - Are different approaches needed for different types of migration field systems (engineered vs. geological regions, crystalline vs. sedimentary host formations)?
 - Where options exist in the procedure, can guidelines be offered for selection?
- What is the demonstrated “state of the art” of TSM-based approaches for measuring, modelling and predicting Kd values for relevant rock/water systems?
 - For modelling and predicting retardation factors in laboratory advection and diffusion experimental systems?
 - For interpreting and predicting the migration of sorbing elements in natural systems? Controlled and uncontrolled “tracer” experiments, natural analogues?
- What is the consensus “best estimate” of the real potential, and likely limits, of TSM for offering support for the PA process, taking the Radwaste disposal time-scale into consideration?
 - What can be done **now** to improve confidence in the current PA process?
 - What additional capabilities are likely to be available in 5 years? in 10 to 30 years?
 - These questions will probably have different answers for each of the principal types of geological host formations under consideration (crystalline rock, sedimentary, salt, ...).
- What are specific, realistic goals for TSM-based sorption research in support of PA?
 - What research should be funded in priority in order to obtain specific results in 3-5 years? Can we propose a collaborative programme corresponding to these priorities.
 - What are the priorities for 10 years? 20 years?
 - We hope to respond at least partially to each of these questions in the following chapters.

3. Thermodynamic Sorption Models

The use of thermodynamic models for understanding and supporting predictions of the composition of chemical systems is well established in the PA field. For example, such models are used for calculating radioelement solubilities and solution speciation, for estimating the composition of waters in equilibrium with engineered barrier materials (vitrified wastes, cements, bentonite...), for evaluating the chemical coherence of information regarding host formation groundwater composition and solid phase minerals, ... Thermodynamic *sorption* models are simply the extension of these “classical” models to encompass certain types of reactions between dissolved species and the surfaces of solid materials. The purpose here is to give a rapid overview of how sorption reactions are included within a thermodynamic sorption modelling framework. There are two major advantages of this for PA Kd-determination programmes:

- Kd studies involving natural materials can be guided by reasoning (expert judgement) based on known chemical and physical principles, and can benefit from information accumulated on simpler, but analogous, systems.
- information and understanding of RN sorption on a given migration field material can be directly incorporated into the same chemical modelling framework used for describing and predicting migration field **groundwater and solid phase geochemistry** and **radionuclide solution speciation and precipitation-dissolution**. This means that a single Thermodynamic Sorption Model may be used to predict variations in RN Kd values for differing migration field groundwater and solid surface compositions.

3.1 Key TSM concepts

All thermodynamic models, TSM included, are based on the assumption that the system reaches and remains at chemical equilibrium, i.e. that all reactions are rapid and reversible, and all thermodynamic models are built around, and require input information concerning, the same fundamental parameters, which are:

1. the **chemical nature** and **total amount** of the different chemical *components* which are present in a given system. Components are a set of fundamental chemical building blocks which can be combined to form all other chemical molecules, or species, which can exist in the system. Components are the basis for defining the total amount of matter present in a closed system, expressed in terms of a total number of *moles* of each component which is present. They therefore serve as a limit on the total amount of all species which contain that component and, therefore, on the chemical composition of the system: i.e. the **Mass (or mole) Balance** requirement.
2. the **component makeup** (stoichiometry) and **thermodynamic stability constant**, K, for each of the other molecules, or *species*, which can exist in the system (in addition to free components). This information constitutes the **Mass Action Law (MAL)** for each species.
3. the model to be used for calculating the **thermodynamic activity coefficients** of dissolved species and components for non-dilute chemical systems. Commonly employed **activity correction models** are Debye-Huckel, Davies, Pitzer, etc.

The component set and species MALs for a given system, taken together, constitute the **Thermodynamic Data Base (TDB)** needed as input, along with the total component concentrations, for calculating the needed output information, i.e. the concentrations of each of the various chemical species (and components) a system contains, at thermodynamic equilibrium, in particular, RN solubility and solution speciation. These calculations generally require specialised computer codes for all but the most simple systems.

Extensive research over the last several decades in the field of “surface chemistry” has clearly shown that the chemical interactions between dissolved radionuclides and natural solid surfaces, i.e. sorption reactions, can be conceptually understood by adapting the same fundamental concepts governing reactions between dissolved molecules. Particularly important was the pioneering work by aquatic chemists P.W. Schindler and W. Stumm, who transferred well established principles for the proton and metal co-ordination chemistry in solution to explain the specific interactions at the solid-water interface, thereby providing a rigorous quantitative blending of specific and non-specific interactions to describe the sorption of ions onto oxides. Many other scientists have contributed to building and reinforcing what has become the paradigm underlying our understanding of sorption phenomena; i.e. thermodynamic sorption models. This theory, developed based on observations of chemical equilibria at the macroscopic scale, has been supported by the “*visual*” evidence of the coordinative arrangements of metal ions at the solid-water interface made possible by recently developed molecular-scale analytical observational techniques, EXAFS spectroscopy and scanning tunnelling microscopy.

The essential adaptations which need to be made to classical thermodynamic models in order to include sorption are as follows:

1. **Define and quantify sorption site components.** The groundwater-contacting surfaces of many natural solid substances (metal oxyhydroxides, clay minerals, humic substances, micro-organisms,...) contain molecular-scale chemical structures capable of chemically reacting with dissolved components. A given solid material may have one to many different types of these *sorption sites* depending on the chemical complexity of the underlying solid matrix. Each type of sorption site can be considered to be a distinct **chemical component**. For example, certain clay minerals have been shown to have at least two types of sorption site components: “ion exchange” sites located on the planar surfaces and “surface complexation” sites located along the edges of the basal planes (cf. examples in chapter 5).

The total amount (moles) of any given sorption site component will depend on the total solid surface area accessible to dissolved molecules and on the site's surface density (number of sites per unit area). If the total surface area of each solid phase present in a given chemical system can be considered to be constant, the total amount of each sorption site component will also be constant: i.e. each sorption site will have its own mass balance constraint.

2. **Define sorption mass action laws.** Sorption of a given dissolved component (RN or other) involves a chemical reaction with a specific sorption site component to give particular sorbed species. Each sorption reaction can be described in terms of an appropriate *sorption mass action law* (i.e. sorbed species stoichiometry and thermodynamic stability constant, K). The overall sorption of a given RN onto a given solid phase will be determined by the sum of all RN sorbed species on all of the solid's sorption site types (e.g. sorption on clay minerals can include the combined effect of species incorporating both basal plane “ion exchange” sites and “surface complexation” sites on mineral edges (see section 3.3). Sorption sites can also react with other groundwater dissolved components (H^+ , Ca^{2+} , K^+ , etc.) to give other sorbed species, i.e. reactions “competing” with RN for sorption sites.

Examples of typical reactions used to represent sorption on different common constituents of natural solid materials are given in Table 1.

3. **Define a correction model for sorbed species.** The principle difference of TSM relative to classical thermodynamic models is that in certain cases special *electrostatic interaction correction models* (see section 3.3) may be needed to account for effects on the chemical behaviour of sorbing ions resulting from the fact that sorption site components are immobilised on solid surfaces and can develop electrical charge.

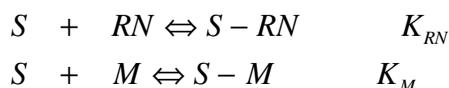
As will be shown in the following sections, the main challenges in deriving a TSM for RN in a given migration field region revolve around finding appropriate answers to each of the foregoing aspects: identifying surface site components and their respective total concentrations, finding a reasonable set of MAL for sorption reactions and, if needed, selecting an approach for compensating for electrostatic effects.

Table 1. Examples of common sorption reactions

Reaction Type	Example Surface Reactions	Typical Solid Phases
Surface complexation	1) $\text{SOH} \leftrightarrow \text{SO}^- + \text{H}^+$ 2) $\text{SOH} + \text{H}^+ \leftrightarrow \text{SOH}_2^+$ 3) $\text{SOH} + \text{Ni}^{++} \leftrightarrow \text{SONi}^+ + \text{H}^+$ 4) $\text{SOH} + \text{Ni}^{++} + \text{H}_2\text{O} \leftrightarrow \text{SONiOH} + \text{H}^+$ 5) $\text{SOH} + \text{UO}_2^{++} \leftrightarrow \text{SOUO}_2^+ + \text{H}^+$ 6) $\text{SOH} + \text{SeO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{SSeO}_4^- + \text{OH}^-$	Metal oxides, oxyhydroxides (e.g. Fe (ferrihydrite, goethite); Al (α, γ -alumina); Si (amorphous silica, quartz); Ti (rutile); Mn (δ -MnO ₂)) Clay mineral “edge” sites Organic substances (e.g. humic and fulvic compounds, polysaccharides, bacterial exopolymers)
Ion exchange	7) $\text{XNa} + \text{Cs}^+ \leftrightarrow \text{XCs} + \text{Na}^+$ 8) $2\text{XNa} + \text{Sr}^{++} \leftrightarrow (\text{X})_2\text{Sr} + 2\text{Na}^+$ 9) $(\text{X})_2\text{Ca} + \text{Sr}^{++} \leftrightarrow (\text{X})_2\text{Sr} + \text{Ca}^{++}$	Clay mineral permanent charge sites (e.g. kaolinite, smectite, illite, bentonite)

3.2 Key parameters determining $K_d(\text{RN})$ values

Under virtually all realistic conditions, sorption of trace amounts of a given RN will involve competition with one or more major geochemical components (e.g. H^+ , Ca^{2+} , K^+ , Na^+ ...) for sorption on a given solid material’s surface sites. In the simplest case, two sorption reactions must therefore be considered, each with its corresponding thermodynamic formation constant, K :



where RN is the radionuclide, S- is the surface site and M is the competing component. Under these conditions, it can be shown (cf. Annexe 1 for a simple derivation) that, for a solid with *specific surface area* A_{sp} (in m^2/kg) and a *surface density of sorption sites*, D_s , (in moles/m^2), **radionuclide K_d** will:

- increase with increasing K_{RN} , D_s , and A_{sp}
- decrease with increasing K_M and competing ion concentration, $[M]$.

The solid mass to solution volume ratio of the system is included in the Kd value (units of m^3/kg)⁵. More specifically, Kd will depend on:

1. The intrinsic **physical-chemical properties of the solid phase sorption sites**, as represented by their contribution to the value of K_{RN} (and to K_{M}). All other parameters being equal, solid phases having sites with stronger chemical affinity for a given RN, i.e. higher K_{RN} (actually higher $K_{\text{RN}}/K_{\text{M}}$ ratio), will have a proportionally higher Kd value. In general, the value of K in a given sorption MAL will be determined in part by the chemical composition and structure of the sorbing solid – the sites present on an iron oxyhydroxide are chemically distinct from those on a silica; different crystalline forms of the same mineral family (e.g. amorphous iron oxyhydroxide, goethite, hematite) should have different surface site characteristics.

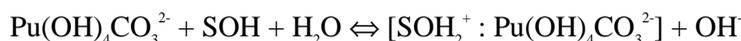
This Kd dependence on the physical-chemical nature of sorption sites is the reason why qualitative, and sometimes quantitative, predictions of the K_{RN} value for sorption of a given RN on different solids can sometimes be made based on the known differences in the solid phase characteristics. Such so-called “Linear Free Energy Relationships” (LFER, see also point 3 below) are strong arguments for TSM-based approaches to predicting Kd values since they show that there is an underlying “order” governing sorption reactions. This in turn means that the wealth of information and understanding regarding the physical-chemical properties and reactions of simpler materials can aid in interpreting, and even qualitatively predicting, Kd values for natural materials, once the predominant sorbing mineral phases have been identified.

2. The **total amount of sorption sites** per unit mass of solid, i.e. the product of the sorption site surface density (D_s) and the solid specific surface area (A_{sp}). The fact that Kd values for PA purposes are generally normalised in terms of sorbing solid mass tends to hide the fact that it is still necessary determine values for these parameters in order to properly account for Kd variations due simply to differences in solid phase geometry, e.g. laboratory ground samples versus *in situ* fracture coatings or porous matrices. A good example of the effect of taking A_{sp} into account is shown by the difference in mass (Kd) versus specific surface area normalised Ka' values for U(VI) and Np sorption on montmorillonite, clinoptilolite, alumina, and quartz given by Turner *et al.* (Oxford – see figure 3).
3. The **physical-chemical properties of the RN molecule**, as represented by their contribution to the sorbed species K_{RN} value. An example of this effect are the variations in Kd as a function of pH for different divalent cations, on the same solid phase and in the same electrolyte, as exemplified by the data for Fe and Al “gels” given in Figures 4a and b (adapted from Kinniburgh and Jackson, 1981)⁶. Here again, knowledge of the physical-chemical characteristics of radionuclide molecules can be used to understand and predict certain aspects of their sorption behaviour. A well known example is the LFER existing between the first hydrolysis constant for various divalent cations and the K values for sorption on various metal oxyhydroxide solids (Dugger *et al.*, 1964, Schindler *et al.*, 1976, Dzombak and Morel, 1990). Figure 5 (after Dzombak and Morel, 1990) shows an example LFER for sorption on ferrihydrite.
4. The **physical-chemical properties and concentration of the competing species, M**. While much of what has been said above also holds for non-RN sorbing components (LFER, etc.), what is more important for PA purposes is that differences or changes in the nature or concentration of M in a migration field chemical system can have a significant effect on Kd(RN). The extremely important effect of changes in H^+ ion concentration (i.e. pH) on cation and anion sorption on oxides has already been shown in Figures 4a and 4b. Significant effects might also be expected

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5. The mass of solid and solution volume are included in the Kd value (Annex 1).
 6. Recalculated assuming both gels to be tri-hydroxides, i.e. $\text{Me}(\text{OH})_3$.

due to changes in the major cation composition of migration field formation water, for example, increasing K^+ or Ca^{2+} concentrations due to co-migration of cement water ions (see Figure 2 for the sensitivity of Ni^{2+} Kd to variations in pH and/or total Ca^{2+} for an aquifer material). It is also likely that certain minor concentration, but high K_M value ions (Al^{3+} , Fe^{2+}/Fe^{3+} , naturally present transition metals - Zn^{2+} , Ni^{2+} , etc.), may be important competing species for high affinity, low total concentration sorption sites (see comments below concerning multiple sorption sites in complex natural solids).

5. While not included in the simplified example given above, it is important to mention the role that **RN dissolved speciation** can play in affecting Kd. In fact, many radionuclides can form dissolved species depending on solution composition, each species having its own particular sorption K value. Since Kd is a global parameter, i.e. reflecting the solid-solution partitioning of the total amount of RN in a system, conditions favouring formation of low K, poorly sorbing, dissolved species will tend to reduce Kd, and vice versa. For example, Sanchez *et al.* (1985) report that Pu(IV) sorption onto goethite involves the following species:



Kd(Pu) will increase in response to any changes in solution conditions which increase the concentration of the dissolved Pu complex, e.g. increasing carbonate concentration should decrease Pu sorption. Although the formation of the mixed $Pu(OH)_4CO_3^{2-}$ aqueous complex is still speculative, the effect of carbonate concentration on Pu(IV) sorption is real.

It is important to emphasise that, while the above extremely simplified example can be considered generally true for a **given sorption site type**, natural systems are always infinitely more complex, generally containing many different types of sites and many major and minor components competing with RN for sorption on each site. How TSM can aid in extracting the Kd information needed by PA from such systems is the subject of chapter 4.

3.3 Ion exchange and surface complexation TSM: variations on a theme

The fact that sorption sites are physically immobilised on a solid surface, coupled with the fact that they are, or can become, electrically charged, means that solid surfaces can **develop a net electric charge** and, consequently, an **electrostatic potential field**. This field can theoretically influence the sorption of charged solution components (i.e. cations, anions) by either promoting (negative surface-cation, positive surface-anion) or inhibiting (positive surface-cation, negative surface-anion) sorption.

The surfaces of natural mineral can be grouped into two broad classes based on the above considerations:

- **Constant Charge Surfaces**, the net electrostatic charge of which remains constant for all solution phase compositions. The most common examples are the permanent, negatively-charged sites created on the basal planes of certain clay minerals by substitution of divalent metal cations for trivalent Al in the crystalline matrix of the octahedral layer, or of trivalent cations for Si(IV) in the tetrahedral layer. Because of their chemical nature, the sorption reaction characteristics of these type sites will largely be determined by the intensity of their **electrostatic interaction** with a given sorbing ion, chemical bonding will play negligible role.
- **Variable Charge Surfaces**, the net charge of which can vary significantly depending on the concentration of one or more dissolved ions. The most common sites exhibiting this

type of behaviour are the hydroxyl groups formed at the solid-solution interface of metallic oxyhydroxides (Fe, Al, Si, Mn, Ti,...) and on the “edges” of clay minerals. These groups can undergo protonation or de-protonation depending on solution pH (H^+) leading to creation of negatively charged, neutral or positively charged surface species (e.g. reactions 1 and 2, Table 1). The composition and molecular structure of these sites allows them to form various types of **chemical bonds** with certain sorbing components, i.e. they can undergo complexation (or co-ordination) reactions similar to those taking place in solution. Electrostatic interactions can influence sorption under conditions where a net charge exists.

Two thermodynamic model variations are generally used for interpreting RN solid-solution partitioning onto these two types of surfaces:

- **Ion exchange (IE)** models for sorption onto constant charge surface sites. In IE models (see example reactions 7-9 in Table 1), sorption site components and sorbed species are always electrically neutral, i.e. charged sorption species are not allowed to exist. Here, the “surface” is effectively considered to include the charge compensating ions. The mass balance for sorption sites in IE models is constrained by the solid’s Cation Exchange Capacity (CEC), which is simply the total number of moles of charge per mass of solid.
- **Surface complexation (SC)** models for variable charge surface site sorption reactions. Charged surface species are allowed to exist in SC models (e.g. reactions 1-6, Table 1). SC models can incorporate an additional correction term for each sorbing ion to account for variations in sorbed species chemical bond intensity, as represented for example by K_{RN} and K_M in the example reactions in section 3.2, resulting from changes in the intensity of a solid's electrostatic field due to changes in the net charge on the solid surface. The now well-established scientific basis for these correction terms is the so-called Electrical Double Layer (EDL) theory (see Dzombak and Morel, 1991 for a clear discussion of this topic). Several EDL model “versions” are actually in common use, reflecting differing hypotheses regarding the positioning of sorbing ions relative to the solid surface, the three most common being the “constant capacitance” model, the “diffuse layer” model and the “triple layer” model.

It is important to stress that, other than these differences in the way of formulating the mass action laws and allowing for correction for the effect of variable charge, IE and SC models both satisfy the essential criteria for thermodynamic sorption models given in section 3.1.

4. TSM-based Strategy for Estimating Kd for Repository Migration Fields

The following sections evoke some of the specific difficulties encountered when developing a TSM for predicting Kd for natural materials, and outlines the essential features of the experimental and modelling strategy generally used for studying these materials.

4.1 Main challenges

Predicting migration field geochemistry

PA models calculate RN solid-solution partitioning for each of the volumes making up potential pathways of radionuclide movement from the waste container to the biosphere: engineered structures (backfill materials, sealing structures), the perturbed “near field” and relatively unperturbed “far field” volumes of the geological host formation, over- or underlying geological formations, biosphere, etc. These volumes are likely to have significantly different physical properties and chemical compositions and, consequently, require different Kd estimations. The basis for any estimation of Kd values which depend on solution composition is a good estimation of the range of geochemical compositions which might exist in the region, i.e. the existing groundwater and solid phase composition, as well as the potential variations in composition resulting from mass transport of non-RN elements into the region due to repository or natural perturbations. Since migration field regions are by definition “open” physical systems, possible future compositions often can be estimated by using a model capable of calculating both the transport of dissolved chemical components into and out of a region, as well as important chemical reactions taking place within each region. Use of such coupled “geochemistry only” modelling can aid during the initial phase of a TSM-based approach in identifying:

1. Regions where groundwater and solid phase compositions will remain relatively constant. These regions can be treated using a single Kd value or an isotherm. An example of this situation is far field RVE with groundwater in equilibrium with formation solid phases.
2. Regions where the groundwater composition varies, but the composition of solid phase minerals governing RN sorption remains constant. An example here would be limited changes in major ion concentrations (H^+ , Ca^{2+} , K^+ , CO_3^{2-} , SO_4^{2-} , etc.) resulting from diffusion of cement water ions into the geological formation.
3. Regions where significant changes in the groundwater composition lead to changes in sorbing mineral composition. These regions will need to be treated both experimentally and in terms of the TSM model as variable sorption site component systems. From a PA standpoint, geochemical modelling may be used to identify periods within the PA time frame during which the solid phase composition remains relatively constant and, consequently, simpler TSM models might be applicable.

Estimating migration field composition over performance assessment time frames can be a very difficult task requiring its own specific modelling and decision making strategy. Here we will assume that geochemical modelling has already been carried out in order to allow us to focus on the specific questions which need to be answered when developing a TSM for RN sorption. It is however

important to point out that many sources of uncertainty in estimating changes in geochemical composition will contribute to K_d value uncertainty, and this will be true whatever the method used for estimating K_d: direct measurements, empirical relationships or sorption TSM.

Determining the nature and composition of natural surfaces

Two major, largely analytical, challenges must be met when developing a TSM for a migration field region:

- How to quantify the surface area of the solid-solution interface present in a given RN sorbing system (laboratory or *in situ*), i.e. the area in contact with the RN-containing solution phase and potential seat of sorption sites. This is the key “physical” parameter determining the total amount of sorption sites associated with a given mass of natural solid material. It is, when complemented with information regarding the volume of contacting solution in a given system, the basic parameter for scaling sorption properties from one system to another (e.g. from K_d values measured in batch systems to K_d values under *in situ* wetted surface to groundwater pore space conditions). While numerous approaches exist for estimating the specific surface area of a solid material sample, it is not always easy to relate measured values to the actual interfacial area which is “sorption active” under a given set of experimental or natural conditions. For example, for porous solids such as the fracture lining material in crystalline host formations where solute diffusion into the porous matrix may be a limiting factor in reaching sorption equilibrium with “internal matrix” sites, the interfacial area which is “sorption available” during “batch” K_d measurements on formation samples at experimental time scales may be much smaller than that acting under *in situ* conditions and at the time scales corresponding to migration field mass transport processes.
- How to identify and quantify the mineral (and/or organic) phases making up the solid-solution interface. This information is needed in order to determine which specific mineral phases are actually furnishing sites for RN sorption, and once these minerals have been identified, the extensive existing database concerning the sorption characteristics of pure mineral analogues can be used as a starting hypothesis regarding the sorption behaviour of the natural material. The difficulty here results from the fact that geological materials are structurally complex and invariably made up of mineral mixtures. In addition, the mineral composition of groundwater contacting surfaces is generally different from the bulk minerals due to alteration processes, and major secondary mineral phases may be covered by thin, difficult-to-detect coatings of other mineral, and possibly organic, substances. If this is the case, it may be these latter, often amorphous, substances which will dominate solid phase sorption characteristics.

Our capacity to provide answers to the above two questions depends largely on advances in analytical techniques specifically oriented towards identifying and quantifying the minerals making up groundwater contacting surfaces. Good examples of the state of the art techniques in this area are given in certain of the studies presented at Oxford and described in Chapter 5 (e.g. Davis *et al.*; Bradbury and Baeyens; Waite and Payne).

Obtaining TSM parameters for natural materials

A TSM requires values for (i) the number of sorption site components and their total amounts, and (ii) the set of mass action laws describing all needed sorption equilibria. Unfortunately, there are virtually no analytical techniques which allow direct measurement of the values for these parameters, especially for natural materials. The principal reason for this is that natural solids generally contain several to many sorption site types bound inseparably together in a single object, making it impossible to measure either the total amount or sorption reaction characteristics of any individual site type. Experimental information on sorption reactions is therefore always macroscopic in nature, measuring the combined effect of more than one site type on the solid-solution partitioning of one or more sorbing components⁷. In fact, the vast majority of sorption data is in the form of measurements of the total dissolved concentrations⁸ of sorbing components in experimental systems containing a known mass of solid and a known volume of solution containing known initial total component concentrations⁹. This data can be transformed to give plots of K_d ¹⁰ for each sorbing component as a function of the total concentration of either the component itself (sorption isotherms), or another sorbing component (H^+ , Ca^{2+} , etc.). A significant part of the process of determining TSM parameters involves seeking an internally consistent and scientifically reasonable set of parameter values capable of reproducing, as closely as possible, these data sets. Once calibrated, the model is tested by predicting K_d values for system compositions other than those used for deriving TSM parameters, while remaining within the domain of model validity.

The above “realities” have several important consequences as far as construction of TSM for PA purposes is concerned, perhaps the most important being the fact that many different sets of TSM parameters, i.e. many different sorption TSM, can generally be proposed for describing the K_d behaviour of a given natural solid phase, all with more or less equally good performance as regards the coherence of model prediction and measured K_d data. This “non-uniqueness” of TSM models for natural solids is often difficult to accept since it seems to imply a lack of rigor in the TSM approach itself, as well as a source of “uncertainty” in the K_d estimation process. This is not at all the case – it is simply the result of being required to select a single deterministic, relatively simple model to represent the properties of an inherently heterogeneous and complex system. This situation means that “expert judgement” will always have a significant role to play when “extracting” the values for TSM parameters from experimental data, which in turn implies that the “correctness” of the particular parameter values used a given TSM model is less important than the experimental and interpretation method employed for obtaining the values. A coherent and theoretically sound methodology offers the best scientifically defensible means of linking a performance assessment K_d selection (and prediction) procedure to the vast body of existing (and future) knowledge regarding the chemistry (and physics) of RN speciation in heterogeneous systems. It also is critical for demonstrating the “chain of decision” linking measurable data with TSM parameter values.

The challenge here is therefore not analytical in nature but rather one of *setting down and applying a scientifically coherent and methodological decision making process* (see below).

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7. In addition to these “resolution limits” regarding TSM parameters, sorption reaction measurements on natural solids are made more complicated, and more uncertain, by various other factors (solid material structural complexity, sample-to-sample composition heterogeneity, kinetically slow reactions, existence of parallel mechanisms such as mass transfer into porous solid phases, etc.).
 8. or pH, i.e. activity, in the case of H^+ .
 9. The total amount of each component brought into the system associated with solid phase sorption sites is generally less precisely known.
 10. or, frequently, the percentage of total component which is sorbed.

4.2 General TSM development methodology

The overall methodology generally used, in whole or in part, for developing TSM for complex natural solid materials is shown in Figures 6 and 7, which roughly divide the process into a sample characterisation and geochemical modelling phase (Figure 6) and a TSM development phase (Figure 7), corresponding to the main challenges mentioned above. Examples of the use of this methodology are given in many of the papers presented at the Oxford Workshop. While not explicitly indicated, in practice there are many feedback loops in the process to allow modification of the experimental and modelling programmes in response to evolving information regarding the sorption reaction characteristics of the natural material. The principal aspects of the method are:

- Analysis of migration field samples to identify and quantify: the “wetted surface” and corresponding contacting groundwater volume (box 2); the mineral phases present on the wetted surface and in the underlying bulk matrix (box 1); the composition of the contacting groundwater (box 3). The surface area and “pore” volume information is needed essentially for scaling TSM calibrated using experimental data for modelling K_d *in situ* (input box 22). The mineral and solution phase composition data are basic input for constructing the geochemical model (box 4). Commonly encountered difficulties involve direct or indirect measurements of the *in situ* values of certain key parameters (e.g. pH, $p\text{CO}_2$, Eh), determining the true dissolved concentration (or total amount) of components participating in sorption reactions or, in certain cases, simply obtaining samples of interstitial fluids (case of clay-rock formations). Good examples of some of the methods used at this stage of the process, and difficulties which can be encountered in their interpretation, were given in the presentations at Oxford by Davis *et al.*, and Waite and Payne in Chapter 5.
- Development of a migration region specific geochemical model (box 4) is generally a progressive, iterative process since, in the end, its essential characteristics must be combined with the TSM for RN and other sorbing components to give the complete thermodynamic sorption model (box 23) for predicting the speciation (i.e. K_d) for those RN given by PA (boxes 7-9). The initial objective of model development is to obtain maximum coherency between system composition data and values calculated using mineral phase solubility and dissolved speciation equilibria contained in the selected TDB (box 6). Among the difficulties frequently encountered at this stage, other than those linked to the analytical uncertainties mentioned above, are large uncertainties in the solubility MAL for certain complex, heterogeneous solid phases (clay minerals in particular) and the fact that sorption MAL are not initially available to account for the effect of ion exchange and surface complexation reactions on the dissolved concentrations of important geochemical components (H^+ , Ca^{2+} , Na^+ , etc.).
- The principal use of the model is to predict how the migration field dissolved concentrations and sorbing solid phase composition (boxes 11-13) will vary due to changes in total component amounts that will result from mass transport into and out of the system as a result of potential perturbation scenarios (box 10). The goal is to be able to identify the range of system compositions which are compatible with identified (or hypothesised) sorbing solid phases, and those situations where significant changes in solid phase composition might take place, with a resulting impact on the nature of the TSM needed to represent RN K_d behaviour. An iterative approach will generally be needed in the case of migration field regions subjected to significant fluxes of externally derived components (e.g. near field rocks subjected to cement waters), since good estimations of the extent and nature of the perturbation will generally require coupling of the geochemical model with a mass transport model (box 12).

- The above information serves as the basis for proposing hypotheses as to the probable mineral (or other) phases likely to govern RN sorption (boxes 14, 13) and the range of system compositions over which Kd estimations will be needed (boxes 11, 13). Generally, one or more minerals known to be capable of undergoing either ion exchange or surface complexation reactions can be identified. In this case, experimental results and existing data bases for sorption on appropriate pure analogue solids can be used as the basis for formulating initial hypotheses regarding the nature of likely sorption reactions (boxes 17-18) for RN, in particular the effect of other components on RN Kd (box 19).
- Much information regarding the general nature of sorption reactions on a given natural material can be obtained by carrying out a limited programme of Kd (or equivalent) measurements for a set of sorbing components specifically selected principally for their capacity to represent a wide range of intrinsic chemical properties, but also for their capacity to act as analogues for certain PA RN (e.g. Cs⁺, Sr²⁺, Ni²⁺, UO₂²⁺, SeO₄²⁻) (boxes 15-16). Comparison of observed variations of the Kd values for Analogue Test Components (ATC) with changing total amounts of either the ATC itself or of key “competing” geochemical components (H⁺, Na⁺, K⁺, Ca²⁺, etc.), i.e. noted here as “scan tests” (box 20), with the Kd responses of known minerals can be used to either confirm (or reject) hypothesised surface phases, or to indicate the nature of the principal sorbing phase(s) present (metallic oxyhydroxide, cation exchange, mixed). This aspect is illustrated by the use by Cho and Hahn (Oxford) of five ATC elements (Cs – alkali metals, Sr – alkaline earths, Co – transition metals, U – actinides, I – anions) to study the sorption properties of a variety of natural materials (granite, gneiss, tuff, andesite) and single minerals (oxides, clays).
- The experimental and modelling programme to be used for developing a TSM for each type of RN of PA interest is defined based on the above information (box 21). This programme (box 22) typically commences with measurements designed to provide an initial estimate of the number and total concentration of sorption site components. This is followed by the step-wise, iterative determination of MAL for the various sorbing components, wherein potential stoichiometries and sorbed species formation constants (eventually different electrostatic correction models, see below) are tested for their capacity to accurately represent experimental data, as well as to predict data not used for model calibration, within a thermodynamic modelling code. This code incorporates a TDB for all necessary solution species for both RN and other components. The work presented at Oxford by Bradbury and Baeyens, Marmier and others provides good examples of this approach.
- The final TSM (box 23) for predicting RN Kd as a function of migration region chemical composition is made up of the essential features of the geochemical model (box 4), the set of sorption site components and corresponding total amounts, the MAL for all sorption reactions, the TDB for all non-sorption site components.

Are electrostatic correction models needed?

As mentioned in section 3.3, different electrostatic correction models exist and are commonly used for interpreting sorption data on natural materials. Since each model will have its own particular variation of the electrostatic correction term in the sorption MALs needed to interpret sorption data for a particular RN or other ion, each model will generally require different K values and possibly stoichiometries to represent the same Kd information. This, coupled with the fact that there is frequently little justification offered for choosing one model over another, has been the source of much of the doubt and confusion in the PA community concerning the “operational status” and “utility” of TSM in general, and those containing electrostatic corrections in particular, for making Kd

calculations. This being the case, the real questions regarding whether or not an electrostatic model should be used in a TSM for performance assessment, and if so which one, revolve around whether the increase in model complexity is justified in terms of both the precision in K_d values required by PA and the quality of the information available on migration field chemistry. We can therefore ask:

- *should an electrostatic correction be used at all?* i.e. will use of a correction in a TSM significantly reduce the uncertainty associated with calculated K_d values relative to those obtained using an uncorrected model, taking into account other major sources of K_d uncertainty (intrinsic sample composition complexity, sample-to-sample variability, experimental error, ...)?
- *if so, which correction model?* i.e. which level of model complexity should be used (diffuse layer, triple layer), again given the contribution of other sources to K_d uncertainty?

In fact, in many cases adding electrostatic corrections does not increase the degree of accuracy between predicted and observed sorption values. For example, Bradbury and Baeyens (1995) obtained a better description of the Zn(II) sorption data on montmorillonite when no correction model was considered. The question of the advantages and disadvantages of using electrostatic corrections in TSM has been critically reviewed by Westall (Westall, 1995). It is nevertheless important to stress that the general physical phenomena potentially responsible for changes in a radionuclide's K_d resulting from variations in surface charge are real and could be important under certain circumstances, in particular for:

- RN which form weak surface complexes in;
- migration field regions dominated by hydrous metal oxide surface phases; and
- which are subject to significant variations in critical solution composition parameters (pH, ionic strength, etc.).

In any case, it would appear that, when an electrostatic correction model is deemed necessary, the simplest model should be used, i.e. the one with the fewest independent "electrostatic" parameters. It would also seem advantageous to the entire PA K_d data gathering and interpretation effort that, whenever possible, the same correction model be used when interpreting RN sorption data. If accompanied by use of a commonly accepted thermodynamic data base, this would facilitate the compilation and inter-comparison of sorption data for geological materials. In any case, the reasons for choosing to use a particular model for representing K_d information in a particular chemical system should always be given and justified.

5. State of the Art in TSM-guided Kd Studies of Natural Materials

Much progress has been made over the last decade in developing the conceptual, experimental and modelling tools needed in TSM-based assessments of Kd values for natural solid materials, i.e. in improving and demonstrating the different aspects of the general strategy outlined above. The essential feature distinguishing TSM for sorption (Kd) from purely empirical expressions is that as much effort as possible is made to relate model parameter values to our best knowledge regarding the chemical composition, and likely sorption reactions, of a particular solid material. Progress in the field of sorption TSM, the state of the art, can therefore be measured at the following levels:

1. Increasing our degree of understanding of simple, single mineral phases: their sorption site composition (chemically distinct surface molecular structures, surface or mass normalised densities), sorbed species stoichiometries and molecular structure, sorbed species intrinsic or conditional formation constants. This effort is very important since it is the basis for reasoning about the likely behaviour of complex materials based on identified, or predicted, mineral phases. Pure mineral phase solids are also probably the only reasonable basis for developing something resembling a thermodynamic data base for “sorption”.
2. Improved methods for identifying, and quantifying, potential sorbing mineral phases present on complex natural solids (i.e. whole rocks). This is essential in order to be able to make use of the qualitative and quantitative information contained in pure mineral sorption TDB in designing Kd experimental protocols and interpreting Kd data.
3. Strategies for determining the surface site composition (number of components and concentrations), and for measuring and modelling the sorption reactions, of complex natural materials. This includes decision making regarding the most appropriate type of TSM model to use.

The following overview purposefully focuses on the work presented at the Oxford meeting for two main reasons. First, in the authors opinion, the balance in presentation distribution between studies involving simple model solid phases (Si, Al, Ti oxides; calcite), clay minerals and complete natural substrates appears to represent fairly well current activity, and the state of the art, in using TSM models as guiding premises for studying the sorption properties of geological materials of interest to PA. Secondly, various relatively recent publications (e.g. Davis and Kent, 1991; Dzombak and Morel, 1990) have thoroughly reviewed current knowledge in the general field.

An important point illustrated by many of the presentations at Oxford is the importance of comparing predictions with measured data and refining the model description or the input parameters in the light of this comparison. This “validation” of models is important to provide confidence that they can be used in a predictive mode, especially for chemical conditions that are similar to those for which direct experimental data are available.

(N.B.: The numbers following the author citations refer to the presentation numbers given in the Oxford meeting programme – Part 3).

5.1 Single minerals and mineral mixtures

The vast majority of the studies regarding application of TSM to mineral substrates has naturally enough focused on single mineral phases, metal oxides and oxyhydroxides constituting the overwhelming majority. Single clay minerals have received an increasing amount of attention over the last 10 or so years, largely because of their proposed use as natural or engineered barrier materials for hazardous waste disposal facilities (radioactive or industrial). Other natural solid minerals (sulphides, calcite, etc.) have been studied to a much lesser degree. These trends reflect an apparent consensus that metallic oxyhydroxide (especially Fe and Al-based) and “clay family” solid phases are likely to play a dominant role in determining trace element solid-solution partitioning in natural systems.

Studies of single natural minerals or synthetic solids differ from those involving more heterogeneous natural materials in that reasonable hypotheses regarding the number and nature of the sorption site components can be proposed based on knowledge of the molecular (or crystallographic) structure of the solid phase. These studies are generally aimed at improving our understanding of Kd-determining phenomena, with the implicit ultimate goal of being able to transpose this information to modelling Kd in the more complex systems of interest to PA. This is illustrated by the fact that many of the research activities focusing on understanding a specific natural material (bentonites, Sellafield site formation rocks, Koongarra solids, Cape Cod and Soulaines aquifer sediments, Wedron sand, ...) also include experimental studies, or use of existing sorption models, of simple minerals known to be present in the whole material.

Clay minerals

Much of the research work presented at Oxford was centred around TSM modelling of the sorption behaviour of clay minerals. The radionuclide Kd characteristics of clay minerals are of interest to PA because of their proposed use in constructing engineered barriers and structures (overpack, backfill, seals and plugs) and because they are important sorbing phases in the geological migration field. This interest has led to devotion of a significant amount of effort over the last several years to improving our understanding of the sorption reactions governing the Kd behaviour of these materials. This effort has had considerable success largely as a result of recognising that the Kd behaviour of a given clay mineral results from the combined effect of cation exchange and surface complexation type sorption sites, the latter corresponding to the silanol (SiOH) and aluminol (AlOH) co-ordination structures created along the “broken edges” of the respective Si or Al sheets. Good arguments, based on known differences in the sorption reaction characteristics of pure silica or alumina minerals, exist for assuming that the aluminol and silanol structures have differing intrinsic chemical reaction characteristics, and therefore to constitute two distinct sorption site components. This conceptualisation, either explicitly or implicitly, has been used to construct TSM for describing and predicting RN Kd values for clay mineral-containing solids (most frequently, bentonites or montmorillonite).

The work of **Marmier *et al.* (4.21)** provides a nearly textbook example of how a TSM based on adding together the sorption characteristics of individual pure mineral phases can, in certain cases, be used to successfully predict the Kd behaviour of more complex minerals. In this study, sorption site total amounts and electrostatically corrected MAL for sorption of H⁺ and various RN analogues (Cs⁺, Ni²⁺, Yb³⁺) were obtained for two pure minerals, alumina and silica, by fitting of experimental sorption data obtained on each solid. A TSM combining the MAL for both solids gave a good representation of the sorption for binary mixtures, if reactions for silica dissolution and binding of H₄SiO₄ on the alumina surface are included. The model was then used to predict the sorption characteristics of two clay minerals, kaolinite and montmorillonite, giving excellent agreement for the former (Figure 8a) but much poorer results for the montmorillonite. This difference was explained by the fact that

sorption on kaolinite is almost exclusively due to surface complexation reactions with SiOH and AlOH edge sites, while the montmorillonite has significant amounts of an additional cation exchange site. If such a site is included in the TSM, the model is capable of accurately representing the experimental data (Fig. 8b).

Bond *et al.* (4.7) also used a similar approach to model pH-dependent sorption of U(VI), Pu and Th onto muscovite and chlorite under oxic conditions. Sorption on muscovite was considered to take place on sites having the same properties as alumina and silica pure phases. A third “goethite” type site was included for chlorite sorption. The authors experimentally determined sorption reaction constants for U(VI) and Pu onto alumina, but used existing literature as a direct source for the remaining parameter values used in the triple-layer sorption model for each of the solids. Model predictions of K_d for sorption of all RN onto both sheet silicates were generally within an order of magnitude of the experimental data across the pH range 5 to 10. The model predicted that silica sites dominated sorption up to pH 10 for U and Pu sorption onto both solids.

Bradbury and Baeyens (3.3) have carried out a very thorough study of Ni (and other ion) sorption on a montmorillonite clay which had been subjected to a purification and conditioning procedure to remove background metal impurities, soluble salts and sparingly soluble solids (calcite) which might complicate determination of the “intrinsic” reaction characteristics of the clay mineral. The sorption of Ni was studied by determining (i) the variation in K_d values as a function of pH and ionic strength for trace total Ni concentrations, and (ii) K_d as a function of total Ni at constant pH. All measurements were made under N₂ atmosphere to eliminate carbonate reactions. Potentiometric titration and Ni sorption data trends were interpreted as indicating that Ni sorption was due to the same two processes as mentioned earlier: cation exchange and surface complexation on two different types of edge sites, one “strong”, one “weak”. The total amount of CE sites was estimated based on the measured CEC, and the total amount of the two SC sites from the potentiometric titration curve. The complete TSM model was constructed progressively as follows:

1. Selectivity constants for Ni, Ca and Zn exchange for Na were determined by fitting sorption edge data as a function of Na electrolyte total concentration.
2. The total amounts of the two SC sites and their respective acid/base constants were determined from potentiometric titration curves.
3. The formation constants for the strong site sorbed species were determined from the corresponding pH sorption edges (at 0.1 N ionic strength).
4. The weak site constants were determined from the sorption isotherms (0.1N ionic strength).

The resulting model, which uses only a single sorption MAL for each of the SC sites and no electrostatic correction, was then used to predict the variation in K_d(Ni) for two other ionic strengths (see Figure 9a). The same TSM was also used to predict the K_d(Ni) behaviour of the unconditioned montmorillonite, the only difference in the model being that the total amounts of the three sites were scaled to reflect the difference in CEC values of the two solids. Figure 9b shows that the experimental K_d at pH 8.2 are significantly higher than the model prediction (dashed line) obtained when using a value reported in the literature for the NiCO₃ dissolved complex. When further investigation revealed that this value was not supported by direct analytical measurements, the authors carried out the experiments needed to determine a more accurate value, which was roughly two orders of magnitude lower than the previous one. The result of using this value is shown by the solid line in figure 9b.

Wang *et al.* (4.16) used a two site (ion exchange and pH-dependent surface complexation) TSM to interpret experimental data for Eu³⁺ sorption onto illite, one of the most abundant clay minerals in the Boom clay. The respective total site amounts were estimated using the ion exchange site capacity and potentiometric titration data. The key reactions determining K_d behaviour were

determined to be: (i) Eu and H⁺ cation exchange, (ii) acid-base reactions of the surface hydroxyl groups and (iii) Eu surface complexation. An electrostatic correction model was needed in the TSM in order to give an acceptable fit to the experimental data.

Turner and Pabalan (4.3) have carried out an extensive experimental and modelling program with the objective of (i) developing a simplified uniform TSM approach to radionuclide sorption based on the use of as many “standard” parameters as possible and (ii) to test the ability of the TSM to reproduce observed K_d(RN) behaviour and to predict K_d for unmeasured system conditions. The study focuses on sorption of U(VI) and Np(V) on a variety of mineral phases (alumina, quartz, montmorillonite, clinoptilolite). Batch sorption experiments were carried out over a wide range of system compositions: pH between 2 and 11, solid mass / solution volume ratio up to 50 g/l, pCO₂ from 0 to 0.01 atm., RN concentration from 10⁻⁸ to 10⁻⁵ M, ionic strength (0.01 and 0.1M). These data, along with selected literature data, were then used as the basis for determining a consistent set of acid-base and surface complexation MAL for the simple oxide solids by progressive optimisation of TSM parameters. Although electrostatic corrections were used, the models were otherwise purposefully kept as simple as possible, i.e. only one site type per solid; a single MAL for each sorbing ion; total site amounts were assumed to be equal to a uniform site density multiplied by the solid's N₂/BET specific surface area. The montmorillonite was modelled assuming non-interacting SiOH and AlOH sites and no cation exchange sites. Figures 10a and 10b show the capacity of the combined SiOH-AlOH model to predict results for K_d(U) and K_d(Np) on montmorillonite as a function of pH.

Ochs and Wanner (4.15) have modelled bentonite sorption of Cs⁺, Sr²⁺ and Ra²⁺ using cation exchange reactions on a single IE site. Reactions with a second protolytic SC “edge” site (with electrostatic activity correction) were added in order to model sorption of Pb²⁺. **Payne (4.4)** used an electrostatically corrected TSM to model U(VI) sorption on a kaolinite. A naturally occurring Ti-rich phase (anatase) was found to have a major effect on U sorption. **Stamberg and Benes (4.17)** modelled sorption of U(VI) on bentonite in the presence of carbonate complexation using TSM with and without electrostatic correction. Simultaneous sorption of six uranium species and carbonate species on positively and negatively charged surface sites was considered. The best fit of batch sorption data was obtained using the diffuse double layer electrostatic correction model, but the differences between models were small.

Ly (4.20) has modelled the K_d characteristics of several clay minerals using a TSM approach based entirely on sorption reactions written as ion exchanges between two electrically neutral phases (liquid and solid). Two principal types of reaction are employed: (i) stoichiometric neutralisation of surface charge resulting either from structural defects or ionisation of acidic functional groups, and (ii) ligand exchange. The number of site types, as well as the corresponding total amount, are estimated by analysis of variations in total sorbed mass of a given ion (K⁺, Cs⁺), as a function of pH. The sorption MAL were determined by optimising model fit to experimental data. Simple solution complexation reaction equilibria are taken into account in the form of Ringböm side reaction coefficients. Figure 11 illustrates the capability of the resulting TSM to represent the variability of K_d values for four elements on smectite (in 0.1M NaClO₄) as a function of varying pH.

*The above examples clearly show that TSM-based approaches are capable of simulating the K_d characteristics of relatively “pure” clay minerals. This means that TSM can be considered as supporting tools capable of providing PA with a basis for assessing the RN retention performance of such materials, eg. certain **engineered barrier systems**.*

Other pure, non-clay minerals

Brady (4.9) has studied the chemical mechanisms governing RN solid-solution partitioning in dolomite-containing systems. Sorption of major ions (Ca, Mg) and various RN (Am, Pu, U, Th, Np) were measured as a function of pH, ionic strength and CO₂ partial pressure. RN sorption was favoured at high pH, and exchange for Ca²⁺ appears to control actinide sorption; high Ca²⁺ decrease actinide K_d values. High pCO₂ values tend to reduce RN K_d values, by increasing dissolved Ca, except in cases where RN carbonate complexes sorb also; the apparent case for Am, possibly for Pu). **Jakobsson and Albinsson (4.11)** have used a TSM (with electrostatic activity correction) to interpret batch experimental data regarding Th sorption onto titanium dioxide, as a function of pH and ionic strength. Initial results suggest that inner sphere complexes with the neutral Th(OH)₄ or positively charged Th(OH)₃⁺ are involved. **Olin *et al.* (4.5)** have also used an electrostatically corrected TSM based largely on literature parameter values for the MAL to interpret experimental data for Ni sorption on several silica solids in synthetic media designed to simulate fresh and saline groundwater compositions.

Davis *et al.* (4.10) have addressed the question of whether or not TSM developed to describe RN K_d in batch systems are applicable at the much higher solid to solution ratios, and dynamic transport conditions, existing in flow-through columns. These authors used the results of batch experiments on a purified and well characterised particulate silica to develop a non electrostatic, 2-site TSM describing U(VI) sorption as a function of (i) pH, (ii) total U(VI), and (iii) the total amount of a U(VI) complexing ligand, the fluoride ion (F⁻). Literature values were used for all aqueous complexes. This model was then coupled with a advective transport code, which was then used to predict the break-through curves for transfer of U(VI) pulses through a silica-filled column, under a wide range of carrier solution compositions (pH, total F⁻). The model was able to give reasonable qualitative predictions (within 30%) of U(VI) transport. The discrepancy might be due partially to the fact that the initial model was determined based on goodness-of-fit to “pH-dependent percent sorption edges”, instead of to “K_d variation as a function of pH” representations (the former reflect poorly K_d variations under conditions leading to high % sorbed).

A similar approach was used in the Winfrith column TSM validation experiment, reported by **Crawford and Bennett (4.8)**. The objective was to use coupled TSM – transport codes to predict both the elution curves and sorbed concentration profiles observed when U(VI) concentration pulses were passed through an intact column of a natural, but nearly 100% silica, sandstone (Clashach sandstone). Independent teams of modellers were provided with experimental (batch system) data for surface titrations of both pure silica and the sandstone, as well as data for U(VI) sorption on the sandstone. Hydraulic characteristics and surface area measurements for the columns were also provided. Column runs were conducted with U(VI) only, as well as in the presence of a competing sorbing cation (Cd²⁺) and two complexing ligands (EDTA, saccharic acid). Modelling results were generally in good agreement with the experimental observations, though they did tend to slightly over-predict U migration, the effect of Cd competition and U de-sorption reversibility.

5.2 Complex natural solids

Various studies have taken up the challenge of interpreting the K_d characteristics of as-sampled complex natural materials in terms of a TSM. The principal difficulty posed by these materials, as compared to purified or synthetic single minerals (or mineral mixtures), is that the identity, amounts and “purity” of the minerals, and other matter, present on the wetted surface are unknown. This makes it difficult to make the same types of a priori assumptions concerning the number of site types or their likely sorption MAL that can be made for known mineral structures. Two types of TSM working hypotheses are possible:

- Assume that the surface is composed of some “mixture” of one to several pure mineral phases whose sorption MAL are known (or can be determined independently in single mineral systems), and that the overall Kd behaviour can be predicted by suitable weighting of the individual mineral contributions.
- Assume the surface composition, and Kd behaviour, is inherently too “complex” to be represented by a mixture of known mineral MAL. Assume, on the other hand, that sorption is governed by the combined effect of reactions with hydrolytic oxyhydroxide site types and ion exchange sites, and that Kd behaviour can be represented by a TSM containing an empirical, “best-fit” defined mixture of generic MAL.

These two approaches are obviously not at the same level from a scientific understanding point of view, and the general consensus is that the first should generally be favoured over direct application of the second. The second option is, however, in the author’s opinion, a viable and practical option when the first “fails” because of excessive system complexity or heterogeneity, especially in a PA context. The principal impact of the first hypothesis is that it necessitates a means of analytically quantifying the **sorption-relevant** amounts of each mineral phase present on the surface of the natural material. This is not generally an easy affair, as shown by the results of the various studies presented at Oxford.

Arnold *et al.* (4.12), for example, have compared U(VI) sorption on a “phyllite” rock, with sorption on its main, **bulk** mineral constituents: muscovite, quartz and chlorite. Their study showed that, while maximum U(VI) sorption on all of the mineral surfaces occurred in the 6 to 7.3 pH range, the phyllite sorbed more uranium than each of its main mineral constituents. They interpreted this result as indicating that some minor mineral constituent of phyllite, or an alteration product formed during the Kd measurements, is dominating the Kd behaviour for U(VI). They hypothesised that small amounts of amorphous iron hydroxide (ferrihydrite), resulting from release and subsequent oxidation of chlorite ferrous iron, might be responsible for this effect. Further batch experiments showed, in fact, that small amounts of ferrihydrite (1 mM) gave almost the same pH dependent Kd response as phyllite. As we shall see, this qualitative evidence of the possible Kd-determining role of trace amounts of secondary minerals, and of iron minerals in particular, supports a common initial working hypothesis used in a number of the other studies. One example is the St. Bees Sandstone exercise in the ChemVal2 sorption project presented by **Crawford and Bennett (4.8)**. In this exercise, groups of independent modellers were provided with surface area and petrographic information regarding this natural rock. This information led to hypothesising that the two likely sorbing phases were silica and ferrihydrite. Based on this, experimental titration and sorption data for Ni on a model silica mineral (MinUSil-5) were generated to provide information for constructing a TSM for Ni sorption on silica; literature values were used for the ferrihydrite MAL. The resulting combined silica and ferrihydrite TSM was able to predict certain important Kd characteristics of this natural material, and indicated that Ni Kd behaviour is dominated by trace amounts of ferrihydrite present as a coating on the silica surfaces.

Siegel *et al.* (4.13) carried out a detailed study of Ni sorption on a quartz sand containing trace amounts of iron oxyhydroxide and kaolinite. The presence and amount of the former was inferred from the quantity of iron released during acid leaching, and the latter by SEM observations of kaolinite platelets on grain surfaces. It was estimated that Fe-oxyhydroxides coat 50 to 90% of the sand surface. The experimental and modelling programme was built around comparison of the pH-dependent sorption of Ni on three model solids (quartz, goethite, kaolinite) with those of the sand, with and without the presence of Li⁺ as a competing ion for ion exchange sites. From a qualitative standpoint, Ni sorption could be interpreted in terms of sorption on goethite sites unaffected by Li⁺ sorption, and competition with Li⁺ for sorption on kaolinite sites. Incidentally, Li sorption on the kaolinite was found to be irreversible, suggesting that this is the only important phase in the sand with

respect to Li sorption. Two electrostatically corrected (triple layer) surface complexation models were developed for representing data for Ni sorption on goethite, the simpler “one-site” model gave poorer fits than the “two-site” formulation incorporating a small fraction of high energy sites. A two site (AlOH, SiOH) EDL corrected model was developed for the kaolinite. In the end, the single site goethite model was found to be capable of representing Ni sorption on the complete sand (see Figure 12). It is interesting to note that these authors also were required to modify the thermodynamic constant used for Ni carbonate solution complexes in order to model observed experimental data (see also Bradbury and Baeyens).

Davis, Kent and Abrams (3.8) presented the results of one of the only cases where a TSM approach was used as the basis for thoroughly studying the coupled effects of chemistry and mass transport on trace element migration over significant distances, representing a fairly long time frame, in a complex natural milieu. In other words, this study is an excellent example for PA of the way TSM can be used for understanding RN migration in the geosphere. In particular, it illustrates virtually all of the decisional and scientific aspects of the TSM approach mentioned in previous chapters. It is for this reason that we have decided to describe it in some detail.

This study focused on understanding, and predicting, transport of Zn (and certain other elements: Pb, Cr, Se) in a shallow sand and gravel aquifer contaminated with secondary sewage effluent. Treated effluent has been dispersed into the aquifer through infiltration beds for roughly 60 years, creating a plume of contaminated groundwater extending more than 5 km down gradient with a width of roughly 900 meters. Steep vertical gradients in chemistry have been created within the aquifer by rainwater infiltration and limited vertical mixing. For example, within a three meter thick transition zone beginning in the recharge water and extending downward into the plume, dissolved O₂ concentrations decrease from several hundred micro-moles per litre to nearly zero, and the pH increases from about 5.5 to around 6.5. The sub-oxic zone of the plume is mildly reducing and contains high concentrations of dissolved manganese and nitrate, but negligible ferrous iron. The core of the plume is anoxic, has a pH of around 6.5, and contains high concentrations of dissolved ammonium and ferrous iron.

In the vicinity of the infiltration ponds, the vertical dimension of the total plume is roughly 25 meters. Zn contamination extends relatively far into the aquifer, with an average vertical dimension of 15 meters at a distance of 50 meters down gradient, and Zn concentrations ranging from 0.3 to 3 µM. At distances greater than 200 meters down gradient from the source, the Zn contamination is restricted to a 3 meter thick transition zone at the top of the sewage plume; the lower boundary of this zone corresponding with the steep increase in pH (5.5 to 6.5) mentioned above. Maximum Zn concentrations in this region vary with distance down gradient from 4 to 12 µM. The leading edge of the Zn plume is sharp, and is located at about 400 meters from the source (Figure 13a). Geochemical modelling indicates that Zn solid-solution partitioning is controlled by sorption processes; Zn-bearing mineral phases are highly under-saturated. Greater than 95% of the total Zn contamination is associated with aquifer sediments due to sorption. The presence of un-reactive sewage effluent components at a distance of roughly 5 km suggests that the average retardation factors for Zn are of the order of 13 for the lowest pH values and within the range of 50-100 at the higher pH values near the centre of the sewage plume.

An extensive solid phase characterisation programme was carried out to identify potential sorption-controlling phases (Coston *et al.*, 1995). The sediments were fractionated based on particle size and diamagnetism, and the specific surface area (BET) and mineralogy of each fraction were determined. Magnetite, hematite and glauconite were identified in the heavy mineral fraction. Chemical extraction methods were applied to each fraction and dissolved Fe, Al, Mn, and P were measured. Micro-scale analysis of the surface of hand-picked grains was carried out using various techniques (SEM-energy dispersion spectroscopy, time of flight secondary ion mass spectroscopy,

auger electron spectroscopy). Batch studies showed that Zn sorption was unaffected by extraction procedures designed to selectively dissolve either amorphous iron oxyhydroxides or crystalline iron coatings. Results indicated that Zn and Pb sorption occurred predominantly on quartz grains, but that the reactivity of these grains was much higher than a purified quartz powder sample. The greater reactivity was attributed to sorption on coatings present on the sand grains composed of surface precipitates of complex mixed oxides and silicates, containing high concentrations of Fe and Al. These coatings are derived from weathering of feldspars and other accessory minerals in the aquifer. K_d (Zn) behaviour was found to vary as a function of location in the aquifer, with strong correlations being observed between metal ion sorption and extractable amounts of Al and Fe, when both were normalised on a surface area basis (Fuller *et al.*, 1996).

Surface complexation TSM (non electrostatically corrected) for Zn sorption were developed based on data obtained in batch experiments on aquifer sediments. Both of the TSM hypotheses mentioned above were tested:

- an aluminol and ferrinol site model, each with two site types, using MAL determined in independent published studies for Zn sorption on poorly crystalline iron and aluminium hydroxides;
- one and two-site “generic” surface complexation models, where Zn sorption MAL and site quantities were determined by fitting the laboratory sorption data.

Model simulations using the aluminol-ferrinol model agreed reasonably well with the experimental data for Zn sorption on aquifer sediments if it was assumed that the site density was greater than that expected based on the sediment BET surface area. This is consistent with the fact that the surface coatings are thick, and had high surface areas.

The distribution of Zn contamination in the aquifer was then simulated using a coupled flow, mass transport and TSM code. The model incorporated the influence of variable chemistry (pH) on sorption (generic site model) and transport of Zn; groundwater flow and dispersion parameters in the transport model were determined from independent field data. The results of simulations carried out over a 54 year time period agree with the important features of the Zn contamination in the aquifer, without any parameter adjustment (See Figure 13a,b). The Zn-contaminated zone deeper in the aquifer is limited to the near-source region by the extensive sorption in the plume core due to the higher pH values. Near the leading edge of the plume, the range of Zn retardation in the simulations due to pH variation was about 22 at the lower pH to about 63 at the higher pH existing in the plume core.

All in all, this study demonstrates quite clearly that the TSM approach can be a valuable tool for estimating K_d values for PA in complex geological environments characterised by spatially and temporally variable chemical conditions.

The ASARR (Koongarra) project, presented by **Payne (3.6)**, **Waite *et al.* (4.2)** and **Cho and Hahn (3.5)** is another example where a TSM approach was used to study the chemical phenomena responsible influencing the migration behaviour of a trace element, in this case uranium, in a complex natural environment over a long time frame. The starting point for this study was an observed spatial distribution of U concentrations in a shallow aquifer, down gradient from an initial source (a uranium ore body). Here an initial working hypothesis, based on the known presence of Fe-bearing secondary minerals in the natural material, was proposed in which it was assumed that uranium K_d on Koongarra natural substrates was dominated by sorption on a single mineral, amorphous iron hydroxide (ferrihydrite). An initial phase of the project was therefore devoted to developing a TSM for U(VI) sorption on this solid phase, over a wide range of conditions (pH, ionic strength, CO_2 partial pressure, U(VI) loading, complexing ligands). This TSM, an electrostatically corrected, 2 site model, was able to represent virtually all of the data regarding U sorption in the single mineral system. This simple

model was, however, not able to correctly predict the uranium Kd characteristics of natural material samples. For example, model predicted Kd variation as a function of pH underestimated observed values by an order of magnitude when total site quantities were estimated as directly proportional to the amount of iron extracted by a “ferrihydrite-specific” procedure (“TAO” curve in Figure 14). This result can be interpreted in several ways:

1. that the number of sites **having ferrihydrite-type MAL** (i.e. similar stoichiometries and formation constant values) must be roughly an order of magnitude greater than that estimated by the TAO procedure. For example, the Fe + Al + Mn DCB curve (Figure 15) shows the result of assuming that the total amount of sites having ferrihydrite type properties is proportional to the sum of the DCB-extractable Fe, Al and Mn. Significant differences subsist however outside the 5 to 8 pH range. An assumption that the entire BET surface area is in the form of ferrihydrite sites significantly overestimates Kd (Figure 14);
2. that non-ferrihydrite sites are responsible for much of the Kd properties of the complex solid. These additional sites will have their own specific total concentrations and surface reaction MAL. In order to include such sites in a “mixture” TSM, additional “simple” phases would need to be hypothesised (Al and Mn oxyhydroxides, organic matter, other) and the corresponding sorption MAL determined. Methods for quantifying the amount of these phases present in the complex material would also need to be developed.

These results led the project to focus strongly on an in depth characterisation of the nature and composition of the natural material solid surface. For example, TEM and SIMS spectra were used to identify Fe, Al, Si and Mg oxide rich secondary mixed mineral phases covering individual sediment grains.

Taken together, these results suggest a certain number of possibilities, or follow-up efforts, from a PA perspective, including:

- hypothesising that it may be possible to use the “ferrihydrite” model to estimate divalent cation Kd, in the 5 to 8 pH range, using the sum of DCB extractable Fe, Al and Mn amounts as an operational estimate of total site quantity. This will require experimental demonstration for a wide range of natural materials of interest to PA;
- continuing to seek a means of constructing a “mixture” TSM for Koongarra materials based on better identification and quantification of sorbing phases other than ferrihydrite;
- examining the utility of using a “generic” TSM modelling approach for representing observed Kd behaviour of Koongarra, and similar complexity, materials. Such an approach could incorporate some “standard” means of fixing the total amount of all sorption sites attributed to any solid material (e.g. a constant site surface density applied to the BET surface area, total extractable Fe, Al, Mn, etc.).

Linklater *et al.* (4.4) also used a somewhat similar logic as the ASARR project in studying U(VI) sorption on a wide variety of far-field rock samples from the Sellafield system: Permo-Triassic sandstones and shales, Carboniferous limestone, volcanoclastic rocks (tuff matrix and fracture infill material). Mineralogical and chemical characterisation (sequential extractions, ...) of natural U distribution indicated that U is at least partially associated with secondary hematite phases. Based on this evidence, these authors hypothesised that a single mineral, hematite, was the dominant active sorbing phase in the whole rocks. Two different formulations of an electrostatically corrected TSM were developed based largely on sorption stoichiometries, selected from those proposed in the literature, for U(VI) and solution ion (Ca, Mg, SO₄) sorption on hematite and related iron oxides. MAL formation constants were obtained by fitting experimental data for U sorption on hematite in simple

electrolyte systems¹¹. Here again, difficulties were encountered in deciding how to estimate the total quantity of “hematite” sites present on a given rock. Two bounding possibilities were considered: one designed to be under-estimating in which the weight percent of hematite in the sample was equated to the percent of hematite surface present per unit mass of rock, and a second designed to be over-estimating where the entire surface area was assumed to be hematite covered. These two site concentration possibilities were used with the two TSM formulations to predict U(VI) Kd on each rock, in the presence of Sellafield groundwater. Here again, as shown in Figure 15, simple models based on an a priori assumption of sorption dominance by a single pure mineral phase fail to give reasonable predictions of the observed Kd behaviour of a variety of complex natural materials, indicating the need for more complex mixture models, or a generic approach.

Wang *et al.* (4.16) have investigated application of a TSM containing reactions with illite and solid and dissolved humic matter for interpreting Kd data for Eu sorption on Boom clay. The illite model is the same as that described previously. The amount and acidity constants for Boom clay humics were determined by titrating organic matter extracted from Boom clay water. Constants for Eu complexation with humics were obtained from an existing TDB. The results of preliminary modelling indicate that reactions with organic matter dominate Eu Kd characteristics, but also that much additional information is needed regarding humic material site capacities and reaction characteristics in the composite system, i.e. humic plus solid substrate.

Yui & Shibutani (3.4) have measured Kd for Cs, Pu(IV), Am(III), Ni on a bentonite backfill (Kunigel V1) under oxidising conditions, and for Se(IV), Tc(IV), Np(IV), Cm(III) under reducing conditions, as part of the PNC PA programme. Bentonite sorption was hypothesised to result from the combined effect of reaction with a cation exchange and a surface complexation (AlOH edge sites) on the Na-smectite, and with surface complexation sites situated on hematite resulting from pyrite oxidation. The different TSM developed to represent experimental data were: Cs, Pu, Am (cation exchange); Se (electrostatically corrected surface complexation on hematite and aluminol edge sites); U, Tc, Np, Cm (electrostatically corrected surface complexation on hematite); Ni (combined CE + SCM). Kd values for U(VI,IV) sorption onto a variety of rock types (bentonite, tuff, granodiorite) under oxidising and reducing conditions in de-ionised and sea water solutions were modelled within one order of magnitude using an electrostatically corrected surface complexation model. Certain of the batch system derived TSM predictions were tested by comparison with the results of diffusion experiments in compacted bentonite. Reasonable correlation was observed between apparent diffusivities for Cs and Se(IV) and those calculated using Kd values predicted by the corresponding TSM in the mass transfer equation. (Figure 16). On the other hand, the Kd extracted from the retardation factor observed for U(VI) diffusion in compacted bentonite was 1-2 orders of magnitude less than the TSM predicted Kd.

11. The capacity of the TSM to predict the results of U(VI) sorption on hematite in systems containing significant concentrations of competing or complexing ions (Ca, SO₄, etc.) was not tested.

6. Conclusions and Recommendations

The significant advances in the field of thermodynamic modelling of sorption processes was clearly demonstrated by the presentations at the Oxford Workshop and by other recent literature. The consensus of the experts present at the Oxford Sorption Workshop, as well as the information gathered in the Status Report indicate that the experimental determination of radionuclide K_d will continue to remain the main source of information for estimating their sorption properties throughout the repository system and that this will continue over a time scale of at least the next five years. Therefore it is acknowledged that the state of advancement of the models is not yet sufficient for their general application in a predictive manner. However, it was recognised that much confidence and transparency can be gained by using chemical reasoning and thermodynamic modelling to guide and support the experimental determinations in a similar fashion to the way equilibrium calculations are used in radionuclide solubility estimations.

Advanced performance assessment of nuclear waste repositories requires the determination of the geochemical evolution of the entire repository system for the various time-dependent scenarios considered (particularly for time-dependent PA exercises). This is normally done by studying the variation of key chemical parameters (pH, Eh, major groundwater composition) in the various parts of the repository system. The variability on the geochemical composition of the system influences the sorption properties of the radionuclides of concern along the migration path. Once the theoretical framework has been more firmly established, chemical thermodynamic sorption models (TSM) may be able to be integrated within a common framework allowing simultaneous consideration of both the geochemical variability of the system and its influence on radionuclide sorption properties, thereby providing support for the selection and uncertainty estimation of radionuclide K_d 's.

The critical parameters needed in order to apply TSM for predicting radionuclide sorption in natural systems, flow wetted surface and detailed mineral characterisation (fracture fillings and coatings), are also needed for transport calculations in PA analyses. Most of the thermodynamic data required to describe the surface interactions between the critical radionuclides and some key mineral surfaces are either available or may be estimated by applying chemical reasoning. Both the theoretical developments and application cases presented at the Oxford Sorption Workshop indicate increasing scientific maturity of the field, as well as the possibilities of application of TSM for predicting radionuclide sorption for PA purposes. However, there is as yet no clear consensus regarding whether or not a single type of TSM can be proposed for treating sorption in all natural systems. In particular, the requirements and the choice of electrostatic correction terms are basically dependent on the relative strength of the radionuclide-mineral surface interaction and the salinity of the aqueous media under consideration. The multiplicity of electrostatic correction models currently in use limits the credibility of the modelling approach. There is a need to move forward in carrying out a systematic, critical evaluation of the various sorption modelling approaches in order to arrive at commonly agreed upon criteria for selecting those which are most appropriate for predicting K_d values for PA needs in evaluating specific RN storage concepts.

From a practical standpoint, TSM approaches offer several specific advantages to the overall performance assessment effort:

Scientific Rationality: The TSM approach is based on basic physical-chemical principles and therefore can be defended at a fundamental level.

Cost effectiveness: The TSM approach should be cost effective over the long term. A great deal of effort has been invested in experimentally determining K_d values for a relatively small number of radionuclides on a wide variety of geological solids. It is now recognised that K_d measured for a given radionuclide/solid phase combination under one set of conditions cannot generally be used to accurately predict the K_d for another set of conditions. A comprehensive TSM based analytical approach should limit the overall effort needed to provide sufficiently accurate predictions of radionuclide partitioning over a wide range of system conditions. This is because the TSM approach aims at identifying the processes and quantifying the fundamental parameters responsible for radionuclide partitioning. While the effort needed to gather this information may initially be substantial in many cases, all properly measured and documented data is useful and contributes to our understanding both of a particular radionuclide/solid/solution system and of the overall validity and limits of the TSM approach. In addition, the inherently cumulative characteristic of TSM information gathering means that its progress can be evaluated and the data gathering process stopped for a given geological system, either when a sufficiently accurate model has been developed and validated or when the TSM approach has reached its limits.

Data reporting and organisation: The logical and internally consistent structure of TSM-based mathematical representations is well adapted for organising solid/solution partitioning data. Such a database could be organised around the component/total concentration/species stoichiometry/stability constant matrix representation already employed in certain numerical speciation programs. Such a representation, combined with a well-organised reference to critical experimental parameters, is essential if the “cumulative” knowledge advantages of the TSM approach are to be fully realised.

Based on the above points, and more generally the results of the Oxford Workshop, we propose the following recommendations to the radioactive waste management community:

1. That the value of TSM in supporting the selection of K_d values be given wider recognition. The choice of K_d values should be supported by TSM wherever possible and documented as part of the justification for parameter selection.
2. That the presentations at the Oxford workshop demonstrated that there were a number of different modelling approaches that could be used successfully to describe similar groups of minerals such as clays. The Radwaste Community makes a dedicated effort to carry out a critical evaluation of the merits of the various modelling approaches as the first step towards achieving a consensus as to the common criteria which should be used when selecting a TSM approach for supporting K_d parameter estimations.
3. That a concerted effort be undertaken to rationalise the large amount of sorption data available in the various national programmes as a first step towards the application of TSM to estimate the magnitude and variability of radionuclide sorption in PA exercises and to guide future experimental work on radionuclide sorption.

These activities were recognised as essential phases for preparing the compilation of thermodynamic data bases to use with TSM for radionuclide sorption.

Furthermore, the need for further testing of TSM for radionuclide sorption was recognised, especially at the field scale. This is an area where international collaboration is particularly beneficial. The present and future field experimental sites could be used for these activities.

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Annex 1

Definition of Kd and Rf

In its most direct sense, a Kd value simply represents the result of an experimental measurement or mathematical calculation of the partitioning, between the solid and solution phases, of the total amount of a specific radioelement present in a closed system containing a known mass of a particular solid material and a known volume of a solution of a given composition. Mathematically, Kd is given by:

$$Kd = \frac{C_{solid}}{C_{soln}}$$

where C_{solid} is the total sorbed RN concentration (e.g. in moles RN per kg solid) and C_{soln} is the total solution phase RN concentration (e.g. moles RN / m³ solution); Kd therefore has the units of volume over mass (e.g. m³/kg).

If a particular constant Kd value can be taken to represent the actual RN solid/solution partitioning which would occur in a given region of the host geological formation, it can be used to estimate the corresponding retardation factor, Rf, for RN mass transfer **relative to non-sorbing solutes** (i.e. Kd = 0). For the simplest case of convective flow through porous formations, Rf can be estimated by $Rf = 1 + (Kd \cdot \rho) / \theta$, where ρ is the solid phase density of the host formation (in kg/m³) and θ is the volume of circulating solution per volume of formation (m³/m³); i.e. Rf is unit-less. Comparable proportional expressions exist for diffusion-dominated mass transport.

In cases where the Kd value varies during the transport time period, other formulations for Rf will be needed. These can vary from mathematical solutions if Kd variation can be expressed by some simple form (linear, logarithmic...) to coupling of a TSM with a transport model.

Annex 2

Derivation of Relationships Given in Section 3.2

Consider a chemical system containing only the following three chemical components:

- a single **radionuclide** component (e.g. Cs, Sr, U(VI)). The total amount of RN in the system at a particular time, expressed in mass or in **moles** (here we will use moles), can be divided by the total solution volume, V_t , to give the **total RN concentration**, C_{RN} . We will also assume that RN has only **one dissolved species** (e.g. Cs^+ , Sr^{2+} , UO_2^{2+} , ...); the dissolved species concentration, in moles/m³, will be denoted [RN].
- a single type of “**sorption site**” component, S_{\equiv} , located on the solid phase surface. The total mass of solid is known, as is the solid’s *specific surface area*, A_{sp} (m²/g), and *surface site density*, $D_{s\equiv}$ (in moles/m²). The total amount of S- is therefore $mass \cdot A_{sp} \cdot D_{s\equiv}$, which we can express in terms of an equivalent total concentration, C_{S-} (in moles S- / m³ groundwater), by dividing by V_t . The solution volume normalised concentrations of sorbed species (see below) will also be denoted by [].
- a single **major ion** component, M, (e.g. H^+ , Ca^{2+} , Na^+ ...) which is naturally present in the groundwater and is also able to react with S-, i.e. to “compete” with RN for sorption on surface sites. M will have its own total and dissolved concentrations, C_M and [M] respectively.

We will further assume that the only reactions which can take place are RN and M sorption onto S- to form the two species S-RN and S-M, with the following stoichiometry's and intrinsic **thermodynamic formation constants**:



The respective K values are proportional to the strength, or intensity, of the chemical bond between S- and RN or M. In addition, we will also assume for demonstration purposes that there are virtually no sites in the “free”, S-, state, i.e. all sites are either as S-RN or S-M. Under these conditions, RN sorption can be approximated by the following exchange reaction, the only one we will consider to be possible by combining equations (1) and (2):



The mass balance for sorption sites will therefore be:

$$C_S = [S - M] + [S - RN] \quad (3.4)$$

Assuming that **thermodynamic equilibrium** is reached, the relative concentrations¹² of all four species can be described by the following MAL:

$$K_{ex} = \frac{K_{RN}}{K_M} = \frac{[S - RN][M]}{[S - M][RN]} \quad (3.5)$$

where K_{ex} is the thermodynamic constant describing RN exchange for M on the sorption site. If we further assume that the dissolved concentration of the major ion M is “fixed” at a constant value by the major ion geochemistry of the “incoming” groundwater and relatively unaffected by changes in C_{RN}^{13} , [M] can be combined with K_{ex} in equation (5) to give a combined **conditional** constant, $k = K_{ex}[M]^{-1}$. Equation (5) can then be combined with equation (4) and rearranged into a form more useful for demonstrating the way various parameters can affect [S-RN], and therefore Kd(RN):

$$[S - RN] = \frac{k[RN]C_s}{1 + k[RN]} \quad (3.6)$$

The variation in RN sorption, log [S-RN], and RN solid-solution ratio, [S-RN]/[RN] can be subdivided into three situations:

1. one where log[S-RN] increases linearly, and [S-RN]/[RN] remains constant as a function of log[total RN]. This behaviour corresponds to conditions where the concentration of sorbed RN, [S-RN], is small with regard to the total sorption site concentration, C_s . Under these conditions, equation (6) simplifies to the following linear equation:

$$[S - RN] = k[RN]C_s \quad (3.7)$$

2. a transition region where $d\log[S-RN]/d\log[RN]$ and [S-RN]/[RN] decrease rapidly due to progressive saturation of sorption sites by RN;
3. one where log[S-RN] remains constant at some maximum value and [S-RN]/[RN] is effectively zero, described by:

$$[S - RN] = C_s \quad (3.8)$$

We will focus here largely on first region-type behaviour since it is the most likely for the trace RN amounts which will be present in virtually all migration field RVE. It is, however, worth noting that saturation-type behaviour might take place under conditions where C_s for a particular site type is small, and/or natural concentrations of the same element (or ones having similar sorption properties) are sufficiently high. Such a situation could be envisaged for the near field components located close to the source, i.e. corrosion products from the canister.

-
12. Activity corrections are not considered for this example.
 13. This assumption is reasonable for open systems where variations in trace element total concentration are “transported” into a reactor containing a fixed solid phase by a constant composition (major element) solution.

Equation (6) shows that $[S-RN]/[RN]$ will be determined by the values of the various parameters making up k and C_s , i.e.:

$$\frac{[S - RN]}{[RN]} = K_{RN} \cdot \frac{1}{K_M \cdot [M]} \cdot \frac{D_S \cdot A_{sp} \cdot mass}{V_t} \quad (3.9)$$

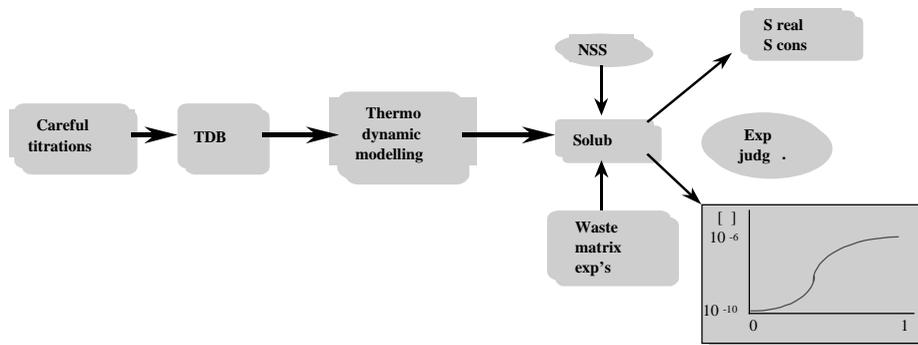
where

$$Kd(RN) = \frac{[S - RN]}{[RN]} \cdot \frac{V_t}{mass} = K_{RN} \cdot D_S \cdot A_{sp} \cdot \frac{1}{K_M \cdot [M]} \quad (3.10)$$

FIGURES FOR PART 2

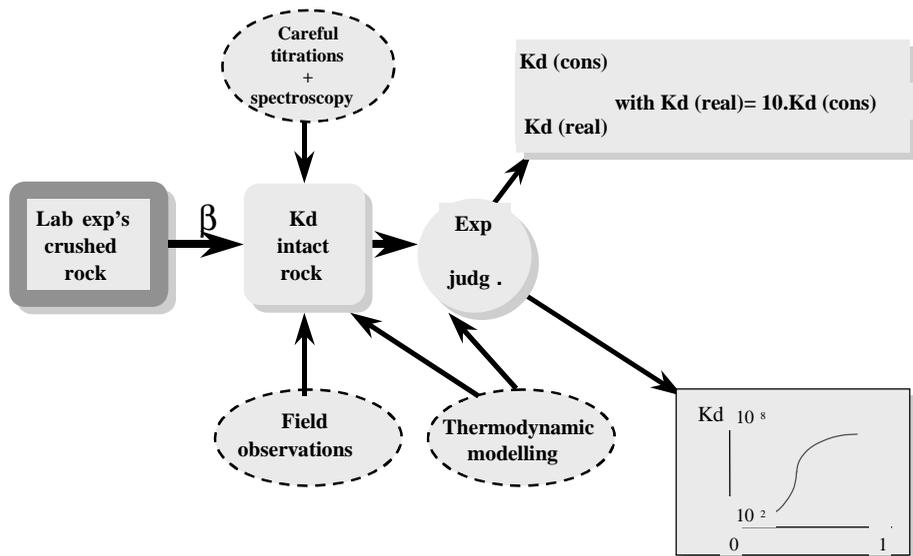
Figure 1. **Analogy between approaches used in selecting solubility (a) and Kd (b) parameters for PA. (The β parameter in Figure (b) is an experimentally determined conversion factor) (Bruno, Oxford)**

TDB: Thermodynamic database
 NSS: Natural system studies
 S real: Solubility, realistic value
 S cons: Solubility, conservative value
 Graphic: Solubility probability function



(a)

Kd (cons): Kd, conservative value
 Kd (real): Kd, realistic value
 β : experimentally determined conversion factor
 Graphic: Kd probability function



(b)

Figure 2. Example of K_d variation for Ni^{2+} sorption on a sandy-clayey aquifer material, as a function of pH and total calcium concentration (Altmann and Chupeau, 1997)

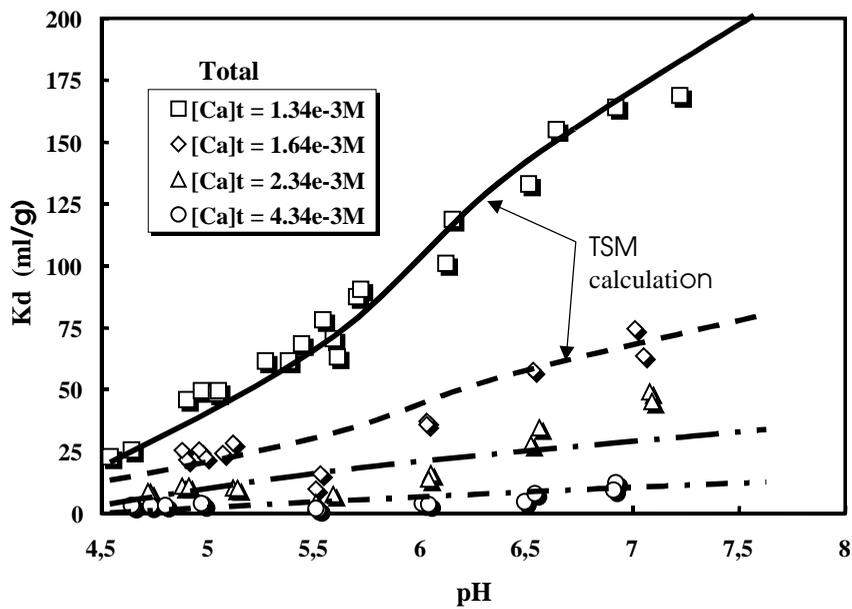
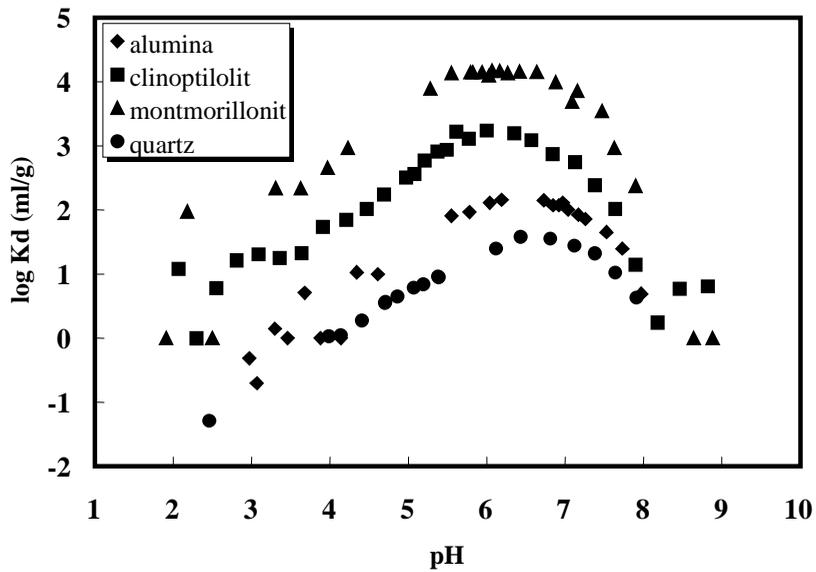
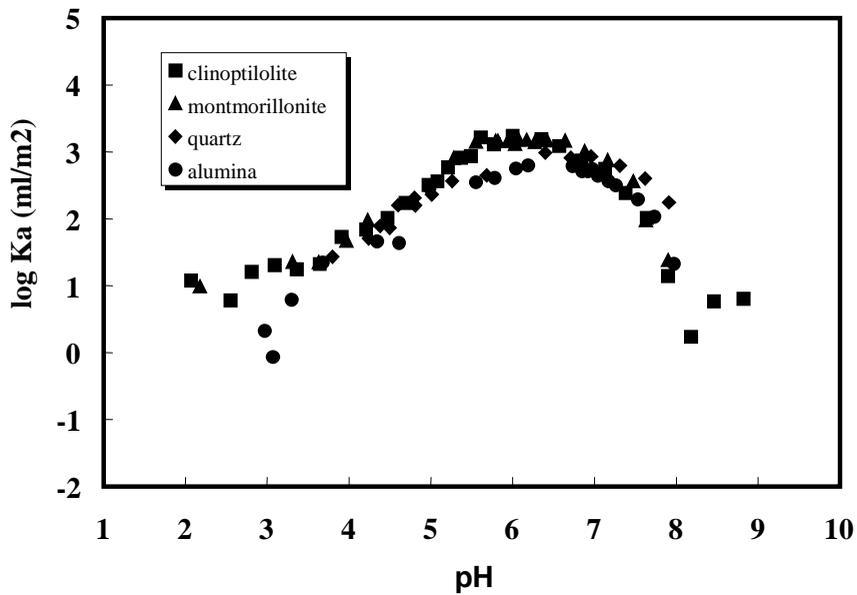


Figure 3. Mass-normalised partitioning coefficient values (figure a) versus specific surface area normalised values (Figure b) for U(IV) sorption on four minerals (Turner *et al.*, Oxford)



(a)



(b)

Figure 4. Variations in K_d as a function of pH for different divalent cations on an Al gel (Figure a) and on a Fe gel (Figure b) in the same electrolyte (adapted from Kinniburgh and Jackson, 1981)

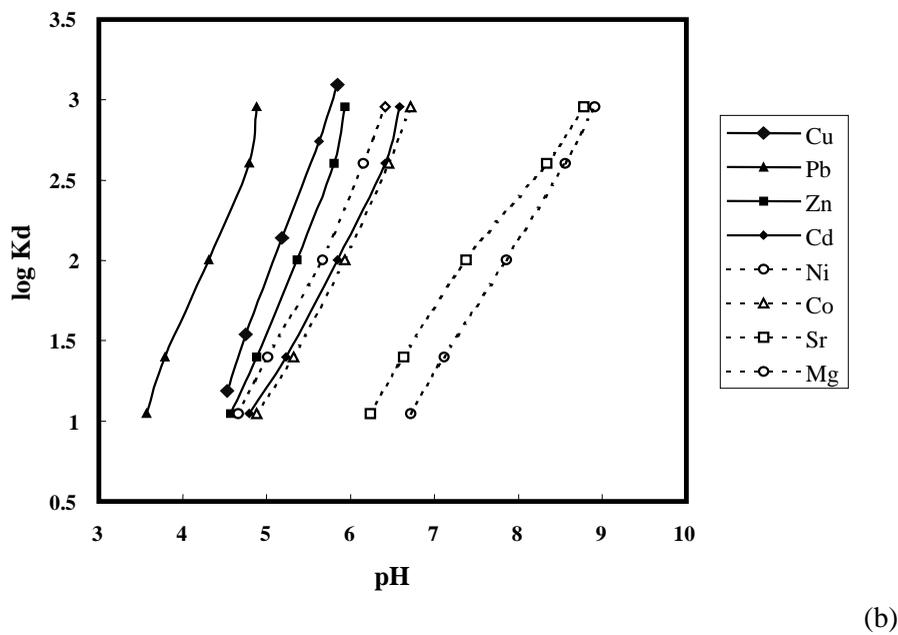
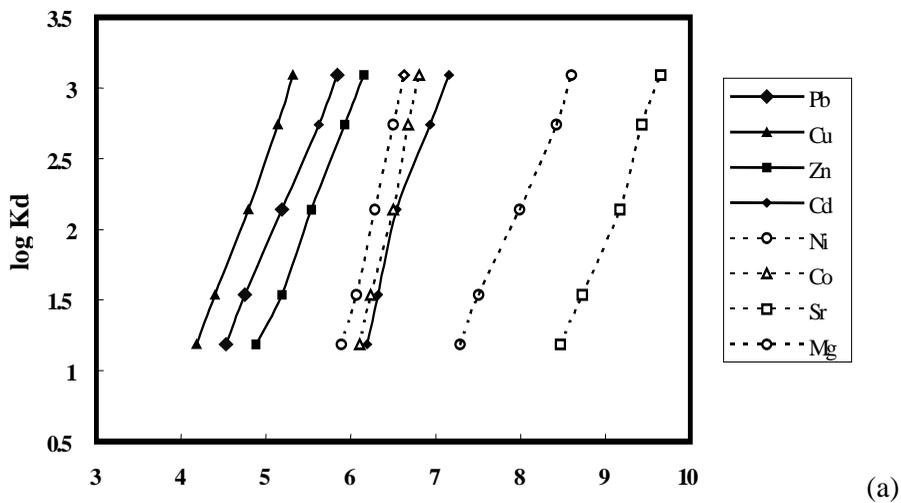


Figure 5. Example of LFER existing between the first hydrolysis constant for various divalent cations and the intrinsic K values for sorption on ferrihydrite (after Dzombak and Morel, 1990)

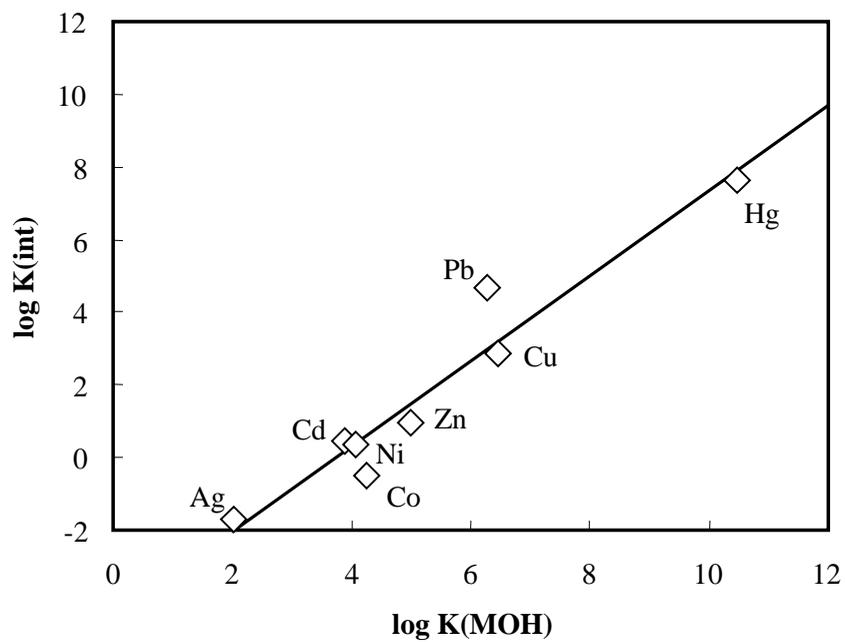


Figure 6. TSM development approach – Sample characterisation and geochemical modelling phase

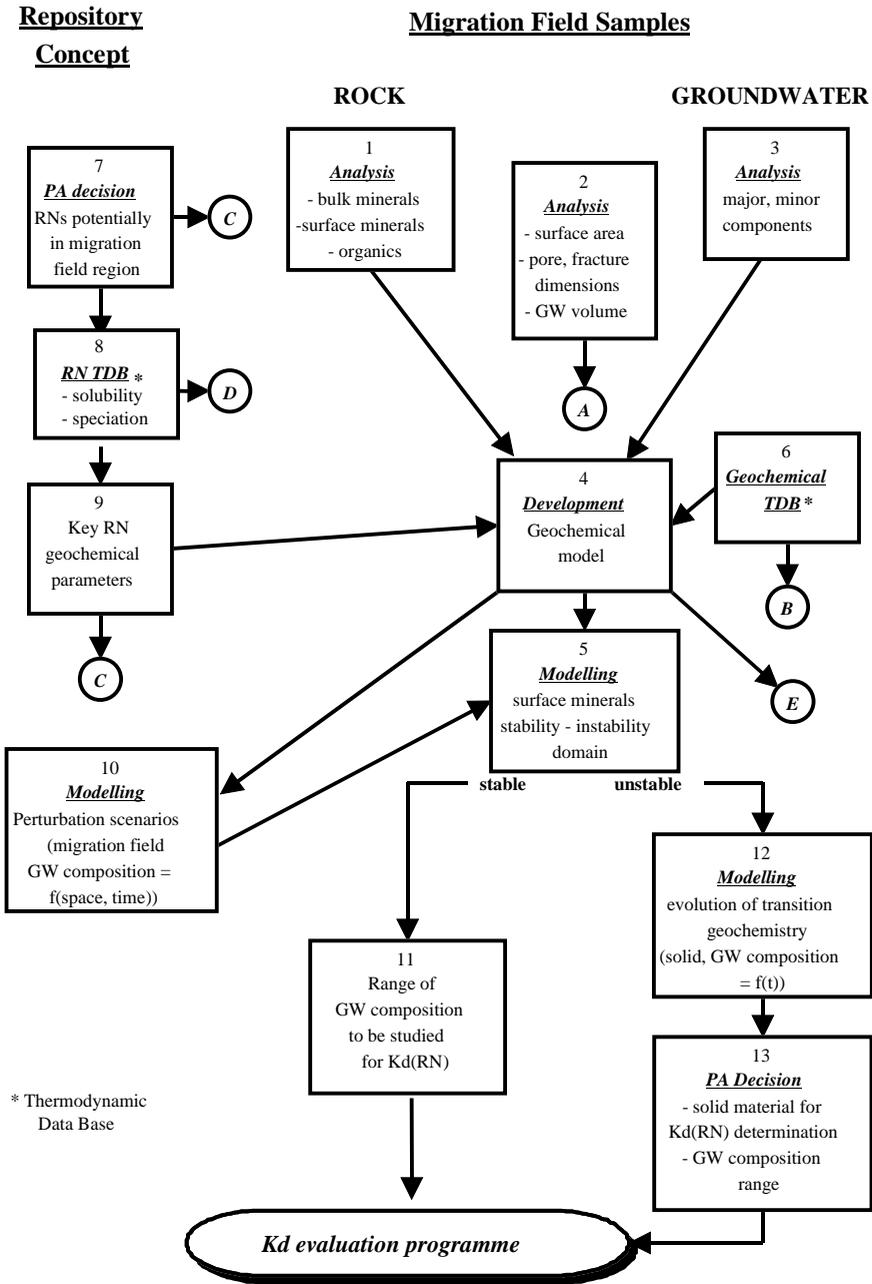


Figure 7. TSM development approach – Model development phase

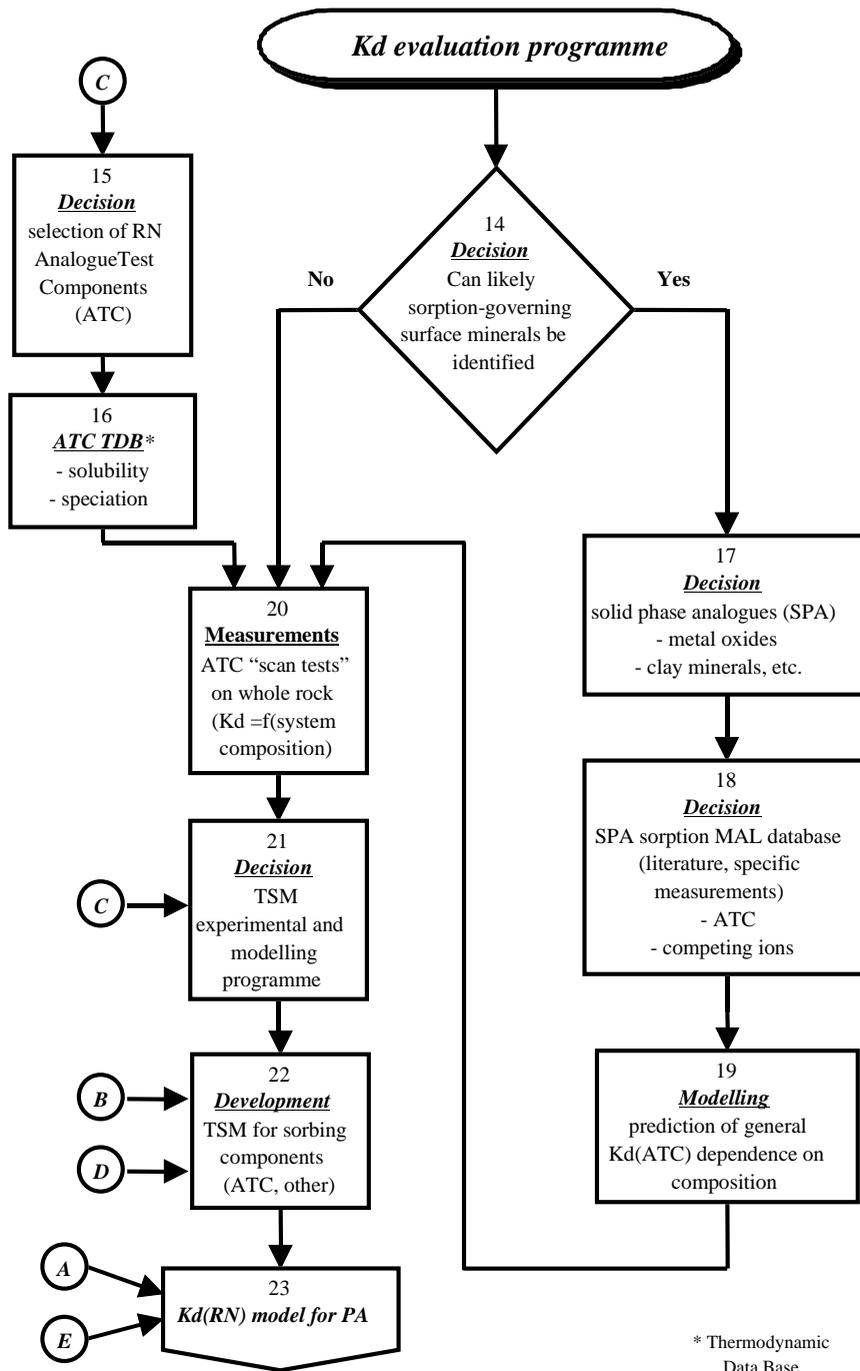
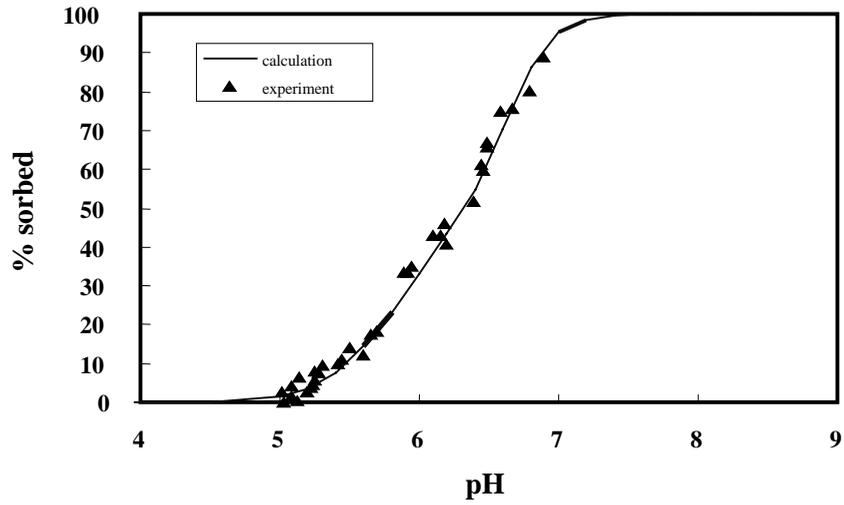
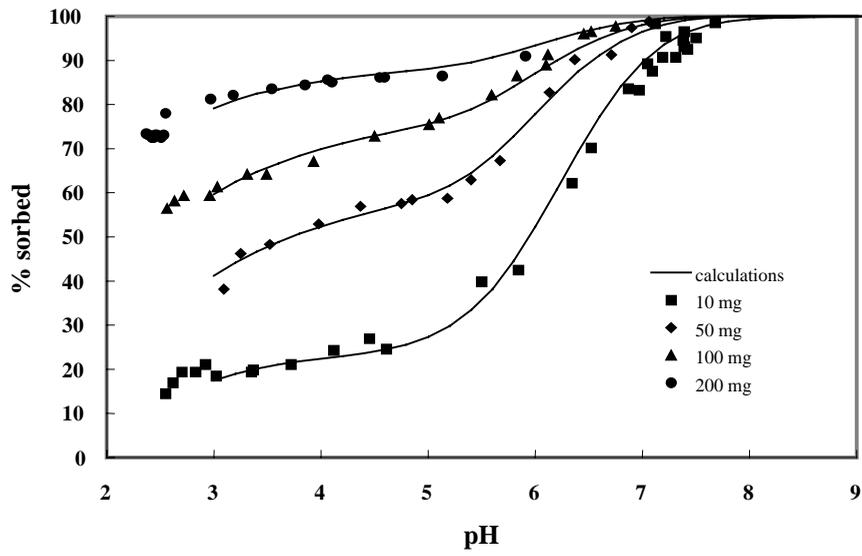


Figure 8. TSM model prediction versus experimental data for Yb^{3+} sorption on kaolinite (Figure a) and on montmorillonite (Figure b). (Marmier, Oxford)



(a)



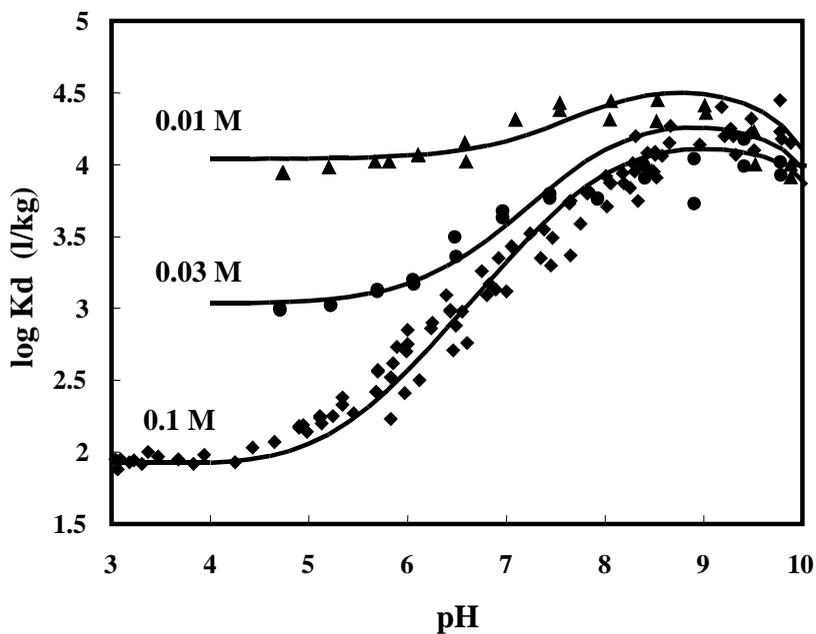
(b)

Figure 9. TSM of Ni sorption on montmorillonite

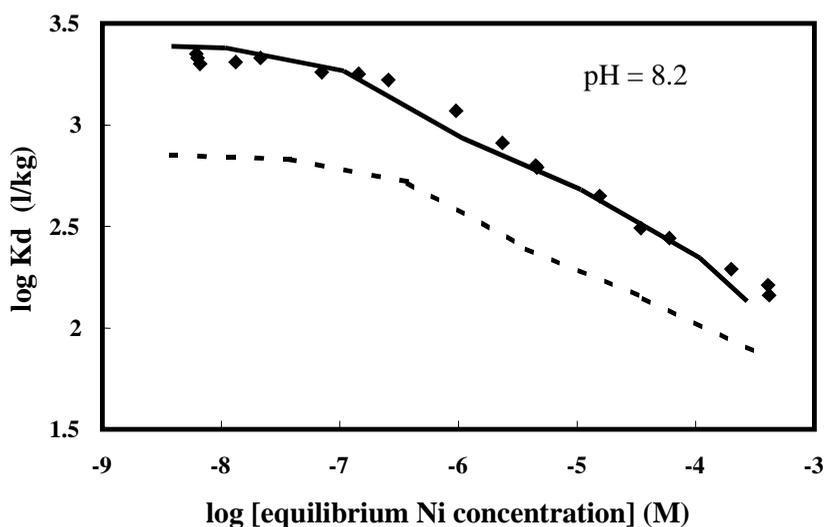
Figure (a): predictions of sorption on conditioned montmorillonite at 0.001 N and 0.01 N ionic strengths by model calibrated at 0.1 N ionic strength.

Figure (b): prediction of sorption on unconditioned montmorillonite (dashed line), prediction after correcting for invalid formation constant for NiCO₃ dissolved complex (solid line).

(Bradbury and Baeyens, Oxford)

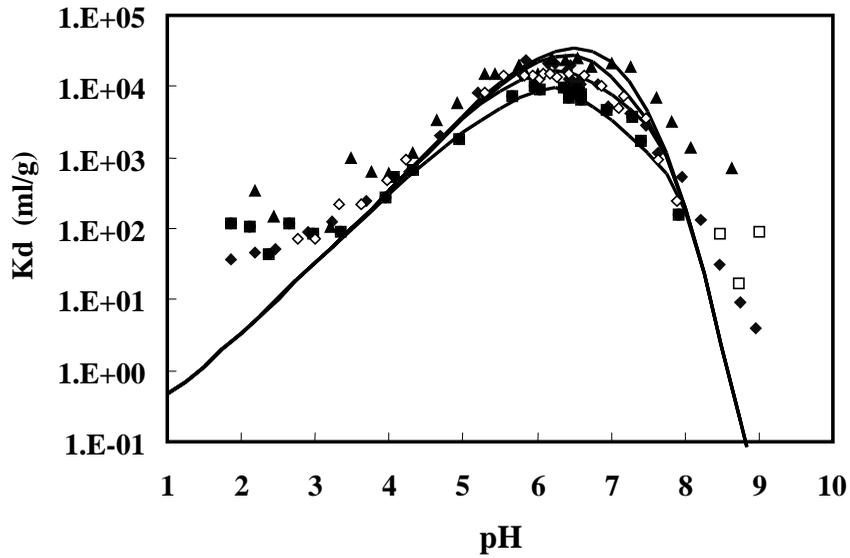


(a)

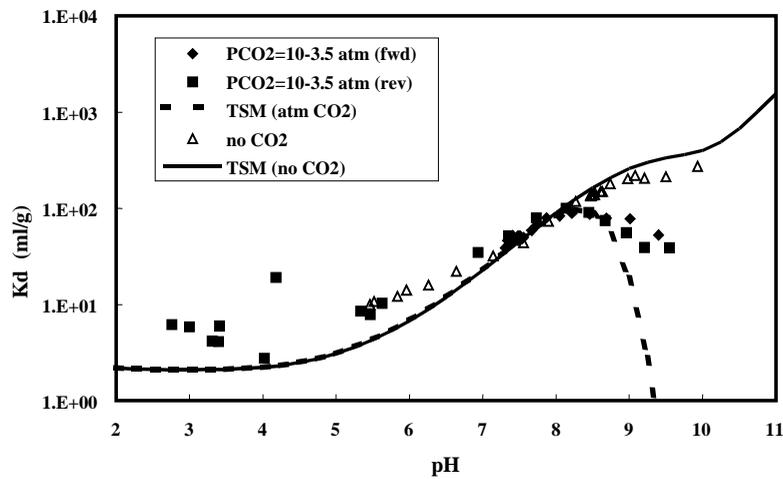


(b)

Figure 10. Examples of the capacity of a two-site type TSM (SiOH, AlOH) to predict K_d values for U(IV) (Figure a) and Np(V) (Figure b) sorption on montmorillonite, as a function of pH and P_{CO_2} (Turner *et al.*, Oxford)



(a)



(b)

Figure 11. Ion exchange TSM modelling of the variability of K_d values for four elements on smectite (in 0.1M NaClO₄) as a function of varying pH (Ly, Oxford)

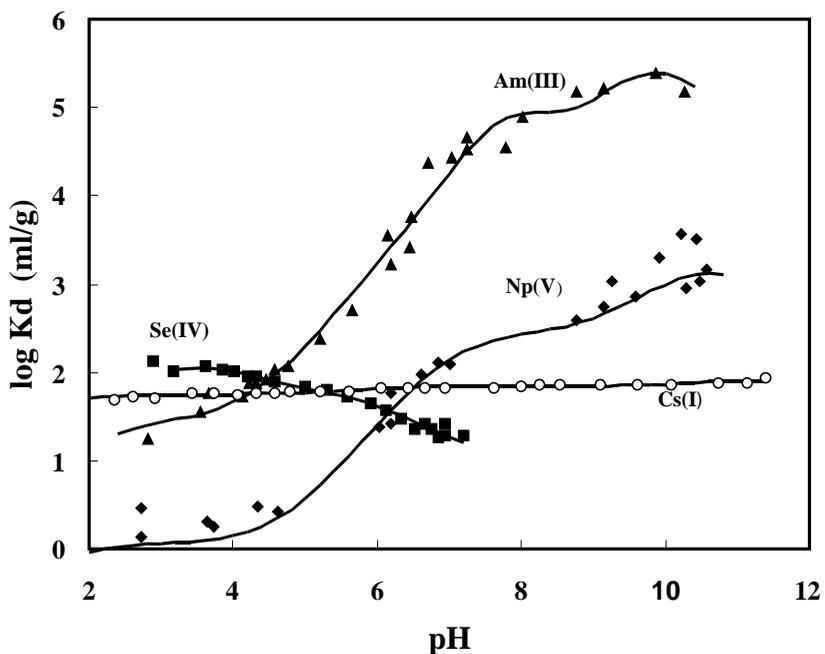


Figure 12. Example of the use of a single site (EDL corrected) TSM developed for representing Ni sorption on goethite for representing Ni sorption on a sand containing trace iron oxide (Siegel *et al.*, Oxford)

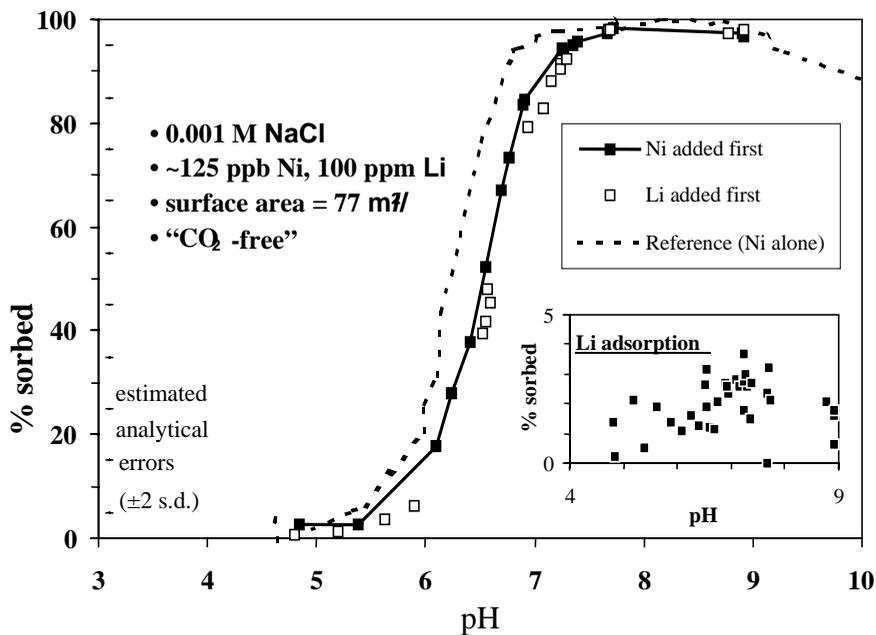


Figure 13. Comparison of the results of simulation of Zn concentrations in a shallow aquifer after 54 years of Zn contamination using a coupled transport plus TSM model (Figure b) with observed Zn contamination (Figure a) (Davis *et al.*, Oxford)

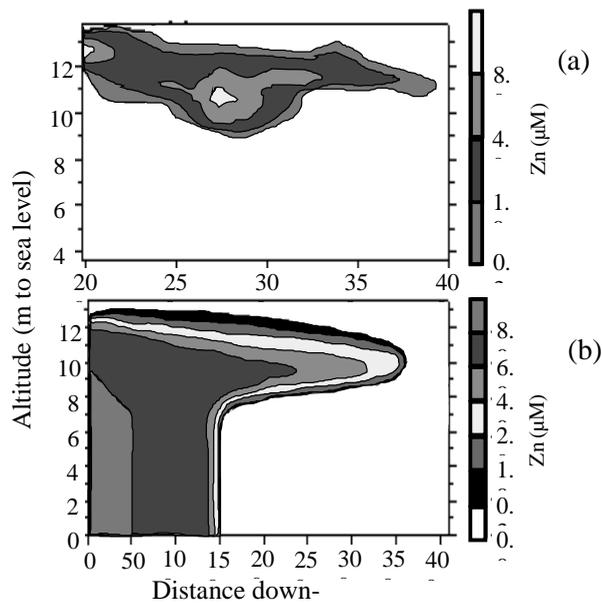


Figure 14. Comparison of laboratory R_d values for U sorption on Koongara W2 material with predictions made using TSM based on a ferrihydrite U-sorption. The curves represent different assumptions for estimating total sorption site amount: (A) only TAO extracted ferrihydrite sites, (B) based on DCB extraction results, (C) based on BET surface area and using the same site density per unit area as ferrihydrite. (Payne, Oxford)

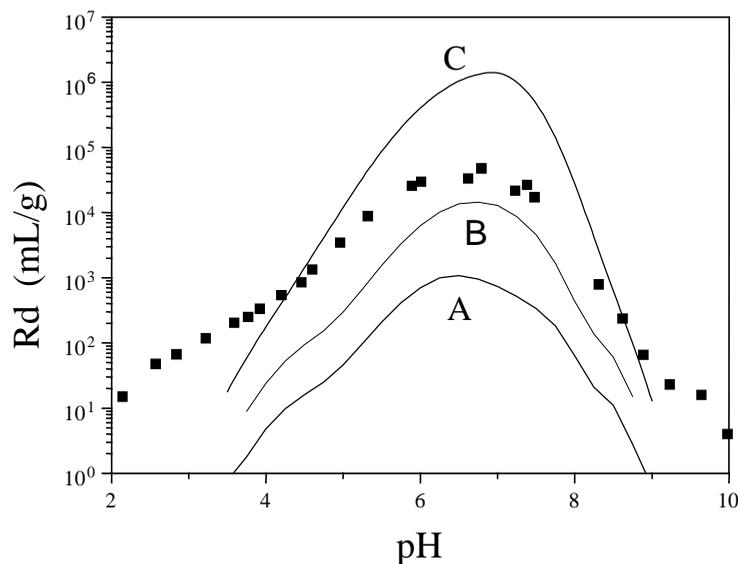


Figure 15. Comparison of measured U(VI) K_d values on 4 rock types (bars) with range of K_d predicted using two different TSM for U sorption on hematite (open symbols-inner sphere U complex, solid symbols – outer sphere U complex) and two hypotheses considered to be bounding for total hematite sites (higher K_d –total surface area, lower K_d - weight percent of hematite = percent of hematite surface present per unit mass of rock) (Linklater *et al.*, Oxford)

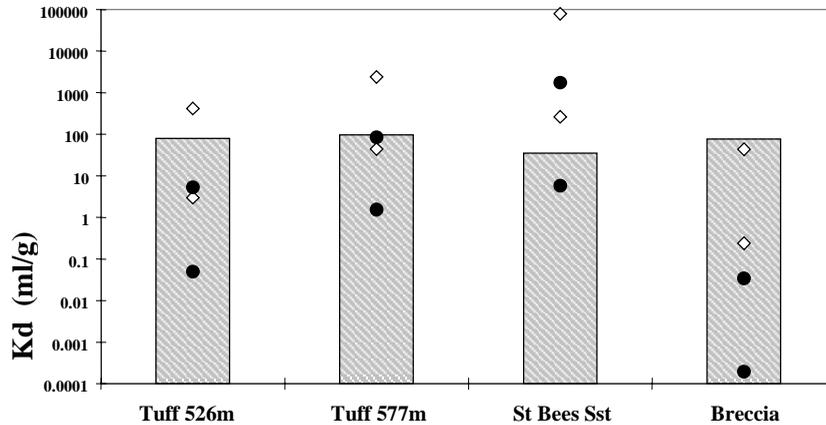
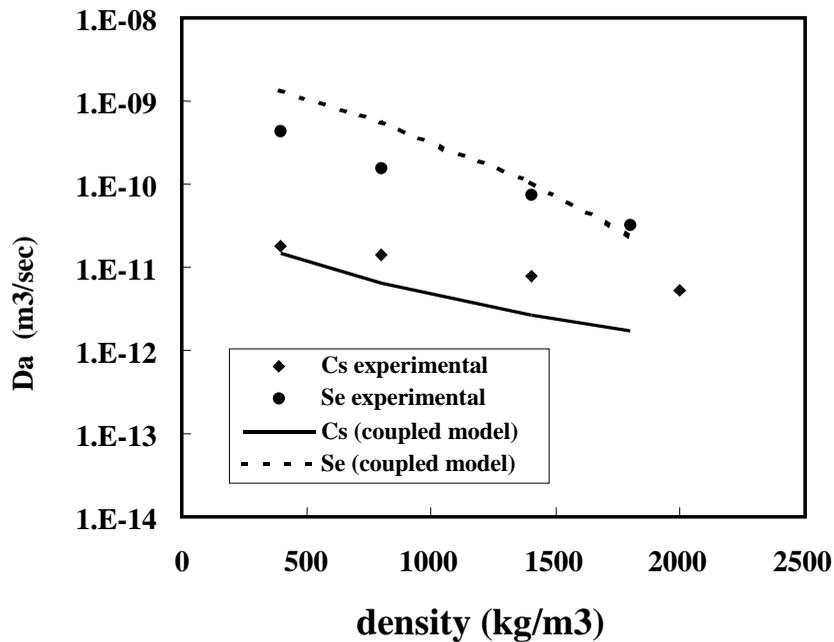


Figure 16. Comparison of apparent diffusion coefficients for Cs and Se predicted using a batch system derived TSM with the results of diffusion experiments in compacted bentonite (Yui and Shibutani, Oxford)



PART 3

**INTERNATIONAL MEETING ON CHEMICAL MODELLING OF
SORPTION IN THE FIELD OF RADIOACTIVE WASTE
MANAGEMENT**

**6-8 MAY 1997,
OXFORD, UK**

SUMMARIES OF PRESENTATIONS

Objectives

The objectives of the meeting were:

- to investigate the potential of mechanistic models for improving confidence in predictions of sorption values for performance assessment;
- to gather new information and promote discussions within the scientific and waste management communities;
- to provide an input to a Status Report on mechanistic sorption modelling that will be published by the NEA and be given the widest possible dissemination.

Background

This international meeting was organised by the Forum on Sorption Modelling for Performance Assessment, set-up within the NEA with the participation of fourteen radioactive waste management agencies and licensing authorities from Member countries. The decision to launch this project arose out of a growing awareness in the radioactive waste management performance assessment community that there would be a greater level of confidence in the use of sorption distribution coefficients (K_d 's) if these were supported by an understanding of the underlying processes.

This activity was a follow up of two previous NEA meetings on related topics:

- radionuclide sorption from the safety evaluation perspective, Interlaken, Switzerland, 16-18 October 1991; and
- informal expert meeting on the use of Surface Complexation Models for representing sorption phenomena in natural systems, Stanford University, Stanford, California, USA, April 5-7, 1993.

Topics covered by the meeting

The meeting concentrated on three topics:

- the demonstration of the usefulness of sorption chemical models to performance assessment with numerous examples where they have been used successfully;
- a review of the practical approach to sorption chemical modelling, identifying key questions facing experimentalists and modellers;
- an overview of what has been done to date with mechanistic models for understanding and estimating K_d 's in natural systems.

Session 1: Kd and Performance Assessment

- Performance assessment context and geochemical context of Kd (Invited papers and discussions)
 - Performance assessor's point of view
 - Reviewer's point of view (safety authorities)

Session 2: Chemical models and Kd for Performance Assessment

- Review of chemical models for sorption (Invited papers and discussions)
 - key parameters and how to get them
 - emphasis on key questions facing experimentalists and modellers

Session 3: Approach to sorption modelling of natural systems

- Strategic approaches to sorption modelling of natural systems (Invited papers and discussions)
 - how it is done : top down and bottom up approaches
 - examples from several projects, including non radioactive waste examples

Session 4: Application of mechanistic models to understanding/estimating Kd's in natural systems

- State-of-the-art (mass action, mass balance sorption models and natural systems) Short oral presentations (15-20 minutes, plus discussion).
 - In order to avoid repetitions with Session 3, contributions will be structured around a questionnaire called Data Sheet (see below).
 - The objective is to learn about practical experiences, not to scrutinise results.

Session 5: Discussion of key questions (Panel discussions)

- Technical / chemical aspects
 - emphasis on model parameters
 - success / failures
 - problems /solutions
- Link to PA, better support of Kd's

Session 6: Consensus, Wrap-up

- Conclusions of the meeting

Presentation of works related to sorption in natural systems

Scientists working in the field of sorption modelling were invited to present their work (mass action, mass balance sorption models and natural systems) in Session 4: State of the art. In order to avoid repetitions with Session 3, and to facilitate comparison of methods, authors were invited to fill-in following questionnaire (Data Sheet).

Data sheet questionnaire and abstract for contributions to session 4

- Author
 - Name
 - Address
 - Telephone
 - Fax number
 - e-mail address
- Solid phase
 - Identify (name of solid)
 - Source (origin of solid)
 - Mineralogy: major & minor components, %, distribution
- Aqueous phase
 - Solution composition: conditions (e.g. time, temperature, batch/flow, oxic/anoxic)
 - Radionuclides
- Brief description of model
 - Surface components, surface species
 - Parameters (measured, calculated, estimated)
 - Thermodynamic data used
 - Codes
- Publications
- Lessons learnt

In addition, authors were invited to provide a one page abstract considering, when relevant, the following key questions.

List of key questions

The purpose of this list was to focus discussions on issues that had been identified as critical to successful use of chemical modelling of sorption in natural systems for the benefit of radioactive waste management. Authors were also invited to consider these questions when preparing their abstract.

Key issues to be considered by the meeting were:

- Kd
- How to identify critical mechanism governing sorption of radionuclides (RN)
 - solid
 - RN
 - solution composition (majors)
- Thermodynamic Data Base (TDB) for aqueous chemistry of RN, etc.
 - activity coefficients
- How do you measure/quantify the real composition of the solid surface
 - phase identification
 - site type

- How much of each site type
 - site specific concentrations
- What are the key reactions between solutes/surface sites
 - stoichiometry, K, H⁺, major cations, RN
- Electrostatics necessary?
 - what conditions
 - which RN
 - what range of system composition
- Are K_d values measured in laboratory the same as those *in situ*?
 - scale, s/s ratio
 - modification of surface composition
- How well compare batch sorption data (K_d's) with K_d's derived from diffusion measurements?
- How does approach used (data/model) support/aid use of K_d's
 - end user
 - why was approach chosen

Authors were given 15 to 20 minutes for oral presentation, not including discussion. No full paper were required but filled Data Sheets and abstracts were available for distribution to participants in advance of the meeting. It is emphasised that the objective of the exercise was to learn about practical experiences of individual experimentalists and modellers, not to scrutinise results.

Programme and Contributions

	Sessions, Objectives, Papers	Authors / Speakers
	DAY 1, Tuesday, May 6	
	Session 0: Introduction	
	<i>General objectives of the meeting</i>	C. Tweed, AEAT
	<i>Recent developments in the UK</i>	A. Hooper, Nirex
	Session 1: Kd and Performance Assessment	
1.1	<i>Sorption in Performance Assessment – the Nirex Perspective.</i>	A. Hooper, Nirex
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	Session 2: Chemical models and Kd for Performance Assessment	
2.1	<i>Key questions, Key parameters</i>	S. Altmann, BRGM
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	Session 3: Approach to sorption modelling of natural systems	
3.1	<i>Acquisition of Sorption Data for the Nirex Performance Assessment</i>	C. Tweed, AEAT
3.2	<i>On the Application of Distribution Coefficients and Mechanistic Sorption Models in Performance Assessments for Repositories in Crystalline Rock</i>	S. Wingefors & R. Arthur, SKI
3.3	<i>A Mechanistic Description of Ni Sorption on Namtomorillonite</i>	M. Bradbury & B. Baeyens, PSI
3.4	<i>A PNC Approach to Increase Confidence in Sorption Coefficients for Near-field Performance</i>	T. Shibutani, PNC
3.5	<i>An approach to Provide a Sorption Database for Performance Assessment</i>	C. Yh, KAERI
3.6	<i>Uranium Sorption Studies within the Koongarra Natural Analogue Project</i>	T. Payne, ASARR
3.7	<i>Determination of Radionuclides Migration Parameters in a Clay Formation: The Belgian Approach</i>	R. Gens, ONDRAF/NIRAS

3.8	<i>Application of a Laboratory-derived Surface Complexation Model for Zinc Adsorption to Field Observations of Zinc Transport in Groundwater</i>	J. Davis, USGS
	Sessions, Objectives, Papers	Authors / Speakers
	DAY 2, Wednesday, May 7	
	Session 4: Application of Mechanistic Models to understanding/estimating Kd's in natural systems	
4.1	<i>Proposal for the Development of Predictive Surface Complexation Models to be Used as a Supporting Tool to Kd Parameters in PA</i>	L. Duro, QuantiSci
4.2	<i>Characterisation of Natural Substrates with Regard to Application of Surface Complexation Models.</i>	D. Waite, UNSW
4.3	<i>Sorption Modeling for Performance Assessment at the Center for Nuclear Waste Regulatory Analyses</i>	D. Turner, SWRI
4.4	<i>Development of a Mechanistic Model of Sorption of U(VI) onto Sellafield rocks.</i>	C.M. Linklater, AEAT
4.5	<i>Modelling Sorption of Nickel on Silica, Goethite, and Kaolinite</i>	M. Olin, VTT
4.6	<i>Pore Water Composition and Bulk Solution in Crystalline Rock and in Bentonite Clay</i>	M. Olin, VTT
4.7	<i>Mechanistic modelling of sorption of Uranium(VI), Plutonium and thorium onto aluminium oxide, muscovite and chlorite</i>	K. Bond, AEAT
4.8	<i>A Summary of Sorption Investigations Performed on Behalf the UK Regulator of Radioactive Waste Disposal</i>	M. Crawford & D. Bennet, Galson
4.9	<i>Dolomite Surface Chemistry and Actinide Retention</i>	P. Brady, Sandia
4.10	<i>Uranium(VI) Transport Modeling under Variable Chemical Conditions Using the Surface Complexation Concept</i>	J. Davis, USGS
4.11	<i>Sorption of Th onto Titanium dioxide</i>	Y. Albinsson, Chalmers
4.12	<i>Uranium Sorption on Phyllite</i>	T. Arnold, Rossendorf
4.13	<i>Ni sorption by a natural sand</i>	M. Siegel, Sandia
4.14	<i>A Model for Radionuclide Sorption onto Cementitious Surfaces</i>	T.G. Heath, AEAT
4.15	<i>Application of thermodynamic sorption models to distribution coefficients of radionuclides in bentonite</i>	M. Ochs, BMG
4.16	<i>Sorption of Europium onto Illite: Mechanistic Interpretations</i>	L. Wang, SCK•CEN
4.17	<i>Modelling of sorption of U(VI)-species, HCO_3^- and CO_3^{2-} on bentonite using SCM</i>	K. Stamberg & P. Benes, Czech Technical University
4.18	<i>Comments on the Use of Kd Coefficient for the Modelling of Radionuclide Migration in Porous Media</i>	K. Stamberg, Czech Technical University

4.19	<i>U sorption by WIPP clay (not available)</i>	J. Leckie, Stanford Univ.
4.20	<i>Ion exchange case</i>	J. Ly, CEA
	Sessions, Objectives, Papers	Authors / Speakers
	DAY 2, Wednesday, May 7	
	Session 4: Application of Mechanistic Models to understanding/estimating Kd's in natural systems	
4.21	<i>Modelling of radionuclide sorption on mixed solids using single oxides surface complexation models</i>	N. Marmier, Reims
4.22	<i>Adsorption of metals and organic acids to kaolinite surfaces</i>	P. Brady, Sandia

	Sessions, Objectives, Papers	Authors / Speakers
	DAY 3, Thursday, May 8 (1/2 day)	
	Session 5: How are we doing vis-à-vis Key Questions (Panel discussion)	
	<i>Objective : Start drawing conclusions. Consider:</i> <ul style="list-style-type: none"> • <i>technical / chemical aspects;</i> • <i>put emphasis on model parameters;</i> • <i>consider success / failures;</i> • <i>review problems /solutions;</i> • <i>consider link to PA, better support of Kd's?</i> 	
	<i>1st subject : Technical, chemical aspects, emphasis on model parameters</i>	
	<i>2nd subject: Link to PA, better support of Kd's?</i>	
	Session 6 : Consensus, Wrap-up	
	<i>Objective: Conclusions of the meeting. Answers to Key Questions. Recommendations?</i>	

Paper 1.1

Sorption in Performance Assessment – the Nirex Perspective

A. Hooper

United Kingdom Nirex Limited

Introduction

Nirex is responsible for the development of a deep geological repository for the disposal of solid intermediate-level and certain low-level radioactive wastes. The disposal concept in the UK is similar to those being considered in several other countries. Caverns will be excavated at depth in a stable geologic setting and the wastes, set in steel or concrete containers will be placed in the caverns. These will then be backfilled with a cement-based material.

The disposal concept makes use of multiple barriers, both engineered and natural, working in conjunction to provide adequate isolation and containment of the waste. The role of the natural barriers includes to control the rate of access of groundwater to the waste, to delay and spread the migration of radionuclides to the biosphere and to limit the probability of disruption by human-initiated or natural events. An important part of the repository development process is the demonstration of adequate safety for future generations.

Long-term safety requirements for the Nirex repository

The long-term safety requirements are defined by the Authorising Departments (ref 1) – of which the Environment Agency takes the lead in England and Wales. Technical requirements include:

- a demonstration of the understanding of the system;
- that quantitative modelling be performed;
- evaluation of individual risk against a target;
- analysis of the performance of individual barriers;
- comparison with radioactivity naturally occurring in the vicinity of the facility.

The main quantitative safety requirement is a target for individual risk to an individual from releases of radioactivity from the repository of 10^{-6} per year – i.e. the risk per year to an individual of a fatal cancer or hereditary defect must be less than 1 in a million. There is no time cut-off for this risk target. The timescale covered by assessment results is a matter for the developer to justify.

The concept of risk implies an acknowledgement that uncertainty will always exist and must be addressed in order to make a safety case. Uncertainty enters into evaluation of the long-term safety performance of a waste disposal facility for several reasons. These include:

- uncertainty as the characterisation of any potential repository site and disposal concept cannot lead to a complete understanding of the present-day situation;

- uncertainty about future environmental conditions such as climate or sea level and of the natural system and how this will influence the system performance;
- uncertainty in future human behaviour, as it affects not only personal exposures to radioactivity but the perturbations to the behaviour of the system;
- the existence of alternative defensible choices of conceptual and mathematical models;
- the effects of simplifications made in the modelling system such that it captures the aspects of interest in the system without unnecessary detail.

Probabilistic safety assessment

The regulatory concept of risk has led to the requirement to use Probabilistic Safety Assessment (PSA). PSA involves using mathematical models whose input parameters, such as radioelement solubilities and sorption, or groundwater flow rates, are uncertain quantities, to which a Probability Density Function (PDF) can be assigned, characterising the uncertainty. Practically, PSA is performed by the “Monte Carlo” method and Nirex uses the MASCOT program for this purpose. The MASCOT model input parameters are set by a process of random sampling and then the whole system is run. This process is repeated a large number of times so as to yield distributions for the output parameters. These outputs can then be analysed to give an analysis of risk. Typical evaluations of risk from the MASCOT calculations are shown in Figures 1 and 2 (Figures 6.6 and 6.7 from Volume 3 of Nirex 95 – ref. 2).

Obtaining probability density functions for input to the mascot model

The characterisation of uncertainty for a parameter such as sorption is a vital aspect of a performance assessment. The approach adopted is to use a structured elicitation process, guided by experts, to assess the uncertainty in a given parameter and so define a PDF for that parameter. The Nirex approach is to derive the functions primarily from experimental data, measured in the laboratory or the field as appropriate. For sorption, a single distribution coefficient K_d for each element is elicited, using the assumption of linear sorption. The PDF's are based mainly on laboratory measurements onto system-specific materials; the Nirex Reference Vault Backfill for the repository near field, and onto site-specific materials for the geosphere. This requirement has led to an extensive laboratory programme to measure sorption under the expected range of chemical conditions in the repository and surrounding geologies. A wide range of experimental techniques have been deployed, including methods for both crushed and intact rocks.

It is important to realise the range of uncertainties incorporated in the PDF is not the same as the uncertainty or error in the laboratory measurement. For example, experiments may measure a sorption distribution coefficient for a given radioelement onto a rock sample. However, the PDF required for a transport calculation is not simply identical to the distribution of experimental values obtained. The PDF must encompass uncertainties about the choice of conceptual and mathematical model as well as corresponding features of the experimental situation such as spatial variability of the measured property, biases in the experiment and differences between the experimental situation and that of the rock mass in which the transport will take place. This process is described in more detail in Reference 3 and will be illustrated for the case of the Nirex '95 treatment of uranium sorption in a companion paper at this meeting. For some parameters, there may be sufficient appropriate data to construct PDF's covering the full range of potential uncertainty. For others, only limited data will be available or the data will be only partly applicable and so an element of expert judgement is applied. In these cases, chemical models are used to support the elicitation.

Role of modelling in the elicitation of PDF's for sorption

The role of chemical modelling in the elicitation process is to supplement the experimental data and assist the process of expert judgement. For example, speciation models can provide information of the likely chemical form of the radioelement in solution and how this may be expected to vary as a function of aspects such as groundwater chemistry, ionic strength, or presence of organic complexants. Knowledge of the important sorbing minerals and their surface chemistries provides the complementary information about the sorbing solid. Mechanistic models, fitted to laboratory data can be used by limited extrapolation to indicate the sorption behaviour as chemistry or mineralogy changes. This information is used to guide the PDF and provides confidence in the elicited distribution but does not necessarily constrain it. Mechanistic sorption models do not provide input directly for Nirex performance assessments.

Other sources of information used to provide confidence in the elicited PDF include:

- NSARP sorption data for sorption onto single minerals;
- Information from the Sellafield Site Characterisation Programme on the distribution of natural radioelements and their association with specific mineral phases within the Sellafield assemblages;
- Information from the literature of sorption onto single minerals and rocks of similar mineralogies to those found at Sellafield.

The role of chemical modelling is seen to be one aspect of a multi-strand approach to increasing confidence in the range of sorption behaviour expected in the Sellafield system.

Sorption in the Nirex '95 assessment

The results of a Probabilistic Safety Assessment for the Sellafield site can be illustrated with the Nirex '95 assessment [ref. 2]. The Probability Density Functions for Sorption onto BVG rocks as used in the Nirex '95 assessment are given in Table 1. For this assessment, sorption PDF's were derived from consideration of sorption onto crushed rock. A correction factor was then elicited to provide data appropriate for an intact rock. Distributions have been elicited for the full suite of radioelements that contribute to risk. For some elements, such as zirconium, direct measurements for sorption have not been made as part of the NSARP and literature data are scarce. The sorption of zirconium was judged to be similar to that of thorium and the same PDF was adopted for both elements. This procedure of grouping elements by chemical analogy is adopted internationally.

A correction factor beta was applied to the values in Table 1 to account for the change in accessible surface area in an intact rock compared with a crushed one. The beta values were also obtained by formal elicitation. Beta values are given in Table 2.

Although the Nirex concept is a multi-barrier concept, the relative importance of the individual barriers differs for different radionuclides, depending on their chemistry, transport properties and half-lives. Sensitivity studies can be performed to assess the relative importance of the various barriers and the information can be used to focus the research programme to meet the requirements of PSA most effectively.

The Nirex '95 assessment showed that the calculated risk was dominated by a very small number of radionuclides: ^{36}Cl , ^{129}I and ^{238}U and its daughters.

Therefore establishing confidence in the behaviour of these nuclides is important in demonstrating the safety of a proposed repository.

In addition, geosphere containment was shown to be important for a further series of radionuclides: ^{59}Ni , ^{79}Se , ^{93}Zr , $^{93\text{m}}\text{Nb}$, ^{135}Cs , ^{242}Pu .

Future developments

The treatment of sorption in Performance assessments is developing as additional information becomes available. The Nirex '97 assessment, currently nearing completion, contains several refinements on the Nirex '95 treatment. These include:

- Revision of the PDF's to reflect the knowledge acquired from recent experimental data for sorption onto Sellafield materials.
- Elicitation of PDF's for lower oxidation states, where these would be expected.
- Refinement of correction factors to convert data to a form appropriate for intact rocks.

The weight attached to the predictions of mechanistic models in the elicitation process will increase as they become more extensively validated for a real system. However, it is envisaged that the role of mechanistic models will remain as support for the experiment data, and not as a replacement for data.

References

1. *Disposal Facilities on Land for Low and Intermediate Level Radioactive Wastes: Guidance on Requirements for Authorisation*, Environment Agency, SEPA and Department of the Environment for Northern Ireland, 1996.
2. *Nirex '95: A preliminary Analysis of the groundwater pathway for a Deep repository at Sellafield*, Volume 3 – Calculations of Risk, United Kingdom Nirex Limited Report S/95/012, 1995.
3. *Information Management*, United Kingdom Nirex Limited Report S/94/002, 1994.

Table 1. Far-field sorption distribution coefficients used in Nirex '95 assessment (BVG unless stated) ($\text{m}^3 \text{kg}^{-1}$)

Element	Probability of sorption being less than stated in the Table						
	0.00	0.10	0.33	0.50	0.67	0.90	1.0
H	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$
C	$1.0 \cdot 10^{-6}$	$8.1 \cdot 10^{-6}$	$1.0 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$	$5.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-1}$	$1.0 \cdot 10^0$
Cl	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$
Ni	$1.0 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	$1.7 \cdot 10^{-1}$	$1.0 \cdot 10^0$	$2.5 \cdot 10^1$	$1.0 \cdot 10^2$
Se	$1.0 \cdot 10^{-2}$	$5.0 \cdot 10^{-2}$	$1.8 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$6.3 \cdot 10^{-1}$	$2.0 \cdot 10^0$	$1.0 \cdot 10^1$
Sr	$1.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$	$2.0 \cdot 10^{-1}$	$6.1 \cdot 10^{-1}$	$1.0 \cdot 10^0$
Zr	$1.0 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-1}$	$3.2 \cdot 10^0$	$2.2 \cdot 10^1$	$3.2 \cdot 10^2$	$1.0 \cdot 10^3$
Nb	$1.0 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-1}$	$3.2 \cdot 10^0$	$2.2 \cdot 10^1$	$3.2 \cdot 10^2$	$1.0 \cdot 10^3$
Tc	$1.0 \cdot 10^{-6}$	$3.0 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	$1.0 \cdot 10^0$
Sn	$1.0 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-1}$	$3.2 \cdot 10^0$	$2.2 \cdot 10^1$	$3.2 \cdot 10^2$	$1.0 \cdot 10^3$
I	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$
Cs ⁽¹⁾	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-2}$	$8.0 \cdot 10^{-2}$	$1.6 \cdot 10^{-1}$	$2.8 \cdot 10^{-1}$	$8.0 \cdot 10^{-1}$	$1.0 \cdot 10^1$
Pb	$1.0 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-1}$	$3.2 \cdot 10^0$	$2.2 \cdot 10^1$	$3.2 \cdot 10^2$	$1.0 \cdot 10^3$
Ra	$1.0 \cdot 10^{-6}$	$3.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$	$6.0 \cdot 10^{-2}$	$2.2 \cdot 10^{-1}$	$1.0 \cdot 10^0$
Ac	$1.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-2}$	$1.0 \cdot 10^0$	$3.2 \cdot 10^0$	$1.0 \cdot 10^1$	$2.5 \cdot 10^2$	$1.0 \cdot 10^3$
Th	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-1}$	$2.7 \cdot 10^{-1}$	$3.5 \cdot 10^{-1}$	$5.5 \cdot 10^{-1}$	$4.0 \cdot 10^1$	$1.0 \cdot 10^2$
Pa	$1.0 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	$2.0 \cdot 10^0$	$4.5 \cdot 10^0$	$1.0 \cdot 10^1$	$2.5 \cdot 10^2$	$1.0 \cdot 10^3$
U	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-1}$	$1.2 \cdot 10^0$	$1.0 \cdot 10^2$
Np	$1.0 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$5.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-1}$	$2.0 \cdot 10^{-1}$	$1.5 \cdot 10^1$	$1.0 \cdot 10^2$
Pu(P-T)	$1.0 \cdot 10^{-1}$	$3.5 \cdot 10^0$	$1.0 \cdot 10^1$	$1.8 \cdot 10^1$	$3.5 \cdot 10^1$	$1.6 \cdot 10^2$	$1.0 \cdot 10^3$
Pu(BVG)	$1.0 \cdot 10^{-1}$	$4.5 \cdot 10^{-1}$	$3.0 \cdot 10^0$	$1.0 \cdot 10^1$	$4.0 \cdot 10^1$	$3.5 \cdot 10^2$	$1.0 \cdot 10^4$
Am	$1.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-2}$	$1.0 \cdot 10^0$	$3.2 \cdot 10^0$	$1.0 \cdot 10^1$	$2.5 \cdot 10^2$	$1.0 \cdot 10^3$

Notes: (1) These data are for intact BVG, and were preferred by the expert group. The factor β should not be applied to these.

P-T Permo-Triassic
 BVG Borrowdale Volcanic Group

Table 2. Nirex '95 values of the factor β for the BVG and for the Permo-Triassic units

Percentile	$\log_{10} \beta$ (BVG)	$\log_{10} \beta$ (P-T)
0	-4.1	-4.0
10	-3.0	-3.5
33	-2.25	-2.25
50	-1.9	-1.45
67	-1.55	-0.7
90	-1.0	-0.1
100	0.0	0.0

Figure 1. **Results of Nirex '95 Assessment: Base-case probabilistic calculation: risk plotted against time for the heterogeneous resource area biosphere model for each of the climate states with terrestrial discharge, and for the temperate climate state with marine discharge.**

Note that the results shown for the Periglacial state include contributions from ^{36}Cl , ^{129}I , ^{226}Ra , ^{230}Th , ^{234}U and ^{238}U only.

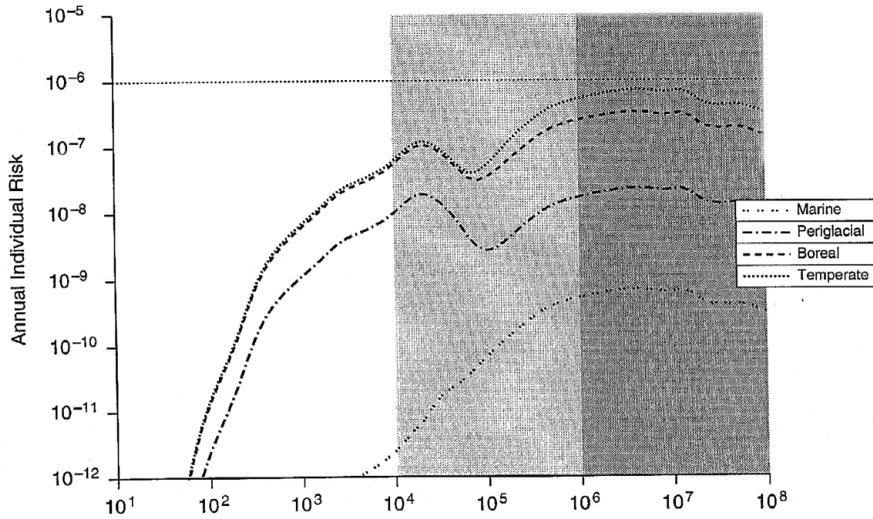
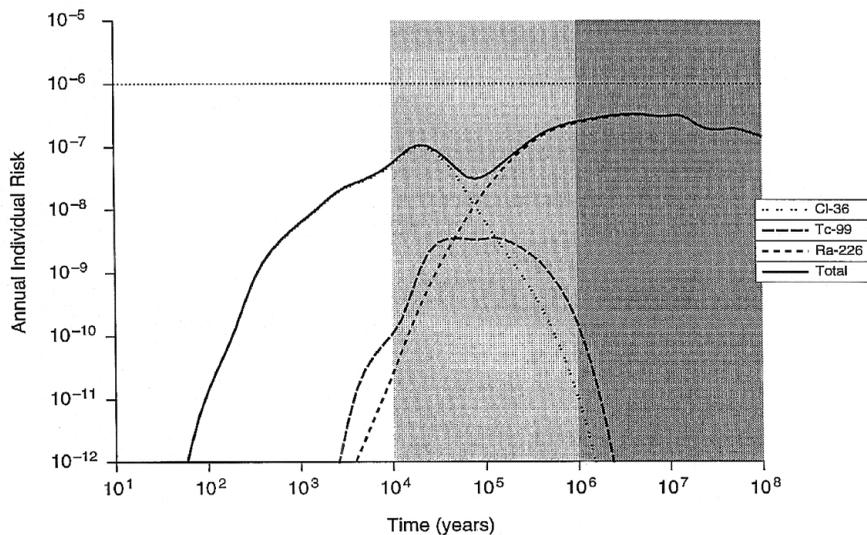


Figure 2. **Results of Nirex '95 Assessment: Base-case probabilistic calculation: Boreal terrestrial risk against time with significant radionuclide contributions**



Kd and Performance Assessment: A Reviewer's Point of View

H. Wanner

Swiss Federal Nuclear Safety Inspectorate (HSK), Switzerland

The construction of a final disposal facility for radioactive waste usually requires a series of licences which, in the case of Switzerland, are granted by the Federal Council (i.e. the Government) based on advice given by the Nuclear Safety Inspectorate (HSK). HSK's task is to review the licence applications. This requires studying the underlying documentation and checking the conclusions of the applicant concerning nuclear and radiation safety, especially long term safety. The review of the long-term safety assessment is therefore a major objective. In the conclusions of HSK's review of Project Gewähr 1985, it was noted that the determination of relevant sorption parameters was problematic because of their manyfold dependencies and of the difficulty to reproduce a specific water-rock system in the laboratory. They also noted the importance of sorption with respect to the safety of a final waste repository, and they concluded that it will be necessary in future to investigate more closely the many open questions in the context of sorption, especially the essential parameters of the specific solid phases. This was an unmistakable call for investigating the mechanisms that govern the sorption processes.

This was 10 years ago. What has happened in the meantime? Increasing awareness is noted in the performance assessment community of the fact that even the most sophisticated separation techniques and the greatest care to eliminate side effects cannot help in answering the inevitable question of the applicability of batch laboratory Kd data to intact rock-water systems. Yet I am not questioning the importance of batch data, on the contrary. The batch technique remains the most practical and the most widely used method for the investigation of interaction mechanisms between solutes and rock surfaces. Increasing awareness is also noted of the disadvantages of independent treatment of chemical (sorption) and physical (migration) processes. Projects to develop coupled models for chemical and physical processes have been undertaken by several organisations. The minimum requirement in this matter is the consistency of the model parameters in both the sorption and the transport (e.g. diffusion) model. However, I have the impression that there are two rather general topics on which consensus has not been reached yet. These are the question about the level of detail required for the analysis of sorption mechanisms on one hand, and the way of dealing with uncertainties on the other hand. Let me give these two subjects some thoughts.

How to deal with uncertainties? This question has led to innumerable discussions, disagreements and misunderstandings in the past. The term "uncertainty" is commonly connected with "error" in a statistical sense, but a statistical basis rarely exists for Kd values because they depend on too many unknown parameters. Hence, the assignment of an uncertainty to a Kd value is usually a priori unscientific and unjustifiable. A common practice to deal with this problem has been to define "realistic" and "conservative" Kd values. In some cases the selected Kd values were described as "realistic-conservative". It is these definitions, especially the term "conservative", that caused many misunderstandings. Examples of interpretations of the term "conservative" range from "worst case"

over “lowest experimental value” and “as low as reasonably to be expected” to “about 10 times lower than realistic”. In existing sorption databases the conservative K_d values are in general about an order of magnitude lower than the realistic ones, largely independent of their experimental basis. For an independent observer this looks like the result of a several years international opinion exchange exercise which had gradually deviated from experimental evidence and scientific experience, and whose only strong point, as it seems, is international consensus. Uncertainties are important enough to be handled in a case-specific manner, rather than in a simplified, categorical way. I would prefer to use specific parameter variations rather than conservative values to analyse the effect of uncertainties. Of course, a mechanistic understanding of the sorption processes greatly facilitates the estimation of uncertainties in the K_d values.

How detailed does our understanding of the sorption mechanisms need to be? This is a legitimate question in view of the time-consuming and costly investigations that are necessary to acquire sufficient knowledge of the solute-solid interactions. The customary K_d values used in the safety analysis need not be replaced by complex surface interaction models. However, our knowledge of the sorption mechanisms needs to be sufficient to understand and support the K_d values. This does not mean that we have to understand each and every detail of the sorption processes, but we need sufficient knowledge to be able to credibly defend the selected K_d values. Information on the sorption mechanisms is essential if experimental data are rare or lacking, because this calls for approximations and estimations concerning the behaviour of the elements or rock surfaces in question. The assumption of analogous behaviour of two elements or two solid phases is only credible (and hence defensible) if there is convincing evidence that the reaction mechanisms are analogous under relevant conditions. It should also be emphasized that the required depth of mechanistic analysis is element-dependent. The safety analysis will reveal which radionuclides have a critical effect on the safety of the repository, and the priority list for mechanistic analysis should be determined by these findings.

As a conclusion, it is nowadays hardly justifiable for a credible performance analysis to use K_d values that were determined in the laboratory, without knowing how the elements in question behave under the relevant chemical conditions, and how therefore the K_d values have to be corrected to reliably predict the *in situ* behaviour of the elements. Mechanistic understanding of the chemical processes that control adsorption of the radionuclides on rock surfaces is not required to the same level of depth for different elements. The level of depth required depends mainly on their long term migration behaviour and, hence, on their relevance to performance assessment. Cooperation between performance assessors and chemists involved in sorption modeling and data acquisition is therefore essential and should be enhanced and improved.

Acquisition of Sorption Data for the Nirex Performance Assessment

C. Tweed

AEA Technology plc, UK

Introduction

Nirex is responsible for the development of a deep geological repository for the disposal of solid intermediate-level and certain low-level radioactive waste. Investigations have been carried out at a site near Sellafield in Cumbria to see if it is suitable as a repository site. The aim of this paper is to outline the Nirex strategy for obtaining sorption data for a Performance Assessment of the Sellafield site, as illustrated by the Nirex '95 assessment.

The overall Nirex approach to Performance Assessment has been outlined in a companion paper for this meeting. It described the use of a probabilistic safety assessment in the UK and the derivation of Probability Density Functions (PDFs) using a structured elicitation process. The PDFs for sorption used in the assessment are primarily based on the results of experimental determinations of sorption onto the various materials characteristic of the repository system. In the near field, this material is the Nirex Reference Vault Backfill – a cementitious material designed to provide the alkaline conditions and sorption capacity that are the principal basis of a chemical barrier to radionuclide migration. Far-field experiments have concentrated on rock samples from the Sellafield site as these provide the most relevant data for the performance assessment of the geosphere at Sellafield.

Assessment basis for treatment of sorption

The following assumptions were made in deriving sorption PDFs for the Nirex '95 assessment:

- The PDFs were derived on the basis of batch sorption R_d values. The correction to R_d values appropriate to intact rock was treated separately by the use of a scaling factor based largely on geometric considerations.
- The assessment model assumes linear reversible sorption. Therefore credit is only taken for short-timescale processes. Coprecipitation and mineralization processes are not included as, on current knowledge, it is difficult to quantify the additional credit that these would offer.
- The sorption values were elicited for elements in their highest expected oxidation states, e.g. uranium as U(VI), selenium as Se(VI). Experiments have shown that elements tend to sorb more strongly in lower oxidation states. Therefore the assessment treatment is expected to underestimate the extent of sorption in the geosphere.

- Sorption data measured at room temperature will be applicable to the repository situation at all times in the future. Sorption behaviour is not strongly temperature-dependent within the expected temperature range.
- The concentration of radionuclides in the geosphere is so small that saturation effects can be ignored.

Research on radionuclide sorption to support the assessment

The radionuclide sorption research on rocks at the Sellafield site comprises three main components:

- laboratory experimental studies;
- geochemical modelling, to build understanding of the sorption process and to enable extrapolation of sorption data to other geochemical environments;
- observation of the behaviour of natural radionuclides in groundwater systems and of the key minerals that control retardation on geological timescales to build confidence in the assessment treatment of radionuclide retardation.

The contribution from these three aspects to supporting the assessment treatment of sorption is outlined below.

Laboratory studies of sorption in the Sellafield system

The standard experimental technique for measuring sorption data is the batch sorption technique. Experiments are generally performed in triplicate using a water-rock ratio of 50:1. The batch technique is chosen as it is quick and reproducible.

Experiments have been performed on a wide variety of Sellafield rocks:

- Permo-Triassic Sediments
 - Calder Sandstone Formation.
 - St Bees Sandstone Formation.
 - Brockram and St Bees Shale.
- Carboniferous Limestone.
- Lower Paleozoic Volcaniclastic Rocks.
 - Borrowdale Volcanic Group (BVG) Tuff matrix.
 - BVG fracture infills.

The experiments have been carried out in site-specific groundwaters in a nitrogen/carbon dioxide atmosphere that reproduced the expected *in situ* partial pressure of carbon dioxide.

The main drawback of the “batch sorption” technique is that it uses crushed rock and therefore may both alter the accessible surface area from the *in situ* value, and also expose fresh surfaces that may show different sorptive properties. Therefore the batch sorption experiments are complemented by a much smaller number of “intact” experiments. The choice of experimental technique depends on the sorptive properties of the radionuclide and the transport properties of the rock sample. For weakly sorbing nuclides, the through-diffusion/sorption technique is used. For strongly-sorbing nuclides, the through-diffusion/sorption experiments did not achieve a steady state

over a timescale of a few years and so the programme now uses transient techniques such as the “rock beaker” technique.

Surface analytical techniques have been used to examine the distribution of the radionuclide between different minerals in the rock to give an indication of the important sorbing minerals in the system. These studies have identified iron oxides as important sorbing minerals in rocks from the Sellafield site.

The Sellafield-specific experiments have been complemented by a series of single mineral experiments, designed to investigate specific aspects of the sorption process and so build up an understanding of the behaviour of the site-specific samples. Sorption isotherms have also been measured, to increase confidence that a linear sorption mechanism is appropriate at the range of conditions expected in the geosphere around a repository.

Geochemical modelling of sorption

Geochemical models are used in the interpretation of sorption experiments to provide confidence in the experimental data. The detailed modelling approach will be described later in this conference. Models for sorption onto hematite are parameterised from the literature where possible and fitted against the experimental data. They can be used by extrapolation to give an indication of sorption on rock samples in a range of hydrochemical environments.

Information from naturally-occurring radioelements at Sellafield

Confidence in the applicability of laboratory measurements to the repository situation is increased by the observations of the occurrence of natural uranium in rocks from Sellafield. Detailed mineralogical and chemical characterisation of samples of BVG has shown that most of the natural uranium is fixed within primary mineral phases but a small amount has been mobilised during water-rock interactions and is associated with secondary hematite. Measurements using sequential extraction techniques have suggested that uranium is not only sorbed onto the iron oxide surface but is incorporated more deeply into the lattice. The absence of this additional mechanism in the laboratory could be due to the much shorter timescales involved, or the fact that the experimental conditions are carefully controlled to minimise mineral dissolution and precipitation.

Example of data elicitation for uranium sorption in the geosphere

A demonstration of the elicitation process for uranium in the Nirex '95 assessment, outlining the role of the various aspects of the programme onto rocks from Sellafield is described below.

The first stage in the elicitation process was to list the main variables to be considered in deriving sorption values. These were identified as:

- groundwater chemistry and ionic strength;
- mineralogy, including both quantities and distributions of important sorbing minerals;
- competing metals, both radioelements and other trace elements.

Extreme outcomes were then considered, together with possible causes.

High values were expected for scenarios when the carbonate concentration in the groundwater was low, so that the speciation was dominated by hydroxy complexes. A high surface area of iron minerals would also tend to increase sorption.

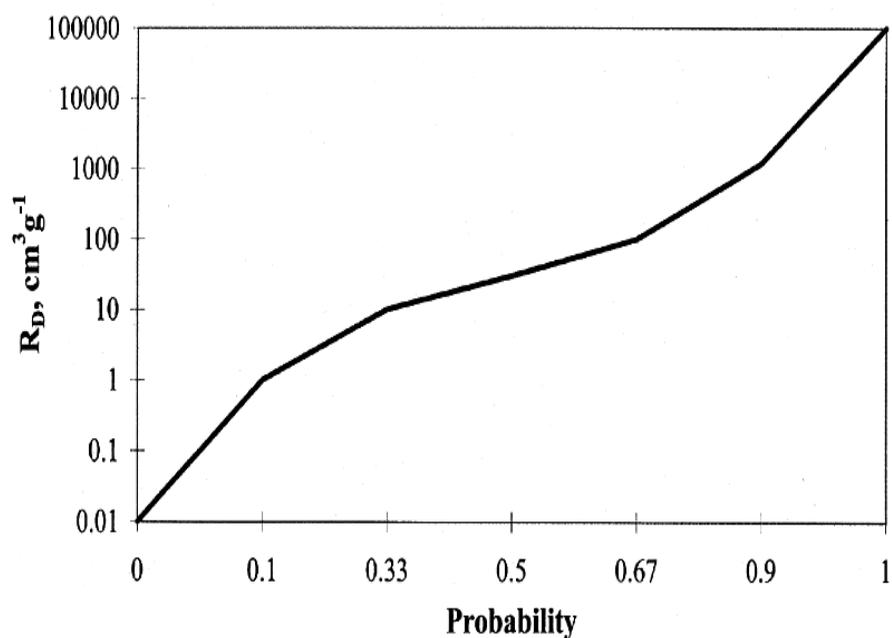
Low R_d values were expected in a high-carbonate system or one with a quartz/calcite dominated mineralogy.

The exact shape of the distribution was then decided by consensus of the expert group.

The resultant PDF for Uranium(VI) in the Nirex '95 assessment is shown in Figure 1.

From this example it can be seen that the elicitation process is heavily weighted towards measured sorption values. The role of mechanistic modelling in the elicitation process is to give confidence that the range of sorption values selected is an accurate representation of the uncertainty. It is thus one component of a multi-strand approach to understanding sorption behaviour. It is envisaged that, as the development of mechanistic models continues, the additional benefit that they bring will increase confidence in the assessment treatment of sorption behaviour in the geosphere.

Figure 1. Cumulative density function for uranium(VI) sorption in the far field



On the Application of Distribution Coefficients and Mechanistic Sorption Models in Performance Assessments for Repositories in Crystalline Rock

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This contribution consists of two parts, one of a more general nature trying to highlight important assumptions made generally in sorption modelling, and the other describing an attempt to apply a chemical thermodynamic model within a performance assessment project.

Modelling of sorption in migration calculations: some implicit assumptions

When modelling advective transport with retardation of radionuclides in natural systems, many simplifying assumptions have to be made in order to get a tractable mathematical formulation. In many cases these assumptions are implicit in the employed set of transport equations and not discussed in any detail. The majority of these assumptions are as valid for use of CTMs as for the Kd concept. A set of such assumptions was identified and discussed in the Project-90 report (SKI Technical Report 91:23) and a condensed version of those assumptions are given below.

- A. The experimental data, behind CTMs or measured Kds, are meaningful in a thermodynamic sense:
- Fully reversible reactions are observed and modelled.
 - Kinetics of reactions and rates of mass transfer in distribution between phases are accounted for.
 - True equilibrium is obtained.

These statements are partially overlapping. Reasons for violation of this assumption are:

- Instability of the sorbent phase: dissolution, e.g. due to future change of geochemical conditions; phase transitions, e.g. of amorphous into crystalline state.
- Ongoing precipitation of the sorbent phase, which leads to coprecipitation.
- Neglect of diffusion in the solid phase, i.e. from the surface to matrix.

Evidently, assumption A holds for both concepts, mechanistic models and Kds.

- B. The migrating nuclide is present only at trace concentration.

This assumption leads to a linear sorption isotherm. It should be noted that assumption B is necessary only for migration models employing a constant Kd. Models are available, which are able to handle non-linear isotherms without direct coupling of chemistry and transport.

C. Constant chemical conditions prevail, in space and time, along the transport path.

Variable or changing conditions can be handled more efficiently by mechanistic models, if data are available and extrapolations are justified.

D. The same and well-defined conditions apply in PA applications as in experiments.

Both concepts have their problems, but CTMs have a clear advantage, at least when applied to “pure” solid phases.

E. The model considers only one sorbent phase.

This is the rule for the both the Kd concept and most of the applications of the CTM models.

Application of a mechanistic sorption model in the SITE-94 performance assessment exercise

This part of the presentation is based on a report contributed by R Arthur (Adaption of Mechanistic Sorption Models for Performance Assessment Calculations, SKI Report 96:34) to the SKI SITE-94 PA project (SKI Report 96:36).

The objective of this work was to bridge the gap between the Kd and mechanistic concepts for sorption, but keeping the constant Kd concept for migration modelling. (The uncertainties connected with the constant Kd approach were judged likely not to be much worse than other assumptions of constant transport parameters, e.g. flow rates, porosities and matrix diffusion parameters.) Another objective was to identify possible new requirements on site characterisations due to application of mechanistic models. In addition, incorporation of CTMs should help in increasing the confidence in migration calculations, although it is recognized that much else also remains to be done.

Sorption of Np(V) on hydrous ferric oxide (HFO) was calculated with the Generalized Two-Layer model of Dzombak and Morel. These data were then applied to a assumed mineral coating of HFO on the whole rock according to Bradbury and Baeyens. The basic assumption is that the rock is fully covered with HFO and that the values of the surface based distribution coefficients K_a are the same for the HFO on the rock and for the HFO itself. The scaling is then made according to the different surface areas, of whole rock and of HFO. For the latter a value of 600 m²/g was adopted. A range of surface areas for whole rock was assumed based on 20% porosity of altered granite and a pore size ranging from 0.1 to 10 mm. Depending on these assumptions the calculated Kds for the whole rock fall between about 0.01 and 10 m³/kg for pH in the range 7 to 8. From these results the value of Kd chosen from direct measurements, 0.01, seems conservative. However, the CTM is possibly extrapolated outside the experimentally verified range at the actual pH of 8.

It is concluded that application of a mechanistic model has provided better insight and, to a degree, supported the chosen Kd value. However, several difficulties remain with the applied concept, e.g.:

- selection of surface areas, site densities and rock structure (porosity, pore size);
- the validity of the assumptions behind the transformation of Kd from HFO to whole rock is uncertain.

A Mechanistic Description of Ni Sorption on Na-Montmorillonite

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Thermodynamic sorption models, based on cation exchange and surface complexation mechanisms have been available for some time. The former mechanism has been used predominantly to describe sorption processes on clay minerals whereas the latter has been mainly applied to relatively simple, pure, single oxide systems. Though the potential for using such models to interpret and predict sorption data in natural systems has been recognised, it is currently unclear whether, and to what extent, they can be used for complex mineral assemblages and water chemistries.

Clay minerals generally form one of the most important mineral components in crystalline and sedimentary rock formations as far as sorption is concerned. For this reason we decided to study a clay mineral and use it as a test material to develop experimental and modelling procedures for describing the uptake of various sorbates. Because of the importance of bentonite as a backfill material in the Swiss concept for a high level radioactive waste repository, Na-montmorillonite was selected.

A purification and conditioning procedure was applied to the SWy-1 Na-montmorillonite (Crook County, Wyoming) in order to remove background metal impurities, soluble salts and sparingly soluble minerals which could influence titration and sorption measurements. The purified clay, in the homo-ionic Na-form, was thoroughly physico-chemically characterised before carrying out batch titration measurements.

The sorption of Ni on conditioned Na-montmorillonite was studied at trace concentrations as a function of pH over a range from ~3 to ~10, at different total NaClO₄ concentrations, to produce so-called "sorption edges". In addition, sorption isotherms were determined at several fixed pH values in 0.1 M NaClO₄. From trends in the sorption edge and isotherm data it was deduced that two main uptake processes were responsible for the sorption behaviour of Ni. The first tended to be dominant at low pH and/or high sorbate concentrations and was strongly dependent on ionic strength. This mechanism was identified as cation exchange and is described in terms of selectivity coefficients. The dependency of sorption on pH and the non-linearity of the sorption isotherms was ascribed to a surface complexation mechanism involving two types of surface hydroxyl groups ($\equiv\text{S}^{\circ}\text{OH}$ and $\equiv\text{S}^{\text{w}}\text{OH}$ sites) at the clay mineral platelet edges having different sorption affinities and site capacities.

Titration and sorption edge/isotherm data were modelled in terms of these two mechanisms with the aid of a computer code called MINSORB. This code allowed the uptake of radionuclides by both mechanisms to be calculated simultaneously, also taking into account competitive reactions from other cations present. From the modelling of the titration results, values for site capacities and protonation/deprotonation constants were deduced. These values were then fixed and used in all further surface complexation modelling of the sorption measurements. The main study was carried out with Ni, but impurity cations present in the system, particularly Zn, had to be examined in addition

due to their competitive effects on Ni sorption. The model, with the derived parameters, allowed all the experimental data from titration measurements through sorption edges to sorption isotherms to be quantitatively described. For the case of Na-montmorillonite it is demonstrated that an electrostatic term in the surface complexation model is not required.

As part of a continuing programme to check the applicability of the model and associated parameters for describing sorption in “natural systems”, Ni sorption isotherms were determined on unconditioned SWy-1 material in more complex water chemistries at pH=7 and 8.2.

The two isotherms were modelled with the parameter set derived for the conditioned Na-montmorillonite and the $\equiv\text{SOH}$ site capacities for the unconditioned clay were obtained by scaling over the respective cation exchange capacities. At pH=7, where the formation of carbonate species was negligible, the fit to the experimental data was good. At pH=8.2, where the thermodynamic data predicted significant concentrations of Ni carbonate species, the model consistently underpredicted the measured R_d values by ~ 0.5 log units.

A literature search revealed that the thermodynamic constants for the Ni carbonate complexes had never in fact been directly measured (Hummel, pers. comm.). Since poor quality thermodynamic data could have been one of the reasons for the inconsistency between model prediction and the experimental sorption results, the Ni carbonate system was investigated and yielded a stability constant for the NiCO_3^0 complex of ~ 2 orders of magnitude lower than the value used in the initial calculations. The Ni isotherm modelled at pH 8.2 using the newly determined stability constant reproduced the sorption isotherm almost exactly.

The ability to model the sorption of radionuclides in natural systems in complex water chemistries depends not only on the development of a good sorption model but also on the thermodynamic data describing the aqueous chemistry of the radionuclide. The quality of this thermodynamic data may well be one of the limiting factors to the future developments of mechanistic sorption models for real systems.

A PNC¹ Approach to Increase Confidence in Sorption Coefficients for Near-Field Performance

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1. Focal points to develop sorption database

PNC¹⁴ has published a comprehensive performance assessment report focused on near field performance in 1992. On the sorption coefficients used for the performance analysis, refinements are required to increase their reliability.

- Reliable sorption database development.
- Mechanistic understanding of sorption and support for sorption database.
- Consistencies of Kd values between batch and intact system.
- Increase in Kd data under reducing conditions.
- The linkage between laboratory and *in situ* measurements of sorption.

2. Procedure for sorption database development

For Second Progress Report in Japan, we have adopted the procedure shown in Fig. 1 to develop sorption database. Firstly we have conducted batch measurements in pure system and surface characterization of pure solid phases and developed intrinsic sorption database including surface complexation and ion exchange constants, surface electrochemical characteristics. Secondly we have checked the reliability of the intrinsic sorption database by comparison of Kd values between batch measurements in complex system such as crushed rock and model predictions. For model prediction we have used the thermochemical database (TDB) of radioelements and a geochemical code. If the reliability is confirmed, we have conducted diffusion measurements to check the reliability in complex intact system. In this way, if we confirm the reliability of the intrinsic sorption database and specify the type of bentonite, rock and groundwater chemistry for the repository, we can predict Kd values for performance analysis.

A critical point for the development of intrinsic sorption database is the reliability of the TDB. The poor quality of the TDB causes the poor intrinsic sorption database. In PNC¹⁴, we have adopted this procedure in the near-field, especially in the engineered barrier system (EBS); compacted bentonite and also tried to apply it to the near-field host rock. However, since the site and geologic formation for the repository have not been fixed, it's very difficult to adopt the procedure in the near-field host rock.

1. PNC is presently JNC.

3. Application of mechanistic sorption model

The status of intrinsic sorption database according to the procedure mentioned above is shown in Table 1. PNC¹⁴ has carried out the batch sorption measurements of Cs and Se, representative of a typical cation and anion respectively, to understand sorption mechanism onto bentonite. Experimental K_d values have been interpreted by cation exchange for Cs and surface complexation for Se. The cation exchange site is assumed to be the interlayer in the smectite and the surface complexation site is the goethite group at the surface of pyrite, which is an accessory mineral in the bentonite. The validity has been confirmed by the comparison between diffusion measurements and sorption model prediction in the compacted bentonite. The results of comparison is shown in Figure 2.

PNC¹⁴ has also carried out the batch measurements of actinides; Pu and Am, and Ni onto bentonite under oxidizing conditions. The sorption of actinides has been interpreted by cation exchanges, because the speciation of Pu and Am indicated cations existence even though the dominant species are anions. The sorption of Ni has been interpreted by ion exchange in the lower pH range and surface complexation at the edge site of smectite in the higher pH range. The Ni combined sorption model has been validated preliminary through diffusion measurements.

Data acquisition under reducing conditions have been progressed under the collaboration with the AEA plc. for actinides; U, Np, Cm and Tc onto bentonite, granodiorite and tuff and these data except for Cm have been interpreted by using surface complexation model assuming that the dominant adsorbent was goethite coated on the bentonite particle and rock material. These mechanistic constants have not yet been validated through the diffusion experiments due to the strong retardation under the reducing condition. The differences of assumptions for mechanistic sorption models mentioned above are the dominant adsorbent; smectite or goethite and the amount of goethite site. These inconsistencies have to be solved through further investigations.

4. Linkage between laboratory and *in situ* measurements

To develop the sorption database for near-field host rock, firstly we have to look into the dominant transport passway in deep underground and to develop the conceptual transport model. Based on the conceptual model, data acquisition should be planned. PNC¹⁴ has conducted the geoscientific research on granitic rock in Kamaishi Mine, north of Japan and accumulated the information related to transport process in deep underground. The fracture system by the observation of the drift wall is composed of three rock zone; fracture fillings, altered and unaltered rock. The conceptual model was proposed to be composed of these three rock zones in the fracture system. The sorption and diffusion data have been obtained on the three rock zones. Sorption data have been obtained for Cs, Se, Pu and U by batch measurements under oxidizing condition. The differences of these elements among three rock zones are not significant. It indicated that the complex conceptual model composed of three rock zones is not needed from the view points of performance assessment.

5. Status in PNC¹⁴

- Mechanistic model has been developed focusing on the bentonite.
- Sorption data acquisition has been progressed under reducing conditions.
- Differences in sorption data in the fracture system have been identified and reflected to the conceptual model.

Table 1. **Development of intrinsic constants for sorption (Surface complexation, Ion-exchange)**

Radioelements	Solid	Atmosphere	Dominant adsorbent	Summary of results
Pu(IV)	Kunigel V-1	air	Na-smectite	ion exchange
Am(III)		reducing	FeOOH	surface complexation
Se(IV)			Al(OH) ₃	
Cs		air	Na-smectite	ion exchange
Ni				ion exchange / surface complexation
U(IV)	Kunigel V-1	reducing	FeOOH	Kd; 1-4 orders of magnitude higher than those under oxidizing conditions, Surface complexation
Tc(IV)	Granodiorite			
Np(IV)	Tuff			

Figure 1. **Procedure for sorption database development for PA**

➔ **Procedure for Sorption Database Development for PA**

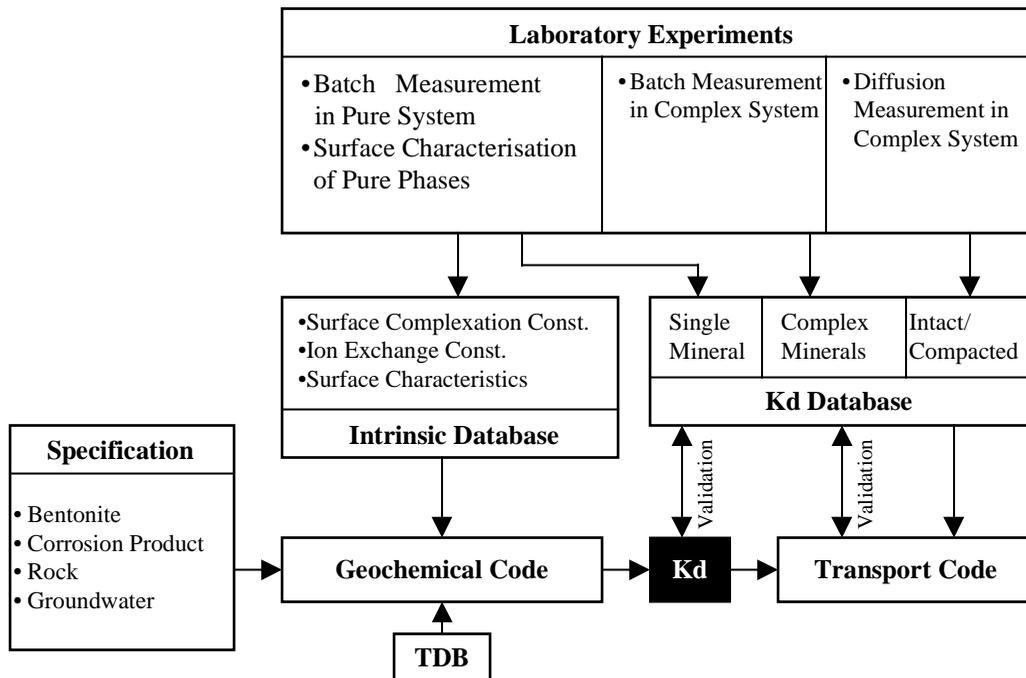
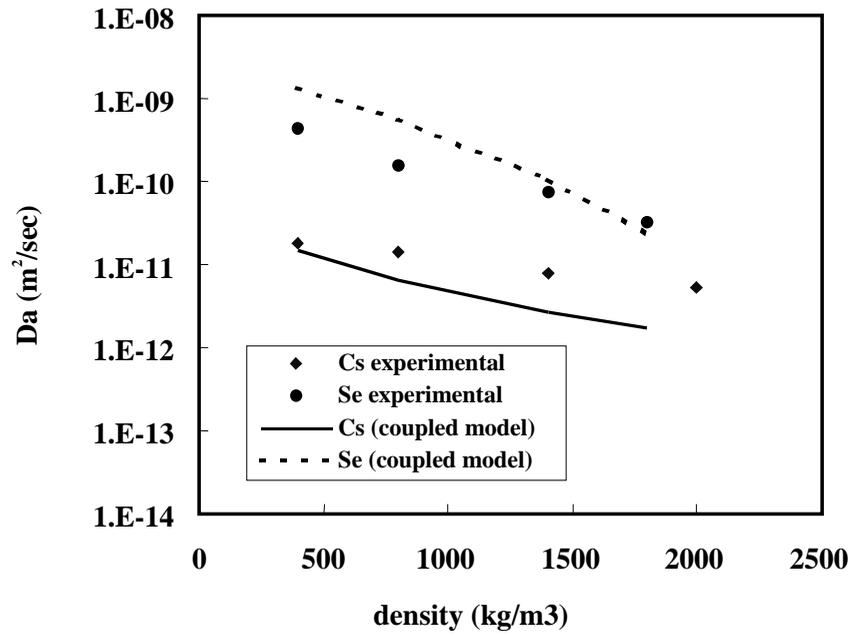


Figure 2. Experimental results and model predictions for apparent diffusion coefficients (Da) of Cs and Se in compacted bentonite



Paper 3.5

An approach to Provide a Sorption Database for Performance Assessment

Y.H. Cho and P.S. Hahn
KAERI, Korea

Experiences and lessons from the past sorption study to provide sorption database for P.A at KAERI will be presented, and an improved approach will be discussed.

(See also Part 2, Section 4.1: “General TSM Development Methodology” and Chapter 5: “State of the art in TSM – Guided Kd Studies of Natural Materials”, section 5.2: “Complex natural solids” for an analysis of results presented)

Paper 3.6

Uranium Sorption Studies within the Koongarra Natural Analogue Project

T. Payne
ANSTO

Introduction

Predictions of the long-term migration of radionuclides in the environment typically involve models based (at least in part) on laboratory sorption experiments. This raises several key questions:

- Can we carry out realistic and appropriate laboratory experiments?
- Can we devise a quantitative model of the results?
- How can results from simple minerals be applied to complex materials?
- Is it valid to simplify complex phenomena (e.g. using Kd values)?
- Is it possible to apply a mechanistic model developed for simple laboratory systems to the field environment?

The ASARR project aims to model U migration over long timescales in the geologic environment. In this project, the Koongarra uranium deposit (Northern Territory, Australia) is being studied as a natural analogue of a nuclear waste repository. The project has provided field and laboratory data that can be used to help answer the above questions.

This paper is in three main sections, each of which focuses on a key part of the sorption work within the ASARR project:

- a) Laboratory U sorption experiments with model minerals (such as ferrihydrite and kaolinite) and development of a surface complexation model (SCM) for the experimental data.
- b) Modeling experimental U sorption results on complex natural materials.
- c) Comparing laboratory sorption results and field partitioning of uranium.

Surface complexation modeling of U(VI) adsorption on ferrihydrite and kaolinite

Uranium(VI) sorption on ferrihydrite and kaolinite is influenced by a large number of factors including: pH, ionic strength, partial pressure of CO₂, adsorbent loading, total amount of U present, and the presence of ligands such as phosphate and humic acid. The effect of complexing ligands may be to enhance or reduce U uptake. The adsorption model being used for ferrihydrite is a surface complexation model with a diffuse double layer, and both strong and weak sites for U sorption. Uranium uptake on a standard kaolinite (KGa-1) is much weaker than U uptake on ferrihydrite under similar experimental conditions. Titanium-rich impurity phases play a major role in U sorption on KGa-1.

Modeling of laboratory experimental results for U sorption on natural materials

As a step towards modeling U sorption in the environment, we are attempting to model laboratory sorption data for experiments involving complex natural substrates from Koongarra. Several approaches to modeling sorption on natural samples have been used. One simplification that has been tried is to assume that one phase (such as ferrihydrite) dominates the system. However, our modeling results have shown that ferrihydrite does not comprise a sufficient proportion of the Koongarra samples to dominate their sorption behaviour.

The most successful approach has been to use the measured surface areas (BET) of natural geologic materials as a normalising parameter, and to model U-sorption using the same site density as ferrihydrite. In simple terms, this may be thought of as approximating the surface with ferrihydrite of equivalent surface area. This approach may seem unrealistic in that natural surfaces are composed of a number of site types with different acid-base chemistry and affinity for the U(VI) species. However, it has the advantage that the U-sorption model for ferrihydrite may be simply transferred to any other mineral assemblage, provided the surface area is known.

Comparison of laboratory U sorption data with in-field measurements

There are usually substantial differences between laboratory and field conditions, and the timescales, spatial extent, and complexity of environmental phenomena cannot be duplicated in the laboratory. Thus, the applicability of laboratory sorption data has been questioned, and it has been claimed that field measurements (“*in situ* distribution coefficients”) provide a more accurate indication of “true” partitioning coefficients.

Before discussing field and laboratory data, it is important to make some comments on sorption terminology. In transport modeling, distribution coefficients (“K_d values”) have often been used to describe the equilibrium partitioning of radionuclides between adsorbed and liquid phases. K_d values may be estimated from the results of laboratory sorption experiments, preferably in which field conditions are closely simulated. However, as laboratory experiments cannot be assumed to be at

equilibrium, we use the term ' R_d ' to express the results of laboratory experiments. Measured R_d values typically vary over a wide range, and are influenced by parameters such as pH, ionic strength, and partial pressure of CO_2 .

In the ASARR project, we have studied in-field U partitioning by comparing the U contents of groundwater and solid phases. The resulting parameter is often referred to as an "*in situ* K_d value". However, processes other than sorption (e.g. precipitation) may influence U partitioning and the system may not be at equilibrium. Consequently, we refer to this parameter as a P (partitioning) value.

In the studies of the Koongarra uranium deposit an extensive suite of laboratory sorption measurements (R_d values) and field partitioning data (P values) has been obtained for U. A valid comparison between field and laboratory data can only be made when the influence of colloids is eliminated and attention is restricted to sorbed or "accessible" uranium species (i.e. excluding precipitates or occluded phases). The correspondence between field measurements and laboratory data improves when the pH values and partial pressures of CO_2 in laboratory experiments are similar to those found in the field. However, factors such as non-equilibrium conditions (attributed to slow kinetic effects) and non-linear adsorption isotherms may result in discrepancies. The results obtained from the Koongarra study indicate that with appropriate control of laboratory conditions and careful field measurements a fair correspondence can be established between laboratory and in-field radionuclide partitioning data.

Determination of Radionuclides Migration Parameters in a Clay Formation: The Belgian Approach

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Summary

This presentation is a summary of papers recently published [1,2,3]. An overview of the major results of the migration programmes is reported in [4].

Host rock

The Boom Clay Formation at the Mol site has been selected 20 years ago as candidate host rock for the deep geological disposal of high level and alpha bearing wastes. This formation is situated between -160 and -270 meters, and is the uppermost Clay Formation of an alternating sequence of clays and sands. The Boom Clay layer was deposited about 30 millions years ago. The main advantages of this tertiary sedimentary formation as long term natural barrier against radionuclides dissemination are:

- self healing properties due to its plasticity;
- low hydraulic conductivity ($K \approx 2 \times 10^{-12}$ m.s⁻¹);
- high sorption capacity for cations;
- slightly alkaline and strongly reducing conditions limiting the solubility and the mobility of many radionuclides.

Performance assessments of the geological disposal of HLW in the Boom Clay have shown that the most effective and reliable barrier of the multi-barrier system is the host Clay layer.

Selected elements

The studied radionuclides (RN) and/or compounds are divided into three categories:

- the critical elements inferred from the performance assessments: ¹⁴C, ⁹⁹Tc, ¹³⁵Cs, ¹²⁹I and ²³⁷Np. The organic matter (OM) occurring naturally in Boom clay is also classified in this group because of its special contribution in controlling the mobility of some radionuclides, especially the actinides;
- the possibly critical elements: Se, Zr, Pd, isotopes U-Pu-Am-Cm, Pa, Ra and Be;
- the non critical elements: tritiated water (HTO), Sr²⁺, Eu³⁺, the haloid anions (I, Br, Cl) HCO₃⁻, organic compounds radio-labelled with ¹⁴C such as sucrose, lactose. The study of this last group of elements has for purpose a better understanding of the migration

mechanisms and allows to simulate the behaviour of some compounds such as the mobile humic acid substances or the trivalent actinides.

Experiments designed to study radionuclides migration

Tests are performed in the laboratory and in the underground research facility. The tests performed in the laboratory are carried out under strictly anaerobic conditions. Depending on the application, real claywater or synthetic claywater is used. The real claywater and the clay core samples are taken from the underground facility. Different types of experiments with different configurations are carried out to determine the migration parameters required for the performance assessments:

- Diffusion experiments: in this case, diffusion is the only mechanism underlying the migration.
- Percolation experiments: solutions are hydraulically forced through the pores of the clay. The radionuclide is measured in the percolate. However, for the strongly sorbed elements, the amount of activity in the percolate is negligible compared to the activity in the solid phase. The activity profile in the clay core is determined after the experiment by slicing the clay plug and measuring the activity in each clay slice. Even under a high hydraulic gradient, diffusion is still the main transport mechanism for the strongly sorbed RN. The migration of the non-or-poorly sorbed tracers is a combination of advective and diffusive transport. Under *in situ* conditions, diffusion remains always the main transport mechanism whatever the chemical species.
- Percolation tests with radio-labelled organic matter: experiments are performed with OM labelled with ^{14}C . Tests with OM double-labelled with ^{14}C and ^{241}Am are also foreseen.

Boom Clay contains about 1-3% OM of which about 0.01% is estimated as mobile. The complexation of radionuclides by OM has a two-fold effect on the safety of the Boom Clay Formation. If immobile organic matter complexes the RN, the presence of OM will retard the migration. On the contrary, if the radionuclides are complexed by the mobile OM, the solubility of the RN will increase and the radionuclides transport would be enhanced. Preliminary results seem to indicate that the OM has a beneficial effect w.r.t. the retention of the actinides, at least for the trivalent ones. They appear to be strongly sorbed on the immobile OM intimately associated with the clay minerals. Furthermore the mobile concentration of the radionuclides seems to be lower when OM is present. An important fraction of the RN is by complexation associated with organic colloids which are partly filtered as well by the backfill (smectite) as by the Boom Clay with as consequence a decreasing of the mobile concentration [6].

The experimental results are interpreted by means of models developed by the CEN•SCK where the tests are performed. The diffusion experiments allow to determine only the apparent diffusion coefficient D_a while the percolation tests give access to the parameters ηR and D_a (η : diffusion accessible porosity, R : retardation factor). The interpretation of R in terms of a mechanistic model accounting for the sorption processes has so far not yet been undertaken.

The goals of the tests performed in the underground laboratory (which is operational since 1984) are:

- validation of the migration parameters acquired in the laboratory under *in situ* conditions;
- validation of the transport models on a large scale (up-scaling factor of the considered volume of 100 000, tests on a scale of a few meters). Till now only the non-sorbed

species have been considered. The theoretical activities in the piezometers are calculated with the code MICOFF also developed by the CEN•SCK [5].

Future works

Besides the completion of the running experiments, new research topics have been identified and in most cases are already under way:

- influence of the concrete backfill for MLW on the migration properties of the Boom Clay (diffusion of an alkaline plume);
- influence of the diffusion of sodium nitrate from bituminized waste (MLW) on the migration properties of the Boom Clay;
- homogeneity of the Clay layer (samples will be taken through the whole layer and migration tests performed with some selected radionuclides);
- study of the osmosis properties of Boom clay (if any);
- temperature effects on the migration properties of Boom Clay;
- determination of the migration parameter in the biosphere (glauconite sands);
- determination of the speciation, solubility and mobile concentration of the redox sensitive elements (Tc, Se, U, Pu, Np).

A major challenge in the near future will be the development of a geochemical code for the Boom Clay which implies the knowledge of the main sorption processes involved. Such a step will help to build the required confidence in the values selected for the PA. Some preliminary works have already been performed.

References

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- [3] B. Neerdael; Geological Radwaste Disposal in Belgium-Research Programme, Review and Objectives; in Geological Problems in Radioactive Waste Isolation, Second Worldwide Review, Edited by P.A. Witherspoon, LBNL-38915/UC-814 (1996).
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Application of a Laboratory-derived Surface Complexation Model for Zinc Adsorption to Field Observations of Zinc Transport in Groundwater

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The surface complexation concept is well accepted in the environmental chemistry research community but it has not yet been applied extensively in modeling natural or contaminated surface and groundwaters. Significant obstacles remain in applying the concept to the heterogeneous mixtures of mineral phases and organic material found in soils and sediments. In particular, the physical and chemical characteristics of the surfaces of natural materials are often not well understood in comparison to those of pure reference mineral phases. Approaches for determining the types and quantities of surface functional groups are not yet developed as routine characterization methods. Electrical double layer (EDL) models that are appropriate for pure monomineralic precipitates may not be appropriate for soils and sediments, which contain mixtures of phases and coatings of variable chemical composition. Although many studies of metal ion and radionuclide sorption by soils and sediments have been reported in the literature, few have approached the problem with a goal of modeling sorption with the surface complexation concept. As a result, there have been very few applications of the surface complexation concept within performance assessment models for radioactive waste repositories or solute transport models that simulate contaminant mobility at polluted groundwater sites.

In this paper we report on an application of the surface complexation concept as a tool for prediction of zinc (Zn) transport in a shallow sand and gravel aquifer contaminated with secondary sewage effluent at Cape Cod, Massachusetts (USA). Treated sewage effluent has been disposed onto infiltration beds at the site for about 60 years and has created a plume of contaminated groundwater that had extended 5.4 km downgradient (in 1994) and was about 900 meters wide. Accretion of recharge water from precipitation on top of the plume, limited vertical mixing, and biological processes have created steep geochemical gradients within the plume. Within a 3 meter thick transition zone, from the accreted recharge water to the top of a suboxic zone of the sewage plume, dissolved O₂ concentrations decrease from several hundred micromoles per liter to nearly zero and the pH increases from about 5.5 to 6.5. The suboxic zone of the plume is mildly reducing and contains high concentrations of dissolved manganese and nitrate, but negligible ferrous iron. The core of the plume is anoxic, has a pH of about 6.5, and contains high concentrations of dissolved ammonium and ferrous iron.

In the vicinity of the disposal beds, Zn contamination extends relatively deep into the aquifer. Up to 50 meters downgradient of the source, the zone of Zn contamination averages approximately 15 meters in vertical thickness. This is somewhat less than the vertical thickness of the sewage plume, which averages about 25 meters. Zn concentrations in the groundwater range from

0.3 to 3 μM . Partitioning of Zn between the groundwater and the sediments is controlled by sorption; Zn-bearing mineral phases are highly undersaturated. Greater than 95 per cent of the total Zn is associated with the aquifer sediments due to sorption.

At distances greater than 200 meters downgradient from the source, the Zn-contaminated region is restricted to the 3 meter thick transition zone at the top of the sewage plume. As mentioned above, there is a steep gradient in pH within this zone, and the lower boundary of the Zn-contaminated region correlates with the steep increase in pH. Maximum Zn concentrations in this region vary with distance downgradient from 4 to 12 μM . Sorbed Zn contamination on the sediments constitutes 90-95 percent of the total Zn. The leading edge of the Zn-contaminated region is sharp and, in 1993-1994, was located 400 meters downgradient from the source. The occurrence of unreactive constituents of the sewage plume at 5 km downgradient, would indicate that the average retardation factors for Zn was of the order of 13 at the lowest pH values in the transition zone and is within the range 50-100 near the center of the plume.

A surface complexation model of Zn sorption was developed from a laboratory study of Zn adsorption by sediments collected from the field site. Quartz and feldspars constituted about 95% (by weight) of the mineral assemblage; accessory minerals included biotite, hornblende, and other ferroaluminosilicates and oxides. The results show that adsorption was dominated by surface coatings containing aluminum and iron; the coatings presumably formed on quartz grains as a result of chemical weathering of feldspars and iron-bearing minerals within the aquifer. Two modeling approaches without EDL correction were tested: 1) One and two-site models, where the chemical identity of the sites was unknown (dummy sites), and Zn sorption stability constants were determined by fitting the laboratory sorption data, and 2) An aluminol and ferrinol site model (each with weak and strong site populations) with the Zn sorption stability constants derived from independent published studies of Zn adsorption by poorly crystalline iron and aluminum hydroxides. For the latter approach, model simulations agreed reasonably well with the experimental Zn sorption data on the Cape Cod sand if it was assumed that the site density of the surface functional groups was greater than expected from the specific surface area of the sand. Analytical and spectroscopic characterization of the sand surface indicated that the surface coatings containing aluminum and iron were thick (>50 nm) and had a high surface area.

The distribution of Zn contamination in the aquifer was simulated with a coupled flow, transport, and equilibrium chemical reaction model (Yeh and Tripathi, 1991). The model incorporated the influence of variable chemistry (pH) on sorption and transport of Zn; parameters of the flow model were estimated from independent experimental data. Simulations were run for a 2-dimensional vertical cross section constructed along a flow line. The groundwater flow field was simulated with horizontal flow and uniform areal recharge. Transport parameters are known from the results of a large-scale tracer test conducted at the site (LeBlanc *et al.*, 1991). The pH gradient was imposed in the model by setting the concentration of an arbitrary buffer entering the model domain at 1 mM and adjusting the ratio of the conjugate acid-base pair with depth to produce the desired pH as a function of depth. Zn was introduced into the model domain by assigning a Zn concentration to groundwater entering along the upgradient boundary. Zn sorption in the simulations was incorporated with the first surface complexation model described above, without any further fitting of data or manipulations.

Simulations carried out for a time period of 54 years agree with the important features of the distribution of Zn contamination in the aquifer. The Zn-contaminated zone deeper in the aquifer is limited to the near-source region by the extensive adsorption in the plume core due to higher pH values. Greater than 200 meters downgradient, the simulations show that the Zn-contaminated region is limited to a narrow zone at the upper boundary of the plume. The location of the leading edge is remarkably similar to that observed. The amount of retardation is similar with either a 1-site or 2-site surface complexation model, but the 2-site model produces a sharper leading edge. Near the leading

edge, the range of retardation in the simulations due to pH variation was about 22 at the lower pH to about 63 in the core of the plume. The case study shows that the surface complexation concept may be valuable as a tool for estimating K_d values for performance assessment where there are spatially or temporally variable chemical conditions.

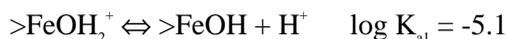
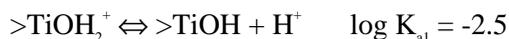
**Proposal for the Development of Predictive Surface Complexation Models (SCM)
to be Used as a Supporting Tool to Kd Parameters in PA**

L. Duro, J. Bruno and B. Honeyman
QuantiSci, Spain

The objective of this work is to correlate the experimental values of Kd to surface complexation model parameters in order to extrapolate the results to natural systems. For this purpose, we have modelled the data obtained by Honeyman (1984) on sorption of Cd onto amorphous iron oxy-hydroxide, on rutile and on mixtures of both solids. Although these mixtures are not very complex and it is a very well controlled lab system, the approach may be used to describe sorption of trace metals on heterogeneous rocks by considering the percentage of each mineral in the rock.

We have not included any electrostatic contribution in the model in order to keep it as simple as possible. The surface equilibria considered are listed below:

Solid surface acidity equilibria:



Surface complexation equilibria:



The best fits for the experiments where a unique solid is present (SSML system) have been obtained with the following set of surface complexation constants:

$\log K_0^{\text{Ti}}$	$\log K_1^{\text{Ti}}$	$\log K_2^{\text{Ti}}$	$\log K_0^{\text{Fe}}$	$\log K_1^{\text{Fe}}$	$\log K_2^{\text{Fe}}$
-1.7±0.4	-8.8±0.6	-20.3±0.4	-4.5±0.5	-10.8±0.8	-19.4±1.0

And these values compare fairly well with the ones obtained in experiments where a mixture of both solids is present (MSML systems):

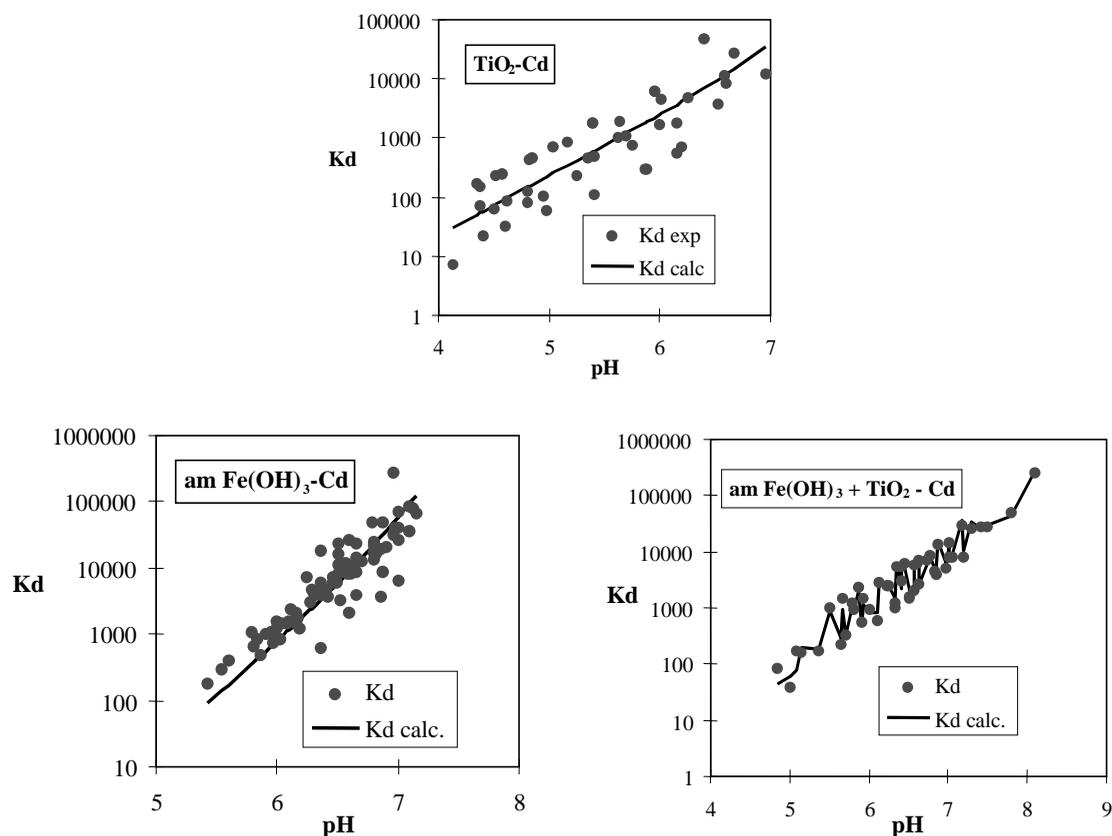
$\log K_0^{\text{Ti}}$	$\log K_1^{\text{Ti}}$	$\log K_2^{\text{Ti}}$	$\log K_0^{\text{Fe}}$	$\log K_1^{\text{Fe}}$	$\log K_2^{\text{Fe}}$
-1.8±0.2	-9.7±0.3	-20.6±0.4	-4.4±0.3	-11.2±0.4	-18.8±1.1

From these sets of surface complexation constants we have used the following expression to obtain the K_d values for each system:

$$K_D = \frac{\sum_{S,q} K_{S,q} \left(\frac{A_s W_s}{1 + \frac{[H^+]}{K_{S,a}}} \right)^q}{1 + \sum_{L,p} K_{L,p} [L]^p}$$

where A_s stands for the density of sorption sites per kg of solid; W_s refers to the weight percentage of each mineral surface in the bulk of the solid; K_{s,a} are the surface acidity constants for each solid surface S; K_{s,q} are the surface complexation constants for each complex q on each mineral surface S, and K_{L,p} represents the aqueous complexation constants of each metal with each aqueous ligand L.

The K_d values obtained by using this expression have been compared with the experimentally determined K_d. This comparison is shown in the following figures:



The results obtained are encourageous and the possibility of applying such approach to complex natural systems will be investigated in more detail with field data.

References

Honeyman, B. D. (1984) Cation and anion adsorption at the oxide/solution interface in systems containing binary mixtures of adsorbents: An investigation of the concept of adsorptive additive. Ph. D. Thesis, Stanford University

Data Sheet

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Solid phase

Amorphous iron(III) oxy-hydroxide
Synthetic

Aqueous phase

Solution composition

T = 25 ± 0.1°C; Batch experiments; oxic conditions.

Radionuclides

Cd; Background electrolyte: 0.1 M NaNO₃

Brief description of model

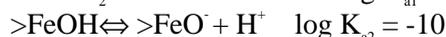
Surface components, surface species

>FeOH₂⁺; >FeOH; >FeO⁻;
>FeO-Cd⁺; >FeO-Cd(OH); >FeO-Cd(OH)₂⁻

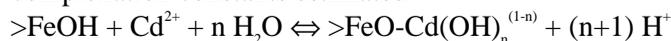
Parameters

Kd measured

Surface acidity constants from the literature



Surface complexation constants estimated



$$\log K_0^{\text{Fe}} = -4.5 \pm 0.5$$

$$\log K_1^{\text{Fe}} = -10.8 \pm 0.8$$

$$\log K_2^{\text{Fe}} = -19.4 \pm 1.0$$

1 unique type of sorption sites

Site density taken from the literature (Davis, 1977): 9.85·10⁻³ moles of sites/g

Surface area (Davis, 1977): 182 m²/g

Thermodynamic data used

Aqueous complexation for cadmium hydroxocomplexes: Baes and Mesmer (*)

Codes

PHREEQC

Home made worksheets

Solid phase

Titanium(IV) dioxide, (α -TiO₂)

Commercial solid. J.T. Baker Co. "Baker analyzed" reagent grade

Aqueous phase

Solution composition

T = 25 ± 0.1°C; Batch experiments; oxic conditions.

Radionuclides

Cd; Background electrolyte: 0.1 M NaNO₃

Brief description of model

Surface components, surface species

>TiOH₂⁺; >TiOH; >TiO⁻;

>TiO-Cd⁺; >TiO-Cd(OH); >TiO-Cd(OH)₂⁻

Parameters

Kd measured

Surface acidity constants from the literature

>TiOH₂⁺ ⇌ >TiOH + H⁺ log K_{a1} = -2.5

>TiOH ⇌ >TiO⁻ + H⁺ log K_{a2} = -8

Surface complexation constants estimated

>TiOH + Cd²⁺ + n H₂O ⇌ >TiO-Cd(OH)_n⁽¹⁻ⁿ⁾ + (n-1) H⁺

log K₀^{Ti} = -1.7±0.4

log K₁^{Ti} = -8.8±0.6

log K₂^{Ti} = -20.3±0.5

1 unique type of sorption sites

Site density (assigned by Honeyman, 1984): 8.75·10⁻⁵ moles of sites /g

Surface area (BET, 100C) = 9.1 m²/g

Thermodynamic data used

Aqueous complexation for cadmium hydroxocomplexes: Baes and Mesmer (*)

Codes

PHREEQC

Home made worksheets

Solid phase

Mixtures of Titanium(IV) dioxide (α -TiO₂) plus amorphous iron(III) oxy-hydroxide

Titanium(IV) dioxide :commercial solid. J.T. Baker Co. "Baker analyzed" reagent grade

Amorphous iron(III) oxy-hydroxide: synthetic material.

Aqueous phase

Solution composition

T = 25 ± 0.1°C; Batch experiments; oxic conditions.

Radionuclides

Cd; Background electrolyte: 0.1 M NaNO₃

Brief description of model

Surface components, surface species

>TiOH₂⁺; >TiOH; >TiO⁻; >FeOH₂⁺; >FeOH; >FeO⁻;

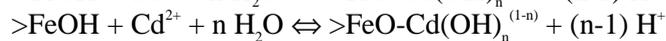
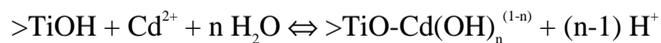
>TiO-Cd⁺; >TiO-Cd(OH); >TiO-Cd(OH)₂⁻; >FeO-Cd⁺; >FeO-Cd(OH); >FeO-Cd(OH)₂⁻

Parameters

Kd measured

Surface acidity constants from the literature (those specified in datasheets 2 and 3)

Surface complexation constants estimated:



$\log K_0^{\text{Ti}}$	$\log K_1^{\text{Ti}}$	$\log K_2^{\text{Ti}}$	$\log K_0^{\text{Fe}}$	$\log K_1^{\text{Fe}}$	$\log K_2^{\text{Fe}}$
-1.8 ± 0.2	-9.7 ± 0.3	-20.6 ± 0.4	-4.4 ± 0.3	-11.2 ± 0.4	-18.8 ± 1.1

1 unique type of sorption sites for each solid

Site density taken from the literature

Thermodynamic data used

Aqueous complexation for cadmium hydroxocomplexes: Baes and Mesmer (*)

Codes

PHREEQC

Home made worksheets

Publications

Honeyman, B. (1984) Cation and anion adsorption at the oxide/solution interface in systems containing binary mixtures of adsorbents: An investigation of the concept of adsorptive additive. Ph. D. Thesis, Stanford University.

Characterisation of Natural Substrates with Regard to Application of Surface Complexation Models

T.D. Waite¹, B. Fenton¹, T.E. Payne², G.R. Lumpkin², J.A. Davis³ and M. McBeath³

¹UNSW, ²ANSTO; Australia

³USGS; USA

While good correspondence between laboratory sorption data and surface complexation modelling results has been obtained for single oxide phase, much poorer correspondence has been obtained for natural substrates. This result arises, at least in part, from the difficulty in ascertaining the identity of sorbing surfaces and in assigning appropriate values for sorbing surface site concentrations.

In an attempt to clarify the nature of possible sorbing phases, we have used a variety of techniques to investigate the surfaces of natural solid substrates from the Koongarra weathered zone. Based on insights gained from the surface characterisation studies, we have then proceeded to assess the applicability of various surface complexation modelling approaches as applied to U(VI) uptake.

Major finding from surface characterisation studies using time-of-flight secondary ion mass spectrometry (TOF-SIMS), high-resolution electron microscopy and microprobe analysis are that:

- most of the uranium either intrinsically present in the weathered zone Koongarra solid investigated (the W2 sample) or subsequently added to the sample was associated with iron-rich coatings;
- these coatings also showed significant concentrations of Al, Si, Mg and P;
- the iron-rich coatings exhibited variable morphology and often possessed some crystallinity (generally exhibiting goethite-like electron diffraction patterns);
- leaching studies revealed that only a small portion of these coatings were removed using Tamms acid oxalate (TAO). A significantly greater fraction (particularly of the iron-rich phases) was rapidly removed using a dithionite-citrate-bicarbonate (DCB) leachant.

Surface complexation modelling using a two-site (strong and weak affinity sites, SOH and WHO respectively) surface complexation model with inner sphere, mononuclear, bidentate complexes of the type SO_2UO_2 and WO_2UO_2 identical to that described for ferrihydrite by Waite *et al.* (GCA **58**, 5465-5478, (1994)) indicated that:

- An assumption that all U(VI) uptake on the natural substrate can be described by adsorption to Tamms acid oxalate (TAO) extractable iron leads to gross underestimation of uptake.
- Use of surface site concentration estimated from dithionite-citrate-bicarbonate (DCB) leached Fe, Al and Mn and assuming a site density identical to that found appropriate for

ferrihydrate (0.875 mol sites/mol of element leached) yields close correspondence between model and batch laboratory sorption data in the pH range 5-8. The site concentration estimated in this way was (surprisingly/fortuitously!) very close to that estimated from surface area using a constant site density of 3.84 $\mu\text{mol sites/m}^2$.

For a low total U(VI) concentration of 3.8 μM , the model slightly underpredicted U(VI) sorption to the natural substrate at $\text{pH} > 8$ but seriously underpredicted uptake at low pH. Much better agreement between model and laboratory data was obtained at a higher U(VI) concentration (10^{-4} M) where the surface coverage was lower and the low pH edge at significantly higher pH.

Data Sheet

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Co-Authors

Names & Affiliation: James A. Davis and Molly McBeath (United States Geologic Survey)
 Brett Fenton (University of New South Wales)
 Gregory R. Lumpkin and Timothy E. Payne (Australian Nuclear Science and Technology Organi-sation)

Solid phase

Identity: W2 (14 metres)
 Source: Koongarra weathered zone
 Mineralogy: Major components: Kaolinite, altered chlorite, iron minerals, mica
 Size fractions: 56% > 1 500 μm , 15 μm < 36% < 1 500 μm , 7.7% < 15 μm
 Surface area of < 15 μm fraction: 52.3 m^2/g

Elemental distribution in fine fraction

Extractant	mg element leached/g of solid							
	Fe	Al	Mn	Mg	Ca	Ti	K	U
Morgans	520	605	7.1	3 930	195	3	370	182
TAO	1 170	1 210	147	246	8	5.7	36	43
DCB	6 770	888	30	128	112	2.9	537	65
HCl	79 200	35 000	126	9 670	12	54	280	130
Fusion	20 800	90 300	35	3 480	31	841	7 840	6.4
Total (mg/g)	108.4	128.1	0.3	17.5	0.4	0.9	9.1	0.43

Aqueous phase

Solution composition, conditions

Batch studies undertaken where extent of uptake of radionuclide on solid phase (< 15 μm component) examined as a function of wide range of system conditions (pH, CO_2 partial pressure, ionic strength, radionuclide concentration, solid substrate concentration).

Radionuclide

Uranium(VI) uptake on solid phase examined in all cases using either the intrinsic U(VI) content or added U(VI). Extent of U(VI) uptake determined after centrifugation by α -spectrometry.

Brief description of model

Surface components, surface species

A two-site (strong and weak affinity sites, SOH and WHO respectively) surface complexation model with inner sphere, mononuclear, bidentate complexes of the type SO_2UO_2 and WO_2UO_2 identical to that described for ferrihydrite by Waite *et al.* (GCA 58, 5465-5478, (1994)) used throughout. Also assumed carbonate surface species of the type SCO_3H^0 and SOCO_3^- and ternary uranyl carbonate surface species of the type $\text{SO}_2\text{UO}_2\text{CO}_3^{2-}$ present at strong and weak sites.

Parameters

Variety of methods used for estimating weak surface site concentrations: i) from TAO-extractable Fe assuming 0.875 mol sites/mole Fe, ii) from sum of DCB-extractable Fe+Al+Mn assuming 0.875 mol sites/mol element, iii) from BET surface area assuming $3.84 \mu\text{m}^2$. In all cases a weak to strong site ration of 580 used (as found previously for ferrihydrite).

Thermodynamic data used

MINTEQA2 data base used but modified for U(VI) species as detailed in Waite *et al.* (1994). The U(VI) constants used are similar (though not in all cases identical) to those prescribed in the NEA database.

Codes

MINTEQA2 has been used in most cases though earlier studies were undertaken using HYDRAQL. FITEQL was used in some instances to obtain estimates for constants.

Publications

The work on the natural substrates has not yet been published though raw data and preliminary modeling results are reported in Waite *et al.* (1992). Details of the modeling approach used here, which is essentially identical to that used for ferrihydrite, are reported in Waite *et al.* (1994).

Waite, T.D., Payne, T.E., Davis J.A. and Sekine, K. (1992). Uranium sorption. Alligator Rivers Analogue Project Final Report, Volume 13. ISBN 0-642-59939-4, DOE/HMIP/RR/92/0823, SKI TR 92:20-13. 106 pp.

Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A. and Xu, N. (1994). Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica Cosmochimica Acta* 58, 5465-5478.

Lessons learned

An assumption that all U(VI) uptake on the natural substrate can be described by adsorption to Tamms acid oxalate (TAO) extractable iron leads to gross underestimation of uptake.

Use of surface site concentration estimated from dithionite-citrate-bicarbonate (DCB) leached Fe, Al and Mn and assuming a site density identical to that found appropriate for ferrihydrite (0.875 mol sites/mol of element leached) yields close correspondence between model and batch laboratory sorption data in the pH range 5-8. The site concentration estimated in this way was (surprisingly/fortuitously!) very close to that estimated from surface area using a constant site density of $3.84 \mu\text{mol sites/m}^2$.

For low total U(VI) concentration of $3.8 \mu\text{M}$, the model slightly underpredicted U(VI) sorption to the natural substrate at $\text{pH} > 8$ but seriously underpredicted uptake at low pH. Much better agreement between model and laboratory data was obtained at a higher U(VI) concentration (10^{-4} M) where the surface coverage was lower and the low pH edge at significantly higher pH.

Sorption Modeling for Performance Assessment at the Center for Nuclear Waste Regulatory Analyses

D.R. Turner and R.T. Pabalan

Center for Nuclear Waste Regulatory Analyses, USA

A fundamental concern in safety assessments of nuclear waste repositories and in nuclear waste management is the potential release of radionuclides, particularly actinides such as U, Np, and Pu to the accessible environment as dissolved constituents in groundwater. An important mechanism for retarding radionuclide migration is sorption onto minerals present along groundwater flow paths, and a quantitative understanding of actinide sorption behavior is important in evaluating the suitability of proposed geologic repositories for nuclear wastes. However, this understanding is complicated by the dependence of sorption processes on various geochemical parameters. These system parameters include aqueous solution properties (e.g. pH, Eh, ionic strength, radionuclide concentration, complexing ligands) and sorptive phase characteristics (e.g. mineral composition, surface area, sorption site density, surface charge), as well as temperature which makes description and prediction of actinide sorption in geochemical systems of variable mineralogic composition and aqueous speciation difficult.

Sorption research at the Center for Nuclear Waste Regulatory Analyses (CNWRA) in San Antonio, Texas has combined experimental and modeling methods to develop a quantitative understanding of sorption processes in support of the U.S. Nuclear Regulatory Commission (USNRC) to help evaluate the suitability of the proposed HLW repository at Yucca Mountain, Nevada.

Batch sorption experiments have been conducted at the CNWRA to investigate the sorption of U(VI) and Np(V) on quartz, clinoptilolite, montmorillonite, and -alumina over wide ranges of experimental conditions. These minerals were selected in part because their mineralogic and surface characteristics, which could potentially influence actinide sorption behavior, are distinct from each other. For example, the points-of-zero-charge (pH_{ZPC}) for quartz, clinoptilolite, and -alumina are 2.9, 3.0, and 9.1, respectively, and pH_{ZPC} values reported for montmorillonite range from 6.5 to 8. Experiments were conducted over a wide range in solution pH (2-11 pH units), solid-mass/solution-volume ratio (M/V) (up to 50 g/L), $\text{P}(\text{CO}_2)$ (CO_2 free to $10^{2.0}$ atm), radionuclide concentration (10^5 to 10^{-8} M), and ionic strength (0.01 to 0.1 M). Results of these experiments as well as literature data were used in determining which of the various geochemical parameters are most important to understanding and predicting U(VI) and Np(V) sorption behavior.

To develop a quantitative understanding of sorption processes and to build a mechanistic modeling capability in support of performance assessment, the CNWRA has used a surface complexation (SCM) approach. Efforts have focused on developing a simplified approach that can be uniformly applied across different radionuclide-mineral-solution systems. While this approach is not intended to be an exact representation of the mineral-water interface, it does provide a useful common starting point for model development and a means for consistent comparison of model results for performance assessment. As a basis for model development, existing potentiometric titration data for a

number of different simple oxides were examined and interpreted using the numerical nonlinear least-squares optimization code FITEQL to develop surface acidity constants for different SCM approaches. Sorption experiments at CNWRA and data from the literature were interpreted using FITEQL to develop a consistent set of binding constants for radionuclide sorption reactions. Relatively simple SCM models were generally sufficient to simulate radionuclide sorption over a wide range in conditions, particularly with respect to pH. Changes in other parameters such as M/V ratios and $P(\text{CO}_2)$ provided additional constraints on modeling parameters; the simplified modeling approach as implemented was tested more severely over the wider range in these conditions, but still provided reasonable results.

Experiments at CNWRA have indicated, for U(VI) and Np(V), a common pattern for actinide sorption that is related to the formation of hydroxy complexes in solution. Geochemical conditions which inhibit the formation of actinide-hydroxy complexes (e.g. low pH, aqueous carbonate complexation) suppress actinide sorption. For different minerals, the similarity in pH-dependence of actinide sorption on quartz, -alumina, clinoptilolite, and montmorillonite and other simple minerals suggest that actinide sorption is not sensitive to the surface charge characteristics of the sorbent as compared to the effect of changing the total number of available sites. Sorption modeling generally provided good agreement between measured and predicted sorption results, indicating that SCMs will be useful in constraining the effects of geochemical parameters on sorption. Limitations to the modeling approach include uncertainties with regard to surface complex stoichiometry, a lack of a consensus on accepted thermodynamic data for many actinides (an uncertainty being addressed by the NEA), and uncertainties regarding realistic site concentrations in mineral-water systems.

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Data Sheet

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Solid phase

Quartz, alpha alumina, clinoptilolite, Na-montmorillonite
NIST (alumina), Wards Scientific
Pure mineral separates

Aqueous phase

Solution composition

Batch experiments,
Oxidizing environment,
20 degrees C,
1-3 weeks,
Controlled CO_2 (atmospheric, CO_2 -free, $1\text{E}-2$ atm)

Radionuclides

U(VI) and Np(V)

Brief description of model

Surface components, surface species

DLM model, with monodentate, mononuclear U(VI) and Np(V) hydroxy species

Parameters

Estimated parameters using nonlinear parameter optimization (FITEQL, Version 2.0)

Thermodynamic data used

NEA thermodynamic data for U(VI), with exception of $\text{UO}_2(\text{OH})_2$ Log $K=-13.0$. EQ3/6 data (release data0.alt.r2) for Np(V)

Codes

FITEQL for parameter optimization, MINTEQA2, Version 3.11 for simulations

Publications

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Lessons learned

These include, but are not limited to:

1. In lab experiments, different minerals exhibited similar pH dependence for sorption which was linked to the onset of hydrolysis.
2. In systems open to CO₂, sorption can be simulated without invoking formation of actinyl-carbonate surface complexes.
3. Consistent application of a simplified model is perhaps adequate from the point of view of performance assessment.

Development of a Mechanistic Model of Sorption of Uranium(VI) onto Rocks from the Sellafield Site

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Radioelement sorption onto a range of rock samples from the Sellafield site investigations by Nirex has been measured as part of the Nirex Safety Assessment Research Programme. Probability density functions (PDFs) for use in performance assessment calculations are elicited based on these measured sorption data. Geochemical models can be used to support the data elicitation process. Geochemical models can be used to determine the aqueous speciation of the sorbing element, and describe possible sorption reactions at mineral surfaces. Models can therefore give confidence in the interpretation of experimental measurements. Additionally, models can be used to extrapolate experimental data to conditions where measurements are unavailable, allowing assessment of sensitivity to key parameters and helping to guide further experimental investigation if necessary.

Both mineralogy and groundwater chemistry vary within the rocks at the Sellafield site. For example, near-surface waters at Sellafield are dominated by dilute, NaHCO_3 water, whereas waters from the basement rocks of the potential repository zone (about 650 metres below Ordnance Datum) are NaCl -dominated with an ionic strength of around 0.5M. The overall objective of the Sellafield sorption modelling is to develop a single, consistent model that can be used for interpretation of data obtained under the range of water/rock environments pertinent to the site. Therefore, the triple layer approach has been adopted so that the model can be applied to a wide range of radioelements, including those whose sorption might be affected by ionic strength. In this paper, the methodology is illustrated in the case of uranium(VI) sorption onto a variety of rock types from the Sellafield site.

When applying the triple layer model approach to sorption onto rock it is usual to select a phase which is considered to dominate the sorptive properties of the rock in question and parameterise the model according to that phase. Within the NSARP, mineralogical controls on sorption have been investigated. Following sorption experiments, surface analytical techniques have been employed to examine radioelement loadings on mineral surfaces. Also, extensive studies of the distribution of natural uranium series elements in rocks from the Sellafield site have been carried out. These studies have shown iron oxides (particularly hematite) to be important sorbing minerals. For this reason, the geochemical model used in this study was based on sorption onto hematite contained within the rock samples. The following steps were carried out during parameterisation and application of the model:

1. Compilation of available data describing the surface reactions of iron oxide minerals, particularly hematite. These data included:
 - measurements of the surface properties of hematite, e.g. surface area, site density and point of zero charge;

- experimental studies of the sorption of relevant elements (uranium, groundwater ions) onto hematite and other iron oxides. Generally these were batch experiments involving pure phases and simple background electrolyte solutions, and typically were carried out as a function of key parameters such as pH, ionic strength, partial pressure of CO₂;
 - spectroscopic studies (e.g. infrared, X-ray absorption) designed to investigate speciation of the sorbed element.
2. Selection of sorption reactions that were consistent with the compiled data regarding the nature of the sorbed complex.
 3. Modelling of the hematite batch sorption data. This stage was a fitting exercise. Equilibrium constants were assigned to the selected reactions so that good fits were obtained to the data. During this step, the philosophy adopted was to achieve the simplest possible reaction dataset that could reproduce all the experimental trends. It is often the case that more than one set of sorption reactions can achieve a good fit to experimental data. To examine the sensitivity of the model to choice of sorbing species, the uranium (VI) calculations were carried out using two different datasets: (i) involving outer-sphere sorption reactions and (ii) involving inner-sphere sorption reactions. It was found that both datasets gave an equally good fit to the experimental data. Both uranium sorption models were therefore investigated in Step 5.
 4. Estimation of the proportion of the rock surface occupied by hematite in the Sellafield rock samples. Two bounding conditions were investigated:
 - the measured weight percent of hematite in the sample was equated to the percent of hematite surface present per gramme of rock. This method was expected to underestimate the amount of available hematite surface because in many samples hematite forms a surface film around other mineral grains. In this case it would follow that sorption would be underestimated;
 - the measured total surface area of the rock sample was used. Using this method it was expected that the amount of hematite surface (and consequently sorption) would be overestimated.

If sorption onto the sample is dominated by sorption onto hematite, then calculations based on these conditions should give a range of sorption values that bound the measured value.

5. Prediction of the amount of uranium(VI) sorption onto rock samples from the Sellafield site for which batch sorption data were available. All aspects of the experimental system were represented in the model, e.g. the groundwater chemistry and the partial pressure of carbon dioxide under which the experiments were carried out.

It was found that the two uranium sorption models (inner-sphere and outer-sphere) gave very different responses when applied to the Sellafield system. The ranges of Rd values calculated using the inner-sphere model were invariably significantly lower than those calculated using the outer-sphere model (by two orders of magnitude). This was unexpected as both models were parameterised using the same single mineral data (Step 3). The differing responses of the models have been related to the effect of competition for sorption sites between radioelements and groundwater ions (e.g. calcium, sulphate). The models were parameterised using experimental data for simple systems where these competitive effects were not addressed. There is therefore a residual uncertainty in applying these models to real rock/groundwater systems. They have not been validated against systems where groundwater ions were present in significant concentrations and possibly include an inadequate representation of competitive effects. Because of this uncertainty, the Step 5 calculations were

repeated, having removed sorption reactions involving calcium, magnesium and sulphate. In the absence of these competing sorption reactions, the ranges of R_d values calculated by the inner-sphere and outer-sphere models were very similar.

Comparison of the calculated ranges of R_d values with the measured R_d values shows that in some cases there is good agreement (for the tuff and sandstone experiments ranges of values calculated by the model overlap with those measured experimentally), while in other cases the model tends to underestimate sorption (for the breccia the calculated R_d values were sometimes several orders of magnitude below those measured experimentally). Underestimation of sorption may be because minerals other than hematite may make a significant contribution to the sorption properties of the rock samples. Surface analytical studies have shown that significant radioelement loadings can be associated with minerals such as ilmenite and chlorite, and single mineral studies have illustrated the potential of alternative minerals (e.g. muscovite, chlorite and clays) to sorb radioelements strongly.

This work has highlighted two key areas of uncertainty in the application of a hematite-based geochemical sorption model to the Sellafield system:

- the treatment of competitive effects in the model is currently untested;
- the role of other mineral phases in controlling sorption onto site-specific samples has not been quantified.

At the current level of understanding, we can “fit” experimental data and use geochemical models as interpretative tools. They can also be used by extrapolation to give an indication of sorption in a range of hydrochemical environments.

Modelling Sorption of Nickel on Silica Goethite and Kaolinite

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The work consists of several studies of nickel sorption on silica as well as some experiments of nickel sorption on goethite and kaolinite. These studies were performed during 1994-1997. The experimental part was carried out in the Laboratory of Radiochemistry (University of Helsinki) while the modelling was done at VTT Chemical Technology.

The objectives of the work were:

- to develop the experimental and theoretical know-how to apply surface complexation modelling;
- to test the predictive power of surface complexation modelling, and
- to find theoretical background for using the chosen values of K_d 's in the performance analysis.

All the studies comprised the preliminary modelling phase, reporting and the subsequent delivery of the results to the experimentalists. The experimental work included the measurement of the specific surface area of the solid phase, the analysis of some important trace elements (Fe and Mn) present in the solid phase, and finally the sorption experiments. All the acidity constants and parameters were taken from the open literature. The silica and goethite systems were modelled by the triple layer model whereas kaolinite by the constant capacitance model.

In the silica experiments, three types of water were used: simple electrolyte, and fresh and saline groundwater simulants. Two different types of quartz – Min-U-Sil 5 and Nilsjö quartz – were used. Although the measured trace element concentrations were low, iron was included in the modelling due to its high influence at high pH-values. Preliminary modelling gave satisfactory results except at low ionic strength, where sorption onto the quartz surface was difficult to quantify with any kind of surface complexation model. This difficulty persisted even in the final modelling phase – at low ionic strength the observed sorption was much higher than modelled. The model predicted much lower sorption for the saline simulant compared to the fresh simulant, which was also experimentally verified.

The goethite system was described quite well even in the preliminary modelling phase (Figure 1), but for kaolinite the same kind of difficulties as for quartz occurred.

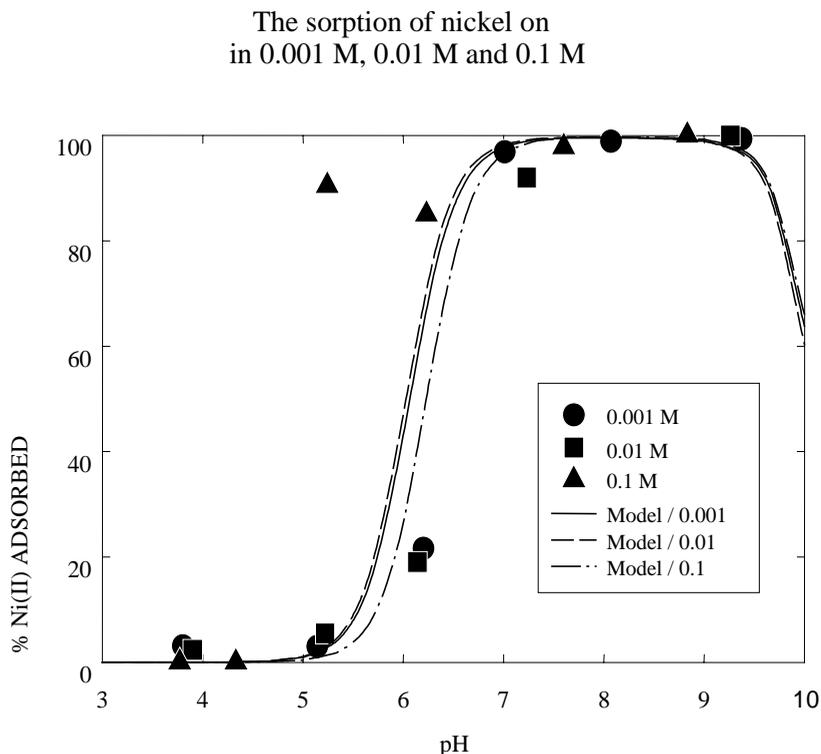
The conclusions were that:

- the most difficult task in applying the surface complexation modelling is either the lack of data or in some cases the high amount of – controversial – data;
- the surface complexation models do have some predictive power, which varies considerably depending on the system under consideration;
- the surface complexation modelling and experiments are invaluable for the understanding the variations in measured K_d -values, giving also valuable hints as to how K_d -measurements should be done.

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- Olin, M. & Lehtikoinen, J. 1997. Surface complexation modelling applied to the sorption of nickel and thorium on silica, and nickel on kaolinite and goethite. To be published as a Posiva report.

Figure 1. The sorption of nickel on goethite at three ionic strengths



Data Sheet

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Solid phase

Quartz
Min-U-Sil 5 and Nilsia quartz
SiO₂
Small amounts of
iron (given as Fe₂O₃·H₂O < 450 µg/g SiO₂), and
manganese (given as MnO₂ < 3 µg/g SiO₂).

Aqueous phase

Solution composition

Radionuclides

- NaOH-NaNO₃, pH = 3- 10
0.001, 0.005, 0.01 and 0.1 mol/L
- Simulated fresh groundwater
- Simulated saline groundwater

mmol/L	b) fresh simulant	c) saline simulant
K ⁺	0.501	22.5
Na ⁺	11.1	171
Ca ²⁺	2.24	79.7
Mg ²⁺	0.889	2.0
Cl ⁻	6.79	356
SO ₄ ²⁻	0.5	–
HCO ₃ ⁻	*	*
Br ⁻	–	1.2
Ionic strength, <i>I</i>	22	440
pH	≈8.1	≈7

* = open to atmosphere

Conditions:

Room temperature, batch, oxic

Brief description of model

Surface components, surface species

Parameters

TLM-model for all surfaces. All manganese and iron parameters are estimated or calculated using data from literature and measured amounts of these elements. For silica the source of the parameter is given in the third column of the table.

Parameter or reaction, X =	SiO ₂		MnO ₂	HFO
Specific surface area, m ² /g	0.8 – 6.0	Meas.	300	600
N _s , sites, nm ⁻²	6	Liter.	55	3
N _s , moles, μmol/m ²	10	Liter.	90	5
Sites per mass, μmol/g	8	Liter.	27 200	3 000
Capacitance of inner layer, F/m ²	1.25	Liter.	1.25	1.40
Capacitance of outer layer, F/m ²	0.2	Liter.	0.2	0.2
XOH = XO ⁻ + H ⁺	-7.8	Liter.	-4.2	-10.7
XOH + H ⁺ = XOH ₂ ⁺	–		–	5.1
XOH + Na ⁺ = XO ⁻ - Na ⁺ + H ⁺	-5.7	Fitted	-3.3	-9.0
XOH + K ⁺ = SO ⁻ -K ⁺ + H ⁺	-5.7	Estim.		-9.0
XOH + Ca ²⁺ = SO ⁻ -Ca ²⁺ + H ⁺	-7.32	Liter.		-6.3
XOH + Mg ²⁺ = SO ⁻ -Mg ²⁺ + H ⁺	-7.32	Liter.		-6.3
XOH + H ⁺ + Cl ⁻ = XOH ₂ ⁺ - Cl ⁻	–	Liter.	–	6.9
XOH + SO ₄ ²⁻ + H ⁺ = SOH ₂ ⁺ -SO ₄ ²⁻		Liter.		9.6
XOH + SO ₄ ²⁻ + 2H ⁺ = SOH ₂ ⁺ -HSO ₄ ⁻		Liter.		14.5
XOH + Ni ²⁺ = XO ⁻ - Ni ²⁺ + H ⁺	-5.5	Fitted	0.0	-2.0
XOH + Ni ²⁺ + H ₂ O = XO ⁻ - Ni(OH) ⁺ + 2H ⁺	-12.4	Fitted	–	–

Codes

HYDRAQL

Thermodynamic data used

Code	Notes	Aqueous species	log K
1000		Ca ²⁺ + CO ₃ ²⁻ = CaCO ₃ (aq)	3.33
1010		Ca ²⁺ + CO ₃ ²⁻ + H ⁺ = CaHCO ₃ ⁺	11.38
1020		Ca ²⁺ + SO ₄ ²⁻ = CaSO ₄ (aq)	2.11
1030		Ca ²⁺ + Cl ⁻ = CaCl ⁺	-0.7
1350		Ca ²⁺ + H ₂ O = CaOH ⁺ + H ⁺	-12.85
1360		Mg ²⁺ + CO ₃ ²⁻ = MgCO ₃ (aq)	2.98
1370		Mg ²⁺ + CO ₃ ²⁻ + H ⁺ = MgHCO ₃ ⁺	11.37
1380		Mg ²⁺ + SO ₄ ²⁻ = MgSO ₄ (aq)	2.41
1385		Mg ²⁺ + Cl ⁻ = MgCl ⁺	-0.13
1740		4Mg ²⁺ + 4H ₂ O = Mg ₄ (OH) ₄ ⁴⁺ + 4H ⁺	-39.8
1960		K ⁺ + SO ₄ ²⁻ = KSO ₄ ⁻	0.880
1962		K ⁺ + Cl ⁻ = KCl(aq)	-1.49
2000		Na ⁺ + CO ₃ ²⁻ = NaCO ₃ ⁻	0.516

Code	Notes	Aqueous species	log K
2005		$\text{Na}^+ + \text{CO}_3^{2-} + \text{H}^+ = \text{NaHCO}_3$	10.48
2010		$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	0.820
12530		$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.33
12540		$2\text{H}^+ + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2(aq)$	16.67
12550		$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	1.98
13595		$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	-13.99
		Minerals	
20000	Calcite	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$	8.48
20002	Aragonite	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$	8.34
20010	Gypsum	$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	4.48
20012	Anhydrite	$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4$	4.31
20130	Portlandite	$\text{Ca}^{2+} + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 2\text{H}^+$	-22.6
20140	Nesquehonite	$\text{Mg}^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} = \text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	5.33
20142	Lansfordite	$\text{Mg}^{2+} + \text{CO}_3^{2-} + 5\text{H}_2\text{O} = \text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	5.49
20144	Artinite	$2\text{Mg}^{2+} + \text{CO}_3^{2-} + 5\text{H}_2\text{O} =$ $\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O} + 2\text{H}^+$	-9.32
20145	Dolomite (dis)	$\text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-} = \text{CaMg}(\text{CO}_3)_2$	16.6
20146	Epsomite	$\text{Mg}^{2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O} = \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.96
20200	Brucite	$\text{Mg}^{2+} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{H}^+$	-16.3
		Gas	
25000		$2\text{H}^+ + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2(gas)$	18.14

Publications

Puukko, E. & Hakanen, M. 1995. Surface complexation modelling: experiments on the sorption of nickel on quartz. Helsinki, Nuclear Waste Commission of Finnish Power Companies, Report YJT-95-12. 20 p.

Olin, M. 1995. Surface complexation modelling applied to the sorption of nickel on silica. Report YJT-95-10. 47 p.

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Olin, M. & Lehtikoinen, J. 1997. Surface complexation modelling applied to the sorption of nickel and thorium on silica, and nickel on kaolinite and goethite. To be published as a Posiva report.

Lessons learned

- Planning and pre-modelling must be done more carefully.
- Silica is not a “simple” system: especially the low ionic strength is problematic.
- Surface complexation modelling had some predictive power in this case.

Porewater Composition and Bulk Solution in Crystalline Rock and in Bentonite Clay

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In real systems, sorption processes often take place inside pores, the dimensions of which are small enough for the diffuse layers of the charged pore surfaces to extend over the entire pore. This extension will cause compositional differences between the bulk and pore waters. If surfaces are negatively charged, anions and cations are repelled from and attracted to the pore space, respectively, which in turn implies differences in solubilities and sorption inside the pores compared to the bulk solution.

We have studied the coupling of surface complexation and diffusion in the model system shown in Figure 1, with the largest and smallest dimension for diffusion simulations and for studying the effect of charged surfaces respectively. The surface charge is caused by a surface complexation reaction. The surface potential and concentrations are calculated by assuming the pore water in equilibrium with some external “bulk” solution, which, for the diffusion boundary condition, is the real bulk solution in contact with the porous sample. Deeper inside the pore, the “bulk” represents a “fictitious” solution composition. A numerical solution to the non-linear Poisson-Boltzmann equation subject to difficult boundary conditions was called for.

Figure 1. Sketch of a diffusion channel. Dimensions in different directions are of different magnitude: $\delta \approx 1 - 100 \text{ nm}$, $\Delta \approx 50 \text{ }\mu\text{m}$, $L \approx \tau L_0$, $L_0 \approx 10 - 100 \text{ mm}$, $\tau \approx 3 - 10$. L_0 is the physical length of the system and τ is the tortuosity correcting for the longer diffusion path through the system.

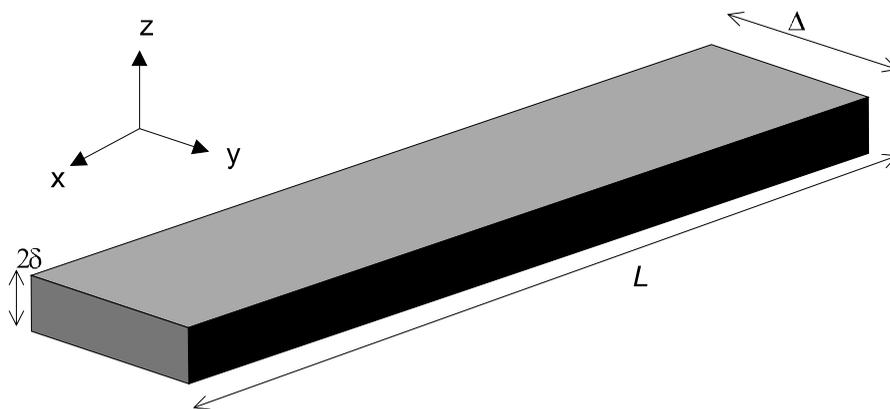
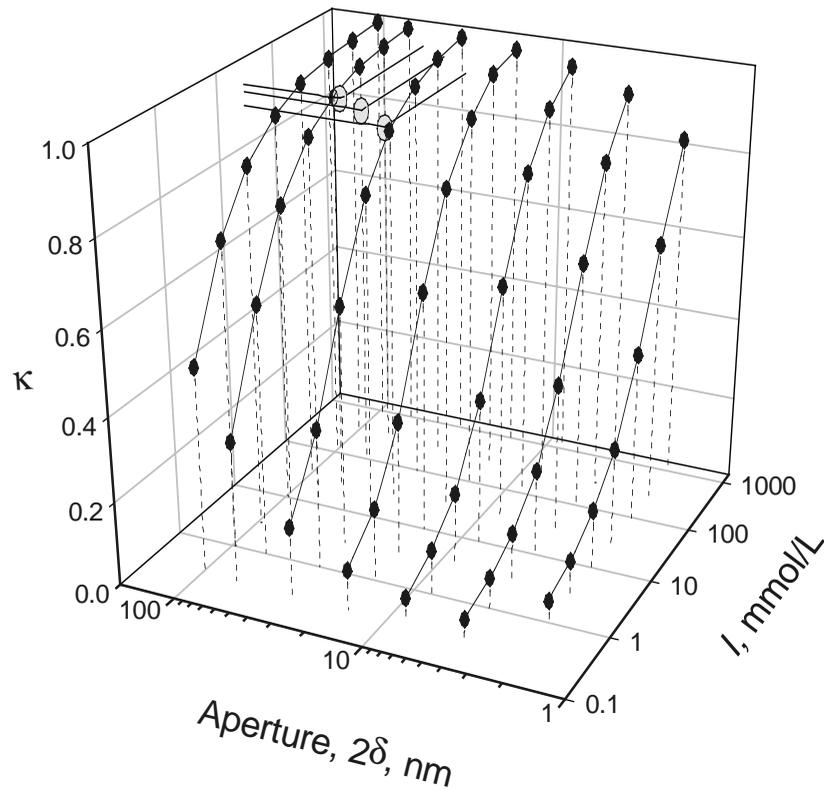


Figure 2 shows some results for anion exclusion in porous rock. The pores are assumed to be covered by silica. It is evident from this figure that both the low ionic strength and the small pore diameter decrease the anion concentration inside the pores thereby essentially changing the chemical conditions. Here, no specific sorption of cations was assumed. The (free) cation concentration is higher by about a factor inversely proportional to the anion exclusion parameter, κ . This may be an explanation for surface diffusion.

The future work includes the solubility and specific sorption studies inside the pores.

Figure 2. **The ratio of concentrations inside the pore and in free water, κ , for a monovalent anion in silica pores at pH 6. Clear anion exclusion is noticed even at high ionic strength in very small pores or in large pores at very low ionic strength. The open symbols denote results from an experimental system.**



Mechanistic Modelling of the Sorption of Uranium(VI), Plutonium and Thorium onto Aluminium Oxide, Muscovite and Chlorite

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Many of the experimental and modelling studies performed under the Nirex Safety Assessment Research Programme have involved site-specific geological materials, and their equilibrated groundwaters. However, these natural systems are complex, and detailed interpretation of the results can be difficult. One approach used to interpret these natural systems is to study component minerals individually and to use this information to build up a representation of the entire system. The current study has looked at radionuclide sorption onto sheet silicate minerals.

Experiments were performed to study the sorption of i) plutonium and uranium(VI) onto aluminium oxide, ii) plutonium and uranium (VI) onto chlorite and muscovite and iii) thorium onto muscovite. (In each case uranium (VI) and plutonium sorption were studied in the same experiment.) Muscovite consists of silica/aluminium oxide sheets with potassium ions in the interlayer sites whereas chlorite has alternate silica/aluminium oxide and iron/magnesium oxide layers. Since many data are available in the literature for sorption onto silica and iron oxides, aluminium oxide was included in the study to parameterise the sorption onto the aluminium-oxygen component of the sheet silicate surfaces.

Thermodynamic equilibrium modelling using the triple-layer sorption model (HARSORB) within the HARPHRQ program has been used to interpret the experimental results. The overall objective of the Sellafield sorption modelling is to develop a single, consistent model that can be used for interpretation of data obtained under the range of water/rock environments pertinent to the site. Groundwater chemistry varies within the rocks at the Sellafield site. For example, near-surface waters at Sellafield are dominated by dilute, NaHCO_3 water, whereas waters from the basement rocks of the potential repository zone (about 650 meters below Ordnance Datum) are NaCl-dominated with an ionic strength of around 0.5M. Therefore, the triple layer approach has been adopted so that the model can be applied to a wide range of radioelements, including those whose sorption might be affected by ionic strength. (HATCHES version 6.0 was used throughout.)

For the aluminium oxide modelling, the standard (single-site) triple-layer sorption model was used. However for muscovite a two-site triple-layer sorption model was employed, with one site (silica) representing the silicon-oxygen component of the sheet silicate surface and the other (aluminium oxide) the aluminium-oxygen component. In the chlorite modelling, a third site type (goethite) was added to the muscovite model to represent the iron-oxygen surface group of chlorite. Parameters to define the interactions between the three sorbing surface sites and the solution species were taken from the literature.

In order to parameterise uranium(VI) and plutonium sorption onto the aluminium-oxygen sites, initial modelling was performed to reproduce experimentally determined R_d values for uranium(VI) and plutonium sorption onto aluminium oxide. This resulted in a refined dataset which was then used, without further adjustment, to simulate the extent of uranium(VI) and plutonium sorption onto muscovite and chlorite.

For uranium(VI) sorption onto the sheet silicates, the model simulations are generally within an order of magnitude of the experimental data across the pH range 5 to 10. The model predicted that radioelement sorption was predominantly onto the silicon-oxygen sites and the background electrolyte components (sodium and nitrate) sorbed onto the aluminium and iron-oxygen sites. Therefore both types of site were required to simulate the experimental data. For plutonium, the model also predicted that radioelement sorption was predominantly onto the silicon-oxygen sites up to pH~10. At pH>10, the sheet silicate minerals are unstable and mineral dissolution/reprecipitation processes could determine the extent of actinide removal from solution.

The two-site model has also been used to simulate thorium sorption onto muscovite, using unrefined literature values to parameterise the interactions between the sheet silicate surface and thorium solution species. Again, the agreement with the experimental data is within an order of magnitude up to pH~10.

A Summary of Sorption Investigations Performed on Behalf of the UK Regulator of Radioactive Waste Disposal

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The Environment Agency of England and Wales (formerly HMIP) is responsible for the regulation of radioactive waste disposal. As part of this responsibility, the Agency is required to undertake a scientific review of the disposer's safety case. To this end, the Agency has funded a wide ranging research programme into scientific disposal issues to enable it to independently assess the adequacy of the disposer's safety case. Key aims of this research programme are to understand processes and performance assessment techniques to model these processes.

As part of its research into the migration of radionuclides through geological media, the Agency has conducted investigations into the modelling of retardation processes. Two investigations are described here: the CHEMVAL 2 sorption project, and the Winfrith column experiments. Both investigations had a number of objectives, including testing the ability of thermodynamic models to predict the retardation of radionuclides by natural geological media.

The CHEMVAL 2 exercise (part funded by the European Commission) provided modellers with experimental data for surface titrations on MinUSil 5 silica and for Ni sorption as a function of pH at two ionic strengths. Also provided were surface area measurements and petrographic descriptions for St. Bees Sandstone, and literature data for modelling Ni sorption onto Fe oxides. The modellers were asked to predict Ni sorption as a function of pH for silica at different ionic strengths and also onto the sandstone. Different modellers used different mechanistic models and assumed differed sorbing species, but there was little difference in the overall quality of modelling results. The position of the midpoint of the sorption edge was correctly predicted, but not the slope of the edge. The slope has subsequently been ratified by other experimental groups. In the case of the sandstone, a small quantity of Fe oxide was observed and modelled as the dominant sorbing phase.

The Winfrith experiments passed U-bearing solutions through intact columns of Clashach Sandstone. Modellers were provided with experimental batch data for surface titrations on silica and the sandstone, and for U sorption onto the sandstone. Hydraulic characteristics and surface area measurements for the columns were also provided. Modellers were asked to predict profiles of sorbed U through the columns and the concentration of U in the effluent solution as a function of time. Runs were conducted just injecting U, and injecting U with Cd, with EDTA, and with saccharic acid to investigate the effects of competition and complexation. The experimental results showed little influence of Cd on U migration but both EDTA and to a more significant degree, saccharic acid were effective in increasing U mobility. The modellers used a fully coupled chemical-transport code (CHEMTARD) which was calibrated using the boundary condition data provided. Dynamic modelling results were in good agreement with experimental observations, although the models tended to slightly

overpredict the migration of U, the effect of Cd competition, and the desorption of U. Some of these overpredictions are clearly an artifact of not modelling kinetic effects.

The results of these two investigations indicate that thermodynamic models can be used to predict sorption by natural media, and that coupled models can be used to upscale laboratory data. However, the lack of confidence in extrapolating the models, especially to more complex natural systems, is such that at least limited experimental corroboration is required, and suggests that the models only be used for interpolation between experimental observations. To build confidence, a sensitivity analysis on model parameters needs to be performed so that the simplest, most robust model can be developed. A similar analysis should be performed on the parameter data to determine if a generic or site-specific database is required. It then needs to be established that each key parameter can be properly determined experimentally or in the field. This will allow the uncertainty associated with the model and its application to be appraised and an assessment of adequacy made by both the safety case proponent and the regulator.

Data Sheet

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Solid phase

- (i) Amorphous silica (Keisegel 60, Merck Ltd.)
BET Surface Area: $432 \text{ m}^2 \text{ g}^{-1}$
- (ii) Clashach Sandstone
Source: Elgin, NW. Scotland.
Mineralogy: > 95 % Quartz rounded grains with silica cement overgrowths and iron oxide coatings. Minor K-feldspar, clay (illite) and lithic fragments.
Porosity: 14 to 29 %
BET Surface Area: $0.8 \text{ to } 1.2 \text{ m}^2 \text{ g}^{-1} \gg 5600 \text{ to } 14000 \text{ m}^2 \text{ dm}^{-3}$
CEC: 0.06 to 0.1 meq/100g

Aqueous phase

(i) Batch Experiments

- a) Protonation/hydrolysis characteristics of silica and Clashach Sandstone
Determined by stepped titrations at ionic strengths of 0.001, 0.01 and 0.1 mol dm^{-3} (HNO_3). pH reduced at start of titrations to ≈ 3 by addition of 1 M HNO_3 . NaOH added in increments at 1 minute intervals until pH stable at ≈ 11 . 1g solid in 55 cm^3 of NaNO_3 electrolyte. Oxidizing conditions. CO_2 removed by purging with nitrogen. $T = 25^\circ\text{C}$
- b) Uranium sorption on silica
Determined by batch experiments at an ionic strength of 0.3 mol dm^{-3} (NaCl) for initial pH values of 4.7 and 5.7. 0.1g solid in 20 cm^3 of NaCl electrolyte. Oxidizing conditions. Uranium (UVI) concentrations between 1.9×10^{-6} and $2.4 \times 10^{-3} \text{ mol dm}^{-3}$. Final pH values between ≈ 4 and 6.5. $T = 25^\circ\text{C}$
- c) Uranium sorption on Clashach Sandstone
Determined by batch experiments as for silica (b above) but with a reduced solid:solution ratio: 0.01g disaggregated (not crushed) sandstone in 20 cm^3 of NaCl electrolyte.

- d) Cadmium sorption on silica
Determined by batch experiments as for uranium (b above) but at ionic strengths of 0.001 M, 0.01 M and 0.3 M (NaCl), and for a range of pH and saccharic acid concentrations.
- e) EDTA sorption on silica
Batch experiments at 25°C at ionic strengths of 0.001, 0.01 and 0.3 mol dm⁻³ (NaCl), for a range of pH (4.7-6.7) and EDTA concentrations.
- e) EDTA sorption on Clashach Sandstone
Batch experiments using ¹⁴C labelled EDTA, at 25°C, at ionic strengths of 0.001, 0.01 and 0.3 mol dm⁻³ (NaCl), for a range of pH (4.5-7) and EDTA concentrations.
- f) Uranium sorption on silica in the presence of EDTA
Batch experiments using ¹⁴C labelled EDTA, at 25°C at ionic strengths of 0.001, 0.01 and 0.3 mol dm⁻³ (NaCl), for a range of pH and EDTA concentrations.
- g) Sorption of saccharic acid on silica
Batch experiments at 25°C at ionic strengths of 0.001, 0.01 and 0.3 mol dm⁻³ (NaCl), for a range of pH and saccharic acid concentrations.

(ii) Column Flow Experiments

Matrix:	Intact Clashach Sandstone.
Core Length:	4 to 30 cm
Core Diameter:	5 cm
Duration:	20 to 60 days
Flow rate:	75 to 300 cm day ⁻¹
Tracer:	³⁶ Cl
Aqueous Conditions:	0.3 mol dm ⁻³ NaCl, T = 25°C, oxic (open to air)
pH:	≈5.6 (the “natural” pH of the sandstone)
Radionuclides/complexants:	Uranium (1 x 10 ⁻⁸ to 4 x 10 ⁻⁶ mol dm ⁻³) in isolation and co-injected with Cd (6 x 10 ⁻⁵ to 1 x 10 ⁻³ mol dm ⁻³), EDTA (1.1 x 10 ⁻⁴ mol dm ⁻³), and saccharic acid (1.2 x 10 ⁻⁴ mol dm ⁻³)

Brief description of model

Single site Triple Layer Model.

Sorbing Species Considered

UO₂⁺², UO₂OH⁺, UO₂Cl⁺, Cd⁺², CdOH⁺, H-EDTA⁻³, H₂-EDTA⁻², H₃-Sacc⁺

Codes

FITEQL for data extraction from batch experiments; CHEMTARD for transport modelling.

Data

Thermodynamic data for solution species from CHEMVAL V6 database. Data for surface reactions derived from batch experiments but supplemented by literature data. Sorption on Clashach Sandstone was assumed to be dominated by amorphous iron oxide coatings on silica grains. Experiments using acid washed Clashach Sandstone, from which the iron oxide coatings had been removed, showed, however, that there was little difference in the degree of uranium retardation.

Publications

R. Sims, T.A. Lawless, J.L. Alexander, D.G. Bennett and D. Read. Uranium migration through intact sandstone: Effect of pollutant concentration and the reversibility of uptake, *Journal of Contaminant Hydrology*, 21, pp 215-228, 1996.

D.G. Bennett and D. Read. The migration of uranium through sandstone, UK DoE Report DoE/HMIP/RR/92.101, 1992.

- D.G. Bennett, S.K. Liew, C.S. Mawbey and D. Read, Development of the CHEMTARD Coupled Chemical Transport Code: Theoretical Overview, UK DoE Report DoE/HMIP/RR/92/036, 1992.
- R. Sims and T.A. Lawless. Effect of cadmium and organics on the migration of uranium through sandstone. Draft report to the Environment Agency for England and Wales.
- D. Ross, E. Falck, J. Alexander and J. van der Lee. Radionuclide migration through sandstone. Batch experiment interpretation and colloid retention model development. Draft report to the Environment Agency for England and Wales.
- D. Ross, R. Sims and P. Warwick. Radionuclide migration through sandstone. A combined experimental and modelling study. Draft report to the Environment Agency for England and Wales.

Lessons learned

Natural sandstone buffers the pH strongly making it difficult to acquire sorption data over a sufficient range of pH for model parameterisation.

Difficulties were experienced in accurately preparing large volumes of experimental solutions at specified trace concentrations of uranium. To allow direct comparison between column test results for uranium obtained with and without Cd, EDTA and saccharic acid, pairs of parallel columns were fed simultaneously from the same reservoir of uranium solution.

Uranium is strongly retarded by Clashach Sandstone under natural conditions (oxidising, pH≈5.6). Sorption is ≈95% reversible over the timescale of these experiments. The presence of cadmium, a potential competitor for sorption sites, had little effect on uranium migration rates. Both EDTA and saccharic acid, however, enhanced uranium migration rates. This suggests that similar interactions that may occur between radionuclides and organics in LLW, ILW and TRU wastes may need to be considered during performance assessment studies.

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Solid phase

(i) *Min-U-Sil 5*

BET Surface Area: 4.4 to 4.5 m² g⁻¹

(ii) *St. Bees Sandstone*

Source: Sellafield, West Cumbria, England.

Mineralogy: 99% Quartz with iron oxide coatings, traces of K-feldspar, and rare amorphous clay (Fe-rich smectite/illite).

BET Surface Area: 3.06 m² g⁻¹ (rising to 3.46 m² g⁻¹ after acid-washing).

Aqueous phase

- a) Protonation/hydrolysis characteristics of Min-U-Sil 5
 Determined by continuous titrations adding 0.01 molar NaOH at ionic strengths of 0.001, 0.01 and 0.1 mol dm⁻³ (NaNO₃). 1g solid in 25 cm³ of NaNO₃ electrolyte. Oxidizing conditions. CO₂ removed by purging with nitrogen. T = 25°C

- b) Nickel sorption on Min-U-Sil 5
Determined by stepped titration experiments adding NaOH at ionic strengths of 0.1, 0.01, and 0.001 mol dm⁻³ (NaNO₃). 12g solid in 180 cm³ of NaNO₃ electrolyte. Oxidizing conditions open to the atmosphere. Sorption measured using ⁶³Ni. Nickel concentration around 4 x 10⁻¹⁰ mol dm⁻³. Final pH values were 10.5 or when 100% sorption was observed. T = 25°C
- c) Nickel sorption on St. Bees Sandstone
Determined by batch experiments as for Min-U-Sil 5 (b above). Sandstone was crushed to fine (<120 mesh) powder.
- d) Fe-oxide sorption data
Taken from Dzombak and Morel (1990).

Brief description of model

This exercise was modelled by five organisations. All used either a Double or Triple Layer Model.

Sorbing Species Considered

Several combinations of Ni²⁺, NiOH⁺, NiO.

Codes

Various.

Data

Thermodynamic data for solution species from HATCHES V5 database. Data for surface reactions derived from batch experiments for Min-U-Sil 5 and literature data for Fe-oxides. Sorption on St. Bees Sandstone was assumed to be dominated by iron oxide coatings on silica grains.

Predictions of sorption using the models correctly predicted the position of the sorption edge, but did not predict a shallow slope for the sandstone or at low ionic strength for the Min-U-Sil 5. The shallow slopes probably reflect more than one site type on the surfaces.

Publications

- D. Read and E. Falck (eds.), CHEMVAL 2. A coordinated research initiative for evaluating and enhancing chemical models in radiological risk assessment. European Commission Report, EUR 16648 EN, 1996.

Lessons learned

Difficulties were experienced in preventing dissolution of the Min-U-Sil 5 affecting results at high pH (> 10). Some experiments were repeated under a nitrogen atmosphere. No effects on sorption due to NiCO₃ species were observed in the experiments, despite being predicted by those models that included such species. The thermodynamic data for these species may require review.

Dolomite Surface Chemistry and Actinide Retention

P.V. Brady,

Sandia National Laboratories, USA

Dolomite surfaces are a common component of soils and sediments and are, in particular, a potentially important sorptive sink if human intrusion into the Waste Isolation Pilot Plant (WIPP) releases actinides into the Culebra Dolomite. Using a limited residence time reactor we have measured Ca, Mg, Nd adsorption/exchange as a function of ionic strength, PCO_2 , and pH at 25°C. By the same approach, but using as input radioactive tracers, we measured adsorption/exchange of Am, Pu, U, Th, and Np on dolomite as a function of ionic strength, PCO_2 , and pH at 25°C. Metal adsorption is favored at high pH. Ca and Mg adsorb in near-stoichiometric proportions except at high pH. Adsorption of Ca and Mg is diminished at high ionic strengths (e.g. 0.5M NaCl) pointing to counterion association with the dolomite surface, and the likelihood that Ca and Mg sorb as outer-sphere complexes. Sulfate amplifies sorption of Ca and Mg, and possibly Nd as well. Exchange of Nd for surface Ca is favored at high pH, and when Ca levels are low. Exchange for Ca appears to control attachment of actinides to dolomite as well, and high levels of Ca^{2+} in solution will decrease K_d s.

At the same time, to the extent that high PCO_2 s increase Ca^{2+} levels, K_d s will decrease with carbon dioxide levels as well, but only if actinide-carbonate complexes are not observed to form (Am-carbonate complexes appear to sorb; Pu-complexes might sorb as well. U-carbonate complexation leads to desorption). This indirect CO_2 effect is observed primarily at, and above, neutral pH. High NaCl levels do not appear affect actinide K_d s.

Data Sheet

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Solid phase

Dolomite from a skarn.

Aqueous Phase

0.005 to 0.5M NaCl, 25°C, flow-through, oxic, Ca, Mg, Sulfate, Np, U, Pu, Am, Th

Brief description of model

Metal exchange on Ca and Mg sites was measured and the effect of sulfate on their magnitude was modeled.

Publications

Brady P. V., J. L. Krumhansl and H. W. Papenguth. Surface Complexation Clues to Dolomite Growth. *Geochimica et Cosmochimica Acta* (60) 727-731.

Brady P. V. and W. A. House 1996. Surface-Controlled Dissolution and Growth of Minerals (Chapter 4 in *Physics and Chemistry of Mineral Surfaces*, CRC Press Ed. P.V. Brady) p. 221-302.

Brady P. V., H. W. Papenguth and J. Kelly J. Ca, Mg and Nd Sorption on Dolomite (In DOE Internal Review; to be subsequently submitted to *Geochimica et Cosmochimica Acta*).

Brady P. V. (Editor) 1996. *Physics and Chemistry of Mineral Surfaces*. CRC Press 352p.

Uranium(VI) Transport Modeling under Variable Chemical Conditions Using the Surface Complexation Concept

J.A. Davis¹, M. Kohler^{1,2}, G.P. Curtis¹ and D.B. Kent¹
¹U. S. Geological Survey, ²Colorado School of Mines, USA

The transport of adsorbing and complexing metal ions in porous media was investigated with a series of batch and column experiments and with reactive solute transport modeling. Pulses of solutions containing U(VI) were pumped through columns filled with quartz grains, and the breakthrough of U(VI) was studied as a function of variable solution composition (pH, total U(VI) concentration, total fluoride concentration, pH-buffering capacity). Decreasing pH and the formation of nonadsorbing aqueous complexes with fluoride increased U(VI) mobility. A transport simulation with surface complexation model (SCM) parameters estimated from batch experiments was able to predict U(VI) retardation in the column experiments within 30%. SCM parameters were also estimated directly from transport data, using the results of three column experiments collected at different pH and U(VI) pulse concentrations. SCM formulations of varying complexity (multiple surface types and reaction stoichiometries) were tested to examine the tradeoff between model simplicity and goodness-of-fit to breakthrough. A two site model (weak- and strong-binding sites) with three surface complexation reactions fit these transport data well. This reaction set was able to *predict* 1) the effects of fluoride complexation on U(VI) retardation at two different pH values and, 2) the effects of temporal variability of pH on U(VI) transport caused by low pH buffering. The results illustrate the utility of the SCM approach in modeling the transport of adsorbing inorganic solutes under variable chemical conditions.

Data Sheet

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Solid phase

Min-U-Sil 30 (brand name)
Pennsylvania Sand and Glass Company, Pittsburgh, PA (USA)
>99% quartz, acid-refluxed to remove traces of iron and aluminum oxides.

Aqueous phase

Solution composition

Typical electrolyte was 0.01M NaNO₃, sometimes with 10⁻⁴M or 5 10⁻⁴M fluoride, 10⁻⁴M total acetate, atmospheric p_{CO2} (NaHCO₃),
U(VI) total concentration range of 10⁻⁹M to 10⁻⁴M.

Room temperature (22°C), oxic conditions, batch and column experiments
Typical equilibration times in batch experiments: 20 hours
Linear flow velocities: 8.7×10^{-4} and 3.5×10^{-3} cm/sec.

Radionuclides

^{238}U , ^{234}U , ^{233}U

Brief description of model

Surface components, surface species:

Surface Complexation Model (SCM) without Electrical Double Layer Model (EDL) used. One, two and three site models studied with two different stoichiometries possible for uranium (VI) adsorption reactions (either one or two protons released per UO_2^{2+} adsorbed).

Surface components were the surface silanol groups, $\equiv\text{SiOH}$, but were represented as either one, two, or three types of silanol groups in one, two, and three site models, respectively.

Surface species were $\equiv\text{SiOH}$, $\equiv\text{SiOUO}_2\text{OH}$ and $\equiv\text{SiOUO}_2^+$ and the various uranium surface complexes (see Kohler *et al.*, 1996).

Parameters (measured, calculated, estimated):

Specific surface area of the quartz measured by gas adsorption (Kr) and BET theory, determined to be $0.33 \text{ m}^2/\text{g}$. Non-porous material. Grain size approximately 8-30 μm .

Total site density of the quartz estimated from U(VI) adsorption edges at 10^{-4} M total U(VI) and 100 g quartz/L. ($3.5 \times 10^{-7} \text{ mol/g}$).

Formation constants for the surface complexes (binding constants) and distribution of sites (strong to weak site concentrations) estimated (see "Publications").

Thermodynamic data used:

"Chemical Thermodynamics of Uranium"; Grenthe *et al.*, 1992.

"Critical Stability Constants"; Vol 6, 2nd suppl.; Smith and Martell, 1989.

Codes:

FITEQL v 2.0 (John Westall, October 1982) for the estimation of binding constants from batch data.

FFSTM (G.P. Curtis and J. Rubin, 1997 in preparation) for solute transport modeling.

Publications

M.Kohler; G.P.Curtis; D.B.Kent and J.A. Davis, 1996, Experimental investigation and modeling of uranium (VI) transport under variable chemical conditions, Water Resources Research, Vol. 32, No.12, Pages 3539-3551, December 1996.

Lessons learned

The uncertainty in parameters for surface complexation models is affected by the type of experiments conducted (batch vs. column) and the range of chemical conditions considered in the experiment. If the range of chemical conditions that must be considered in PA modeling or some other application is known, a surface complexation model can be simplified to eliminate unnecessary parameters, including components and species. That is, the required complexity of the surface complexation model depends on the range of conditions that must be considered in the model. The results of the study illustrate that reactive transport models that combine aqueous chemical speciation and surface complexation provide a powerful tool for predicting the complex transport behavior that may occur under variable chemical conditions.

Sorption of Thorium onto Titaniumdioxide

A.M. Jakobsson and Y. Albinsson

Department of Nuclear Chemistry, Chalmers University of Technology, Sweden

The sorption of thorium onto titanium dioxide from aqueous solution was studied as a function of both pH (1-7) and ionic strength (0.005-0.05 M NaClO₄) in a CO₂ free environment at low thorium concentration (10⁻⁷-10⁻⁸ M). The concentrations were measured with ICP-MS. Titaniumdioxide has been chosen to represent minerals of a low/medium point of zero charge and because it is relatively insoluble and thorium to represent tetravalent actinides. The experimental method employed is batchwise where the pH of the individually prepared samples is measured after separation of the phases. The first and second acid dissociation constants, pKa1 and pKa2 of the titaniumdioxide surface were determined from potentiometric titrations. Preliminary results indicate the formation of innersphere complexes for Th as the sorption is independent of the ionic strength. The thorium sorption sharply increases between pH 2 and 3. All the data are to be modeled using a triple layer surface complexation model with the code FITEQL.

Data Sheet

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Solid phase

Titaniumoxide
Degussa Corporation, Pigm. division, P.O. Box 2004, New Jersey 07608

Aqueous phase

Solution composition

0.005 - 0.05 M NaClO₄; 2 days contact time, ambient temperature, batch experiments, anoxic

Radionuclides

²³⁴Th

Brief description of model

This part is not finished at the moment.

Codes

FITEQL

Lessons learned

Check the concentration. In our case was the concentration of ²³²Th the dominating.

Sorption of Uranium(VI) onto Phyllite

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The sorption of U(VI) on phyllite and on the main mineral constituents of phyllite, muscovite, quartz, chlorite and on various feldspar minerals (oligoclase, labradorite, and orthoclase) was studied in batch experiments under ambient pressure in the pH range of 3.5 to 9.5 using an uranium concentration of 1×10^{-5} M. With the exception of chlorite, which was studied using the size fraction smaller than 40 μm , batch experiments with phyllite and the above listed minerals were carried out using the size fraction of 63-200 μm and a to solid solution ratio of 1g/20mL. The study showed that sorption of uranium on the various mineral surfaces had its maximum in the pH range of 6.0 to 7.3. However, the maximum amount of uranium sorbed onto each individual mineral was different and ranged from 45% of the initially added uranium for quartz and labradorite to almost 90% for muscovite and oligoclase, 95% for chlorite and 97% for phyllite. It was found that the rock phyllite was sorbing more uranium than all of its main mineral constituents. There was a good agreement between the sorption curves for phyllite and chlorite up to a pH of 6.5. At higher pH values (> 6.5) chlorite and all of the above listed mineral were sorbing less uranium than phyllite. Reasons for this is not clear at the present time.

It appears as if minor mineral constituents of phyllite or its alteration products formed during the batch experiments may be responsible for dominating the sorption behaviour of phyllite. Additionally conducted batch experiments with ferrihydrite, which may form during alteration reactions with chlorite, revealed that small amounts of ferrihydrite (1 mM Fe) showed almost exactly the same sorption behaviour as phyllite. Chlorite which contains ferrous iron may be altered due to water-rock-interactions during the batch experiments, and iron may be leached out of the chlorite. In the solution, the ferrous iron becomes oxidised to ferric iron which subsequently hydrolyses and eventually precipitates as a secondary iron hydroxide or iron oxy-hydroxide mineral. This may then be responsible for sorbing the major amount of uranium from the solution.

Data Sheet

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Solid phase

Phyllite, (Western Erzgebirge in Saxony/Germany)
Chlorite, (Grimsel, Switzerland)
Muscovite, (California, U.S.A.)
Quartz, (Merck, p.a., 0.2 - 0.8 mm, washed and calcined)
Albite, (Iveland, Norwegen)
Orthoclase, (La Cabrera, Guadarrama, Spanien)
Oligoclase, (Risør, Norwegen)
Labradorite, (Pauls Islands, Labrador coast)

Aqueous phase

Solution composition

With and without ionic strength adjustments, sodium perchlorate (NaClO₄, 0.1 N)
50-60 hours contact time 25 EC
Batch experiments with phyllite and with its mineral constituents (see above), open to the atmosphere

Radionuclide

Uranium(VI)

Brief description of model

Surface components, surface species

This part is not finished yet.

Parameters (measured, calculated, estimated)

BET surface area is already measured for the above named minerals and the rock phyllite itself. Total site density will be determined

Thermodynamic data used

From Grenthe *et al.*, 1992 (Grenthe, I., Fuger, J., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., Wanner, H., 1992. Chemical Thermodynamics of Uranium, 1st ed., Elsevier Science, Amsterdam.

Codes

FITEQL, Version 3.2
HYDRAQL
EQ3/6

Publications

Arnold, T., Zorn, T., Bernhard, G., Nitsche, H. Sorption of Uranium(VI) onto Phyllite. Submitted to Chemical Geology.

Lessons learned

When evaluating the sorption capacity of natural rocks, the minor mineral constituents and possibly forming alteration products have to be taken into consideration.

Ni Sorption by a Natural Sand

M. Siegel

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Data Sheet

Author

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Solid phase

A natural sand and its 3 component minerals were studied.

Natural sand: Wedron 510 Quartz Sand

Source: St. Peter sandstone, sold by Wedron Silica Corp., Wedron, Illinois, 60557, USA

Mineralogy:

major: quartz

trace: kaolinite, mixture of iron oxyhydroxide phases

Chemical composition: 99.99% SiO₂

Trace elements in bulk rock (ppm):

Li (1.5); Na (1.7); Mg (24.7); Al (2830); K (2.5); Ca (55); Ti (83); Fe (242); Ni (0.2); Br (1.7)

Trace elements in bulk fine (<74 micron) fraction (ppm):

Li (2.5); Na (9.6); Mg (118); Al (11300); K (20); Ca (222); Ti (892); Fe (2280); Ni (2); Br (<0.8)

Trace elements in surface (hot 6 N HCl leach) of fine (<74 micron) fraction (ppm):

Li (0.1); Na (0.9); Mg (84.6); Al (1200); K (1); Ca (198); Ti (13); Fe (1180); Ni (0.9); Br (nd)

BET Specific surface area: 0.08 m²/g

Component Solid Phases:

1. synthetic goethite

Synthesized by the method of Atkinson *et al.* (1967)

BET specific surface area: = 33.8-45.4 m²/g

2. Min-U-Sil 5 quartz

Fe content: 357 ppm extractable in boiling HCl

source: U.S. Silica, Berkeley Springs, West Virginia

BET specific surface area: = 4.05-5.81 m²/g

3. Kaolinite

Fe content: 1270 ppm extractable in boiling HCl

source: kaolin powder, U.S.P., J.T. Baker Co.
BET specific surface area: = 24.6 m²/g

Aqueous phase

Solution composition

0.001 or 0.1 M NaCl electrolyte; pH range: 4-10; competing cation: Li (100 ppm).
Equilibration time: 8-12 hr pre-equilibration; 8-12 hr equilibration (“overnight”)
Temperature: room temp, about 22°C,
Batch test: Wedron sand: 58-78 m²/l (20 g sand /20 ml solution)
 goethite: 4.8-55 m²/l
 Min-U-Sil5: 124-247 m²/l
 kaolinite: 124 m²/l
Oxic atmosphere: atmospheric pCO₂ for pH <7.5;
 (total carbonate = 10-3.74 M maintained by addition of NaHCO₃ at
 higher pH)

Radionuclides

Ni (100 - 230 ppb)

Brief description of model

Surface complexation parameters were derived for the component minerals. The Ni sorption edge measured on the Wedron sand was compared to those calculated using the properties of the component minerals.

Surface components, surface species

Wedron 510 sand is more than 99% quartz in bulk mineralogy, yet its adsorption behavior is dominated by iron oxyhydroxide and kaolinite, two trace components. The presence of Fe-oxyhydroxide is inferred from the quantity of Fe leached during an acid wash. Fe-oxyhydroxides probably coat most (50–80%) of the available surface area in the raw sand. Kaolinite platelets were observed on sand grain surfaces by SEM. Qualitatively, the adsorption properties of the sand can be adequately modeled as a two-component system. Ni adsorption occurs primarily on the iron oxyhydroxide, on sites where Li does not compete; some of the Ni adsorbs to kaolinite, and competes with Li for adsorption sites on that mineral. Competition with Li leads to diminished Ni adsorption by both the raw sand and pure kaolinite. Ni adsorption by goethite is insensitive to the presence of Li, suggesting that in the sand, iron oxyhydroxide could not be the site of the Li-Ni competition. The presence of the carbonate cement is inferred from potentiometric titration of the raw sand and the amount of Ca and Mg that is leached by acid-stripping. Li adsorbs irreversibly, suggesting that kaolinite is the only important phase in the sand with respect to Li adsorption.

Two triple-layer surface-complexation models were developed for simulating Ni adsorption onto goethite. The models were fit to Ni adsorption data in batch systems with approximately 5 and 50 m²/l goethite, under both CO₂-free and air-equilibrated conditions. The adsorption stoichiometry is modeled as a 1:1 SONi⁺ inner-sphere complex. The simpler one-site model performs poorly at lower surface concentrations when optimized at the higher surface concentration. The two site model contains a small fraction of high energy sites and fits data for both goethite concentrations. A quantitative model of Ni adsorption onto kaolinite was also developed; attempts to develop a model for quartz were less successful. The Ni-adsorptive properties of the sand could be simulated using the 1-site goethite model assuming an iron oxyhydroxide surface area of 28 m²/l in the sand/solution system. This corresponds to a specific surface area of the iron coatings of approximately 600 m²/g.

Parameters (measured, calculated, estimated)

Goethite:

Surface area calculated from BET: 58 m²/l.

Inner-layer capacitance (C₁): 1.20 F/m² – calculated from potentiometric data with FITEQL

Outer-layer capacitance (C₂): 0.20 F/m² – Davis *et al.* (1978)

Site density: 2.31 sites/nm² - as advocated by Davis and Kent (1990).

Fraction of high Ni affinity sites: 0.038 – This work (two-site model only).

Formation constants for surface species (pK values):

SO⁻ = 9.9, SOH₂⁺ = -7.9 – van Geen *et al.* (1994)

SO-Na = 8.9, SOH₂-Cl = -8.84 – calculated from potentiometric data with FITEQL.

SOCO₂⁻ = 4.23 – van Geen *et al.* (1994)

SO^{II}Ni⁺ = -0.613 – single site inner sphere complex calculated from sorption data with FITEQL.

SO^{II}Ni⁺ = 0.5 – IS complex calculated from sorption data with FITEQL (2-site model).

SO^INi⁺ = -1.8 – IS complex calculated from sorption data with FITEQL (2-site model).

Min-U-Sil-5 Quartz:

Surface area calculated from BET data: 265 m²/l

Inner-layer capacitance (C₁): 2.0 F/m² – calculated from potentiometric data with FITEQL.

Outer-layer capacitance (C₂): 0.20 F/m² – Davis *et al.* (1978)

Site density: 6 sites/nm² – estimated from other studies in literature.

Formation constants for surface species (pK values):

SO⁻ = 6, SO-Na = 7 – calculated from potentiometric data with FITEQL.

SOH₂⁺ = 2 SOH₂-Cl = 3 – calculated from formation constants for SO⁻, SO-Na assuming pH_{zpc} = 2.

SO^{II}Ni⁺ = 7.7 – outer sphere complex visual fit from sorption data calculated with HYDRAQL.

Kaolinite:

AlOH and SiOH sites

Surface area calculated from 10x value of BET measurements: 1240 m²/l

Site density: 6 sites/nm² – as advocated by Xie and Walther (1992).

Inner-layer capacitance (C₁): 2.4 F/m² – from Riese (1982).

Outer-layer capacitance (C₂): 0.20 F/m² – Davis *et al.* (1978)

AlOH sites

Fraction of total sites: 0.5 – as advocated by Riese (1982)

Formation constants for surface species (pK values):

SO⁻ = 7.4 – from Riese (1982).

SO-Na = 7.4 – from Riese (1982).

AlONi⁺ = 2.1 – IS complex; visual fit from sorption data calculated with HYDRAQL.

SiOH sites

Fraction of total sites: 0.5 – as advocated by Riese (1982)

Formation constants for surface species (pK values):

SO⁻ = 6.25 – from Riese (1982).

SO-Na = 3.5 – from Riese (1982).

SiONi⁺ = 7.7 – outer sphere complex; value from Min-U-Sil used.

Thermodynamic data

Thermodynamic calculations were carried out with using a critically evaluated set of formation constants for aqueous Ni species. Sources of data include compilations by Baes and Mesmer (1976), Mattigod and Sposito (1977), Wagman *et al.* (1982), van Geen *et al.* (1994).

The formation constants for Ni carbonato-complexes are two orders of magnitude lower than the values commonly used in the literature. The lower values are consistent with the results of Ni solubility measurements in batch systems with low concentrations of CO₂ and Ni adsorption experiments at high pH.

Codes

HYDRAQL 94 (Ward, 1995), a revised version of HYDRAQL (Papelis *et al.*, 1988) and FITEQL 2.0 (Westall, 1982).

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Lessons learned

1. Acid-cleaning procedures strongly effect surface properties of sand and Min-U-Sil quartz reference.
2. Sorption properties of sand were dominated by trace mineral coatings.
3. Dissolution of minerals (esp. SiO₂) and change in ionic strength during potentiometric titration introduces uncertainty in data interpretation and model fitting.
4. Uncertainty in effective surface area of clays has strong effect in calculated SCM parameters.
5. Large number of adjustable parameters in SCM and large number of reasonable interpretations of data produced from each experimental technique makes unique set of model parameters unattainable. A large degree of subjectivity is unavoidable.

A Model for Radionuclide Sorption onto Cementitious Surfaces

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In a Nirex repository for low and intermediate level wastes, a high-calcium cementitious backfill would be specified. Sorption onto this Nirex Reference Vault Backfill (NRVB) and onto cementitious encapsulation grouts would play an important role in retarding the release of radionuclides from the near field of a repository. In this work, a thermodynamic sorption model was developed that is consistent with the available experimental data and that allows prediction of radioelement sorption onto cementitious materials of varying calcium-silicon ratio (Ca/Si). The diffuse-layer model (DLM) has been applied, which includes the electrostatic interaction between a sorbing ionic species and a charged interface, but does not require the extra surface parameters associated with more detailed surface complexation models. It is assumed in the development of this modelling study that the surface is dominated by calcium and silicon sorption sites. The composition of the aqueous phase and the properties of the cementitious surface vary with the calcium-silicon ratio (Ca/Si) of the solid material.

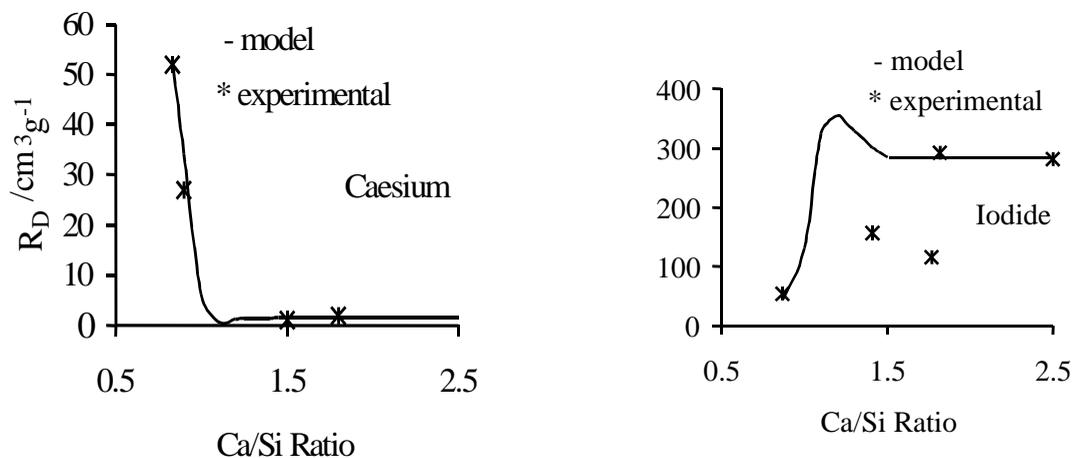
For any given system, Ca/Si is fixed and the pH and the aqueous calcium and silicon concentrations are calculated using the Berner model [1]. The surface properties of the cementitious solid are also dependent on the Ca/Si ratio. Two types of surface site are included: calcium sites ($>CaOH$) and silicon sites ($>SiOH$). Each type may take up or lose protons. In addition, sorption of calcium ion onto silicon sites may occur, creating further calcium surface sites. The proportion of calcium surface sites is therefore dependent on the calcium ion concentration and the pH, which in turn are dependent on Ca/Si. This mole fraction of calcium surface sites, $x_s(Ca)$, is a key parameter in the model.

It is fundamental to the model that the equilibrium constants for the surface equilibria ($\log K^{int}$) do not keep the same values for solids of different Ca/Si. This is not unexpected since, for example, a calcium surface site is unlikely to behave identically when it is located on a calcium-rich surface and on a silicon-rich surface. The approach adopted was to select $\log K^{int}$ values for each surface equilibrium at $x_s(Ca) = 0$ (silica surface) and at $x_s(Ca) = 1$ (calcium hydroxide surface), based on literature values or the fitting of experimental data wherever possible. At $0 < x_s(Ca) < 1$, the $\log K^{int}$ values are assumed to vary linearly with $x_s(Ca)$, between the two sets of limiting values.

The surface model has been applied to predict the surface potential of cementitious solids after equilibration with pure water, at varying Ca/Si. Both the equilibrated pH and the surface potential are dependent on the Ca/Si. The surface potential is negative at low Ca/Si (weak calcium sorption) but positive at high Ca/Si (strong calcium sorption). This trend is also found in reported zeta potential measurements.

Radionuclide sorption is incorporated into the model by surface complexation of the major aqueous species with the surface sites. The model has been applied consistently to a range of batch sorption data including caesium and iodide sorption onto calcium silicate hydrate phases (see Figure 1), and to the sorption of several radionuclides onto a high calcium cement (NRVB). The model predictions under saline conditions are also consistent with the available data.

Figure 1. Sorption of caesium and iodide as a function of Ca/Si ratio



This work has been reported in more detail in reference [2]. The model has been used to support the sorption data used in assessment calculations.

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Application of Thermodynamic Sorption Models to Distribution Coefficients of Radionuclides in Bentonite

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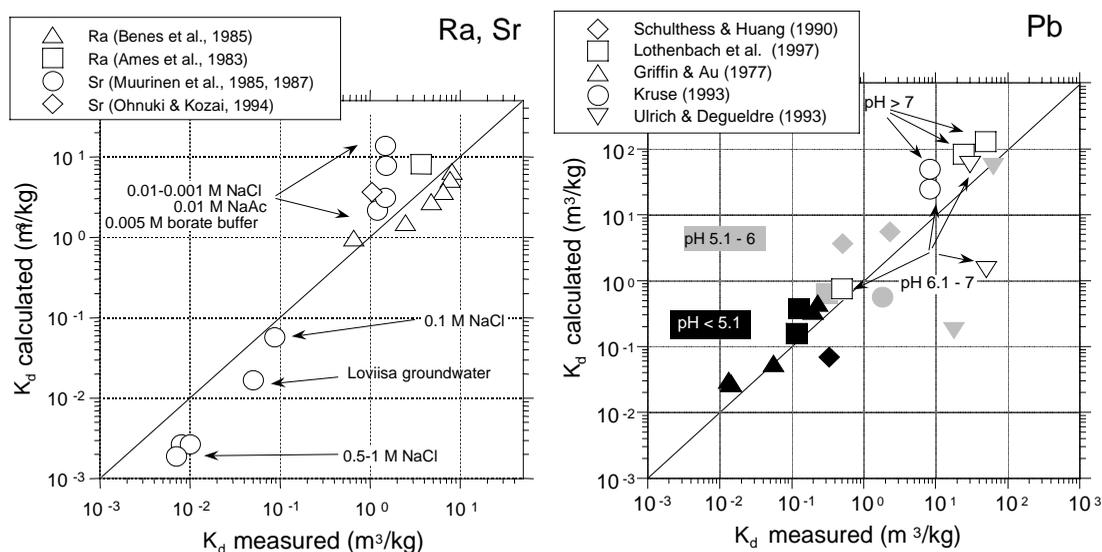
Like the disposal strategies of other countries, the Japanese disposal concept for high-level radioactive waste envisages the use of compacted bentonite as backfill material. The bentonite backfill is probably the most effective and predictable barrier on the entire migration path. High priority is therefore given to the thorough understanding of the processes affecting radionuclide transport in compacted bentonite. Sorption reactions of radionuclides on bentonite are of particular importance regarding their retention.

Sorption of radionuclides is quantified through distribution coefficients (K_d values) that may be used directly in performance assessment calculations. Typically, K_d's relevant for performance assessment are selected based on compilations of experimental sorption data (sorption databases) and expert opinion. While this process may lead to reasonable results, it is usually very difficult to follow by third parties.

Thermodynamic (“mechanistic”) sorption models are very effective tools for supporting and facilitating the selection of K_d values. Calculations carried out with such models can be used to (1) evaluate the quality of experimental sorption data, and (2) predict K_d values for situations where no experimental data are available.

Here, we present the application of thermodynamic models to calculate K_d values for radionuclides on bentonite, using elements with different behavior for illustration: Ra and Sr do not form important complexes in aqueous solution and interact with bentonite through ion exchange, while Pb forms complexes and solid phases with e.g. hydroxide and carbonate ions, and sorbs through surface complexation as well as ion exchange. Thus, the sorption behavior of these elements in bentonite is described by simultaneously addressing their solution/solid speciation and ion exchange as well as surface complexation reactions. At the same time, the model is used to calculate the solution composition and bentonite surface speciation as a function of the solid/water ratio, based on the bentonite model developed by [1, 2]. To model the behavior of Ra/Sr and Pb, relevant ion exchange and surface complexation constants are selected from the open literature [3, 4] and incorporated in the bentonite model. A comparison of model results and experimental K_d's is provided in the figure below. All model results are calculated using the same set of thermodynamic constants, i. e., in no case were the constants modified in order to obtain a better fit.

Figure 1. A comparison of calculated and measured K_d values for Ra and Sr (left) and Pb (right) on different bentonites and smectites. Measured K_d values are taken from the references indicated. Calculation of K_d values is explained in the text.



This plot shows that the model used is able to predict K_d 's for Ra and Sr reasonably well over a wide range of conditions, including 0.001-1 M NaCl and a synthetic groundwater. It becomes apparent that these elements can be treated analogously, and that a major factor governing the distribution of Ra and Sr is the solution concentration of cations able to compete for the available ion exchange sites. This stresses the importance of the composition of the input solution and the amount of soluble impurities contained in the different bentonites for Ra and Sr sorption. The model used also describes Pb sorption well for a number of different situations. Solution pH is a dominating factor regarding sorption of Pb, which adsorbs onto bentonite both by ion exchange and surface complexation. Ion exchange takes place at the structural charge sites of smectite and dominates adsorption at pH values below 5, whereas at higher pH values surface complexation is more important. At high pH values, the precipitation of solid Pb-carbonate or -oxide has to be taken into account in order to explain the experimental data.

The model discussed here can be used to identify relevant sorption processes, as well as other factors that determine experimental K_d 's, such as impurities contained in bentonite and artefacts (precipitation). K_d 's can be modeled over a very wide range, indicating that such models may be used for predictive purposes.

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Data Sheet

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Solid phase

Bentonite:	Kunipia-F, Japan	99% smectite, traces of quartz and calcite, 0.071% NaCl, 0.005% KCl, 0.694% CaSO ₄ .
	Kunigel-V1, Japan	46-49% smectite, 29-38% quartz, 2.1-6.6% calcite, 0.5-0.7 % pyrite, traces of other minerals (not considered), 0.001% NaCl, 0.004% KCl, 0.38% CaSO ₄ .
	MX-80, Wyoming (USA)	88.6% smectite, 10% quartz, 1.4% calcite, 0.007% NaCl, 0.34% CaSO ₄ .

Pure montmorillonites

Aqueous phase

Solution composition: conditions

1. The solution composition is always calculated as a function of the solid/water ratio, and the composition of the input solution, assuming equilibrium.
2. The amount of impurities in bentonite available for dissolution may be varied.
3. Calculations are performed in the present case for 25°C and batch systems (other temperatures can be handled, and flow-through systems can be simulated).
4. For the present presentation, only oxic systems are considered, but redox equilibria may be handled through the model used.

Radionuclides:

For the solid phase considered here (bentonite), data on Cs, Ra, Sr, Pb, as well as major electrolyte cations are available (for e.g. simple oxides, data on a number of other elements are available)

Brief description of model

Surface components, surface species

Ion exchange sites (permanent charge sites) at the siloxane surface of clays.

Surface site: Z, surface species: e.g. NaZ, CaZ₂.

Surface complexation sites at the "edge surface" of clays.

Surface site: SOH, surface species: e.g. SOPb⁺, (SO)₂Pb.

Parameters:

Most ion exchange and the SOH-site hydrolysis data are evaluated from measurements, other ion exchange and surface complexation data are taken from the open literature. Bentonite characteristics (composition, surface site density) are measured for some bentonites (e.g. MX-80), but need to be partly estimated in some cases.

Thermodynamic data used

For aqueous-phase thermodynamic data, the database used in connection with MIN_SURF (see below) is usually relied upon. This database includes the contents of the Nagra TDB (Pearson and Berner, 1991; Pearson, Berner and Hummel, 1992) but contains also additional species which were part of earlier versions of MINEQL. These additional species have been partly revised and listed by Pearson, Berner and Hummel (1992).

Codes

MIN_SURF (Berner, 1993) is a surface and solution chemical speciation code based on MINEQL/PSI and DSURF (Dzombak and Morel, 1990). MIN_SURF uses the diffuse double layer model to calculate surface complexation reactions in the solid surface/water interface, the formalisms used to calculate double layer characteristics are based on Hunter (1981) and de Levie (1990). The code MINEQL/PSI corresponds to the code MINEQL/EIR, made available for the NEA data bank in 1986 (OECD/NEA, 1986).

The BMG-version of MIN_SURF includes the possibility to model ion exchange reactions, using either the mole fraction or equivalent fraction approach to calculate the activity of the exchanger species.

Publications

The basic surface chemical model for bentonite is published by Wanner *et al.*, 1994 (Radiochim. Acta 66/67, 157-162), the ion exchange model developed for Cs by Wanner *et al.*, 1996 (Fresenius J. Anal. Chem. 354, 763-769). Publications regarding the application to K_d values of Ra, Sr and Pb are in preparation, as well as a publication on the integration of an ion exchange and mechanistic diffusion model for Cs.

Lessons learned

K_d values determined in batch and diffusion experiments can be explained and predicted by the above model. In particular for compacted bentonite, the most critical uncertainties are more related to the (lack of) characterisation of the solid phase (soluble impurities) and experimental conditions, rather than the actual model parameters.

Sorption of Europium onto Illite: Mechanistic Interpretations

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Sorption of europium onto illite – one of the most abundant clay minerals present in Boom Clay (the candidate host rock for HLW disposal in Belgium) was studied. The batch sorption results are interpreted by a multi-site sorption model based on the surface complexation approach. Our sorption conceptual model is based on a fundamental hypothesis: clay mineral possesses two types of reactive sites, i.e. permanently charged cation exchange sites and pH dependent surface complexation sites. Further on, the mechanisms assumed are demonstrated by fitting the sorption data with the two mass action constants, i.e. surface complexation constant ${}^{\text{Eu}}K_{\text{int}}$ and selectivity coefficient ${}^{\text{Eu}}K_{\text{c}}$. The surface site concentrations are quantified by cation exchange capacity (CEC) and titration measurements. The CEC of the illite is 71 $\mu\text{eq/g}$ and the total site density of the surface hydroxyl group is 1.35 $\mu\text{eq/g}$. The key reactions between solutes/surface sites identified are: (1) europium exchange onto the illite surface; (2) proton exchange onto the illite surface; (3) proton association/dissociation of the surface hydroxyl groups; (4) surface complexation of europium with the surface hydroxyl groups. The titration and the sorption data are fitted with the FITEQL program using the diffuse layer model. The results indicate that the electrostatic term is necessary to obtain an acceptable fit. The K_d value measured on clay suspension in laboratory is always higher than that of measured under *in situ* condition on reconsolidated clay cores. The discrepancy may be due to the different accessible surface site densities encountered under the two conditions. The intrinsic and predictive features of the mechanistic approach can help to evaluate the uncertainty coming from empirical K_d 's for increasing the confidence in the performance assessment calculations. Moreover, the data obtained concerning the surface and solution speciation can be used by transport modeller to interpret the *in situ* migration experiments. The multi-site model used in this study was chosen mainly because of the success of the surface complexation modelling (SCM) on oxide/hydroxide system. Our objective is to extend the SCM to clay minerals and later to natural organic matter which are the main sinks for radionuclides in Boom Clay. It appears from this study that the multi-site model based on the surface complexation and ion exchange mechanisms can give a quantitative description of europium sorption onto illite.

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Solid phase

Identify: Silver Hill Montana illite

Source: Source Clay, USA.

Mineralogy: major components (Hower *et al.*, 1966): SiO₂ (55.1%); Al₂O₃ (22%);
minor components: K₂O (8%), Fe₂O₃ (5.3%), MgO (2.8%).

This clay was further purified in our laboratory for removing carbonate and organic matter. Finally, the clay was transformed to sodium form before use.

Aqueous phase

Solution composition:

Sodium perchlorate (NaClO₄, 0.02~0.5 N);

3~7 days equilibrium; room temperature;

Batch; oxic for sorption; anoxic for titration.

Radionuclide:

Europium, Eu(NO₃)₃, 10⁻⁸ M.

Brief description of model

Surface components, surface species

Illite surface is considered possessing two types of reactive sites which are responsible for sorption. They are (1) the permanently charged site arising from isomorphous substitution within the crystal lattice and (2) the variably charged surface functional groups due to the ionisation of the surface hydroxyl groups (S-OH) at the broken edges of the clay particles. The surface species considered in this study are: (1) Europium sorbed due to cation exchange (ill₃-Eu); (2) Europium surface species due to the surface complexation reaction (S-Oeu²⁺).

Parameters (measured, calculated, estimated)

1. BET surface area: measured.
2. total site density for the surface hydroxyl group: fitted (FITEQL) from the acid/base titration data.
3. Cation Exchange Capacity (CEC): measured by ²²Na⁺ isotopic dilution and Cobaltihxmmine methods.
4. acidity constants of the surface hydroxyl group: fitted (FITEQL) from the acid/base titration data.
5. surface complexation constant: fitted (FITEQL) from the sorption data.
6. selectivity coefficient K_c for europium: measured.
7. selectivity coefficient K_c for proton: fitted from the sorption data.

Thermodynamic data used

EQ3/6 database (Lawrence Livermore National Laboratory, V8.R5, 1996).

Codes

1. FITEQL (Herbelin and Westall, 1996): for data optimisation;
2. CHESS (van der Lee, 1993): for sorption calculations.

Lessons learned

1. Selectivity coefficients for cation exchange cannot be treated as thermodynamic constants. The value of selectivity coefficient is function of ionic strength. Due to the difficulty for defining the surface activity coefficient of cation exchange site, the selectivity coefficient has no intrinsic meaning. The selectivity coefficient for europium in this study is treated as a fitting parameter.
2. Difficulties for pH measurement is encountered concerning electrode calibration, back titration for compensating the effect of clay dissolution, influence of purification procedure on pH measurement, etc.

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Modelling of Sorption of U(VI)-species, HCO_3^{1-} and CO_3^{2-} on Bentonite Using SCM

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We have been seeking parameters characterizing the interaction (sorption and desorption) of radionuclides with solid phase, suitable for description of migration of radionuclides in porous media. These parameters need not necessarily be the K_d factors, as K_d is not suitable parameter in the case of non-linear sorption isotherm (see attached text).

In this paper, modelling of uranium sorption on bentonite has been studied as the method of examining the mechanism of the sorption and obtaining the parameters sought.

The modelling has been based on the assumption that the sorption takes place on the “edge sites” of clay minerals in bentonite. These sites occur in three forms, SO^{1-} , SOH^0 and SOH_2^{1+} , whose proportion depends on the pH, ionic strength and two protonation reactions. The equilibrium constants of the reactions were determined from titration curves obtained with bentonite SABENYL and synthetic granitic water. In the same system, sorption of uranium(VI), HCO_3^{1-} and CO_3^{2-} was experimentally studied as a function of pH. The data set so obtained was examined using three types of surface complexation models, while the sorption was described by 6 tentative reactions for six U(VI) species and by two reactions for HCO_3^{1-} and CO_3^{2-} with the edge sites.

It has been found that the experimental data can be reasonably well described by all three models, differences among the models are rather small in this respect. $\text{UO}_2(\text{CO}_3)_2^{2-}$ seems to be the prevailing uranium form sorbed, sorption of UO_2^{2+} , $\text{UO}_2\text{OH}^{1+}$ and UO_2CO_3 takes place to the less extent. The equilibrium constants for the sorption of these uranium forms were obtained, as well as those for the adsorption of HCO_3^{1-} and CO_3^{2-} .

See Data Sheet Questionnaire for more details.

Data Sheet

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Solid phase

Bentonite SABENYL

KERAMO, Obrnice, Czech Republic

- a) mineralogical composition: montmorillonite + nontronite 70%, quartz 7.9%, muscovite +illite 6.9%, goethite 6.6%, feldspar 5% and anatase 4%,
- b) chemical composition: SiO₂ 41%, Fe₂O₃ 12%, Al₂O₃ 11%, CO₂ 1.04%, TiO₂ 3.5%,

Aqueous phase

Solution composition and conditions

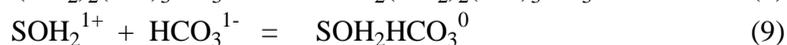
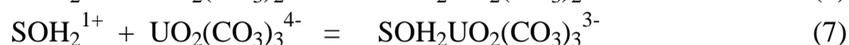
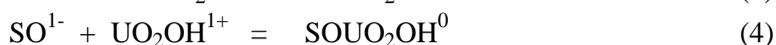
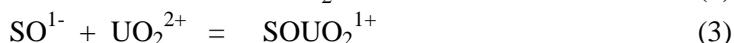
- a) Synthetic granitic water (mol.l⁻¹): Na 2.3x10⁻³, K 1.1x10⁻⁴, Ca 3.6x10⁻⁴, Mg 1.8x10⁻⁴, Cl 2x10⁻³, SO₄ 1.1x10⁻⁴, CO₃ 1.8x10⁻³.
pH = 8.2. Ionic strength = 0,1 (NaNO₃).
- b) Equilibration time ≥ 48 hours, room temperature, batch arrangement, oxic conditions.

Radionuclide

²³³U - starting concentration 6.67x10⁻⁷ mol.l⁻¹.

Brief description of model

Three types of surface complexation models were used for the description of the equilibrium states of sorption of U(VI)-species and anions HCO₃¹⁻ and CO₃²⁻, namely Constant Capacitance Model (CCM), Diffuse (double) Layer Model (DLM) and the so-called Chemical Equilibrium Model (CEM, where Boltzman's factor equals one, i.e. the electrostatic surface charge is not considered). The behaviour of the system studied was described by the equations of protonation of surface group SO¹⁻ (1) and (2), sorption of U(VI)-species (3) - (8) and sorption of carbonates (9) and (10) :



The experimental data, namely the titration curves of bentonite and the dependences of U(VI) and carbonates sorption on pH (approximately 3-9.5), were evaluated using our own computer codes (see below), by means of which the following parameters were obtained: equilibrium constants of the reactions (1)-(10), site density ΣSOH and, in the case of CCM, Helmholtz capacitance G.

Bentonite powder was characterized by specific surface area (44.4 m².g⁻¹) using BET method, by total cation exchange capacity (0.88 mval.g⁻¹) and granulometric analyses (82.5% below 0.01 mm).

The stability constants taken from MINTEQ-A2 code were used to the calculation of the abundance of U(VI) species in the aqueous phase.

Four codes were constructed: P33 and P35 for the evaluation of titration curves of bentonite or similar materials, P34 for the evaluation of dependencies of carbonates sorption on pH and P38

for the evaluation of U(VI) sorption on pH. Code P38 makes it possible to choose suitable complexation reaction(s) and to calculate the corresponding equilibrium constant(s).

Lessons learned

1. The calculated parameters corresponding to the individual models (CCM, DLM, CEM) depended to some extent on the type of model used and partly on the starting estimations of the values of parameters to be calculated, because non-linear regression method had to be used for the calculation.
2. The time of calculation depended in some cases also on the starting estimations, especially if the experimental data for $U(VI) = f(pH)$ were evaluated using the code P38.
3. The sorption of $UO_2(CO_3)_2^{2-}$ has been found as the main reaction participating in the fixation of U(VI) on the bentonite surface in the pH interval studied. The following uranium species seem also to participate at the fixation: UO_2^{2+} , UO_2OH^+ and UO_2CO_3 .
4. The best fit of the experimental data was obtained when the reaction (8) was not considered, as seen from the lowest sum of square deviations of the experimental from calculated values. In this case, the ability of different models to describe the experimental pH dependence of sorption of uranium decreased in the order $DLM \geq CCM > CEM$, but, the differences between the models in this respect were small.

Comments on the Use of Kd Coefficient for the Modelling of Radionuclide Migration in Porous Media

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Most of the mathematical models of migration describe the interaction of radionuclides with solid phase by means of Kd . This approach is, however, strictly correct only if the sorption/desorption isotherm is linear ($q=Kd C$, where q is the equilibrium concentration of radionuclide in the solid phase and C is the equilibrium concentration in the liquid phase). Then Kd can be used for calculation of the retardation coefficient R using equation (1):

$$R = 1 + (\xi/\varepsilon)Kd \quad (1)$$

where ξ denote bulk density and ε is porosity. (It holds: $(\xi/\varepsilon) = (\rho/\Theta)$, where ρ is the solid phase density of the host formation and Θ is the volume of circulating solution per volume of the host formation.)

The general equation for the retardation coefficient is derived by rearrangement of 1D equation of non-equilibrium dynamics of sorption/desorption (2) of radionuclides, under the assumption of equilibrium conditions, namely by means of the following procedure [equations (2)-(5)].

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \frac{\xi}{\varepsilon} \frac{\partial q}{\partial t} - \lambda \left(C + \frac{\xi}{\varepsilon} f(C) \right) \quad (2)$$

Because the quantity q is the so-called composite function, which can be expressed as $q=f(C)$, its first derivative by t is given by the equation (3):

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} = f'(C) \frac{\partial C}{\partial t} \quad (3)$$

If the migration takes place under the conditions of the equilibrium dynamics, then $f'(C)$ is the first derivative of the equilibrium isotherm function $q=f(C)$ and $\partial q/\partial t$ in the equation (2) can be substituted from the equation (3). After rearrangement, the equation (4) is obtained:

$$\frac{\partial C}{\partial t} \left(1 + \frac{\xi}{\varepsilon} f'(C) \right) = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \lambda \left(C + \frac{\xi}{\varepsilon} f(C) \right) \quad (4)$$

The expression in parenthesis on the left-hand side of the equation (4) is usually designated as retardation coefficient (R) and it is evident, that it corresponds with the equation (1) on the assumption that $f'(C) = Kd$, i.e. if $q = Kd C$. By means of the last rearrangement, the well-known 1D-equation of equilibrium dynamics (5), including the equation (6), can be derived:

$$\frac{\partial C}{\partial t} = \frac{D}{R} \frac{\partial^2 C}{\partial x^2} - \frac{u}{R} \frac{\partial C}{\partial x} - \frac{\lambda}{R} \left(C + \frac{\xi}{\varepsilon} f(C) \right) \quad (5)$$

$$R = 1 + (\xi/\varepsilon) f'(C) \quad (6)$$

The symbols used denote: D – dispersion coefficient (if u converges to zero, D converges approximately to the diffusion coefficient), u – flowrate of liquid phase through the pores, t – time, x – length parameter, λ – decay constant. Other symbols were explained above.

It can be derived that the fraction u/R ($= v(C)$) represents the convective component of the rate of individual concentration point moving in the axial direction (in the direction of x -axis, i.e. in the direction of the flow of liquid phase) through the bed of solid phase and having the total concentration $C_{sum} = C + (\xi/\varepsilon) f(C)$.

We see from it that:

- (i) The retardation coefficient (see equation (6)) generally depends on the first derivative $f'(C)$ of the function of equilibrium isotherm $q=f(C)$ and therefore, in the case of nonequilibrium isotherm, is a function of concentration of radionuclide (or component studied) in liquid phase.
- (ii) The values of the rate of individual concentration point ($= v(C)$) and of the so-called effective dispersion (diffusion) coefficient ($= D/R = D_{eff}(C)$) depend on the retardation coefficient and generally on the concentration.

From the point of view of the application of Kd - model ($q = Kd C$, linear equilibrium isotherm) for the description of sorption/desorption in the migration process, it is necessary to know the systems, where the retardation coefficient is constant. Two types of such systems according to the theory of chromatography exist:

- (i) The isotope exchange systems, the equilibrium isotherms of which are in principle linear. Certainly, there are a lot of other systems having the linear equilibrium isotherm in the concentration interval studied, as some systems where the individual sorbing components (radionuclides) are present in a very low concentration – lower than, e.g. 10^{-7} - 10^{-10} M. But it is necessary to take into consideration, that the form of the isotherm depends not only on the radionuclide concentration, but also on the sorption capacity of the given solid phase, on the concentration of ligands, competitive components, pH and so on.
- (ii) The system having the so-called favourable (concave, i.e. if $C_1 < C_2$, then $f'(C_1) > f'(C_2)$, $v(C_1) < v(C_2)$, $D_{eff}(C_1) < D_{eff}(C_2)$) equilibrium isotherms, in the case of which – after certain time of migration, i.e. after the stabilization of the migrating sorption front (if $v(C_1) = v(C_2)$) – the retardation coefficient is the function of $(Kd)_0$ ($= q/C_0$, C_0 is starting concentration in liquid phase) and R is constant ($R = 1 + (\xi/\varepsilon)(Kd)_0$).

However, if the systems are characterized by the so-called unfavourable (convex, i.e. if $C_1 < C_2$, then $f'(C_1) < f'(C_2)$, $v(C_1) > v(C_2)$, $D_{eff}(C_1) > D_{eff}(C_2)$) equilibrium isotherms and, because the value of retardation coefficient is a function of concentration C , the migrating sorption front of the given

component is washed away (i.e. extended in the axial direction, in the direction of the flow of liquid phase). In such a case, strictly speaking, the first derivative of the function $q=f(C)$ must be used to the calculation of retardation coefficient (i.e. for each integration step in the course of solution of migration dynamic equation (5)) and $f'(C)$ cannot be approximated by the value of Kd .

Conclusion: Before the application of Kd coefficient (Kd model) for the modelling of radionuclides migration in porous media, especially so if the important systems are studied, the form of sorption/desorption equilibrium isotherms should be experimentally verified in the concentration interval of the given components (radionuclides) considered in the liquid phase. And only on the basis of this information, the application of Kd or $(Kd)_0$ should be chosen.

Paper 4.20

Ion Exchange Case

J. Ly
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Modelling of the sorption on clay minerals:

- Description of sorption mechanisms in terms of the ion-exchangers theory.
- Influence of the compaction on sorption.

(See Part 2, Chapter 5: “State of the Art in TSM – Guided Kd Studies of Natural Materials”, section 5.1: “Single minerals and mineral mixtures” and Figure 11 for an analysis of results presented).

Modelling of Radionuclides Sorption on Mixed Solids Using Single Oxides Surface Complexation Models

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In this work, surface complexation model was used to reproduce sorption behaviour of different solids surfaces, and to predict performance of their mixtures. Tested minerals were single oxides (alumina, silica, hematite), clays (kaolinite, montmorillonite), and zeolites. Using the methodology described as following, results of calculation were confirmed by experiments.

In a first step, modelling of alumina, silica and hematite was performed. Surface sites concentrations have been measured using saturation experiments, and surface acidity and complexation constants extracted by fitting results of batches experiments. These data were used in a first prediction try of binary oxides mixtures behaviour. Then, the obtained calculated curves were compared to experimental one's for both acid-base titration and sorption experiments. The cations chosen for these sorption experiments were cesium (I), nickel (II) and ytterbium (III). If experimental and calculated curves were superimposed for alumina-hematite mixtures, results for alumina-silica one's could not be reproduced using this chemical description. As an example, sorption of ytterbium has been overestimated when 15 mg of alumina and 50 mg of silica are used, and underestimated for a mixture composed with 50 mg of each solid. Then, a second modelling was performed, taken into account silica dissolution and binding of dissolved H_4SiO_4 on alumina surface. This new chemical description has been able to account for results of three different alumina-silica mixtures. Bindings of H_4SiO_4 on alumina was confirmed by independent experiments.

The second step of the study was based on the assumption that clay minerals surfaces may be described as "chemical" mixtures of alumina and silica, keeping the same surface constants. Using such simplification, modelling of clay surfaces is the same as the one used to describe alumina-silica mixtures. A first comparison of experiment and calculation was made with kaolinite. The results showed that the behaviour of this surface can be reproduced using the only two different types of surface sites present on alumina and silica. The second clay tested is montmorillonite. For the theoretic description of its surface, three different types of sites had to be used. If silanol and aluminol sites are still present with the same constants fitted from oxides experiments, one ion-exchange site has to be added. The surface constants of this new type of site, not present on the previous tested surfaces, were fitted.

The methodology used, beginning with a very simple surface and going through more and more complicated ones, permits to have a minimum number of adjustable parameters. With the data set obtained in this way, and the above chemical description of the surface equilibria, behaviours of clays-oxides and clays-zeolite mixtures have been calculated without any adjustable parameters.

Adsorption of Metals and Organic Acids to Kaolinite Surfaces

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Kaolinite surface charge can be described by proton donor and acceptor reactions occurring on edge Al sites, and by proton donor reactions occurring on edge Si sites. Edge Al sites are hypothesized to control pH-dependent sorption of metals, though there also appears to be minor pH-independent sorption of hard acids (Cs^+ and Sr^{2+}) on basal planes. Si site acidity at the kaolinite-solution interface differs minimally from that of pure SiO_2 , whereas Al sites became appreciably more acidic when a part of the kaolinite matrix. Increasing temperature decreases the pK values of Al and Si proton-exchange sites. Calculated site densities indicate either an elevated participation of edges (or substantial contribution from basal planes) in the development of surface charge. Independent evidence from scanning force microscopy points to a higher percentage of edge surface area due to thicker particles and basal surface steps than previously assumed.

Molecular modeling of the proton-relaxed kaolinite structure has been used to establish the elevated acidity of edge Al sites, to independently confirm the crystallochemical controls on surface acidity, and to establish likely bonding geometries for adsorbed organic acids, such as oxalate. Unidentate binding of metal ions on Al sites is suggested by constant capacitance model fits to measured metal sorption curves.

Data Sheet

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Solid phase

Kaolinite (KGa-1); Washington Co. Ga, USA

Aqueous Phase

0.1M NaCl, 25-70°C, batch, oxic, Cs, Sr, Cd, Ba, Zn, Oxalate, Acetate

Brief description of model

FITEQL was used with both a constant capacitance and triple layer model to determine proton/hydroxyl adsorption stoichiometry and temperature dependent metal-binding (unidentate) constants.

Publications

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