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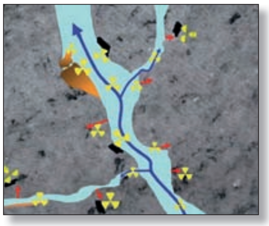
# Thermodynamic Sorption Modelling in Support of Radioactive Waste Disposal Safety Cases

## NEA Sorption Project Phase III



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# Thermodynamic Sorption Modelling in Support of Radioactive Waste Disposal Safety Cases

## NEA Sorption Project Phase III

NEA No. 6914

NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

# ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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- to assist its member countries in maintaining and further developing, through international co-operation, the scientific, technological and legal bases required for a safe, environmentally friendly and economical use of nuclear energy for peaceful purposes, as well as
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# Foreword

This report is the outcome of Phase III of the NEA Sorption Project conducted as a co-operative project under the auspices of the Integration Group for the Safety Case (IGSC) of the OECD/NEA Radioactive Waste Management Committee (RWMC).

Sorption is one of the most important processes with regard to the prevention or retardation of migration of radionuclides present in a radioactive waste repository towards the biosphere. Nearly all radioactive waste management organisations use equilibrium distribution coefficients ($K_d$) to represent the effect of sorption in their performance assessment (PA) calculations, and there is a general desire by these organisations to have scientifically robust arguments for showing that selected $K_d$ values and associated uncertainty management are based on a demonstrable and credible knowledge base. The overriding objective of the NEA Sorption Project, which began in 1997 and is now in its third phase, has been to demonstrate the potential of thermodynamic sorption models (TSMs) for improving confidence in the representation of radionuclide sorption in the context of radioactive waste disposal.

The results of the first phase of the Sorption Project (NEA, 2001) illustrated the capacity of TSMs for representing radionuclide sorption on both simple and complex solids, but also showed that there was great diversity in the different TSMs (formulation, parameter values) proposed for sorption of the same or analogous radionuclides in seemingly comparable geochemical systems. In order to respond to, and to understand the origins of this situation, a second phase of the project was initiated in 2000 in the form of a comparative modelling exercise. The results of Phase II (NEA, 2005) demonstrated the overall usefulness, robustness and scientific defensibility of TSMs for quantifying and predicting $K_d$ in the framework of PA, and the value of TSMs in quantifying the geochemical factors that determine $K_d$ was shown for a variety of systems. Phase II also showed that some critical issues and needs remain with regard to the practical implementation of TSMs for PA and building safety cases (modelling decisions, choice of fundamental parameters, etc.), in particular:

- knowledge of the effects of modelling strategies and decision making during TSM development on the final TSM used for justifying $K_d$ for the safety case;
- identification of appropriate methods for determining the various TSM parameter values;
- development of a scientific foundation for applying TSMs to complex and intact materials (host rocks, engineered barriers, soils…);
- transparent documentation by modellers regarding modelling decisions;
- assessment of uncertainty effects on TSM output quality.

The objective of Phase III of the NEA Sorption Project, which began in November 2007, was to address these issues by sponsoring the preparation of guidelines for TSM development and application within the framework of PA/safety case building. This report's primary audience is the sorption modelling community and other users of $K_d$ in developing safety cases. Its principal goal is to educate modellers and the "safety case" community about appropriate and useful TSM applications for systems relevant to radioactive waste disposal concepts, and to provide “guidelines” for TSM development and parameterisation.

Phase III of the Project was made possible by the participation and financial support provided by 14 organisations representing 12 countries:

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|---|---|
| ANDRA | France |
| ANSTO | Australia |
| ENRESA | Spain |
| GRS | Germany |
| ENSI, NAGRA & PSI | Switzerland |
| JAEA | Japan |
| KAERI | Korea |
| NDA | United Kingdom |
| NRC | United States |
| ONDRAF/NIRAS | Belgium |
| POSIVA | Finland |
| RAWRA | Czech Republic |

The project was overseen and guided by a Management Board composed of one representative from the funding organisations per country. The report was prepared by a team of three experts in the field of TSM development (Dr. Michael Ochs, Dr. Tim Payne and Dr. Vinzenz Brendler), aided by a number of other internationally known scientists (see list of external experts). The Management Board would like to express its appreciation for the quality and intensity of their work.

The Management Board also wishes to express its gratitude to the OECD/NEA for its excellent secretarial, logistic and publishing support.

On behalf of the NEA Sorption Project Phase III participating organisations cited above,

Scott Altmann
Andra
Phase III Management Board Chairman

## *Acknowledgements*

The authors would particularly like to acknowledge the contributions by the external experts and the stimulating discussions with them, as well as with associated scientists and experts in the field. Also very gratefully acknowledged are the support by, and critical discussions with, the members of the Management Board and the respective waste management organisations. Thanks are also extended to the NEA staff and Management Board members who were of much help with regard to logistical aspects.

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# Overview and purpose

A common central safety function of radioactive waste disposal facilities is the prevention or sufficient retardation of radionuclide (RN) migration to the biosphere. Performance assessment (PA) exercises in various countries, and for a range of disposal scenarios, have demonstrated that one of the most important processes providing this safety function is the sorption of radionuclides on the surfaces of the various solids phases encountered along the migration path, as expressed by $K_d$ values (NEA, 2001). Confidence in PA, and therefore in the predicted safety of a repository (or predicted risk from a contaminated site), will depend to a significant extent on the confidence in, and the justification of, the quantification of radionuclide sorption. Thermodynamic sorption models (TSMs) offer the potential to improve the incorporation of sorption processes in the overall safety case.

However, as demonstrated by the outcome of the previous phase of the NEA sorption project (Phase II), one of the central issues in applying TSMs in the context of radioactive waste disposal is the justification, and credibility, of specific modelling decisions (NEA, 2005). This includes the choices of fundamental model parameters, and the method of model application to PA-relevant substrates. Specifically, the following needs exist:

1. Awareness of the effects of modelling strategies and decision making during TSM development.
2. Transparent documentation by modellers regarding modelling decisions.
3. Identification of appropriate methods for determining the various TSM parameter values.
4. Development of a scientific foundation for applying TSMs to complex and intact materials (such as host rocks, engineered barriers and soils).
5. Justification of conceptual choices and quantification of uncertainty effects.

The purpose of Phase III of the NEA Sorption Project was to develop recommendations and guidelines for TSM development and application within the framework of PA/safety case building that address the above topics. An additional goal of this report is to educate modellers and the "safety case" community about appropriate and useful TSM applications to relevant systems.

### Note on format

Recommendations and other key features of the text are given in:

> Grey boxes – which highlight key messages and give recommendations associated with particular parts of the experimental or modelling process.

# 1. Thermodynamic sorption models and radionuclide migration

## 1.1 Sorption and radionuclide migration

### *1.1.1 Potential role of TSMs for supporting $K_d$ in performance assessment*

In order to evaluate the risks that may be associated with the disposal of radioactive waste, PA places particular emphasis on an important pathway having significant potential for causing a safety-relevant release of radioactive substances. This pathway is groundwater transport of radionuclides from the repository to the biosphere. Due to the number and complexity of the processes that need to be considered, PA calculations typically rely on selected key parameters for quantifying RN migration. The chemical processes relevant for the transport of RNs are often described through the following two parameters (although some PA programmes rely directly on measured retardation factors):

- The maximum solubility ($C_{sat}$) of the RN in the various geochemical environments.
- A $K_d$ value which quantifies the distribution of a dissolved RN between the solution and the solid phases present along relevant transport pathways.

Typically, calculations employing selected values for these parameters are undertaken for specific volumes (representative volume elements, RVEs) along the migration path within which it is assumed that local thermodynamic equilibrium is reached (Appelo and Postma, 1993). An RVE is defined as a volume of a porous medium that is sufficiently large to allow the definition of mean properties while the effects of variations from one pore to another are negligible[1] (de Marsily, 1986). As will be explained in more detail below, $K_d$ is a conditional parameter (i.e. dependent on the specific conditions under which it is measured). As such, $K_d$ values selected for PA need to be valid for the specific predicted conditions at a given disposal site during the time frame of possible RN release. Consequently, $K_d$ is one of the most critical parameters in many PA scenarios, implying that confidence in PA may be significantly dependent on confidence in $K_d$.

In addition, in some cases, the uncertainty associated with $K_d$ estimation is a significant component of the overall uncertainty of the safety case. As such, it is clearly desirable to improve the conceptual models for estimation of $K_d$ values. A reduction of uncertainty in $K_d$ values, as well as an increase in confidence with regard to the overall process of selecting $K_d$, will serve to increase confidence in PA and strengthen safety cases. One way to reduce the uncertainty in $K_d$ values is to base their selection and justification on the scientific foundation of thermodynamic sorption models.

### *1.1.2 Sorption, distribution coefficients and retardation of RN migration*

Performance analyses in the context of radioactive waste repositories are based on specific repository concepts which include the engineered barrier, host rock and

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[1] At the same time, an RVE is sufficiently small to allow the approximation of parameter variations from one domain to another by continuous functions (de Marsily, 1986).

surrounding geosphere systems. Typical PA transport models represent these systems in terms of discrete volumes containing specific substrates (mineral assemblages) and ground- or pore water solutions. Each compartment is usually considered to be homogeneous (i.e. no spatial variability of geochemical or other properties) and generally invariant over time, for a given calculation. To quantify the effect of sorption on radionuclide transport, the PA models generally require an estimate of sorption for each radioelement in each compartment.

The total amount of a radionuclide in a model compartment is the sum of all dissolved and solid forms. The solid forms include precipitated, co-precipitated and sorbed phases. Sorbed phases comprise the proportion of the RN that is bound on mineral surfaces, and are therefore considered to exchange with the pool of dissolved radionuclides. These sorbed RN can be released (desorbed) into the aqueous phase, and the equilibrium between dissolved and adsorbed phases is therefore of critical importance in assessing RN mobility.

The distribution coefficient ($K_d$) is defined as the ratio of the sorbed concentration of an element “X” to its dissolved concentration:

$$K_d = \frac{amount\ of\ element\ \text{"X"}\ sorbed\ per\ unit\ mass\ of\ substrate}{amount\ element\ \text{"X"}\ dissolved\ per\ unit\ volume\ of\ solution} \tag{1.1}$$

and typically has units such as mL/g or L/Kg. The amount of element (in both numerator and denominator) can be expressed in convenient units (such as moles or Bq).

One of the attributes of a $K_d$ value is that it can be incorporated into radionuclide transport models used for migration predictions. If one assumes that the amount of sorption is proportional to the dissolved radionuclide concentration, this can be described by a single $K_d$ value. In this simple case, referred to as the “linear isotherm”, the retardation of a pollutant front in simple porous media is given by the retardation factor $R_f$:

$$R_f = 1 + \frac{\rho_b}{\varepsilon} \cdot K_d \tag{1.2}$$

where $\rho_b$ is the bulk density and $\varepsilon$ the porosity. $R_f$ can also be expressed as the ratio $\overline{v} / \overline{v}_c$ where $\overline{v}$ is the average linear velocity of the groundwater and $\overline{v}_c$ the velocity of the point on the concentration profile of the retarded constituent where the concentration is half that of the input concentration, which is assumed to be constant (Freeze and Cherry, 1979). Thus, the retardation factor represents the retardation of the movement of the pollutant relative to the flowing groundwater. Therefore, $K_d$ is directly related to the migration of the radionuclide in the groundwater. While this is a greatly simplified example, it serves to illustrate the key point that $K_d$ directly influences modelled radionuclide mobility. A similar expression holds for systems where diffusion is the predominant transport phenomenon, with the reference velocity being defined in terms of the diffusion front associated with a non sorbing solute. In many situations the governing equations are considerably more complex, particularly in fractured media.

The sorption of RNs can be studied in laboratory sorption experiments. In a typical batch sorption experiment, a measured mass of a geological material of interest (such as a clay barrier or a sample of host formation material) is shaken with a solution containing a known quantity of RN under well-controlled conditions followed by separation of the solid and solution phase (e.g. centrifugation, filtration). The experimental results can be converted directly to a $K_d$ value using the following equation:

$$K_d = \left(\frac{C_{init} - C_{equil}}{C_{equil}}\right)\frac{v}{m} \tag{1.3}$$

where $C_{init}$ and $C_{equil}$ denote the initial and equilibrium concentration of a sorbing element in the solution phase, and v and m are the volume of the aqueous phase and the mass of the sorbent, respectively.[2] Equations 1.2 and 1.3 taken together show that the experimental $K_d$ value is a key parameter for modelling radionuclide mobility in the environment. However, measurement of $K_d$ in laboratory experiments and the translation of the $K_d$ values to real world situations (particularly those involving spatial heterogeneity and changes over time) is not necessarily straightforward. For this reason it is important to combine these experimental results with a rigorous theoretical framework as the basis for interpreting sorption phenomena.

### 1.1.3 *Sorption and other processes affecting RN mobility*

In the present report, the term "sorption" is used to describe surface chemical interactions between aqueous species (particularly those incorporating radionuclides) and solid sorbents (single minerals such as iron oxides or clays; or mineral assemblages, such as sediments or rock samples). The term "$K_d$" is used exclusively in this broad sense. The generic sorption process on the surface of a mineral can involve a number of specific processes, such as:

- ion exchange (due primarily to electrostatic forces, for example uptake of a cation on the negatively charged surface of a clay mineral);
- surface complexation (in which an ion interacts with a mineral surface site in an analogous way to the formation of a complex in solution, usually involving co-ordinative chemical complexes).

These processes (and the chemical equations describing them) will be discussed in more detail in subsequent chapters. In addition to sorption processes, a number of additional (and sometimes ill-defined) processes may affect the rate of radionuclide transport, including:

- Mineral precipitation, which limits the maximum dissolved concentration of RNs by the formation of sparingly soluble solid phases of the corresponding element. These solids may include pure compounds, such as metal (hydr)oxides or carbonates.
- Formation of solid solutions, whereby RNs are accommodated in the structure of another mineral. Solid solutions may form through simultaneous co-precipitation, or through the incorporation of RNs into the structure of previously formed solids. In the latter case, the formation of a solid solution phase is typically preceded by the surface interaction of RNs and solid mineral phases (i.e. by a sorption step).
- Other physical processes including matrix diffusion (exchange of solute mass through molecular diffusion between fluid in fractures and fluid in the rock matrix), filtration effects, etc.

Therefore, appropriate conceptual models are required for the various surface processes in order to adequately model RN migration.

Many simplified models of sorption have been developed. Sorption isotherms relate the amount of adsorbed contaminant to its dissolved concentration, and may take into

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2. Note that some authors prefer to describe the results of sorption experiments with the Rd parameter, which is identical to $K_d$ as defined in Equation 1.3, but equilibrium is not assumed.

account some of the properties of the solid phase, such as a finite population of sorbing sites. Commonly used isotherms include the Langmuir and Freundlich isotherms (Morel and Hering, 1993). The isotherm approach is most useful if little or no variation in chemical conditions is expected, since isotherm models do not explicitly consider RN speciation. However, as will be shown in the following section, $K_d$ values can be significantly dependent on chemical conditions, which implies that more fundamental mechanistic approaches are needed to describe sorption processes.

### 1.1.4 *Dependence of $K_d$ on geochemical conditions*

The importance of $K_d$ as a geochemical factor describing radionuclide migration has led to the compilation of a number of $K_d$ databases intended for use in PA applications (Sheppard and Thibault, 1990; Jung *et al.,* 2001; JAEA, 2008a). While these compilations are useful in demonstrating the range of $K_d$ values for a specific RN, and in some cases trends of sorption as a function of conditions, the data cannot be extrapolated to a wide range of conditions due to the conditional nature of $K_d$. On the other hand, systematic sets of $K_d$ values compiled in such databases can be used to calibrate or test TSMs.

The strong dependence of $K_d$ on geochemical conditions can be demonstrated using the example of U(VI) sorption on ferrihydrite (a nanocrystalline iron oxyhydroxide). Figure 1.1a shows the sorption of U(VI) as a function of pH and of the aqueous concentration of an important complexing ligand [carbonate, expressed in terms of equilibrium with a given partial pressure of carbon dioxide ($p\mathrm{CO}_2$)]. The sorption data are expressed both as percentage sorbed against pH, and $K_d$ values (inset) as a function of pH. The $K_d$ representation is particularly useful for discriminating the two sets of experimental data where the sorption of uranium is close to 100%. An important conclusion from Figure 1.1a is that the $K_d$ value is strongly dependent on the conditions, varying by orders of magnitude following changes in the chemical speciation of U(VI) and of the surface as a function of pH and $p\mathrm{CO}_2$ (i.e. dissolved carbonate concentration). Note that the chemical speciation will be influenced by a range of other important ligands as well as competing ions. It follows directly that an accurate description of the aqueous chemistry of a given RN is a prerequisite for sorption modelling.

Similarly, the system redox potential (Eh), which determines the oxidation state of the sorbing radionuclide, is extremely important. Each oxidation state of an RN has its own unique chemistry and sorption behaviour. It follows from Equation 1.2 that the retardation of an RN in a porous medium (such as an aquifer or a soil) would be significantly affected. In other words, transit times could vary by orders of magnitude depending on the environmental conditions determining Eh.

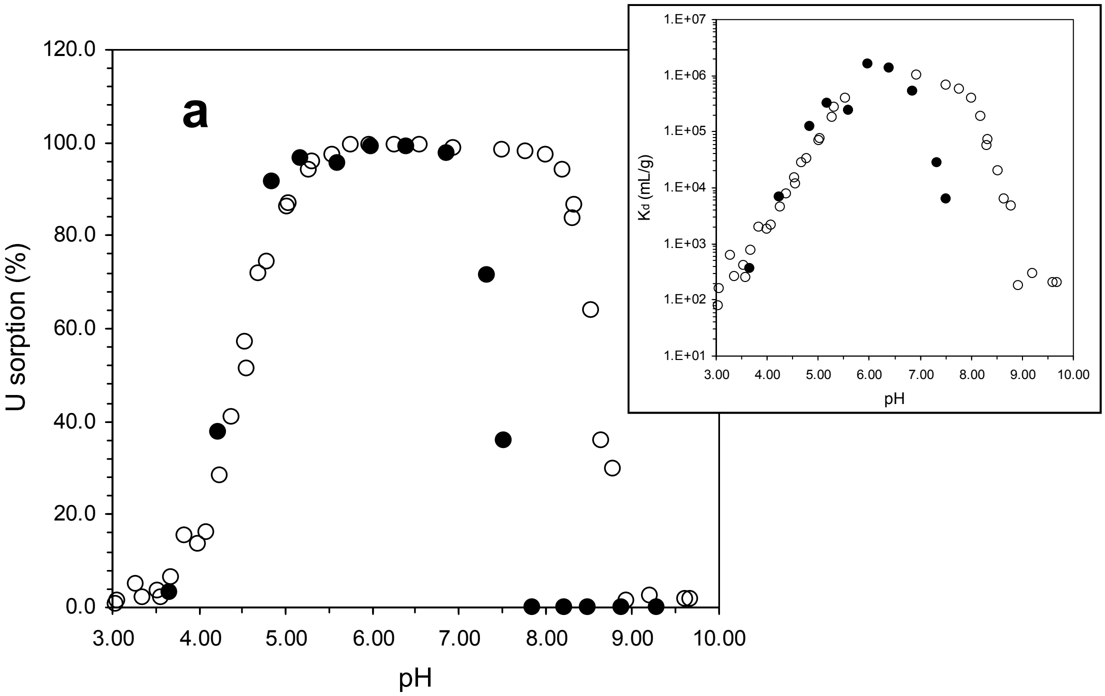
Figure 1.1b illustrates the pH dependence of the $K_d$ for U(VI) sorption on different solid phases, under similar conditions. A significant feature is that, although the magnitude of sorption at a given pH differs between the three substrates, the *trend* of sorption vs. pH is approximately similar. This suggests the underlying sets of chemical reactions may have some similarities for the different materials.

The example underlines the importance of a detailed understanding of both the solution phase components and nature of the solid phase in determining RN sorption. In this and other similar examples, the following factors play an important role:

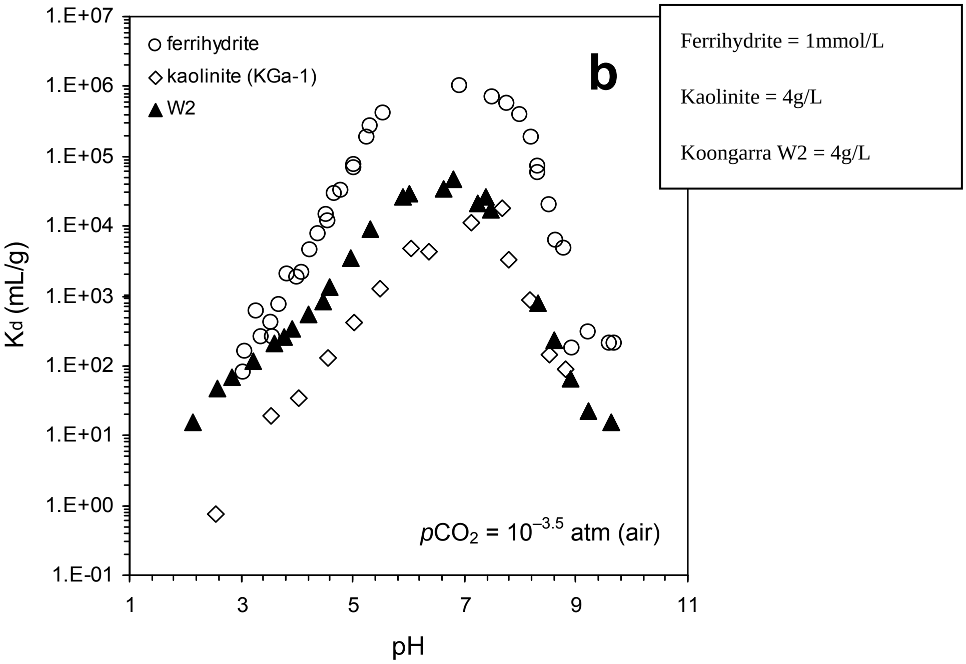
- type and amount of mineral surfaces available for sorption; and
- composition of the aqueous solution (including pH, RN concentrations, ligands such as carbonate or natural organics).

**Figure 1.1: Sensitivity of $K_d$ for U(VI) sorption on geochemical conditions**

a) U(VI) uptake on ferrihydrite (percentage sorbed vs pH) for systems equilibrated with two partial pressures of carbon dioxide (○– air; ●- $p\text{CO}_2$ = 0.01 atm). Inset shows $K_d$ vs pH for the same data set (U=1µmol/L, Fe=1mmol/L, 0.1M $\text{NaNO}_3$)



b) $K_d$ for U sorption on ferrihydrite, kaolinite and a sample of weathered schist from the Koongarra uranium deposit



Source: Payne, 1999.

## 1.2 Applications of TSMs in radioactive waste disposal studies

### *1.2.1 General role of TSMs in radioactive waste management*

The role of TSMs in radioactive waste management depends on each specific application. Nevertheless, it is possible to identify two general ways in which TSMs can support safety cases for radioactive waste disposal, which are by providing:

1) a scientific basis for the range of $K_d$ values used for an RN included in the safety case; and
2) an interpretive tool for assessing changes in $K_d$ values in response to changes in chemical conditions. The range of conditions may cover alternative PA scenarios and future evolution of system variables.

A TSM coupled within a reactive transport model can be used to simulate the spatial and temporal character of the $K_d$ distribution that is due to evolving chemical conditions (Curtis *et al.*, 2006; Curtis *et al.*, 2009).

TSMs are therefore a useful tool to identify, characterise and eventually parameterise the basic phenomena that are usually described by a $K_d$ value or range of $K_d$ values. Analysis of measured sorption data using TSMs ties the measured $K_d$ values into functional and quantitative relationships between the extent of RN sorption and environmental parameters (such as pH, concentrations of the various components, binding site densities). In this way, TSMs may provide scientific support for measured sorption data, which in turn increases confidence in the $K_d$ values derived from such measurements.

### *1.2.2 Specific applications of TSMs*

The form and mode of implementation of a TSM is dependent on the modelling objectives (for example, in terms of the level of detail required). It is impossible that, for a real-world system, the model will incorporate the most detailed or chemically accurate description of all possible sorption and related processes (as might be feasible for simplified laboratory systems). However, a well-formulated TSM can be much more realistic in terms of its representation of chemical processes than simpler $K_d$-type models.

Therefore, the exact formulation of the TSM, and its applicability in the context of radioactive waste disposal will be dependent on the specific situation. However, in general the potential uses of TSMs within safety analyses and safety case building can be summarised as:

- Application to support specific $K_d$ estimates in the frame of PA calculations, through:
    - direct estimation of RN distribution coefficients to provide approximations for parameter spaces that are difficult or time-consuming to access experimentally (for example, to supplement limited site-specific data);
    - indirect support of experimentally measured $K_d$ values through explanation and justification of measured data, increasing confidence for $K_d$ values measured under complex site-specific conditions;
    - sensitivity and uncertainty analyses regarding the influence of variability and uncertainties in geochemical conditions on $K_d$;
    - interpolation or extrapolation from existing datasets to other conditions;
    - scoping calculations to estimate the possible effect of different scenarios on $K_d$ values.

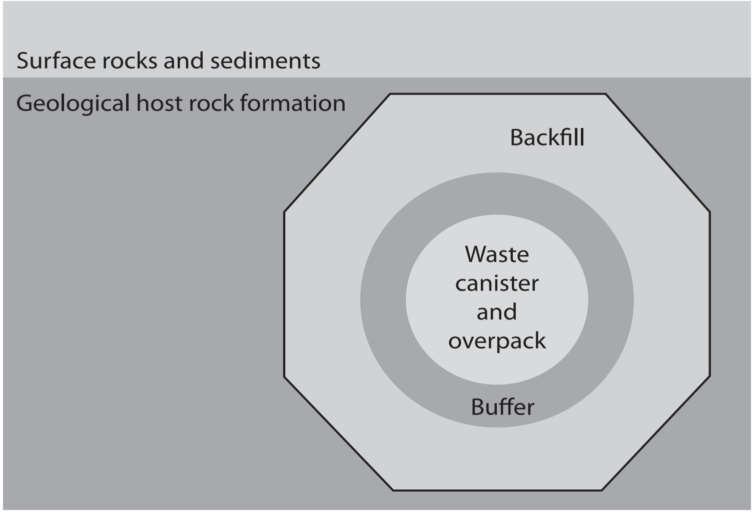
- Guidance of experimental $K_d$ acquisition programmes, for example through:
  - the selection of parameter spaces to be covered using sensitivity analyses;
  - the optimisation of experimental design through screening calculations (for example, identifying the most critical conditions for experimental measurements);
  - the interpretation and consistent combination of sets of laboratory data;
  - the interpretation of sorption data obtained on site-specific samples, using TSMs calibrated on the basis of laboratory data;
  - the detection of gaps in the database for experimental study;
  - the filling of data gaps with estimates based on TSMs, possibly complemented by the application of thermodynamic relationships and chemical reasoning.
- Building confidence with regard to the quantification of radionuclide sorption under various conditions within the larger framework of safety case building.

The above applications of TSMs are grounded in the importance of $K_d$ for safety analyses on one hand, and in the highly conditional nature of $K_d$ on the other. However, uncertainty and possible variability of relevant geochemical parameters, as well as the complexity of natural and engineered systems, may make it impossible to experimentally determine radionuclide sorption systematically for every compartment and all sets of conditions. Therefore, experiments with site-specific conditions may be supplemented by an often much larger set of data for approximated, simplified, or generic systems. Because TSMs provide a consistent and quantitative framework for linking (geo)chemistry with radionuclide sorption, they represent an ideal tool for integrating all available types of sorption information.

### *1.2.3 Important substrates and their sorption characteristics*

The radioactive waste disposal concepts which are being implemented (and/or assessed) in many countries are complex systems containing many components, each with a specific safety function (Figure 1.2).

**Figure 1.2: Generic radioactive waste disposal concept**



Modelling the future behaviour of RNs in such a system is a complex undertaking. Depending on the repository concept, this involves simulating the interactions of RN with the surfaces of such materials as:

- bentonite/clay backfill;
- remnant materials derived from repository components such as canisters (e.g. Fe-oxides);
- host-rock (which may be crystalline rock, plastic or hard clay formation, or other sedimentary rock);
- rock fractures, and fracture in-filling minerals, in the far-field;
- complex natural materials such as sediments and soils.

An important observation from consideration of the radioactive waste disposal system (Figure 1.2) is that it consists of a range of complex materials, derived from the waste itself, the barrier materials, the engineered components of the repository and the surrounding natural environment. It is noted that the interactions of radionuclides with this range of materials are not necessarily governed by sorption processes, a specific example being incorporation of RN in concrete. Nevertheless, the modelling of sorption on complex materials is an issue of central importance for PA purposes.

A survey of the scientific literature on modelling adsorption reveals that most attention, and development of TSMs, has been focused on simplified model systems (for example, simple oxides and clays). The experimental techniques and modelling approaches for simple systems (such as metal oxides) have become highly sophisticated. While there have been increasing attempts to use TSMs to describe sorption in complex systems, this field is still maturing. In fact, many of the experimental techniques applicable to studying sorption in simple systems cannot be applied to complex systems, and the application of TSMs to complex materials requires considerable simplifications and assumptions regarding the nature of the surfaces and RN interactions. The development of TSMs for complex materials of relevance to PA applications is an important theme of the present volume (see Chapter 4).

### *1.2.4 Substrates not considered for the present guideline*

This guideline book focuses on surface sorption (surface complexation, ion exchange) and on the thermodynamic models which can describe these processes. Surface sorption processes are relevant for most substrates of importance in the context of radioactive waste disposal, including various (hydrous) oxide minerals, clays and other phyllosilicates, primary minerals such as quartz and micas, but also solid organic matter. Accordingly, these substrates are addressed in the present guideline document.

Some other substrates which are relevant to PA are much more reactive in terms of their bulk properties and therefore not suitable for sorption modelling by TSM. Prime examples are the Ca-Si-hydrates (CSH) and other minerals constituting hardened cement paste. CSH minerals can change their Ca/Si ratio and their structure rapidly as a function of the composition of the surrounding solution. At the same time, the Ca ions in the CSH structure are easily exchanged against other cations that fit into the Ca/Si-framework. Because of the amorphous nature of CSH, this process is not very selective. As a result, CSH can take up trace elements by a variety of incorporation processes. Other minerals in hydrated cement paste show such behaviour to some degree. Exchange of Ca ions against other cations in the mineral lattice is also a common feature of trace element uptake by carbonates. Trace elements may also be incorporated during the crystallisation process (e.g. freshly precipitated Fe-hydroxides) or diffuse into the interior of certain amorphous minerals.

While surface sorption is typically the first step in the overall uptake process of trace elements, various other processes occurring over approximately the same timescales can often not be clearly distinguished from sorption. As a result, TSMs are not considered to be adequate tools for the description of trace element uptake by such substrates. Therefore, hydrated cement and other substrates featuring high bulk reactivity are not included in the present guideline.

## 1.3 Requirements for a scientifically defensible, calibrated TSM applicable to radioactive waste disposal

### *1.3.1 Definition of model purpose*

The development of a TSM for radionuclide sorption typically involves, at several points, making choices within a range of options. The purpose of the present section is to better define how a TSM, applicable within the context of geochemical modelling for radioactive waste disposal, can be developed in a scientifically defensible way.

The first step is to define the objectives of the modelling. If the aim is to fit only the available experimental sorption data as closely as possible then "physico-chemical reasonableness" is less important than a convenient mathematical form. A shortcoming of this approach is that it is only applicable to the range of experimental conditions studied. While this purely descriptive modelling approach might improve radionuclide transport predictions in some cases, it lacks the scientific confirmation that can be achieved with detailed chemical characterisation. Thus, this simple fitting approach is not a significant advance over measuring $K_d$ values. At the other extreme, one may aim to produce a comprehensive model that is compatible with all available data and theoretical constraints. This is difficult to achieve, as is demonstrated by the ongoing debate about sorption models, even for relatively simple systems. It is improbable that such a fundamental approach can be applied to the complex real-world systems of interest to radioactive waste disposal safety cases in the foreseeable future.

Therefore, the model's purpose determines the complexity required. While it appears difficult to transfer a detailed "state-of-the-art" TSM developed to explain well-defined laboratory data to the complex radioactive waste disposal situation, it is clear that "mechanistic" or "semi-mechanistic" reasoning can, and should, be included in model development. Furthermore, the requirement that the model should represent reality implies that the associated parameter values (which represent "real" properties of the system) must lie within "reasonable" ranges. Such a constraint does not apply to variables which have been extracted by simply fitting experimental data.

An intermediate objective between a purely fitted approach and a fully mechanistic model is therefore appropriate for real systems. In such an approach, the goal of the TSM may be understood as simulating the macroscopic state of the system whilst remaining broadly consistent with the results of molecular-scale structural investigations and other fundamental constraints. This simulation may be applied to known experimental conditions or under conditions, or at times, beyond the experimentally accessible range. This type of TSM approach for modelling sorption is more complex than empirical approaches, such as $K_d$ values or isotherm models. However, it offers a method for directly coupling all relevant sorption and geochemical equilibria in a common thermodynamic framework.

### *1.3.2 Model quality and applicability*

The quality of a sorption model can be assessed against the following characteristics:

- an appropriate level of complexity;
- documented and traceable decisions;

- internal consistency;
- limitations on the number of adjustable parameter values;
- an adequate fit to a comprehensive calibration data set;
- capability of fitting independent data sets.

A TSM can be developed at various levels of complexity. A simplified model may be considered preferable to a model having numerous fitted parameters which cannot be properly constrained (NEA, 2005). On the other hand, a complex model having several "derived" parameters (including some which have been optimised) may be more reasonable than one with a smaller number of adjustable and physico-chemically meaningless parameters.

Although not all parameters are present in some models, defensible and *documented* choices must be made with respect to all model components that are present. These choices must be justified and consistent with each other. Unfortunately, in many published cases, it is not clear why a certain choice has been made. If various parameters are taken from different sources, a TSM can become internally inconsistent. Thus, *traceability* of the TSM components is necessary and it is therefore recommended that the rationale for model parameters should be documented (NEA, 2005)

The quality and uniqueness of fit to a calibration data set are determined by the quality and breadth of the data, the number of model parameters that can be directly measured, and the validity and rigor of the modelling approach. To demonstrate these concepts, consider a calibration data "set" for a radionuclide consisting of a single $K_d$ value. Clearly, a TSM could be calibrated to this single data point with zero error. However, since a TSM typically has several model-dependent parameters, it follows that the calibration of this TSM would be non-unique, that is, there would be several possible ways to fit the model output by varying the model-dependent parameters. Thus, in order to properly calibrate a TSM, it is necessary to collect a comprehensive, high quality calibration data set in which sorption is measured over a large range of conditions, spanning all scenarios in which the TSM will be potentially applied.

While fitting the experimental data is clearly important, it is also necessary to limit the number of model-dependent parameters. A decision can be made to fix some parameters at "reasonable" values as a way of constraining the number of "adjusted" or "fitted" parameters. In general, the fewer the number of "adjusted" model-dependent parameters, the greater will be the scientific confidence in a specific TSM. For this reason, spectroscopy can be of great utility to TSM modelling if surface species can be uniquely identified and used to constrain TSM calibrations (Arai *et al*., 2006). Although minimising "adjusted" model-dependent parameters achieves a greater uniqueness-of-fit for a specific TSM, it is still possible that an alternative TSM formulation could achieve a superior fit mathematically. Thus, it is incumbent upon a modeller to demonstrate which alternatives were considered.

There is a fundamental requirement for internal *consistency*. As detailed in following chapters, there is a documented interdependence of TSM parameters within a given model framework (Goldberg, 1991; Hayes *et al*, 1991; Lützenkirchen, 1999). Thus, selected parameter values (including aqueous thermodynamic data) must be taken from compatible sources or alternatively re-calculated within a self-consistent TSM framework (Dzombak and Morel, 1990; NEA, 2005; Guillaumont *et al*., 2003) (methods of recalculation are presented in Chapter 3).

An important test of a TSM is its ability to fit independent data sets measured for a different set of conditions, by different investigators, or for another mineral preparation or mixed mineral assemblage. A properly calibrated TSM should be capable of predicting $K_d$ values for conditions that are interpolated within the range of conditions in the calibration data set (NEA, 2005). A stronger test of a calibrated TSM is whether it can be extrapolated to conditions beyond those considered in the calibration data set. This extrapolation test may reveal that certain model parameters need to be adjusted, or that a new surface species needs to be added to the TSM. Testing a TSM's performance to describe data from different investigators may reveal the importance of experimental error or differences in methods for directly measurable model parameters.

- The objectives of the TSM must be defined at the outset. This may influence the range and types of experiments required as well as the modelling approaches.
- Model development should proceed according to a defined and self-consistent model framework.
- All modelling decisions should be properly documented, including justification for incorporated features and rationale for excluding alternatives.
- The model-specificity and interdependence of model parameters, which often limits the transferability of parameters from one model to another, should be recognised.

## 1.4 Current status of TSMs in radioactive waste management

The current status of TSM modelling for radioactive waste management applications can be evaluated from the outcomes of the previous stage of the NEA sorption project (NEA, 2005; Payne *et al.*, 2006). In that exercise, various modelling teams appointed by radioactive waste management organisations modelled selected sorption data sets using the TSM approach. The systematic comparison of the independent models generated within this project enabled the underlying assumptions, robustness, range of applicability, and data requirements of the models to be assessed. This permitted an overall evaluation of the general features, limitations and attributes of various modelling approaches.

A highly positive outcome of the NEA Phase II project was that the sorption models were able to reproduce trends, and in most cases magnitudes, of $K_d$ values for a variety of mineral substrates and aqueous chemical conditions (pH, $p\mathrm{CO}_2$, etc). This demonstrated the fundamental benefits of the TSM approach in its ability to handle geochemical variability. However, the individual models for each test case tended to diverge substantially in important component features. For example, in a test-case involving U(VI) sorption on quartz, all modelling teams achieved a good fit to the sorption data, despite incorporating highly dissimilar sets of chemical sorption reactions. Similarly, it was shown that adequately fitting models could be produced independently of whether electrostatic correction terms were included in the chemical sorption equilibria. Another test case showed that models could fit the sorption data adequately with a large range of sorption site concentrations on the solids, extending over two orders of magnitude. It was also demonstrated that the number of fitted model parameters was a major factor in determining the final model performance. The ability of the various TSMs to fit the data adequately despite the major differences in individual modelling choices is therefore partially attributable to the degree of parameter fitting in the TSM approaches, as implemented in that project.

It was concluded that sorption modelling was not yet adequately standardised, particularly for complex materials. While the TSM approach is highly promising, and in many ways superior to empirical $K_d$ values, further development and standardisation is desirable in order to achieve widespread application of TSMs in a scientifically defensible and consistent fashion. This is the need addressed by the present volume.

# 2. Theoretical basis of TSMs and options in model development

Chapter 1 discussed the critical role of sorption processes within PA for radioactive waste disposal. It demonstrated the importance of understanding sorption within each compartment of the geochemical model used to simulate the evolution of the repository system. Figure 1.1 showed that sorption is strongly dependent on geochemical conditions, and that it is possible to develop a mechanistic explanation of these variations. It follows that an improved understanding of, and ability to model, the key processes of sorption, as well as their dependence on geochemical conditions, would be an important advance towards increasing confidence in PA.

The purpose of this chapter is to present the theoretical basis of thermodynamic sorption models (TSMs). The final sections discuss some of the major choices available to the modeller and the impact of those modelling decisions on model performance.

## 2.1 Conceptual building blocks of TSMs and integration with aqueous chemistry

TSMs share many of the same conceptual building blocks that are present in widely accepted equilibrium models for solution chemistry. A basic assumption is usually that the system is at chemical equilibrium, in other words, there are no ongoing processes that require consideration of chemical kinetics.[1]

The fundamental conceptual components within such an equilibrium chemistry framework are:

- The definition of the *chemical components* which are present. Components are a set of fundamental building blocks which can be combined to form all the chemical species which can exist in the system. Chemical elements or simple ions are often selected as components (e.g. $Na^+$, $Cl^-$, $UO_2^{2+}$), but other choices are possible, so long as they meet the requirement that no component can be expressible as a combination of other components. For example, $H_2O$, $H^+$ and $OH^-$ cannot all be components because they are not independent of each other.
- The identification of all *species* which can be formed by combining one or more components (i.e. components are also species). For example, the bicarbonate ion $HCO_3^-$ is a species that could be considered to be made up of the components $H^+$ and $CO_3^{2-}$. It is very important to appreciate that the definition of each species depends on the selected set of components.

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1. It is emphasised that this does not mean that the evolution of the entire repository system is ignored – however it does imply that computations generally assume that local equilibrium has been reached in each model compartment (representative volume element) for which thermodynamic calculations are performed. It is also noted that some computer codes allow slow dissolution of minerals coupled with other reactions at equilibrium.

Having specified the chemical components and species present in the system, it is then possible to define relationships which enable the amounts of individual species present at equilibrium to be calculated. These include the following:

- The mass balance requirement by which the combined concentrations of all species containing a given component must equal the fixed total quantity of that component.
- The mass action law (MAL) for each species. The activities of all chemical species and components involved in a chemical reaction are related by a thermodynamic stability constant (usually expressed as log K) according to the stoichiometry defined in the MAL.
- The underlying thermodynamic database (TDB) containing the stability constants for all relevant dissolved (and solid) species. For many RNs as well as related auxiliary elements, high-quality TDBs have become available through the OECD/NEA (see www.oecd-nea.org/dbtdb/).
- The model to be used for calculating the thermodynamic activity coefficients of dissolved species (common examples being Debye-Huckel, Davies, Pitzer equations, see Grenthe *et al.*, 1997).

The key point that distinguishes TSMs from other representations of sorption (such as isotherms) is that they share a common conceptual basis with aquatic chemistry. As an example, consider the simple adsorption reaction of a metal ($M^{2+}$) on a hydroxylated surface site (denoted >SOH). Here the metal ion displaces a proton according to the reaction:

$$>SOH^0 + M^{2+} \Leftrightarrow SOM^+ + H^+ \tag{2.1}$$

The chemical components involved in this reaction can be defined as: $M^{2+}$, $H^+$ and $>SO^-$. The aqueous species are $M^{2+}$ and $H^+$ and the surface species are >SOH and $SOM^+$. Each of these species is defined relative to its components by chemical relationships (for example, the surface species >SOH is expressed by the reaction $>SOH \leftrightarrow >SO^- + H^+$). The mass balance constraint requires that the sum of all species containing the surface site is fixed (which could include other species in addition to >SOH, $SOM^+$, and $>SO^-$). The activities of all aqueous species are determined using the applicable activity correction. Finally, the activities of all species are related by the equilibrium constant (K) for the various reactions, in equations known as mass-action laws. (These are discussed in more detail below, where, for example, the equilibrium constant for reaction 2.1 is given by Equation 2.18.)

## 2.2 The TSM representation of sorption and relationship with $K_d$ values

As noted above, TSMs place the modelling of sorption within the same conceptual framework which is applied in aqueous chemistry. In the formalism of aquatic chemistry, it is considered that the total amount of (for example) a divalent radionuclide ($M^{2+}$) in solution could comprise species such as hydrolysis products ($MOH^+$, $M(OH)_2^0$), a carbonate complex ($MCO_3^0$), etc. Therefore, the total amount of M in solution is the stoichiometric sum of all the individual species containing $M^{2+}$.

In an analogous way, the total sorption of a radionuclide is, in a TSM, considered to be made up of the sum of different types of sorbed species on the surface. For example, consider the binding of $NpO_2^+$ to a surface site. We can summarise this process with surface reactions such as:

$$>SOH^0 + NpO_2^+ \Leftrightarrow SONpO_2 + H^+ \tag{2.2}$$

Here the total concentration of adsorbed neptunium in the system is the sum of all surface species containing Np. Many additional surface reactions may need to be considered apart from the simple reactions in Equations 2.1 and 2.2. For example, a second type of surface species involving $M^{2+}$ might involve binding of $M^{2+}$ by two adjacent negatively charged ion-exchange sites ($>Z^-$) to give the surface species $Z_2M$. Many other types of binding are possible, and these are discussed in more detail in Section 2.3.5. Analogously to the aqueous phase, the total amount of the RN sorbed is comprised of the sum of all relevant surface species.

Thus, the definition of $K_d$ (given in Equation 1.1) can be re-written:

$$K_d[\mathrm{m}^3/\mathrm{kg}] = \frac{\text{stoichiometric sum of surface species of RN [moles/kg]}}{\text{stoichiometric sum of aqueous species of RN [moles/m}^3\text{]}} \tag{2.3}$$

or more exactly (using the terminology introduced above for a divalent RN $M^{2+}$) as:

$$= \frac{(>\mathrm{SOM}^+) + (>\mathrm{SOMOH}) + (\mathrm{Z_2M}) + .....}{[\mathrm{M}^{2+}] + [\mathrm{MOH}^+] + [\mathrm{MCO}_3^0] + .....} \tag{2.4}$$

The denominator in Equation 2.4 is a direct output of the chemical speciation model for the aqueous phase. Similarly the numerator could be calculated by a TSM, pre-supposing that the associated chemical reactions (such as Equation 2.2) could be accurately described (and assigned equilibrium constants), followed by normalisation in terms of the mass concentration of solid in the system (kg/m$^3$).

In summary, TSMs offer the possibility to accurately describe and model adsorption, whereby surface uptake is described using chemical reactions with associated equilibrium constants, in an analogous way to solution speciation calculations. As such, sorption can be directly integrated into chemical speciation models (for example, computer codes such as MINTEQA2 or PHREEQC). Coupled geochemical/transport models incorporating aqueous speciation, sorption, and mass transport (diffusion, convection) are also possible (Yabusaki *et al.*, 2008; Curtis *et al.*, 2006). However, in the present volume the focus is on the application of TSMs as a scientific support for $K_d$ estimation and the interpretation of sorption phenomena.

## 2.3 Theoretical basis of TSMs

### *2.3.1 Main concepts*

As noted above, the TSM approach is based on a set of surface adsorption reactions, each with an associated equilibrium constant. Dzombak and Morel (1990) summarised the basic concepts of the model:

- Sorption takes place at specific types of co-ordination or ion exchange sites, having different quantities and characteristics.
- Sorption reactions can be described with mass law equations.
- Surface electrostatic charge results from the sorption and proton transfer reactions.
- The effect of surface charge on the free energy of surface complex formation can be accounted by applying a correction factor from electrical double layer theory to equilibrium constants for surface reactions.

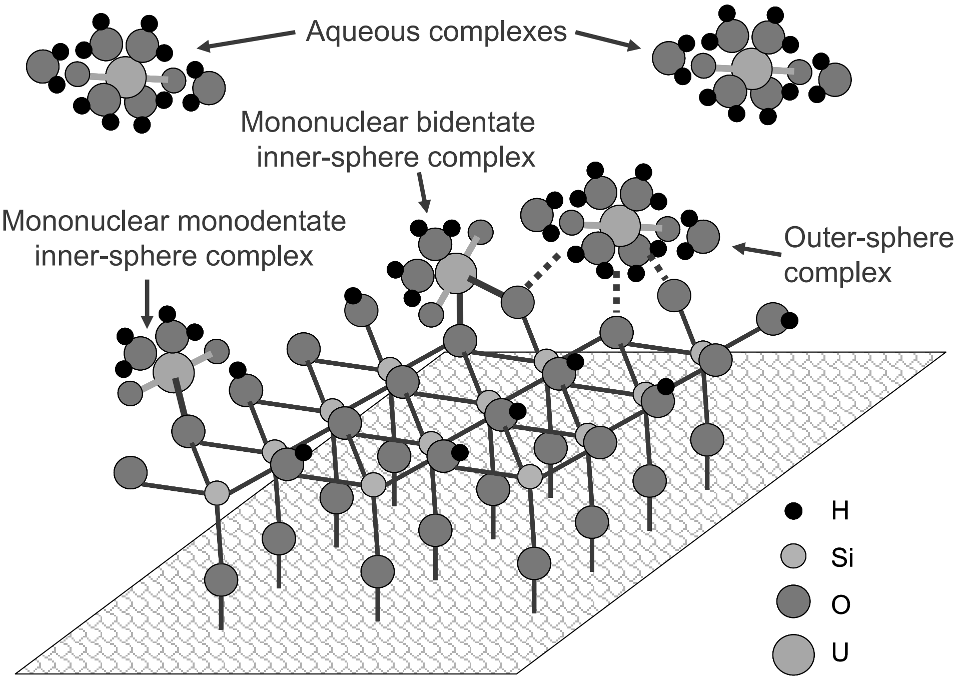
Each of the above aspects of the TSM is discussed below.

### *2.3.2 Mineral surfaces*

All mineral surfaces contain chemical functional groups with which radionuclides interact through sorption, ion exchange, or hydrogen bonding. The surface atoms have insufficient bonding (lower co-ordination than needed for chemical stability), and will react with water to form surface hydroxyl groups. While a number of interactions of RNs with these surface groups are possible (discussed further in Section 2.3.5 and Chapter 3), a distinction is often made between "inner sphere" and "outer sphere" surface complexes. When forming an inner sphere complex, there is a direct bond between the surface and the adsorbed species. In contrast, a species forming an outer sphere complex retains its shell of co-ordinated water molecules, and therefore lies in a plane at a greater distance from the surface (Figure 2.1). As a result, this species is associated with the surface only by electrostatic forces which are weaker than inner sphere type bonds. Regardless of the exact nature of bonding of sorbed species on the surface, it is clear that the number and types of surface sites are a critical TSM component.

**Figure 2.1: Inner sphere and outer sphere surface complexes on a metal oxide surface are distinguished by the types of chemical bonding between the aqueous ion and the surface site**

The inner sphere complex is directly bound to the surface, whereas in the outer sphere complex the ion retains its hydration sphere and attaches to the surface via electrostatic forces. U(VI) sorption onto a silica surface is used here as illustrative example.



A specific example of a metal oxide sorbent of environmental significance is goethite (an iron oxide). The various cleavage planes of the goethite 110 surface (shown in Figure 2.2) contain hydroxyl groups that are co-ordinated to one, two, or three iron atoms, and each of these hydroxyl groups has a different chemical reactivity (Hiemstra and van Riemsdijk, 1999). Structural models for specific mineral phases allow the estimation of the number of functional groups per square nanometre of each cleavage plane. The densities of groups that outcrop on the various crystal and cleavage faces of a mineral can be estimated from known crystal structures (Koretsky, 2000), with calculated site densities in the range of 4-30 sites/nm$^2$.

**Figure 2.2: Illustration of the co-ordination of hydroxyl groups on a particular (110) surface of goethite**

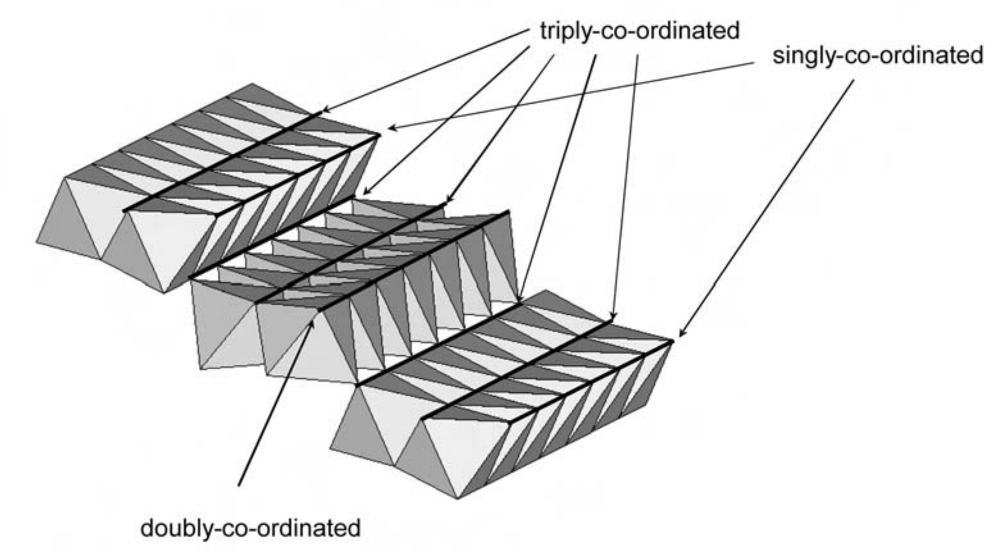
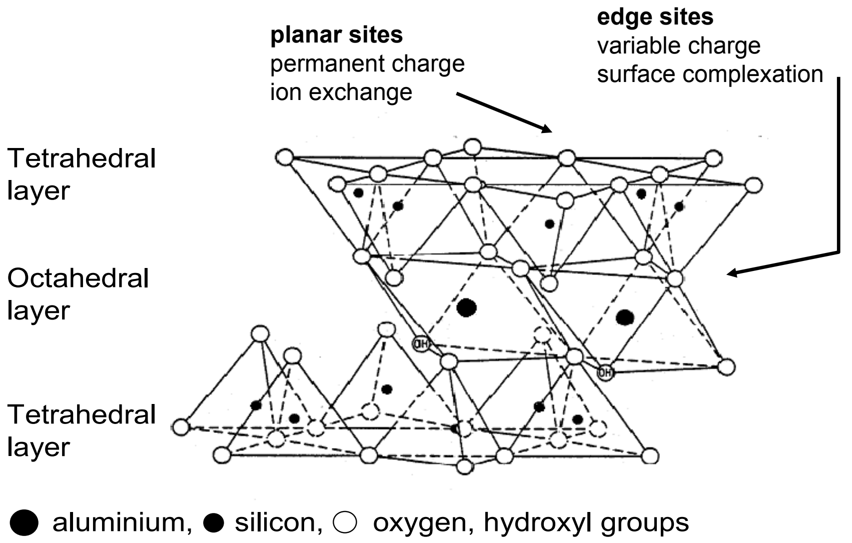


**Figure 2.3: Schematic representation of a 2:1 clay mineral platelet with surface sites indicated**



Source: Modified after Grim and Kulbicki, 1961.

Clay minerals are comprised of composite sheets consisting of layers of aluminium-oxygen octahedra and silicate tetrahedra (Figure 2.3). Substitution of lower-charged cations (for $Al^{3+}$ or $Si^{4+}$) gives rise to permanent structural charge that is compensated by complexation of cations in ditrigonal cavities between the layers and on the outer planes (ion exchange sites; Sposito, 1984). These cations are exchangeable with others in the aqueous phase (ion exchange reactions are discussed further in Section 2.3.6). Although cations typically form outer sphere complexes with ditrigonal cavities, there are exceptions where a cation forms an inner sphere complex (e.g. $K^+$ binding in mica). Binding at the abundant ditrigonal siloxane sites is predominantly electrostatic in nature and relatively weak bonds are formed. Stronger bonds (surface complexes) can be formed with either cations or anions at the edges of clay layers, where the octahedral and tetrahedral layers of the clay crystallites terminate (Figure 2.3). Surface hydroxyl groups at these layer terminations are similar in nature to those formed on oxide crystal plane cleavages.

### *2.3.3 Surface site hydrolysis*

The evolution of TSMs may be traced back to detailed studies of the origin of surface charge on oxides which appeared in the 1960s. In a key paper, Parks and de Bruyn (1962) concluded that the surface charge on hematite develops as a result of reactions of surface hydroxyl groups, which they expressed as:

$$>\mathrm{Fe(OH)}_2^+ \Leftrightarrow >\mathrm{FeO}_2^- + 2\mathrm{H}^+ \qquad (2.5)$$

These investigations were continued in subsequent years, and the theory was generalised to other oxide surfaces (Parks, 1967).

The basis of the TSM approach emerged during the early 1970s, and was distinguished as being the "surface complex formation model in which hydrous (metal) oxide surface groups >Me-OH are treated as complex forming species" (Stumm *et al.*, 1976). In this model, the acidity constant $K_{a1}^{app}$ for the deprotonation reaction of a surface site (>S):

$$>\mathrm{SOH}_2^+ \Leftrightarrow >\mathrm{SOH}^0 + \mathrm{H}^+ \qquad (2.6)$$

is given by

$$K_{al}^{app} = \frac{[>\mathrm{SOH}^0]\{\mathrm{H}^+\}}{[>\mathrm{SOH}_2^+]} \qquad (2.7)$$

The activity coefficients of the surface species are assumed to be equal. $K_{a1}^{app}$ is an apparent equilibrium constant because it is dependent on the surface charge. There is an analogous equation for the removal of the second proton:

$$>\mathrm{SOH}^0 \Leftrightarrow >\mathrm{SO}^- + \mathrm{H}^+ \qquad (2.8)$$

$$K_{a2}^{app} = \frac{[>\mathrm{SO}^-]\{\mathrm{H}^+\}}{[>\mathrm{SOH}^0]} \qquad (2.9)$$

In the TSM, surface functional groups undergo acid-base reactions similar to ligands or metal ions in aqueous electrolyte solution. With increasing pH, the surface hydroxyl groups lose protons and the surface charge becomes more negative. This surface site hydrolysis can be studied by acid-base titrations, typically in the presence of 1:1 electrolytes (e.g. $NaClO_4$, $NaNO_3$).

Currently, two options for modelling surface site hydrolysis are generally in use:

(i) the 2-pK approach (described above) which can be characterised by the two deprotonation steps represented by chemical Equations 2.6 and 2.8. SOH° can be viewed as a generic surface group, which can yield or take up a proton. In this mechanism, which was originally proposed by Parks (1965), two consecutive deprotonation steps of the surface species $SOH_2^+$ are considered; and

(ii) the 1-pK approach, which is characterised by one de-protonation step

$$>SOH_2^{+0.5} \Leftrightarrow >SOH^{-0.5} + H^+ \qquad (2.10)$$

This simplified 1-pK formalism can be applied without substantial loss of accuracy compared to the equivalent 2-pK model, but with fewer parameters. In particular cases, the 1-pK model can also be interpreted as a special case of the more comprehensive MUlti-SIte Complexation (MUSIC) model (Hiemstra and van Riemsdijk, 1996).

The acidity constant in this case is given by

$$K_{H^+}^{app} = \frac{[>SOH^{-0.5}]\{H^+\}}{\left[>SOH_2^{0.5}\right]} \qquad (2.11)$$

### 2.3.4 *Surface charge and electrostatic double layer models*

The uptake of ions at a mineral surface changes the surface charge, which means an electrostatic double layer model (EDL) is often a component of the overall TSM in order to correct for the effects of surface charge on equilibrium constants. A number of electrostatic models for the interface have been developed and applied to modelling sorption (Westall and Hohl, 1980). The most commonly used are: the diffuse double layer model (DLM), the constant capacitance model (CCM), the basic Stern model (BSM), and the triple-layer model (TLM). An introduction to the various EDL models is provided in Davis and Kent (1990). Briefly, EDL models take into account the charge produced at the surface (which is balanced by counter-ions located in the adjacent solution layers) and the electric potential ($\Psi$) arising from this charge, as a function of the surface charge density ($\sigma$) and of the distance from the solid surface (x).

It is worth noting here that, in cases where the chemical contribution to the free energy of adsorption dominates over the electrostatic contribution, a non-electrostatic model (NEM) is an alternative to using a specific EDL model. Simple NEM models have been widely applied in the literature to interpret sorption experiments.

The main differences between the EDL models are the number of adsorption planes (single or multiple), and how the relations between the charge density and the electrostatic potential at these planes are defined. In CCM and DLM, only one adsorption plane exists, so that they have a limited capability to distinguish between inner- and outer-sphere bound ions (discussed in 2.3.2 above). The BSM and TLM consider two adsorption planes, and also offer the capability of accounting for the specific adsorption of electrolyte ions. To account for the different reactivity of various sites (Figures 2.2 and 2.3), multi-site surface complexation models combined with the charge distribution between surface planes (CD-MUSIC) were also developed (Hiemstra *et al.*, 1989; 1996).

As noted above, EDL TSMs incorporate a correction term for the electrostatic effects. As formulated by Stumm and co-workers, the apparent constant, $K_{al}^{app}$ for reaction 2.7 is related to the intrinsic acidity constant of the acid group in a hypothetical completely charge-less surrounding, $K_{al}^{app}$ by

$$K_{al}^{int} = K_{al}^{app} \exp\left(\frac{-F\Psi}{RT}\right) \qquad (2.12)$$

where $\Psi$ is the effective potential difference between the surface site and the bulk solution, F is the Faraday constant, and R is the universal gas constant. Equation 2.12 illustrates how the TSM accounts for the contribution of the surface charge to the free energy of deprotonation. More generally, the TSM takes into account the effect of surface charge on the sorption of any species, in which case Equation 2.12 becomes

$$K^{int} = K^{app} \exp\left(\frac{\Delta Z\, F\, \Psi}{RT}\right) \qquad (2.13)$$

where $\Delta Z$ is the change in the charge of the surface species due to the sorption reaction. Note that in the NEM the value of K does not vary as a function of surface charge since the Coulombic term is neglected, i.e. there is no distinction between $K^{int}$ and $K^{app}$.

In order to apply Equation 2.12, an expression for $\Psi$ is required. As noted above, there are a number of models for the interfacial region including the constant capacitance model, triple layer model and CD-MUSIC model. For example, in the diffuse layer model for the solution side of the interface in a symmetrical electrolyte with a valence Z, the surface charge density $\sigma$ (C/m$^2$) is related to the potential at the surface by:

$$\sigma = 0.1174c^{½} \sinh (Z\Psi \times 19.46) \qquad (2.14)$$

where c is the molar electrolyte concentration (Dzombak and Morel, 1990). The net charge on an oxide surface arises from proton transfer reactions together with surface coordination reactions by other cations and anions. The net charge density is given by

$$\sigma = F\left[\Gamma_H^* - \Gamma_{OH}^* + \sum (Z_M \Gamma_M^*) + \sum (Z_A \Gamma_A^*)\right] \qquad (2.15)$$

Here $\Gamma^*$ is the sorption density (in mol/m$^2$), and $Z_M$ and $Z_A$ are the valences of the sorbing cations and anions. Equations 2.13 to 2.15 form the basis for the TSM with a diffuse double layer at the oxide surface.

The number of TSM parameters is, of course, dependent on the way in which the EDL is incorporated in the model. Among electrostatic models:

- The DLM has only 3 parameters: the protolysis constants ($K_{al}^{int}$ and $K_{a2}^{int}$) and the total number of surface sites ($N_s$).
- The CCM incorporates the capacitance parameter $C_1$ in a simple charge-potential relationship ($\sigma_0 = \Psi_0 C_1$) and has 4 parameters ($K_{al}^{int}$and $K_{a2}^{int}$, $N_s$ and $C_1$).
- The TLM includes the electrolyte surface binding constants as well as the capacitance of both the inner and external Helmholtz layers. It has a total of 7 parameters ($K_{al}^{int}$ and $K_{a2}^{int}$, $N_s$, $K_{x+}$, $K_{y-}$, $C_1$ and $C_2$).
- The BSM assumes that $C_2 = C_1$, thus it has one fewer parameter than the TLM in the 2-pK form and two fewer parameters (i.e. $K_H^{int}$, $N_s$, $K_{x+}$, $K_{y-}$, $C_1$) in the 1-pK formulation.

As shown above, the key feature distinguishing a TSM from a simple $K_d$ representation is that chemical equations, and often electrostatic terms, are incorporated in modelling sorption. There are several comprehensive accounts of TSM applications in aquatic chemistry and geochemistry, using various EDL models (Westall and Hohl, 1980; Stumm, 1992; Davis and Kent, 1990). These authors provide many examples of models for trace metal sorption (such as Cr, Cd, Cu, Zn, Pb and Ni) on simple oxides and other minerals.

### *2.3.5 Radionuclide surface complexation reactions*

The modelling of the sorption of radionuclides using a TSM is, in principle, identical to modelling of a similar non-radioactive species. In all types of TSMs, RN uptake is modelled as a chemical reaction involving the RN and a surface site (represented by >S). There are several important types of reactions that must be considered, including simple adsorption reactions, reactions to form both inner or outer-sphere complexes (in TLM and BSM only), reactions involving simultaneous ligand sorption (to form ternary surface complexes), reactions involving multiple surface sites (multidentate sorption), as well as more than a single sorbing species on each site (polynuclear adsorption). This section briefly introduces each type of reaction and demonstrates how it is possible to construct a consistent TSM containing a range of realistic and relevant surface reactions.

Adsorption of a z-valent cation ($M^z$) such as $Ni^{2+}$ or $Eu^{3+}$ on (hydr)oxide surfaces is typically represented by one or more monodentate mononuclear hydrolysis-type reactions:

$$>SOH^0 + M^Z \Leftrightarrow >SOM^{Z-1} + H^+ \tag{2.16}$$

$$>SOH^0 + M^Z + H_2O \Leftrightarrow >SOMOH^{Z-2} + 2H^+ \tag{2.17}$$

Intrinsic equilibrium constants for these reactions are usually defined as:

$$K^{int}_{M,1} = \frac{[>SOM^{Z-1}]\{H^+\}}{[>SOH^0]\{M^z\}} \tag{2.18}$$

$$K^{int}_{M,2} = \frac{[>SOMOH^{Z-2}]\{H^+\}^2}{[>SOH^0]\{M^Z\}\{H_2O\}} \tag{2.19}$$

Similar to that for the aqueous complexes, intrinsic adsorption constants are referenced to the infinite dilution at zero surface electrostatic potential and (usually) to 1 M standard state at ambient pressure and temperature of interest.

Adsorption of anions (e.g. $SeO_4^{2-}$, $SeO_3^{2-}$, $CrO_4^{2-}$, $SO_4^{2-}$) is usually represented as a ligand exchange or a ligand attachment reaction:

$$>SOH^0 + L^y + H^+ \Leftrightarrow > SL^{y+1} + H_2O \tag{2.20}$$

$$K^{int}_{L,x} = \frac{[>SL^{y+1}]\{H_2O\}}{[>SOH^0]\{L^y\}\{H^+\}} \tag{2.21}$$

$$>SOH^0 + L^y \Leftrightarrow >SOHL^y \tag{2.22}$$

$$K^{int}_{L} = \frac{[>SOHL^y]}{[>SOH^0]\{L^y\}} \tag{2.23}$$

At relatively high dissolved [$M^z$], the formation of polynuclear (e.g. binuclear) surface hydroxo complexes can be considered:

$$>SOH^0 + 2M^z + H_2O \Leftrightarrow >SOM_2OH^{2z-2} + 2H^+ \tag{2.24}$$

This is analogous to the formation of polynuclear solution complexes at higher concentrations. Note how, in this representation, two M atoms are bound to a single surface site.

$$K^{int}_{2M,2} = \frac{[>SOM_2OH^{2z-2}]\{H^+\}^2}{[>SOH^0]\{M^z\}^2\{H_2O\}} \tag{2.25}$$

Cations, such as uranyl $UO_2^{2+}$, are known to bind to two or more surface oxygens, which can be represented as a bidentate reaction:

$$2>SOH^2 + M^z \Leftrightarrow >S_2O_2M^{z-2} + 2H^+ \tag{2.26}$$

$$K^{int}_{2,M,1} = \frac{[> S_2O_2M^{z-2}]\{H^+\}^2}{[SOH^0]^2\{M^z\}} \tag{2.27}$$

Some cations are thought to form ternary surface complexes with anions ($L^y$) such as $CO_3^{-2}$. This leads to a surface species that involves both M and L on the surface, which is expressed via reactions such as:

$$>SOH^0 + M^z + L^y \Leftrightarrow >SOML^{z-1-y} + H^+ \tag{2.28}$$

$$K^{int}_{M,1,L} = \frac{[>SOML^{z-1-y}]\{H^+\}}{[>SOH^0]\{M^z\}\{L^y\}} \tag{2.29}$$

Formulation of mass-action laws, together with associated equilibrium constants, for these multidentate surface complexes can be problematic (see discussion in Kulik, 2009).

### *2.3.6 Ion exchange reactions*

Ion exchange reactions involve electrostatic interactions between an ion and a permanently charged surface (e.g. basal planes on clay platelets). The difference relative to surface complexation is that there is no formation of covalent bonds with an atom contained in the solid matrix (i.e. only outer sphere complexes are formed). Ion exchange is stoichiometric and in most cases there is some preference (selectivity) of one ion over another by the exchanging surface (Sparks, 1995). The classical ion exchange models assume that all permanent charges are balanced by exchangeable ions (e.g. Sposito, 1984), i.e. that there is no effective potential difference between the surface and the bulk solution (this simple concept has limitations for compacted clays; see Chapter 4).

For monovalent ions, such reactions are particularly simple:

$$X^-Na + M^+ \Leftrightarrow X^-M + Na^+ \tag{2.30}$$

with the selectivity constant

$${}^{M}_{Na}K^{a}_{ex} = \frac{x(X^-M)\cdot\{Na^+\}}{x(X^-Na)\cdot\{M^+\}} = \frac{[X^-M]\{Na^+\}}{[X^-Na]\{M^+\}} \tag{2.31}$$

representing the selectivity of the ion-exchange site with regard to either $Na^+$ or $M^+$. Here $X^-$ stands for the cation exchange site, with the total cation exchange capacity (CEC) being expressed in charge equivalents per kg of NaX solid; *x*() represents the mole fraction of the ion on the exchanger. The CEC of a material is usually measured by a standard technique involving saturating it with an index cation (such as $NH_4^+$) removing excess salts of the index cation and then displacing the index cation with another cation.

The amount of index cation displaced is then calculated (Sparks, 1995). Isotope dilution methods are also in use (Baeyens and Bradbury, 2004).

There are several ways of representing heterovalent ion exchange. The most frequently used reaction (for a divalent ion such as $Ni^{2+}$) is

$$2X^{-}Na + M^{2+} \Leftrightarrow X_2^{-}M + 2Na^{+} \tag{2.32}$$

with the equilibrium selectivity constant

$${}^{M}_{Na}K^{a}_{ex} = \frac{x(X_2^{-}M)\cdot\{Na^{+}\}^2}{x(X^{-}Na)^2\cdot\{M^{2+}\}} \tag{2.33}$$

However, the experimental data on ion exchange are usually presented in the charge equivalent fraction scale *E* as the Gaines-Thomas (GT) selectivity coefficients:

$${}^{M}_{Na}K^{a}_{GT} = \frac{E(X_2^{-}M)\cdot\{Na^{+}\}^2}{E(X^{-}Na)^2\cdot\{M^{2+}\}} \tag{2.34}$$

with $$E_{XNa} = \frac{x(X^{-}Na)}{c_S V_S \cdot CEC} \qquad E_{X_2M} = \frac{2x(X_2^{-}M)}{c_S V_S \cdot CEC} \tag{2.35}$$

where $c_S$ is the NaX solid concentration (in kg), $V_S$ is the volume of suspension, and CEC is the cation exchange capacity in equivalents per kg.

Sorption of many RNs by natural clay-containing materials is often dominated by the clay mineral component which typically has a high surface area. The accessory minerals, such as carbonates, are mostly relevant with regard to the pore water composition. According to the structure of the common 2:1 clay minerals, sorption takes place on two entirely different types of surfaces (see Figure 2.3):

- The planar siloxane surface is crystallographically well defined and chemically relatively inert. Sorption by ion exchange refers to the exchange of counterions.
- The edges of the clay platelets feature exposed Al, Si and O atoms with broken bonds, forming amphoteric hydroxyl surface functional groups similar to a typical metal oxide surface.

It follows from the above that a TSM for describing RN sorption in clay materials needs to include the surface complexation and ion exchange parameters for the RN, plus the ion exchange coefficients for all exchange reactions involving major cations and surface complexation reactions of these species if relevant.

## 2.4 Example of TSM for uranyl sorption

This section will illustrate some of the foregoing key TSM concepts using the example of uranium sorption, which has been the subject of numerous experimental and modelling studies.

A TSM for U(VI) adsorption on ferrihydrite was developed by Waite *et al.* (1994). As with many other metals, the uptake of U(VI) on geological materials increases with increasing pH, up to approximately pH 6.0 (Figure 2.4). In brief, the experimental data were interpreted using the computer code FITEQL (Herbelin and Westall, 1994) with the thermodynamic data for aqueous U(VI) reactions taken from Grenthe *et al.* (1992). In micromolar U solutions, the uranyl ion, $UO_2^{2+}$ hydrolyses with increasing pH, and other species such as $UO_2OH^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$ are formed. At near neutral pH and under atmospheric conditions, negatively charged uranyl carbonate complexes such as $(UO_2)_2CO_3(OH)_3^-$ and $UO_2(CO_3)_3^{4-}$ begin to predominate.

The computer modelling was guided by the results of physical examination of the substrates (and associated adsorbed U(VI)) using Extended X-ray absorption fine structure (EXAFS). The EXAFS analysis of the surface of the ferrihydrite showed that U(VI) formed mononuclear bidentate surface complexes. The details of this example are given in Table 2.1. The diffuse double layer electrostatic model was used in this example.

U(VI) uptake on ferrihydrite was modelled as the uptake of $UO_2^{2+}$on weak and strong bidentate surface sites (denoted as $Fe_w$ and $Fe_s$ respectively), with the surface species being $(> FeO_2)UO_2$, an inner sphere, bidentate complex. The same reaction stoichiometry and surface structure were assumed to occur on both the weak and strong sites, and the optimised log K values were determined by least squares residual minimisation using the FITEQL code. The suite of surface reactions included protonation and deprotonation of surface sites, together with adsorption of carbonate ions. For the latter reactions, strong and weak surface sites were assumed to have the same reaction constants. A ternary uranyl-carbonate surface complex was included in the suite of surface reactions on both site types in order to provide a satisfactory fit to the experimental sorption data under conditions of elevated $pCO_2$ and high pH values (Table 2.1). Subsequent spectroscopic studies have confirmed the existence of this species (Bargar *et al.*, 2000).

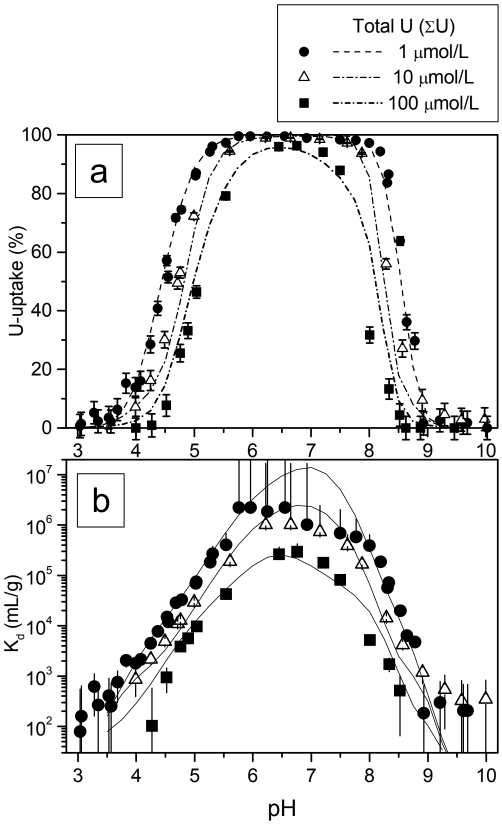
The TSM curves in Figure 2.4 were computed using the surface species and parameters summarised in Table 2.1, to simulate the data in both the percentage sorbed and $K_d$ format. The TSM simulates well the decrease in U(VI)-sorption at high pH values in these air-equilibrated systems (imposed $pCO_2$). This is due to the stability and weak sorption of uranyl carbonate complexes that are dominant at these pH values. The models also reproduce the lower $K_d$ values at higher total U, which is a consequence of the filling of high affinity surface sites.

The model simulations in Figure 2.4b show that the TSM can be applied to calculate $K_d$ values which may be utilised in performance assessment. This potential application is one of the central subjects of the present volume.

**Table 2.1: Summary of surface reactions of uranium sorption on ferrihydrite**

| Surface site type | Weak ($>Fe_W$) | Strong ($>Fe_S$) |
|---|---|---|
| $pK_{a1}$ | 6.62 | 6.62 |
| $pK_{a2}$ | 9.24 | 9.24 |
| U sorption reactions and log K values | $(>Fe_s(OH)_2) + UO_2^{2+} \Leftrightarrow (>Fe_sO_2)UO_2^0 + 2H^+$<br>(log K= -2.35) | |
| | $(>Fe_w(OH)_2) + UO_2^{2+} \Leftrightarrow (>Fe_wO_2)UO_2^0 + 2H^+$<br>(log K= -6.06) | |
| | $(>Fe_s(OH)_2) + UO_2^{2+} + CO_3^{2-} \Leftrightarrow (>Fe_sO_2)UO_2CO_3^{2-} + 2H^+$<br>(log K= 4.33) | |
| | $(>Fe_w(OH)_2) + UO_2^{2+} + CO_3^{2} \Leftrightarrow (>Fe_wO_2)UO_2CO_3^{2-} + 2H^+$<br>(log K= 0.24) | |

**Figure 2.4: Model of U(VI) sorption on ferrihydrite, showing the computation of both (a) percentage sorbed and (b) $K_d$ using a TSM approach**



## 2.5 Options in TSM development

One of the key issues associated with the application of TSMs for simulating sorption is the degree of uncertainty and uniqueness associated with the formulation of the model. For example, if we consider the case-study of U(VI) presented in the previous section, one could question whether the results would be equally satisfactory if a different electrostatic (EDL) model had been used. Other modelling choices could also be examined, for example the stoichiometry of the surface reactions, or the underlying thermodynamic data. These types of questions associated with model choices and uncertainty are considered in this section.

The various sources of uncertainty associated with TSM model development can be considered to fall into several groups:

- model conceptual uncertainty;
- parameter uncertainty; and
- numerical dispersion.

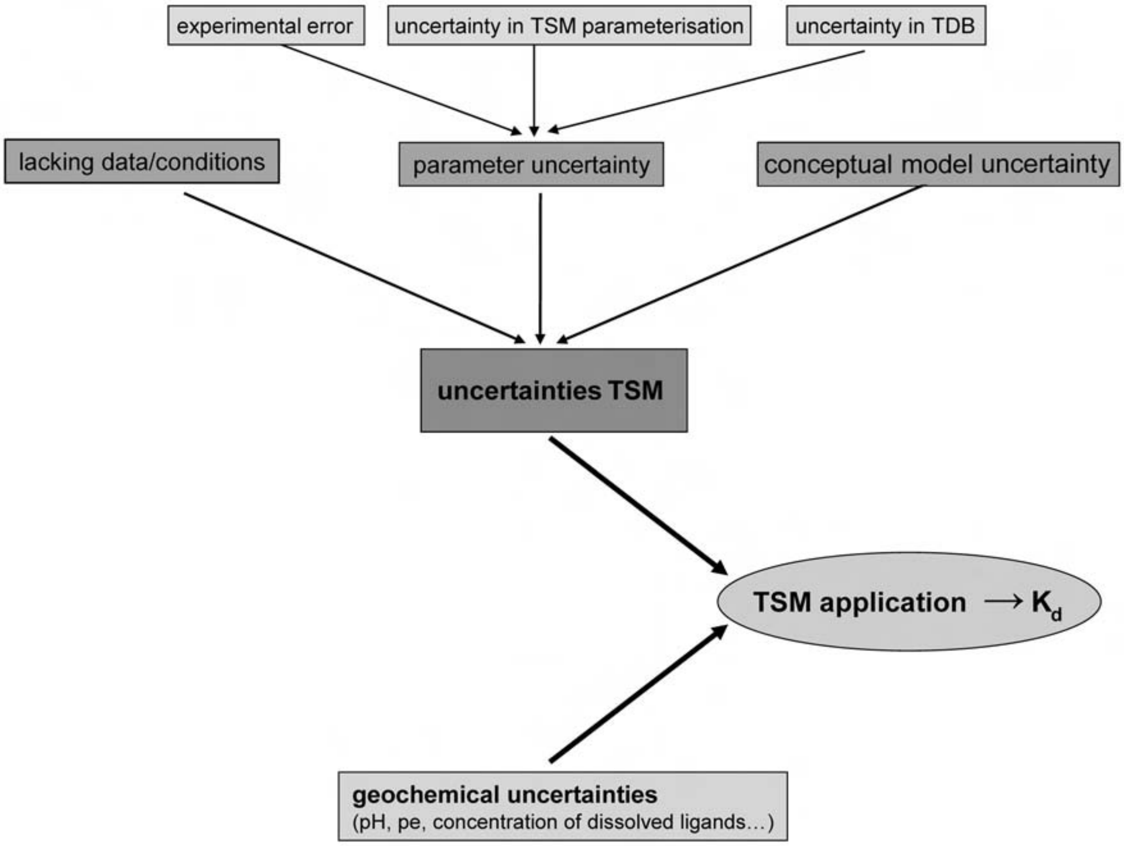
Figure 2.5 illustrates how these various types of uncertainty interact within the context of TSM applications.

*Model conceptual uncertainty* represents the lack of confidence about the conceptual model (including chemical, physical, and mathematical components) being a valid formulation of the system. In the framework of TSM applications, this includes speculative surface species, missing reactions and phases, or errors in the electrostatic double layer (EDL) representation. As there is not just one model to be considered, but rather a combination of different concepts for physico-chemical phenomena, the term "conceptual uncertainty" will be used here. The analysis of the results of these types of uncertainties is entirely different from a sensitivity analysis, in which one investigates the results of a range of parameter values on the model outputs. Conceptual uncertainties can be investigated by running test computations with alternative models. Furthermore, they can be assessed through model validation by comparing model predictions with data sets that are independent of the data used to develop the model. The next sections provide more details and an illustrative example.

*Parameter uncertainty* considers the uncertainty about the true value of the parameters used in the model equations. Such uncertainties (originating from uncertain auxiliary data such as the thermodynamic data describing the aqueous speciation, experimental errors, errors in the characterisation of the physico-chemical environment, and the numerical fitting of the experimental raw data to a model) may be due to a lack of knowledge or to the random character of the parameter value. This topic is discussed in detail in Section 3.5.

*Numerical dispersion* arises from limited precision of computer-implemented codes, often materialising in internal computational rounding errors. Usually it is only encountered in very complex models or models requiring extremely high numbers of iteration cycles. It is thus not considered here, as TSM models generally do not fall into such a category. Furthermore, verification tests have shown that computational errors are of much lower importance than uncertainties due to conceptual modelling and/or parameter values. This has been shown in several verification studies of total model intercomparison where all models used the same expressions and parameter values (Klos *et al.*, 1993).

**Figure 2.5: Schematic representation of sources of uncertainty (from JAEA, 2011)**



Of particular significance in considering TSM development are the consequences of the number of modelling choices that are available during model development. These modelling decisions result in conceptual uncertainty, with a particularly important issue in the context of TSM applications being the possible non-uniqueness with respect to the number and type of model parameters. A decision may be supported by experimental evidence or theoretical considerations, or may simply be based on expediency of fitting. Whereas decisions about surface species can be supported by spectroscopic and quantum chemistry tools (see Chapter 3), decisions regarding binding site types and number of protolysis steps mostly rely on "quality-of-fit" criteria, similar to the selection of the electrostatic term.

The model development requires decisions to be made on several key issues:

- the proposed set of surface species, i.e. their number, stoichiometry and denticity (number of bonds to binding sites per surface species);
- how surface binding sites of different reactivity are distinguished (often related to distinct crystallographic planes or lattice positions);
- the inclusion of a single type of sorption binding site, or two sites (e.g generic weak and strong sites), or multiple sites;
- incorporation of specific surface sites (silanol, aluminol etc.) or generic sites (identified e.g. as >SOH);
- the assumption about the number of protolysis steps of the surface groups: 1-pK vs. 2-pK;
- the use of different representations for the electrostatic interactions (i.e. double layer model).

## 2.6 Illustration of TSM development and effects of modelling choices

This illustration is based on the sorption of Np(V) onto hematite as described in Test Case 1 in the NEA Sorption Project Phase II (NEA, 2005). Five possible paths through the decision-making process (Figure 2.6) are followed, and the differences in the model outcomes are summarised and discussed. The critical points are presented in a way such that these examples can serve as a direct illustration of the potential effects of decisions on model development.

All examples have several aspects in common: The experimental raw data are identical and originate from Kohler *et al.* (1999). They comprise 52 data points, falling into 6 subsets, with the following variable parameters: pH, ionic strength, solid-liquid ratio, $[Np]_{total}$, and $pCO_2$. The same source also supplied the experimental value of 14.4 $m^2/g$ for the specific surface area of hematite used throughout all examples. The auxiliary data to describe the aqueous chemistry are taken from Guillaumont *et al.* (2003). The selection of surface protolysis constants, surface binding site densities, and surface complex formation constants utilised the mineral-specific sorption database $RES^3T$ (Brendler *et al.*, 2003). Where needed, the normalisation concept of Kulik (2002) was applied to reduce the variability of the model with respect to the surface site density.

Note that in order to keep efforts at a reasonable level, an "abbreviated" model development approach was followed:

- It was not attempted to obtain the best possible model description of the experimental data by specifically fitting the TSM parameters (as one would typically do). Instead, for the purpose of illustrating possible effects of different decisions on model outcome, TSMs were constructed by directly using previously published TSM parameters on similar systems (details are explained in the following sections).

- Constraints on formal model consistency were relaxed in terms of protolysis constants and associated EDL models. For example, protolysis constants derived with a DLM were directly accepted for a CCM. It has been shown before (Richter *et al.*, 2005a; Richter and Brendler, 2008) that the resulting effect on numerical values for protolysis constants is smaller than their respective error. In case of the Np-surface complexes, chemical analogies between various iron(hydr)oxides were exploited to obtain log K values.

**Figure 2.6: Generalised decision tree for TSM modelling choices**

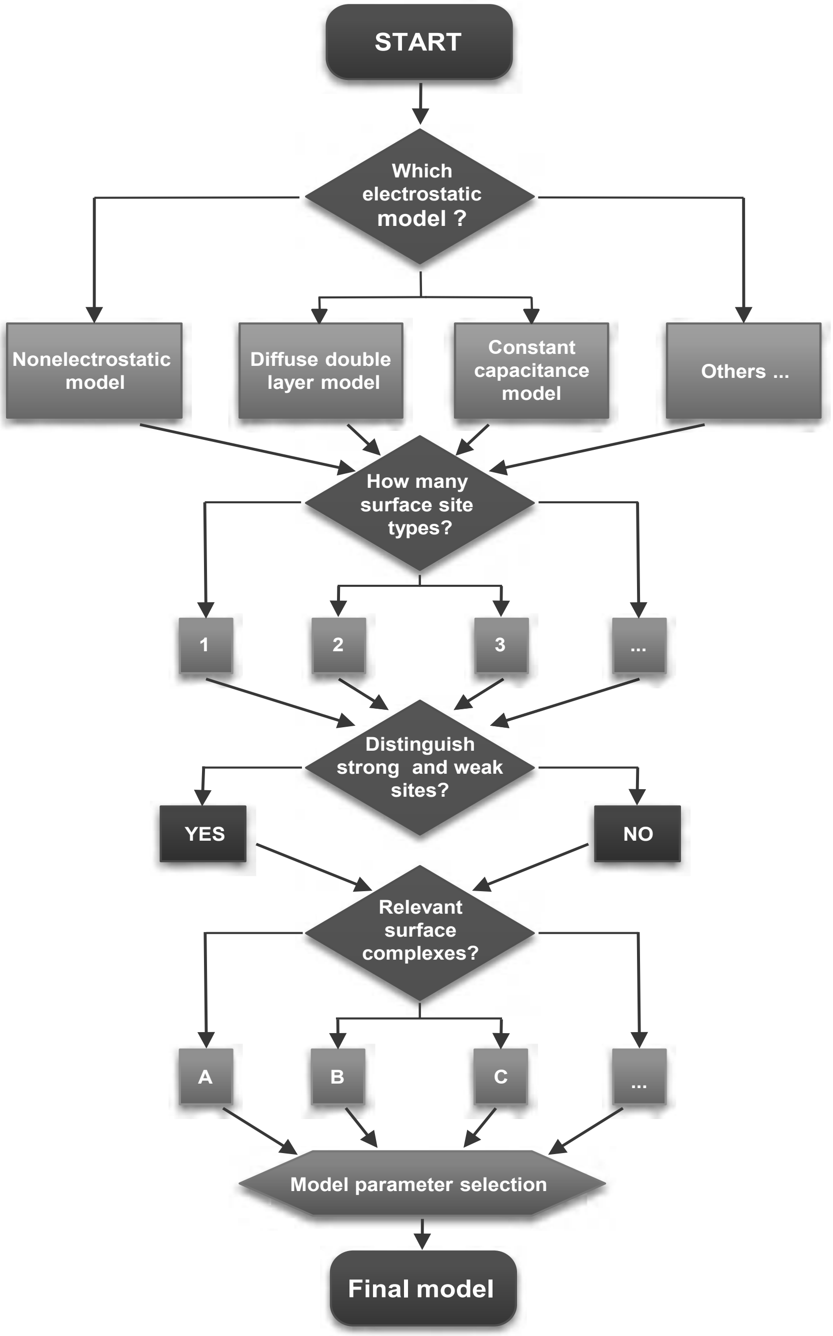


**Table 2.2: Summary of model choices applied to Np(V) sorption onto hematite**

The different electrostatic models were briefly introduced in Section 2.3.4 and are discussed in more detail in Chapter 3.

| Example | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Electrostatic model | DLM | NEM | DLM | DLM | CCM |
| Number of site types | 1 | 1 | 1 | 1 | 1 |
| Protolysis steps | 2 | 2 | 2 | 2 | 2 |
| Strong/weak sites | No | No | No | Yes | No |
| Number of complexes | 3 | 3 | 4 | 4 | 3 |
| Ternary complex | N | N | Y | Y | N |

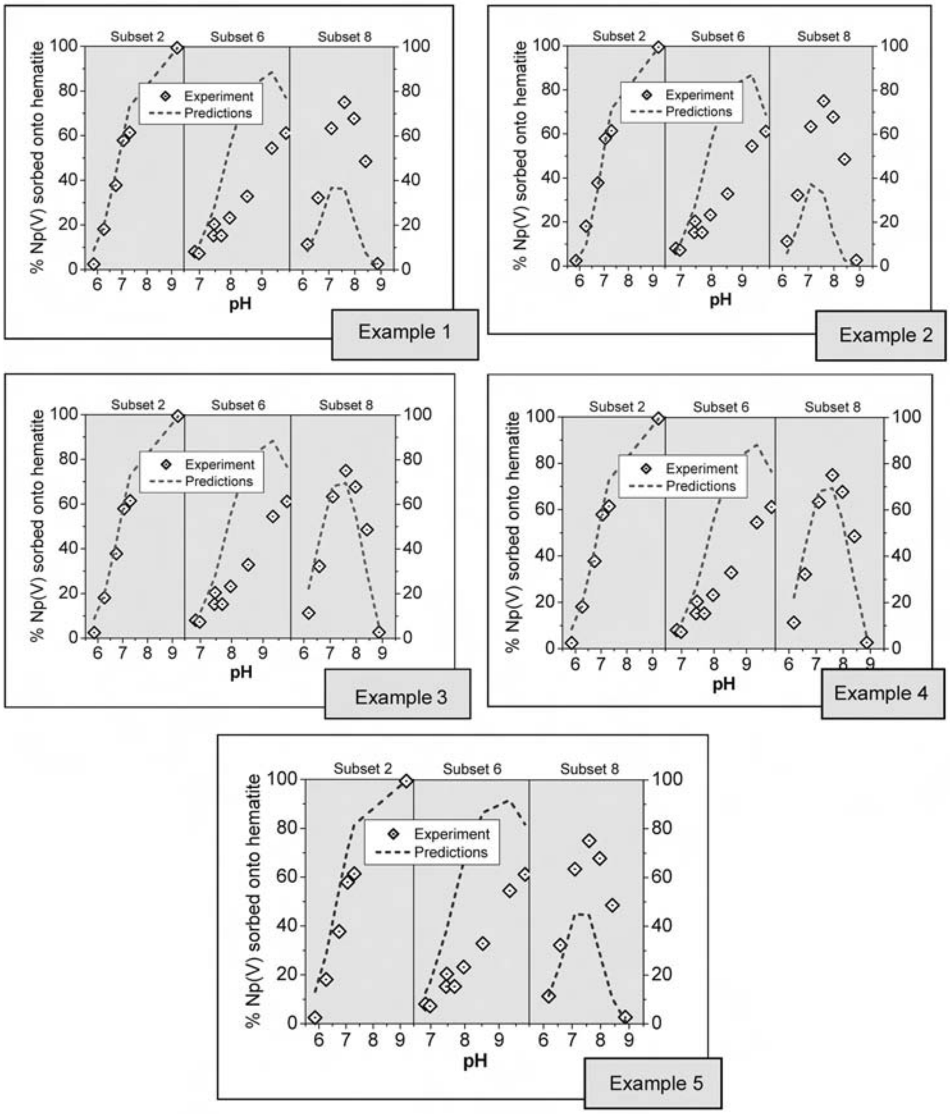
All computations were performed as forward calculations (without fitting) with the FITEQL code, version 3.2 (Herbelin and Westall, 1996). The presentation of the various model responses is based on the criteria applied during Phase II of the NEA Sorption Project, i.e. sorption represented as % sorbed rather than logarithms of distribution coefficient $K_d$.

The results of the five illustrative model calculations are summarised below and in Figure 2.7:

- The first example illustrated a simple approach using the diffuse double layer model (DLM), only one surface type but two protolysis steps, no distinction between strong and weak binding sites, and three surface complexes with no ternary surface species. This example followed the paradigm of keeping the model as simple as possible, utilising a minimum number of adjustable parameters. As can be seen, there are serious deviations in the predicted amount of Np sorption for the data subset with the lowest hematite loading and with the highest carbonate content (data subset #8).
- The second example is based on the following decisions: no electrostatic corrections (NEM), only one surface type but two protolysis steps, no distinction between strong and weak binding sites, and three surface complexes with no ternary surface species. This approach may be seen as even more simplified than example 1, which is identical in terms of decisions apart from the EDL-correction. The number of parameters required is identical to example 1. The parameter values were kept constant to focus exclusively on the effect of simply changing the electrostatic term. The results were similar to the first example.
- The third example used the following branches of the decision tree: DLM, one surface type, two protolysis steps, no distinction between strong and weak binding sites, and four surface complexes, including one ternary Np-$CO_3$-hematite species. This example is similar to the first one, but with a more detailed chemical model. As can be seen from the figure, there is a noticeable improvement of the model simulation for the data subset with a high carbonate content, i.e. with increased carbon dioxide partial pressure (data subset #8) – which is explained by the inclusion of the ternary carbonate containing surface species.
- The fourth example illustrates the following decision path: DLM, one surface type, two protolysis steps, different strong and weak binding sites, and four surface complexes including a ternary Np-$CO_3$-hematite species. The example is similar to example 3, except for the additional differentiation between strong and weak binding sites on the hematite surface. The quality of sorption prediction is similar to example 3, because only the log K value for one surface reaction is adjusted to a value specific for strong binding sites.
- The fifth example illustrates the following decision path: constant capacitance model (CCM), only one surface type but two protolysis steps, no distinction between strong and weak binding sites, three surface complexes not including ternary surface species. There is again some similarity with example 1, but the CCM requires a capacitance

value as additional parameter. Furthermore, the reaction constants are selected in a different way, so that a direct comparison of examples 1 and 5 illustrates the combined effects of using a different electrostatic correction term and of using adapted thermodynamic constants for surface protolysis and surface complexation. The results show an over-prediction for data subset # 2 in comparison to example 1.

**Figure 2.7: Results from five different TSM fitting strategies**



For details of modelling, see Table 2.2 and subsequent text. These illustrative graphs (percentage Np sorbed) pertain to three representative data subsets: #2 (1 g/L hematite (Hem), 0.12 μ M $[\mathrm{Np}]_{\mathrm{total}}$, 0.01 M $NaClO_4$, air with < 5 ppm $CO_2$) , #6 (0.1 g/L Hem, 1.24 μM $[\mathrm{Np}]_{\mathrm{total}}$, 0.1 M $NaClO_4$, air with < 5 ppm $CO_2$), and #8 (1 g/L Hem, 0.11 μM $[\mathrm{Np}]_{\mathrm{total}}$, 0.1 M $NaClO_4$, $N_2$ with 1.5% $CO_2$) from the raw data published by Kohler *et al*. (1999).

As can be seen from the example outcomes, some choices (in particular choices regarding the set of surface species) may affect TSM results, while others clearly appear to be less critical. A comparison of the different data subsets included in Figure 2.7 also shows that the degree to which model choices affect the respective results is also strongly dependent on the actual dataset.

On the other hand, this illustration also shows that some features (insufficient description of data at the lowest solid-liquid-ratio, poor model fits in the neutral pH range and for the intermediate level of carbonate, represented by subset #6) were independent of the model choices tested. This can be seen as an indication that a basic model feature (most likely the formation of a certain surface species) is missing. In such a situation, the effects of other model choices become secondary.

It needs to be recalled in this context that these illustrations rely on TSM parameters derived from the literature. Such an approach may be typical for initial stages of a model development programme or for scoping calculations. It is likely that specific fitting of the parameters to the data would show further differences between the various model designs. For example, it can be imagined that the introduction of a second (strong) surface site, as in example 4, with site density and equilibrium constants for the related surface reactions treated as adjustable parameters, would improve the mathematical fit to the data. On the other hand, basic shortcomings as illustrated for data subset #6 would become apparent during the fitting process (e.g. when different model decisions lead to the same deviation of model results from the experimental data).

Irrespective of the resulting model fit, it is not recommended to rely on arbitrary decisions when developing a TSM, but to follow a defensible and consistent strategy. However, it has to be realised that qualified decisions can only be based on sufficient experimental constraints and/or information (sorption data as a function of conditions, spectroscopic information on surface species, etc.). The information derived from such sources can substantially improve the justification for specific modelling decisions and these issues are further discussed in the following chapters.

## 2.7 Summary: TSMs for constraining $K_d$ values – impact of modelling choices

TSMs share a number of key building blocks and conceptual components with aqueous chemistry, and consequently provide a method of modelling the contribution of sorption to the movement of radionuclides in the vicinity of a repository in a way that is consistent with the thermodynamic treatment of aqueous species. Thus, the application of TSMs can increase the confidence in $K_d$ values which are utilised in PA studies in radioactive waste disposal.

The applicability of the TSM approach for calculating experimental $K_d$ values across a range of conditions was demonstrated by the case study of uranium sorption on ferrihydrite (summarised in Table 2.1, Figure 2.4). One of the main issues associated with the application of TSMs is the number of modelling choices which can lead to multiple models for the same data sets. The model conceptual uncertainties surrounding the application of TSMs were illustrated in the case study of Np(V) sorption on hematite, where a number of similar modelling approaches were used to simulate the data with varying degrees of success.

While it is not possible to recommend a single, "best" decision-path applicable for all situations, the decisions that need to be made when setting up a TSM should not be viewed as random. Reasonable and traceable decisions should normally be possible when all available information for a specific case is considered. The information given within this document is aimed especially at providing guidance to modellers for evaluating the available data and making the expert judgments that are required to make reasonable decisions – and also at highlighting the requirements for explaining and documenting such decisions.

The subsequent chapters will be concerned with outlining a scientifically rigorous and defensible basis for the selection of TSM components and the associated parameter values, as well as strategies for decision making and for the documentation of the choices made. The features of TSMs will be described in more detail in Chapter 3.

# 3. Determination of parameters for TSMs

## 3.1 Overview of experimental determination of TSM parameters

In this chapter, experimental methods for parameterising TSMs are presented, i.e. approaches to measure or estimate fundamental TSM parameters. The various TSM components (specific surface area, surface binding site types and their densities, surface site hydrolysis, electrostatic parameters, stability constants of the surface complexes) are discussed separately for conceptual clarity, although they are interdependent. Thus, the typical strategy (which can be adapted to specific needs) is firstly to determine values for the specific surface area of the solid substrate. In the next step, one has to define an initial set of relevant binding site types (which can later be refined) and then to determine the respective site concentrations. An EDL model is typically selected at an early stage, because the data processing depends on the type of EDL model (see Section 2.3.4). It is usually difficult to estimate EDL parameters and/or surface protolysis constants independently of site densities, so these parameters may be determined simultaneously. The next step is then to perform sorption experiments, the results of which can be used to derive surface complexation constants. As these experiments will also allow the refinement of parameters determined in earlier steps, iteration cycles are often appropriate.

For most of the steps described above, it is possible to derive estimates (literature values, chemical analogues, approximations using algorithms, etc., see Section 3.2 for details). They can assist in optimising experiments or be used as a first approximation for experimental values.

The discussion in this chapter is restricted to relatively simple systems, focusing on single mineral sorbents such as oxides or clays. The development of TSMs for radionuclide sorption on these materials serves as an illustrative introduction to many of the phenomena applicable to the more complex systems of specific interest to radioactive waste disposal. The issues surrounding the application of the TSM approach to these more complex materials are discussed in Chapter 4.

While they are normally not directly applicable to PA, simple systems can be relevant for safety analyses and safety cases in several ways:

- Simple systems help to gain a detailed understanding of the fundamental sorption processes (thus increasing confidence in conclusions and data derived).
- TSMs for single minerals can serve as components of models for complex systems. In various cases the sorption in complex systems is dominated by one single mineral phase (e.g. montmorillonite in bentonite).
- Knowledge acquired for simple systems can indicate plausible starting points for building models applicable to complex systems.

When setting up a TSM it is important to carefully examine the experimental data with respect to other/additional processes which may be responsible for removing the dissolved radionuclide from solution; such as precipitation, surface precipitation or formation of solid solutions.

### 3.1.1 *Surface areas, surface binding site types and their densities*

The *specific surface area* (SSA) of a solid phase, usually expressed in m²/g, can be measured by many different methods. In descending order according to their usage, they include BET sorption isotherms obtained with different gases, geometrical calculations based on crystallographic data (restricted to large, non-porous particles with simple geometry; often based on images obtained from scanning electron microscopy – SEM), water vapour adsorption, ethylene glycol monoethyl ether (EGME) adsorption, Sears' method [for silica particles of colloidal size; titration with sodium hydroxide in a medium of 20% sodium chloride between pH 4 to 9 (Sears, 1956)], methylene blue adsorption, or rhodamin B adsorption. Because milling and grinding produce additional surfaces, the SSA must be related to a certain (average) grain size. Here, simple sieving procedures are useful, but more advanced methods such as laser diffraction can be used to determine the grain size distribution patterns for the particles present in a given experimental system.

The BET gas adsorption method (Davis and Kent, 1990) measures gas adsorption isotherms (typically nitrogen gas, but also argon, krypton, xenon or mixtures thereof), and the data interpretation is based on generalisation of the Langmuir isotherm to an infinite number of adsorbed layers (Gregg and Sing, 1982). The BET analysis is valid for a wide variety of solid phases. However, there are problems in applying the analysis to phases with significant microporosity or to clay minerals (gas adsorption does not occur to a great extent on clay interlayer surfaces). Determination of the true specific surface area of clay can be accomplished using polar organic compounds, which penetrate the interlayer region of expandable clays. One of the most common compounds used is EGME (Heilman *et al.*, 1965, Eltantawy and Arnold, 1973, Cihacek and Bremner, 1979), others are water vapour (Xu *et al.*, 2000), methylene blue (Sposito, 1984), or rhodamin B, (Soerensen and, Wakeman, 1996). Pabalan *et al.* (1998) have argued that the edge surface area of clay minerals can be estimated as approximately 10% of the total external surface area (see also Test Case 4 in NEA, 2005). Based on structural considerations, Tournassat *et al.* (2004) propose a specific edge surface area of 8.5 $m^2/g$. For the basal plane surfaces, they give a corresponding value of 26.6 $m^2/g$. This would result in a total external SSA of about 35 $m^2/g$, which is in the range often observed in BET measurements. Montavon *et al.* (2009) deduce a specific edge surface area of 11 $m^2/g$ from atomic force microscopy measurements.

> The specific surface area is usually best determined by a multi-point BET measurement, whereas in the case of clays, EGME may be an alternative. It can be useful to characterise the grain size distribution, which is typically related to the SSA.

The total amount of proton-reactive surface sites per unit mass of solid (moles/g) can be determined by several methods, including:

- Tritium exchange: this method yields high values, close to crystallographic estimates.
- Proton titration: this method assumes that the surface at low pH can be saturated by protons. The difference in proton uptake between the point of zero charge and the plateau is taken as a measure of the "proton active" site density.
- Test adsorbate saturation: this method assumes that at some pH the maximum amount of test adsorbate corresponds to 100% occupancy of the surface sites.

The surface site density (SSD), a key TSM parameter expressed as moles/$m^2$, can then be estimated by dividing the number of sites by the specific surface area.

Certain authors (Dzombak and Morel, 1990; Davis and Kent, 1990) have proposed adopting a single constant total (conventional) site density of 3.84 µmoles/m$^2$ for all oxide solids in order to develop a uniform modelling approach across a wide range of adsorbing materials.

The next decision is how to allocate the total surface site concentration among different possible binding site types which may be present on the mineral surface. For most minerals, one can commence with binding site types described in the literature. Note that some binding sites may be inaccessible for certain sorbing species, or their amount may be negligible. The concentration range expected for the sorbing species may determine whether or not a distinction between strong and weak binding sites is useful.

Adsorption across a range of adsorbate concentrations is often modelled with an assumption of non-equivalent sites. In two-site models, the sites are referred to as "high affinity" (strong) and "low affinity" (weak) sites. The most common approach in modelling adsorption data is to determine the density of "strong" sites by numerical optimisation techniques (Davis *et al.*, 1998), and to define the weak sites as the difference relative to the total site concentration. If experimental data are collected over a wide enough range in adsorbate concentration, a 3-site model may be justified (Davis *et al.*, 2004a). In many radionuclide migration scenarios, the radionuclide is present at an extremely low concentration and therefore knowledge of the density of "strong" sites may be very important in model simulations.

New site types should only be added when an improvement in numerical optimisation is observed and where the optimisation does not proceed beyond the experimental error associated with the adsorption dataset. The principle is (as in many other cases) to make the model as realistic as reasonable, while remaining as simple as possible.

### *3.1.2 Surface site hydrolysis*

As explained in Section 2.3.3, the acid-base reactions on the mineral surfaces can be described by either one or two protolysis reactions, often referred to as the 1-pK and 2-pK approaches. These reactions can be studied by acid-base titrations, typically in the presence of 1:1 electrolytes. An important attribute of the 1-pK approach is that the logarithm of the stability constant corresponding to the surface chemical reaction can be directly inferred from experimental data, because it is identical to the point of zero charge (PZC). This is the pH at which the surface has no electric net charge. It can be measured by interpreting titration data, or by direct means such as electrophoresis.

While titration experiments are widely applied to determine the stability constants of protolysis reactions, they are subject to various complications, particularly at pH extremes where dissolution of solids can contribute to the proton balance. For example, gibbsite (an aluminium-hydroxide) dissolves at low pH values, releasing three hydroxide ions per dissolved aluminium ion. Depending on the pH, the dissolved aluminium ion will also hydrolyse, thereby consuming some of the released hydroxide ions. Another complexity is that the increasing consumption of protons or hydroxide ions at the extremes of the pH range means that small errors in pH measurements will have increasing impact on the calculated proton balance. Both problems can be addressed (but not eliminated) by appropriate experimental design, for example, by adding greater amounts of solid (surface) to the system. Although the techniques are not fully standardised and the macroscopic titration data do not generally resolve either the protonation mechanism or the electrostatic model, titration data are usually the basis of development of surface hydrolysis schemes. A good overview of the requirements for titration experiments (as well as other methods applicable for sorption investigations) can be found in Lützenkirchen *et al.* (2002).

### 3.1.3 *Electrostatic double layer (EDL) model*

The different ways in which the EDL can be incorporated within TSMs were detailed in Section 2.3.4. It was demonstrated that the different models have different numbers of adjustable parameters, as summarised in the following table. One or two protolysis constants (according to the number of assumed surface protolysis steps) must be added to this list for each EDL model (except for the NEM where this is not required).

**Table 3.1: Number of additional EDL parameters required to describe surface properties in contact with a 1:1 electrolyte**

| EDL representation | Additional EDL parameter required |
|---|---|
| NEM | None |
| DLM | None |
| CCM | One (capacitance) |
| TLM | Four (capacitances of inner and external Helmholtz layers, surface binding constants for anion and cation of the background electrolyte) |
| BSM | Three (capacitance, surface binding constants for anion and cation of the background electrolyte) |

At present, there is no widely accepted method to experimentally determine the capacitance $C_1$ (see Section 2.3.4) for oxides or other minerals, although some techniques [such as electrochemical atomic force microscopy (ECAFM)] are promising in this field (Nishimura *et al.*, 2002). Hayes *et al.* (1991) suggested a $C_1$ value of 1.0 $F{\cdot}m^{-2}$ for the CCM and a $C_1$ value of 0.8 $F{\cdot}m^{-2}$ for the TLM, "unless another value gives substantially better fits". However, the inner capacitance is related to the distance between the plane 0 and the plane β (β, in nm) by

$$C_1 = \varepsilon_\beta / 1.131\beta \qquad (3.1)$$

where $\varepsilon_\beta$ is the permittivity of free space (Davis *et al.*, 1978). Given physically acceptable values for $\varepsilon_\beta$ (6 - 50) and β, corresponding to the distance of closest approach of hydrated ions (2.3 - 4.3 Å), $C_1$ should not be outside the range of 0.1 to 2 $F{\cdot}m^{-2}$ (Hayes *et al.*, 1991). The value for $C_2$ is set to a value of 0.2 $F{\cdot}m^{-2}$ in nearly all published TLM parameterisations, thus reducing the number of variable parameters within this model to 6.

The majority of published TSM data is based on either the DLM, the CCM, the TLM, or the NEM. The specific treatment of the background electrolyte within the TLM requires additional experimental data on major electrolyte ion sorption in order to apply it to natural waters of complex composition. $C_1$ should not be outside the range of 0.1 to 2 $F{\cdot}m^{-2}$. The value for $C^2$ is set to a value of 0.2 $F{\cdot}m^{-2}$ in nearly all published TLM parameterisations.

### 3.1.4 *Formation constants for surface species (log K values)*

A standard experimental method of studying interactions between an adsorbing species and mineral surfaces is to conduct "batch experiments". In a typical batch sorption experiment, a measured mass of a geological material of interest (such as a pure oxide or a clay mineral) in a finely dispersed state is agitated in a solution containing a known total amount of sorbing species under well-controlled chemical and physical conditions. The experimental results can be converted directly to a $K_d$ value using Equation 1.3.

In a well-designed experimental programme, radionuclide uptake should be studied as a function of a wide range of solution parameters (see e.g. Payne *et al.,* 2001). Often the careful interpretation of a comprehensive set of sorption data can yield important input for sorption models. For example, the simple pH dependence ("pH-edge") is a basic input parameter to estimate surface complexation constants using numerical optimisation codes such as FITEQL (Herbelin and Westall, 1994, 1996 and 1999). An influence of ionic strength on sorption is sometimes interpreted as indicating outer sphere surface complexes. The effect of increased RN concentration on the position of the pH edge can demonstrate the need for "strong" and "weak" sites in the sorption model. Typically in sorption models for oxides, these sites are differentiated only by the equilibrium constants for RN sorption and their site populations. In other words, the site density and log K for sorption reactions on these sites (e.g. Equation 2.18) have two different values. Usually it is assumed that the population of strong sites is much less than that of the weak sites. Thus, a wide range of experimental sorption data is essential to constrain the TSM, with a variation in several parameters (e.g. pH, concentration of RN, solid-liquid-ratio, $CO_2$ partial pressure). The experiments should also cover a wide sorption range between 0% and 100% sorption. This may require pre-experiments to determine an optimal solid-to-liquid ratio (SLR).

Simple batch adsorption experiments are an important tool in development of sorption models. Considerable thought must be put into their design, as various factors can influence the results, including equilibration time and method of solid-liquid separation (Dzombak and Morel, 1990). It is strongly advised to perform kinetic experiments to find the minimum time required to reach sorption equilibrium (or at least when the rapid initial phase of sorption is complete). The choice of centrifugation or filtration to separate the phases (and the filter pore size) can significantly influence sorption results, particularly in cases of high percentage uptake on the solid. Thus, it is often advisable to use ultracentrifugation or ultrafiltration to ensure separation of colloidal materials. Filter materials that have minimal sorption of RN should be selected, and if possible preloaded with the sorbing element being investigated. Another typical source of error in sorption experiments can be sorption of the RN onto the container walls. Whilst this effect can be minimised by a suitable choice of container materials (after scoping experiments) it is desirable to independently measure the amount of RN removed from the solution due to sorption on glass or plastic. This can be done by acidifying the container after phase separation (e.g. using analytical grade 0.1 M $HNO_3$) to strip the RN sorbed by the walls. The acid solution can then be analysed separately.

Furthermore, care must be taken to not exceed solubility limits as this will impose an alternative mechanism for RN removal from solution, i.e. (surface) precipitation, which is not described by sorption equilibria. Solubility limits of all potential solid phases should be computed and carefully assessed. However, it should be noted that phases do not necessarily precipitate if the saturation index exceeds unity, i.e. mineral phases may become oversaturated in solution. Sorption edges (i.e. RN sorbed as a function of pH) can be examined to see whether they conform to the typical S shaped sorption edges (e.g. Figure 1.1a). A steep abrupt edge with increasing pH may indicate precipitation of a RN hydroxide or other solid phase (Payne *et al.*, 1998). It can also be important to check whether the RN of interest is a trace constituent of the solid phase under investigation. This is particularly the case for elements having isotopes which are commonly found in natural materials (for example, natural uranium or caesium in soils). In such cases, the total elemental concentration is the sum of natural and added forms, and the respective soluble amount must be determined *a priori* and corrected for during data processing.

It is very important when assessing possible sorption reactions in a given RN/mineral system that a comprehensive range of surface reactions be considered at an early stage, ideally during experimental design. This enables appropriate experimental conditions to be selected and controlled (and later taken into account during modelling).

Experimental variables such as the compositions of the contacting gas phase (e.g. exclusion of air or imposed partial pressure of $CO_2$) can be an important issue for redox sensitive radionuclides or where carbonate is important, as is the case for many actinides (which may form ternary complexes).

Other types of experiments apart from batch experiments which can yield RN retardation factors include flow-through experiments (column tests) as well as static diffusion type tests. The interpretation of these types of experiments must incorporate a mathematical description of flow and/or diffusion processes as well as sorption terms. With these additional factors correctly described, the derivation of sorption data is possible from these types of experiments.

It must be emphasised that adsorption experiments only give information on the change in the ratio of the sum of sorbed RN species relative to dissolved RN species (cf. Equation 1.1), as a function of experimentally imposed changes in component total concentrations or activities. Such experiments do not give direct information on the molecular nature of surface species. While potential dominant species can be inferred by testing different chemically plausible stoichiometries and using numerical optimisation codes to determine the corresponding equilibrium constants, a good fit is not proof of the molecular correctness of the sorbed species. Detailed physical and mineralogical examination of mineral assemblages should be undertaken to determine whether sorption of an RN is likely to be dominated by association with the surfaces of specific mineral phases. The atomic environment of the RN should be probed using techniques such as EXAFS (discussed below) to determine the nature of the bonding environment and whether precipitation or oxidation state change has occurred. Therefore, spectroscopic information should be used where possible to constrain choices for sorption reactions, as discussed in the next section.

It is essential to check for processes other than sorption that may remove RNs from the solution.

The experiments must cover wide ranges of surface coverage and ensure proper phase separation (accounting for the possible presence of colloids). Dissolution and secondary phase formation should be checked. Artefacts such as container wall sorption must be avoided. Parameters such as pH, ionic strength, RN concentration, ligand concentration, temperature or $CO_2$ partial pressure should be systematically varied.

### 3.1.5 *Characterising adsorbed surface species*

Spectroscopic methods give valuable information on which processes are dominant on the surfaces, and which surface species can be expected. However, virtually all of these methods require significantly different conditions from those expected in the environment (rather high sorbing component concentration, vacuum, high energy influx during the measurement, etc.). Ideally one should combine various methods.

Various advanced techniques can provide independent evidence of the type of surface complexes that should be tested when developing a TSM to fit $K_d$ data.

*Extended X-ray absorption fine structure (EXAFS)* – synchrotron-based X-ray absorption spectroscopy (Brown and Sturchio, 2002) provides information on the co-ordination sphere (i.e. type of neighbouring atoms, bond length and coordination number) of the X-ray absorber. For example, EXAFS spectroscopy of RNs on clay minerals can be used to distinguish between sorption on ion exchange and edge sites (Papelis and Hayes, 1996).

Similarly, EXAFS can be used to distinguish between various forms of adsorbed and precipitated species. The radionuclide surface coverage and total contaminant concentration are usually unrealistically high in EXAFS studies, which may limit the applicability of the results. EXAFS results are more applicable to co-ordination at weak sites, and it is usually assumed that bonding is similar on strong sites. Nevertheless, such spectroscopic studies provide useful constraints for TSMs.

*X-ray absorption near-edge spectroscopy (XANES)* can provide information about the symmetry of atom groups and the oxidation state of the probed element (Waychunas, 1987; O'Loughlin *et al*., 2003).

*GIXAFS* – This technique applies EXAFS to planar substrates with grazing incidence of the beam (Waychunas, 2002). An early application of this technique to metal ion adsorption onto an oxide surface was published by Bargar *et al.* (1996). Subsequent application by Denecke *et al.* (2003) involved the determination of the orientation of the uranyl ion on mineral surfaces. More recently, the uranyl ion was studied by Catalano and Brown (2005) using a combination of GIXAFS and x-ray standing waves.

*X-ray photoelectron spectroscopy* yields relatively rapid information on oxidation states of adsorbates, but has also been applied in adsorption studies, both for acid-base studies of mineral surfaces (Shchukarev, 2006) and in studies involving other adsorbates.

*X-ray reflectivity, X-ray standing waves (XSW), crystal truncation rods (CTR)* – These methods applying X-ray reflectivity to mineral surfaces have been reviewed by Fenter (2002). XSW is applied to investigate the structure of surfaces and interfaces with high spatial resolution and chemical selectivity. Synchrotrons have facilitated the application of this interferometric method to a wide range of problems in surface science, including the study of mineral water interfaces (Bedzyk and Cheng, 2002). Besides the determination of adsorbate structure, it is also possible to study properties of the electrical double layer (Fenter *et al*., 2000). Crystal truncation rod (CTR) measurements allow detailed determination of atomic structure at the surface.

*Time resolved laser fluorescence spectroscopy (TRLFS)* – This technique has been widely utilised in studies of aqueous complexation and processes occurring at various liquid/mineral interfaces [for U(VI), Am(III), Cm(III), as well as Eu(III)]. It has been applied to several questions involving the speciation of uranyl in environmental systems (Geipel *et al*., 1996; Bernhard *et al.,* 2001). Applied to clay systems, it has allowed the identification and quantification of the different species sorbed onto various types of clay minerals. TRLFS distinguishes between various sorption mechanisms based on the shape and position of the fluorescence emission spectra and the corresponding fluorescence decay (outer-sphere, inner-sphere, and surface precipitation). The spectral shift and/or splitting of the emission band compared to that of the aquo ion clearly indicate a change in local co-ordination environment of the metal ion. The lifetime of the excited state contains information about the hydration state of the sorbed species.

*Vibrational spectroscopies* – These techniques encompass ATR-FTIR or sum-frequency surface vibrational spectroscopy techniques, which can be applied *in situ*. The methods are sensitive to IR (and in some cases Raman) active modes of surface species (surface hydroxyls, adsorbates and interfacial water). The ATR-FTIR technique was pioneered by Anderson and co-workers (Tejedor-Tejedor and Anderson, 1986). The application of ATR-FTIR to the study of inorganic ion adsorption was recently reviewed by Lefèvre (2004). The technique typically involves covering the ATR crystal by a layer of colloidal particles on which the vibrational spectra then are collected. The approach has been predominantly applied to the study of anion adsorption on mineral surfaces. However, it has also been applied to uranyl(VI) (Ulrich *et al*., 2006) and neptunyl(V) (Müller *et al*., 2009). Systems involving ternary surface complexes are of particular interest (Pasilis and Pemberton, 2008).

*Non-linear optic methods* – This family of techniques is extremely surface sensitive and has been applied to anion adsorption on oxide minerals (Kataoka *et al.*, 2004; Shen and Ostroverkhov, 2006). These techniques can be used to study effects on interfacial water structure caused by the addition of adsorbates, but there has been no application to radionuclide adsorption. The non-linear optic technique, second harmonic generation, is typically applied to ideal single crystal surfaces (occasionally suspensions have been reported). It has been applied to uranyl – oxide systems (Dossot *et al.,* 2006). This technique is highly surface sensitive and also allows quantification of amounts adsorbed onto small surfaces such as single crystal samples. The non-linear optics techniques yield information on water structure and may be applicable to assess the contributions from dipole orientations to the free energy of adsorption, a detail which is presently included in surface complexation models by some groups (e.g. Hiemstra and van Riemsdijk, 2006).

- Spectroscopic methods (ideally a combination of several techniques) give valuable information on dominant processes and species on the surface.
- However, virtually all of these methods require significantly different conditions from those found expected in the environment (rather high sorptive concentration, vacuum, high energy influx during the measurement, etc.).

### 3.1.6 *Extracting numerical values of TSM parameters from experimental data*

This section briefly summarises the estimation of model parameters (for example, log K values) from experimental data (such as the data for RN sorbed as a function of pH). Parameter estimation can be done by graphical methods; by "trial and error" using a forward speciation calculation routine (i.e. systematically varying parameters until a good fit to the data is obtained); or by an inverse modelling (i.e. parameter fitting) routine. Graphical methods (such as "Kurbatov" plots, which were used before chemical speciation codes became available) may bias the results and are therefore not recommended. Trial and error calculation is tedious, and not amenable to statistical interpretation that can be obtained with modern inverse-modelling routines. This can be important in order to evaluate the uncertainty intervals of fitted parameter values.

Since the early 1980s, the computer code FITEQL has been extensively used as a comprehensive fitting routine that includes the chemical equilibrium speciation solver plus an optimisation subroutine (Herbelin and Westall, 1994, 1996 and 1999). More recent approaches combine a robust, generic external parameter optimisation shell (such as UCODE (Poeter and Hill, 1998; Poeter *et al.*, 2005) with a chemical speciation program capable of integrating TSMs (such as MINTEQA2 (Allison *et al.*, 2006), or PhreeqC (Parkhurst and Appelo, 1999), but FITEQL can also be used by operating it in forward mode). The available parameter optimisation shells have numerous options which encompass:

- coupling of various sets of observations and comparison with the results calculated within one chemical speciation program;
- coupling of various speciation solvers with the problem of interest;
- scaling of observations and observation types to constrain fitted parameter values.

In inverse modelling programs, the adjustable parameters are optimised such that an objective function (constructed using other measured parameters) is minimised. This process is always chemical model dependent (e.g. dependent on aqueous speciation, complexation constants, activity coefficients, site density, selection of surface complexes and EDL corrections). The adjustable parameters are usually equilibrium constants for surface species, as well as some parameters of the chosen EDL model (e.g. capacitance).

The objective function (in the present context) is a measure of differences between specific calculated (modelled) and measured (provided) properties of the experimental aquatic chemical system. Its most common mathematical form is a (weighted) sum of squares of such differences. In inverse modelling, selected input parameters of the chemical speciation model are adjusted so as to minimise the objective function. Table 3.2 shows the types of parameters that can be encompassed in the modelling approach.

**Table 3.2: A typical range of system properties considered in the numerical optimisation process**

(data should be obtained for a wide range of conditions: pH, ionic strength, solid concentration, total ion concentrations, etc.)

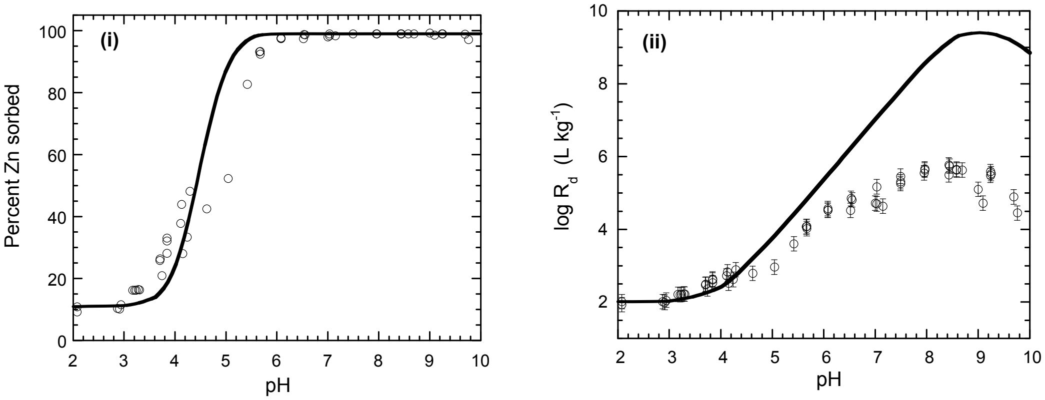
| System property | Parameter description |
|---|---|
| Ion (RN) uptake | Concentrations of the ions remaining in the solution for each experiment |
| Proton uptake | Measured pH values versus titrant additions in potentiometric titrations |
| Surface potential | Variation of relative surface potential as a function of pH |
| Zeta-potential | Electrophoretic mobilities obtained as a function of pH, ionic strength, etc. |

Measured properties (or their simple functions) can be fit to entire data sets; or systematically to respective (sub)systems (i.e. separately for pure solution data, surface acid-base data and uptake data). An improper choice of the objective function may bias the outcome of the fitting exercise. Utilisation of the raw data for fractional ion uptake (i.e. percentage adsorbed as a function of pH) will emphasise the pH range of the sorption edge. On the other hand, if adsorbed RN concentrations are used, the model fit can be biased towards the pH range where the RN is predominantly adsorbed. To avoid such effects, the experimental $K_d$ values should be used, optionally with weight coefficients (lowest for regions of minimal or near-total sorption).

An example of the differences in quality-of-fit obtained with different objective functions is demonstrated in Figure 3.1. Here a model fit to data expressed in terms of %-sorbed [Figure 3.1(i)] provides a poor fit to the experimental $K_d/R_d$ data in Figure 3.1(ii). As will be discussed further below, the $K_d$ representation is preferred for derivation of TSM model parameters.

**Figure 3.1: Sorption edge data for Zn measured on Na-montmorillonite at 0.1 M $NaClO_4$**

(i) Data presented as % sorbed versus pH; (ii) data presented as experimental distribution coefficient (log $R_d$) versus pH. The curve is the best fit obtained with the DDL-model.



Source: Bradbury and Baeyens, 1997.

A model is acceptable if it describes the experimental data within the errors of measurement. Thus, experimental error *estimates* should be associated with each data point. Unfortunately, data sets rarely contain adequate error quantification. If quantified, they are associated with the y-axis quantity (such as $K_d$) but rarely with the x-axis quantity (frequently pH or aqueous ion concentration).

In summary, the choice of the objective function is difficult and many options are available. The best option, involving raw data (or $K_d$ values) with weight factors obtained from the experimental error estimates, is technically possible, but concomitant experimental data are often missing. Further data reduction down to intrinsic equilibrium surface complexation constants ($K^{int}$) is strongly model-dependent because it requires knowledge of site density, activity coefficients for aqueous and surface species, and parameters of the chosen EDL model. In optimisation shell-based approaches, this data reduction occurs simultaneously with the fitting. This means that the chemical model, including aqueous and surface species, EDL model, and equations for activity coefficients, must be completely defined initially.

Presentation of sorption data in "% sorbed" values is common in the environmental sciences literature, where pH sorption edges [e.g. Figure 3.1(i)] usually provide the main part of the data sets used in modelling. However, there are a number of reasons why the $K_d$ representation is preferred:

- When represented as $K_d$, sorption edges are largely independent of the solid to liquid ratios.
- The sorption curves, when presented in terms of $\log(K_d)$ values, are more sensitive to the parameter values, especially log K for sorption reactions.

In a "% sorbed" representation the fits are strongly biased towards the narrow pH range covering the steeply rising portion of the sorption edge and give much less weight to the pH region where high sorption is occurring (>95% sorbed). In radioactive waste management and environmental sciences, where the migration of radionuclides/contaminants is of central interest, the quantity of critical importance is the concentration of radionuclides/contaminants in the groundwater along the flow path. Representing the sorption data in terms of distribution coefficients rather than "% sorbed" reflects more closely the sensitivity of the aqueous concentrations to changing conditions and it is preferable that TSMs be fitted using $K_d$ values where possible.

From a practical point of view, it is recommended to use $\log K_d$ as measure for the quality of fit; for fitting experimental sorption raw data, an alternative would be $[RN]_{dissolved}$ (see NEA, 2005, for a detailed discussion).

Fitting experimental sorption raw data:

- it is recommended to use $\log K_d$ (or $[RN]_{dissolved}$) as measure for the quality of fit.
- a combination of an optimisation shell code and a geochemical speciation code can provide significant computational benefits.

### *3.1.7 Parameter derivation from re-interpretation of existing experimental data*

The preceding sections discussed the various parameters which form part of typical TSMs and methods of experimentally determining them. Because many of the parameters are model-dependent, it follows that they cannot be directly transferred from one model to another without re-calculation. In principle, if the original experimental data are available, it should be straightforward to re-derive parameters, using any desired model framework. Indeed, there are several examples where existing experimental sorption data have been re-interpreted using a modelling approach that differs from the original work.

Perhaps the most extensive effort was undertaken by Dzombak and Morel (1990), who surveyed numerous published experimental and modelling studies of sorption on hydrous ferric oxide (HFO). All existing experimental data for HFO were evaluated, and those results that were considered to be of sufficient quality were re-interpreted in a consistent model framework, which included a DLM interface model with a fixed site density on the HFO surface. These authors documented their data selection and the criteria for rejection of other data sets. More recently, a similar re-interpretation has been carried out for goethite (Mathur and Dzombak, 2006).

Re-interpretation and standardisation of titration and sorption data on clay systems has also been undertaken. For example, the acid base titration data measured on montmorillonite and modelled using a non-electrostatic model (Bradbury and Baeyens, 1997; 2000), have been re-modelled several times using various modelling approaches (e.g. Kraepiel *et al.*, 1999; Tournassat *et al.*, 2003). Kraepiel *et al.* (1999) also remodelled the sorption data of Ni and Zn on montmorillonite. The conclusion drawn from such exercises is that in all cases, a quantitative description of the data could be demonstrated, but the validity of any single model could not be assessed.

The published studies involving re-interpretation of existing data (some of which are mentioned above) can be classified into three groups:

(1) The same TSM is retained (in terms of surface reactions, $\log K^{int}$, EDL model), but different site density (site capacity) parameters are employed.

(2) The same or similar EDL model is used, but multidentate adsorption reactions (e.g. reaction 2.26) are employed instead of monodentate.

(3) The previous experimental data are re-fitted with a different set of protolysis/adsorption reactions and a different EDL model.

It is obvious that case (3) requires a complete re-fitting of the whole experimental data set. This has also been done in the past for cases (1) and (2), although in case (1) it might be sufficient to convert protolysis and surface hydrolysis/ligand exchange constants from one site density to another (see Section 3.2.1).

> Re-modelling of experimental sorption raw data from external sources may increase the available TSM parameter set in a consistent way, without requiring new experimental work.
>
> - It is essential to evaluate carefully the raw data and the associated experimental detail.
> - Numerical data are preferred to data derived from digitised graphs.

Case (2) has emerged recently due to advanced synchrotron-based and molecular modelling studies, which have revealed that on (hydr)oxide surfaces, many cations bind to two or even four surface oxygens. This led to some attempts at re-modelling the available data using 2- and 4-dentate surface complexes. For instance, Ridley *et al.* (2004) remodelled previous data (Ridley *et al.*, 1999) for a number of cations on rutile at various temperatures using multidentate complexes [a discussion of the thermodynamic aspects of the re-derivation of $K^{int}$ values for multidentate surface complexes is given in Kulik (2006, pp. 227-233)].

A significant obstacle in re-interpretation of published sorption data is that the experimental adsorption or titration data are seldom published in their original form. Often, the experimental data are presented as graphical plots (e.g. % sorbed versus pH, adsorption isotherms, etc.), and this is not always sufficiently accurate for remodelling. If the experimental solid to liquid ratio is not optimally chosen, the "% sorbed" data at high sorption percentages (e.g. >95%) may have a large uncertainty. This is illustrated by returning to Figure 3.1(i), in which a Zn sorption edge on montmorillonite is presented as "% sorbed" values. The data could be modelled with an electrostatic term in the mass action equation (DDL model, see Bradbury and Baeyens, 1997) in both the protolysis and Zn surface complexation reaction. The fit to the data is apparently very good. However, if the same Zn sorption data are plotted as log $K_d$ versus pH [Figure 3.1(ii)] the fit has an error of as much as 4 log units.

## 3.2 Theoretical estimation methods of selected model parameters

The preceding sections have defined the key TSM parameters, and described methods for determining them from experimental measurements. However, there are a number of reasons why it is desirable to have methods available for estimating the required parameters for TSMs. For example:

- to establish whether experimental parameters are consistent with theoretical predictions;
- to ascertain whether derived constants are consistent with previous experiments and modelling results;
- to verify whether parameters derived from experimental and fitting methods are chemically and physically reasonable;
- to transfer TSM parameters from one model framework to another, particularly if raw experimental data are unavailable.

We have already considered the re-deriving of TSM parameters from published experimental data in a consistent fashion (as discussed in Section 3.1.6). In this section we consider:

- re-scaling of literature values of adsorption constants in a rigorous fashion and in particular avoiding inappropriate combinations of parameter values (Section 3.2.1);
- ensuring that numerical values for physically meaningful parameters correspond with reasonable theoretical values for these parameters (Section 3.2.2).

### *3.2.1 Scaling of literature values*

In this section, we consider the issue of whether, and how, parameter values from existing TSM models can be re-calculated in a consistent TSM model framework, when system-specific experimental data are not available.

In many of the earlier publications on sorption modelling using TSMs, the site density $\Gamma_C$ was an adjustable parameter, which resulted in strong inter-dependences between model parameters [i.e. between $\Gamma_C$ or $[>S]_{tot}$ and the fitted $K^{int}$ values (Goldberg, 1991; Hayes *et al.*, 1991)]. Dzombak and Morel (1990) recognised this, and re-fitted all data for HFO using a two-site model (with two fixed $\Gamma_C$ values, one for "weak" and one for "strong" sites). This enabled comparison of $K^{int}$ between cations and anions, as well as the construction of linear free energy relationships (see below) which related the surface complexation constants of different ions.

An alternative to re-fitting TSMs from the original experimental data is to utilise simple formulae for re-scaling the $K^{int}$ values to the same $\Gamma_C$ (or $\Gamma_o$) parameter values, provided that the reaction type and species "denticity" are defined. When re-scaling the site capacity between different specific surfaces and solid-water ratios, the total amount of sorption sites in the system sets the site mole balance:

$$n_{S,Tot} = c_S A_S \Gamma_C = c_S q_C \tag{3.2}$$

This equation is necessary for re-scaling the sorption model parameters, especially for multidentate surface species. The (molar) solid concentration $c_S$ (g dm$^{-3}$), and the specific surface area *SSA* (in m$^2$ g$^{-1}$) or the sorption capacity $q_c$ (total moles of site ligand per unit mass of the sorbent) must be known. If *SSA* has not been measured, it can be estimated from the mean particle size and density (Parks, 1990). The particle morphology is especially important for clay minerals where *SSA* values measured with BET can vary widely, even for the same sample. Furthermore, in many modelling studies with clays it has been useful to allocate the total surface area between various site types, such as basal planes and edge sites.

The site density (number of sites per nm$^2$) can be inferred using crystallographic information on the arrangement and densities of variously-co-ordinated oxygen sites on predominant mineral particle planes (Koretsky, 2000). In the absence of such information, the site density parameter $\Gamma_C$ for proton-reactive sites can be chosen as a selected conventional value such as $\Gamma_o$ = 20 µmol·m$^{-2}$ (Kulik, 2002), 1.66 µmol·m$^{-2}$ (Sverjensky, 2003), or 3.84 µmol·m$^{-2}$ (Davis and Kent, 1990).

For a sorption reaction with the free site >S or the >SOH species on the left-hand side (e.g. Equation 2.2), the following relationship between $K^{int}$ values is valid, if all other properties of the system and the TSM (except the site density) are kept constant:

$$\frac{K_M^{int\,2}}{K_M^{int\,1}} = \frac{\Gamma_{C1}}{\Gamma_{C2}} \tag{3.3}$$

where $\Gamma_{C1}$ is the first and $\Gamma_{C2}$ is the second value of site density (see pp. 194-196 in Kulik, 2006). Applying a similar analysis to the n-dentate binding reaction (e.g. Equation 2.26, where n = 2), the following relationship is obtained:

$$\frac{K_{nM}^{int\,2}}{K_{nM}^{int\,1}} = \left(\frac{\Gamma_{C1}}{\Gamma_{C2}}\right)^n \tag{3.4}$$

which shows that the conversion factor becomes far more significant for multidentate binding. For example: in converting from $\Gamma_{C1}$ = 3.84·10$^{-6}$ mol·m$^{-2}$ (Dzombak and Morel, 1990) to the value of $\Gamma_{C2}$ = 1.66·10$^{-5}$ mol m$^{-2}$ (Sverjensky, 2003), the conversion will be:

$K_M^{int2} = 0.23 \cdot K_M^{int1}$ for monodentate binding

$K_{2M}^{int2} = 0.053 \cdot K_{2M}^{int1}$ for bidentate, and

$K_{4M}^{ini2} = 0.0028 \cdot K_{4M}^{int1}$ for tetradentate binding.

The strong dependence of $K^{int}$ value on the site density, which is amplified in cases of multidentate binding, underlines the importance of the site density parameter in TSMs [see also the final report of Phase II of the NEA sorption project (NEA, 2005)].

In closing, it is noted that, while synchrotron spectroscopic data clearly indicate that some cations are bound to two or four surface oxygen atoms when adsorbate concentrations are high, this may not apply at trace concentrations. For these sites, the microscopic configuration is unknown, due to the detection limits of spectroscopic techniques. Therefore, the respective 2- or 4-dentate adsorption reactions may not be applicable and it may be preferable to represent adsorption formally as monodentate binding, particularly for "strong" sites.

Scaling of literature values:

- helps in the comparison of TSM parameters obtained from different experimental studies;
- allows chemical plausibility to be checked and the detection of outliers.

### *3.2.2 Theoretical considerations and linear free energy relationships*

Following the original work published in the early 1960s (Parks and de Bruyn, 1962), the pH of zero surface charge ($pH_{PZC}$ or isoelectric point) has been recognised as an important property of mineral (hydr)oxide surfaces. Several methods exist to relate $pH_{PZC}$ to the crystal-chemical properties of minerals (including its dependence on temperature). It is also possible to predict intrinsic adsorption constants for metal cations and anions on minerals, based on the analogies between hydrolysis and ligand exchange reactions on surfaces and in bulk aqueous solution, expressed in correlations known as linear free energy relationships (LFER). A simple but comprehensive correlation approach can be used to predict TSM parameters ($pH_{PZC}$, 2pK protolysis and electrolyte adsorption constants) from the bulk ion and mineral properties. This is referred to as the SBE model, based on its incorporation of terms for solvation (Pauling) bond strength, and electrostatics (Sverjensky, 1994; Sverjensky and Sahai, 1996).

The seminal work of Schindler and co-workers led to the general acceptance that the adsorption reactions of transitional metal cations on amphoteric (hydr)oxide surfaces are energetically similar to cation hydrolysis reactions in aqueous solution. Schindler and Stumm (1987) established a correlation between intrinsic surface complexation constants, for adsorption of $Fe^{3+}$, $Fe^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$, and $Mg^{2+}$ on amorphous silica, and the aqueous hydrolysis constants $\beta$ for these cations:

$$\log_{10} K_S^{int} = -0.09 + 0.62 \log_{10} \beta \tag{3.5}$$

This correlation works reasonably well both for mono- and bidentate surface species. Other early correlations of this kind were constructed for minerals including $\gamma$-$Al_2O_3$ (Hachiya *et al.*, 1984), and $\alpha$-FeOOH and $Fe(OH)_3$ (Balistrieri and Murray, 1981).

In their systematic study of metal and anion adsorption on HFO in the DLM framework, Dzombak and Morel (1990) developed LFERs relating the intrinsic adsorption- and the aqueous hydrolysis constants for mono- and divalent cations. For the "strong" $>^{s}SOH$ sites, the following regression equation was obtained:

$$\log_{10} K_1^{int} = -4.374 + 1.166 \log_{10} K_{MOH} \tag{3.6}$$

where $K_1^{int}$ corresponds to reaction (3.13) and $K_{MOH}$ is the first hydrolysis equilibrium constant (from Baes and Mesmer, 1976). For the "weak" $>^{w}SOH$ sites an analogous LFER was derived:

$$\log_{10} K_2^{int} = -7.893 + 1.299 \log_{10} K_{MOH} \tag{3.7}$$

The uncertainty of such LFER predictions for many metals (except Pb) is often between 0.5 and 1.0 pK units. Mathur and Dzombak (2006) later extended this LFER approach to a number of cations adsorbed on goethite $\alpha$-FeOOH.

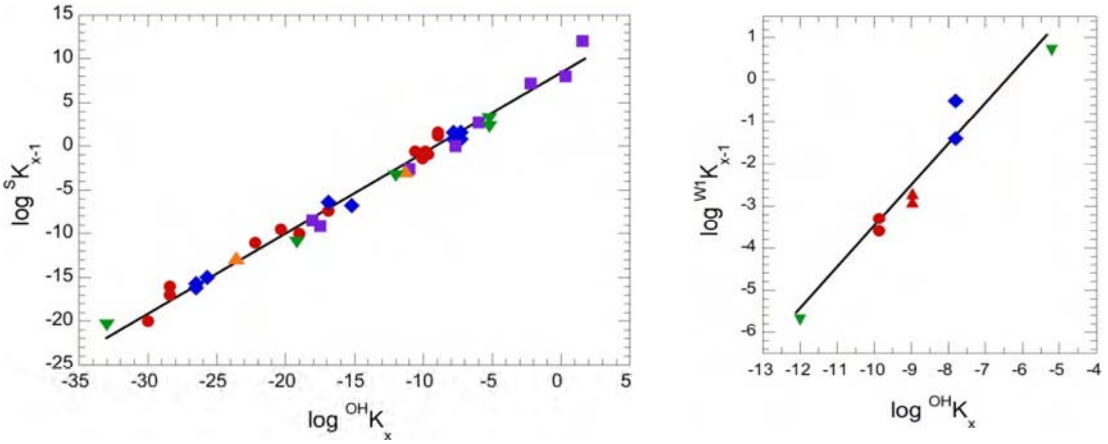
The above examples involving LFERs are applicable to adsorption on metal oxides. LFERs have also been used for predicting cation adsorption on natural clay minerals such as montmorillonite and illite (Bradbury and Baeyens, 2005a; 2009), as shown in Figure 3.2. These correlations can be used to fill significant gaps in sorption databases, particularly where data for important radionuclides are either unavailable or of questionable quality. Bentonites (containing high contents of montmorillonite) are used in various repository concepts and hence the data and values covered in the LFERs (Figure 3.2) are relevant for providing information about sorption relevant to performance assessment studies. Some of the most important elements in this category are Pd(II), Pb(II), Pu(III), Zr(IV), U(IV), Np(IV), Pu(IV) and Pa(IV).

While the reader is referred to the original literature for full details of these methods, the important conclusion from this section is that, while the intrinsic equilibrium constants for adsorption reactions are often determined from fitting of numerical data, there are important relationships (LFERs) that govern the expected values of these constants. Two of the main implications of this are that:

(i) TSM parameters (specifically log K values) data can be checked for consistency with other measured values; and

(ii) in the absence of experimental data, LFERs can be used to estimate the required equilibrium constants.

**Figure 3.2: LFERs for cation adsorption on clays**



Left: Correlation of surface complexation constants of species sorbing on the strong sites of montmorillonite with the corresponding hydrolysis constants. Red circles: Mn(II), Co(II), Cd(II), Ni(II), Zn(II); blue diamonds: Eu(III), Am(III); violet squares: Sn(IV), Th(IV); orange triangles: Np(V); green inverted triangles: U(VI). Right: Correlation of surface complexation constants of species sorbing on the weak sites of montmorillonite with the corresponding hydrolysis constants. Red circles: Ni(II); red triangles: Zn(II); blue diamonds: Eu(III); and green inverted triangles: U(VI).

Application of linear free energy relationships (LFER):

- LFERs are a well established estimation method, namely between log K values for surface complex formation and aqueous hydroxy complex formation.
- Additionally, correlations based on terms for solvation (Pauling) bond strength, and electrostatics may serve as guidance.

## 3.3 Case study: sorption modelling of trivalent lanthanides/actinides on illite

As an illustrative example of the concepts described in this chapter, the sorption modelling of a trivalent lanthanide, Eu(III) and actinide, Am(III) on the clay mineral illite is described. This example is particularly relevant to the disposal of radioactive waste, since illite is present at significant levels in many clay mineral rich host rock formations under consideration for repository sites, such as the Opalinus Clay of Switzerland (NAGRA, 2002), Callovo-Oxfordian formation in France (ANDRA, 2001), and Boom Clay in Belgium (ONDRAF/NIRAS, 2001). The experimental data and modelling associated with this case study are also discussed by Bradbury and Baeyens (2005b, 2009).

To understand and model the interaction of aqueous metal species at the clay mineral/liquid interface over a broad range of pH, background electrolyte and sorbate concentration, both cation exchange (e.g. Equations 2.30, 2.32) and surface complexation (e.g. Equations 2.16, 2.17) reactions need to be considered. Mass action equations are used to describe acid/base behaviour (see Chapter 2.3.3), cation exchange reactions (Chapter 2.3.6) and surface complexation (Chapter 2.3.5). The 2-Site Protolysis Non-Electrostatic Surface Complexation and Cation Exchange (2SPNE SC/CE) model (Bradbury and Baeyens, 1997) is used here as an example.

Four different types of experiments are necessary to derive the parameter values required in the 2SPNE SC/CE model:

- Acid/base titration measurements to yield weak site capacities ($\equiv S^{W}OH$) and protolysis constants ($K_a$).
- Sorption experiments at trace Am/Eu concentrations as a function of pH at a fixed ionic strength (sorption edges). These measurements allow strong site ($\equiv S^{S}OH$) surface metal binding constants ($^{S}K$) to be derived.
- Sorption measurements as a function of Eu/Am concentration at constant pH and ionic strength (sorption isotherms). Weak site surface metal binding constants ($^{W}K$) are obtained from these data, together with estimates of the strong site capacity.
- The cation exchange model requires the cation exchange capacity (CEC) of the clay mineral (Section 2.3.6) and the selectivity coefficients between trivalent Eu/Am and the cation of the background electrolyte. Separate measurements are required to provide the former value, whereas the latter values are obtained from sorption edge measurements in the low pH region.

The parameter values contained in a sorption model cannot all be measured independently, and hence fitting parameters to experimental data is an integral part of the modelling process. The modelling approach is illustrated below utilising examples of titration data for illite (Figure 3.3), sorption edges for Eu(III) and Am(III) (Figure 3.4), and an Eu(III) isotherm [with $^{241}$Am tracer used to label Am(III)] (Figure 3.5). An iterative procedure is necessary using additional data sets (not shown here), such as sorption edges/isotherms measured at different pH values and ionic strengths, to refine the parameter values and produce an internally consistent set of model parameters.

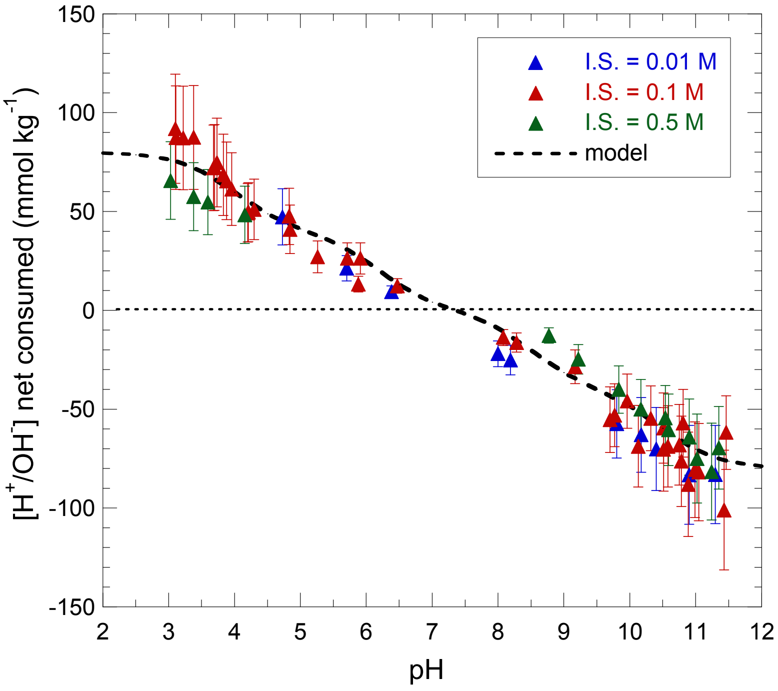
*Acid/base titration modelling*: In this part of the modelling a series of iterations are followed in which the first step is to find a "best set" of parameter values, distinguishing two weakly-sorbing site types. The "weak 1" type sites fitted the acid region of the plot (Figure 3.3) whereas the "weak 2" type sites primarily model the alkaline region of the curve. Subsequently, individual parameter values were changed in order to fine tune the parameter set to give the best fit to the data within the measurement error bars. These parameters were then fixed for the modelling exercise for the sorption edges.

*Cation exchange*: In the acid region of sorption edges (Figure 3.4) where the Eu/Am $K_d$ values are constant and independent of pH, the uptake is interpreted as cation exchange on the permanently charged planar sites. Appropriate specific equations, based on the general equations given above (2.31 and 2.33), are used to fit a selectivity coefficient to the experimental data. The selectivity coefficient and CEC are fixed and included in all further calculations.

*Sorption edges:* In the modelling of sorption edges a stepwise approach is adopted, as illustrated in the following example for Am undergoing surface complexation. The initial step is to calculate the aqueous speciation of Am in the pH range and ionic strength used in the sorption measurements.

**Figure 3.3: Titration data for Na-illite carried out in 0.01 M, 0.1 M and 0.5 M $NaClO_4$**

The curve is the modelling result obtained using the parameters and values given in the table below the figure.



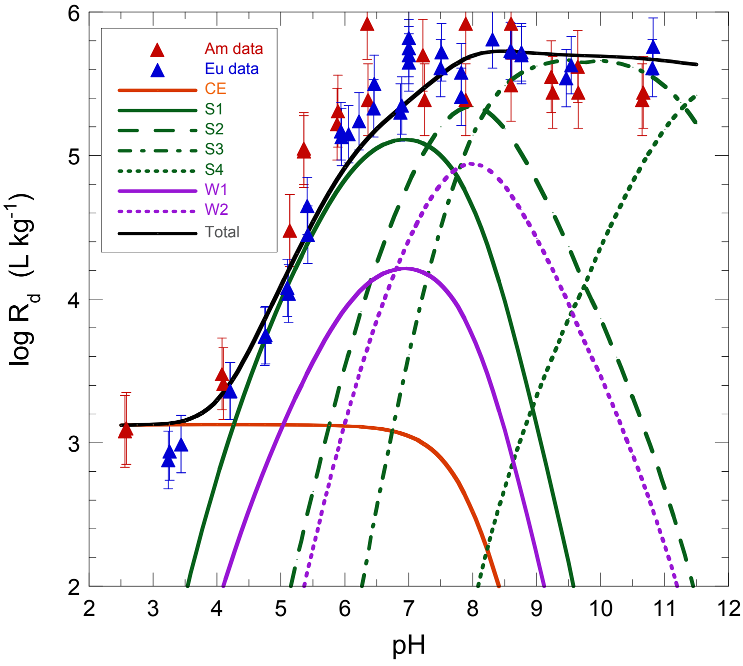
| Amphoteric edge sites | |
|---|---|
| $>S_SOH$ | $2 \times 10^{-3}$ mol/kg |
| $>S_{W1}OH$ | $4.0 \times 10^{-2}$ mol/kg |
| $>S_{W2}OH$ | $4.0 \times 10^{-2}$ mol/kg |

| Protolysis reactions | log K | | |
|---|---|---|---|
| | $>S_SOH$ | $>S_{W1}OH$ | $>S_{W2}OH$ |
| $> SOH + H^+ \Leftrightarrow > SOH_2^+$ | 4.0 | 4.0 | 8.5 |
| $> SOH \Leftrightarrow > SO^- + H^+$ | -6.2 | -6.2 | -10.5 |

Source: Bradbury and Baeyens, 2009.

**Figure 3.4: Eu(III)/Am(III) sorption edges on Na-illite measured in 0.1 M $NaClO_4$**

The curves are modelling results obtained using the parameters and values contained in the tables given below Figures 3.3 and 3.4.



| Cation exchange reaction | log $K_c$ |
|---|---|
| $3Na - illite + Am^{3+} \Leftrightarrow Am - illite + 3Na^{+}$ | 1.9 |
| Surface complexation on strong sites | log $^{S}K$ |
| $> S^{S}OH + Am^{3+} \Leftrightarrow > S^{S}OAm^{2+} + H^{+}$ | 2.7 |
| $> S^{S}OH + Am^{3+} + H_2O \Leftrightarrow > S^{S}OAmOH^{+} + 2H^{+}$ | -4.5 |
| $> S^{S}OH + Am^{3+} + 2H_2O \Leftrightarrow > S^{S}OAm(OH)_2^0 + 3H^{+}$ | -12.9 |
| $> S^{S}OH + Am^{3+} + 3H_2O \Leftrightarrow > S^{S}OAm(OH)_3 + 4H^{+}$ | -24.1 |

Source: Bradbury and Baeyens, 2009.

In the pH range where the dominant aqueous species was the free $Am^{3+}$ cation, the first and simplest surface complexation reaction to be considered was:

$$>S^{S}OH + Am^{3+} \Leftrightarrow >S^{S}OAm^{2+} + H^{+} \tag{3.8}$$

Often, the situation occurs that the rising edge of the sorption curve, and the sorption plateau at higher pH, cannot be fitted simultaneously with a single surface complexation reaction: any approximate fit to the former results in a substantial under-estimate in the latter. In this case, the procedure was to fit a log $^{S}K$ value for reaction 1 (Equation 3.8) describing the rising part of the edge. This best fit constant is then fixed in the following modelling steps. Next, a surface reaction with the first hydrolysis species was considered, Equation 3.9, and the process repeated and so on for the second, Equation 3.10, and the third, Equation 3.11, hydrolysis species until a first fit to the whole sorption edge was obtained.

$$>S^{S}OH + Am^{3+} + H_2O \Leftrightarrow >S^{S}OAmOH^{+} + 2H^{+} \tag{3.9}$$

$$>S^{S}OH + Am^{3+} + 2H_2O \Leftrightarrow >S^{S}OAm(OH)_2 + 3H^{+} \tag{3.10}$$

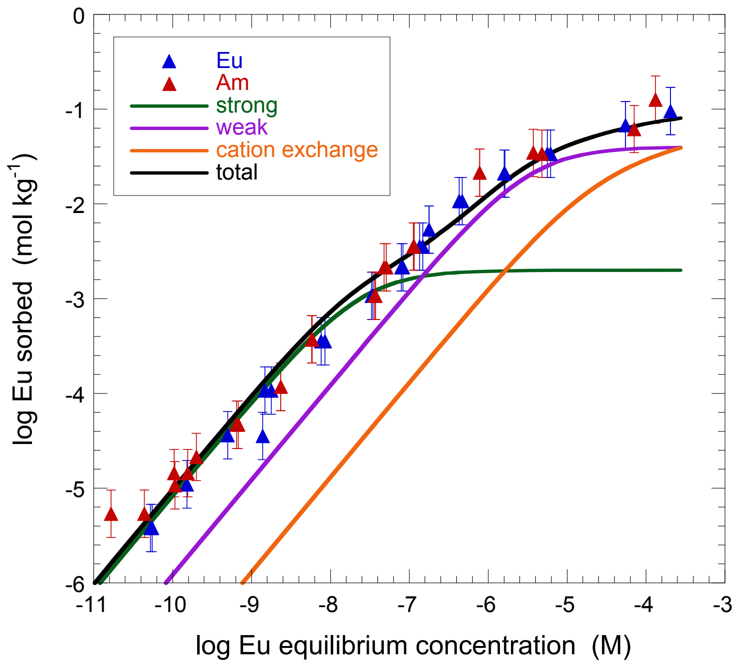
$$>S^{S}OH + Am^{3+} + 3H_2O \Leftrightarrow >S^{S}OAm(OH)_3^{-} + 4H^{+} \tag{3.11}$$

An iterative procedure then followed to find the best fit to the data and "fine tune" the surface complexation constants.

*Sorption isotherms*: Surface complexation constants (${}^{W1}K$) for the weak sites are obtained by fitting the sorption isotherm data and keeping all previously derived parameters fixed (Figure 3.5). A further fine tuning of the constants then followed by recalculating the sorption edges with the full set of values for the strong and weak sites and finally the sorption isotherms were remodelled. The contributions to the total sorption of Eu/Am on illite of all surface species (cation exchange, strong and weak sites) considered in the model are shown in Figure 3.5.

**Figure 3.5: Sorption isotherm of Eu(III) (labelled with $^{241}$Am) on Na-illite in 0.1 M $NaClO_4$ at pH 6.1**

The curves are modelling results obtained using the parameters and values contained in the tables given below Figures 3.3 to 3.5.



| Surface complexation on weak sites | log ${}^{W}K$ |
|---|---|
| $>S^{W1}OH + Am^{3+} \Leftrightarrow >S^{W1}OAm^{2+} + H^{+}$ | 0.5 |
| $>S^{W1}OH + Am^{3+} + H_2O \Leftrightarrow >S^{W1}OAmOH^{+} + 2H^{+}$ | -6.2 |

Source: Bradbury and Baeyens, 2005b.

## 3.4 Indicative values for certain TSM parameters

In this section, indicative values for several selected TSM parameters are provided. These indicative values are based on an effort made within the NEA Sorption Project Phase III (i.e. are not taken from a previously published review). The values represent averages of original experimental data, mainly relying on the literature data contained in the RES$^3$T database (Brendler *et al.*, 2003). The data selection procedure itself excluded all values that are i) of uncertain origin and ii) declared by the original authors to be literature values, averages from other papers or estimates. Thus, only original experimental values were used for the averaging process.

For a variety of minerals (or mineral groups), indicative values for certain parameters can be obtained by examining values available in the literature for specific surface area (SSA), binding surface site density (SSD), and surface protolysis constants. Stability constants for RN surface complexes are not considered here, because of their strong dependency on the underlying TSM characteristics (sites, protolysis constants, EDL-type).

Thus, the indicative values listed below are all mineral-specific parameters. A pooling of mineralogically-similar material has been done for those minerals for which there is only very limited published data. All minerals for which there are no published formation constants for surface complexes have been eliminated.

*Specific surface area (SSA) values* – Compilations of SSA values often exhibit multi-modal distributions that are correlated to specific experimental conditions or analytical methods. For example, the EGME method tends to include the internal surfaces of swelling clays, whereas the BET method does not and, consequently, provides smaller SSA values. Thus, both categories have been treated separately for montmorillonite and illite in Table 3.3. The data subset selected by potential users will depend on the specific application. Generally, the mean values presented in Table 3.3 are derived from a lognormal distribution function (assumed to be the best approximation for this parameter). This proved successful for most cases. Only quartz does not exhibit a clear peak and has on average the lowest SSA values, which leads to the stated error being larger than the value itself.

*Surface site density (SSD) values* – As outlined in Section 3.1.1, the selection of SSD values offers a certain degree of freedom, in so far that this value can be treated as a scaling factor. There are respective transformation equations to adjust the values for pK and log K as shown below. Commonly used values for SSD are 2.31 nm$^{-2}$ (following Turner and Sassman, 1996), 12.05 nm$^{-2}$ (Kulik, 2002) or 10.00 nm$^{-2}$ (Sverjensky, 2003).

The SSD values presented in Table 3.3 were derived assuming a normal distribution of the published SSD values, which can only be considered as an approximation. A problematic case is boehmite, for which only two inconsistent SSD values of 1.7 nm$^{-2}$ and 9.0 nm$^{-2}$ have been published, so probably the average of the values from the chemically similar gibbsite (4.53 nm$^{-2}$) and amorphous alumina (8.19 nm$^{-2}$) is closer to reality, providing an SSD of about 6.4 nm$^{-2}$ for boehmite. For those minerals possessing several chemically distinguishable reactive surface groups (e.g. silanol and aluminol surface sites on clay minerals) generic sites have been used here. This affects both SSD and pK values.

*Surface protolysis constants (pK values)* – Concerning the surface protolysis, the 2-pK model (see Section 2.3.3) has been selected as there are much more data published for this approach compared to the 1pK model. Since the values of pK and SSD are generally not independent, a methodology to compare and average thermodynamic constants originating from different sources is required. Thus the normalisation concept introduced by Kulik (2002) was applied, that defines a reference binding site density $\Gamma_n$ common for all minerals.

The respective equation is:

$$\log K^n = \log K^{ex} + \log(\Gamma_{ex}/\Gamma_n) \tag{3.12}$$

with the indices **ex** meaning the experimental value and **n** the normalised value. In the special cases of protolysis constants, this equation becomes:

$$pK_1^n = pK_1^n + \log(\Gamma_{ex} / \Gamma_n) \tag{3.13}$$

for the first deprotonation step:

$$>XOH_2^+ \Leftrightarrow XOH + H^+ \tag{3.14}$$

and into

$$pK_2^n = pK_2^{ex} - \log(\Gamma_{ex}/\Gamma_n) \tag{3.15}$$

for the second one:

$$>XOH \Leftrightarrow >XO^- + H^+ \tag{3.16}$$

Following that computation, all pK values in Table 3.3 were normalised to a reference binding site density of 2.31 sites/nm$^2$ (Turner and Sassman, 1996). The above equations allow for adjustments of pK (and log K) parameters to any other preferred SSD. A side effect of such normalisations is that pK values (and thus the acidities of binding sites) become comparable. This helps to check whether a specific pK value is sensible in the chemical context of the associated surface binding group.

Table 3.3 gives indicative values of some basic TSM parameters for a range of minerals. These values are intended to assist in evaluating the plausibility of TSM parameters obtained from experiments or by extracting/scaling literature information. They are not intended to be used as substitutes for experimental data relevant to the specific system of interest.

The values in Table 3.3 are averaged over a range of specific mineral samples. Hence, there is a relatively large uncertainty for each value, which includes sample-specific spread. This again highlights the need for system-specific data (experiments or specific extraction of literature information) in the development of a defensible TSM.

**Table 3.3: Indicative values for some TSM parameters of important minerals or mineral groups (marked by *), uncertainties represent 2σ (95% confidence level)**

These values are not intended to be used as substitutes for experimental data but may rather assist in evaluating the plausibility of TSM parameters for a specific system of interest obtained from other sources.

| Mineral / mineral group* | SSA in m²/g | SSD in sites/nm² | $\mathbf{pK_1^n}$ | $\mathbf{pK_2^n}$ |
|---|---|---|---|---|
| Hematite | 14 ± 5 | 5.47 ± 2.07 | 6.28 ± 0.36 | 10.21 ± 0.33 |
| Goethite | 47 ± 6 | 4.28 ± 0.82 | 6.72 ± 0.29 | 10.56 ± 0.19 |
| Hydrous ferric oxide | 166 ± 22 | 7.47 ± 2.34 | 5.79 ± 0.31 | 9.79 ± 0.39 |
| Magnetite | 4.6 ± 3.8 | 5.86 ± 2.71 | 4.38 ± 0.41 | 9.13 ± 0.47 |
| Other iron oxides*[a] | 73 ± 23 | 5.96 ± 4.86 | 5.05 ± 0.81 | 9.39 ± 0.25 |
| Quartz | 0.59 ± 0.81[h] | 5.67 ± 2.20 | -1.26 ± 1.07 | 7.28 ± 0.54 |
| Amorphous silica | 171 ± 56 | 5.79 ± 1.93 | -0.74 ± 1.06 | 7.78 ± 0.35 |
| Boehmite | 134 ± 44 | 6.36 ± 3.00 | 6.05 ± 0.56 | 11.07 ± 1.06 |
| Gibbsite | 12.5 ± 9.2 | 4.53 ± 2.08 | 6.93 ± 0.87 | 10.97 ± 0.67 |
| Amorphous alumina | 68 ± 36 | 8.19 ± 4.43 | 6.59 ± 1.01 | 10.35 ± 0.55 |
| Titanium oxides*[b] | 26 ± 18 | 6.53 ± 1.69 | 3.54 ± 0.32 | 8.34 ± 0.33 |
| Kaolinite | 13.7 ± 2.7 | 1.89 ± 0.59 | 4.09 ± 0.59 | 9.69 ± 0.58 |
| Montmorillonite[f] | 41 ± 18 | 2.41 ± 0.74 | 5.73 ± 1.70 | 8.66 ± 1.22 |
| Montmorillonite[g] | 650 ± 100 | | | |
| Illite[f] | 36 ± 13 | 2.39 ± 1.01 | 6.69 ± 1.02 | 9.07 ± 1.48 |
| Illite[g] | 76 ± 46 | | | |
| Feldspars*[c] | 0.53 ± 0.47 | 4.05 ± 1.90 | 4.13 ± 3.25 | 8.46 ± 2.00 |
| Mica*[d] | 2.5 ± 2.1 | 3.81 ± 2.39 | 6.50 ± 2.22 | 9.78 ± 1.99 |
| Vernadite | 226 ± 48 | 8.14 ± 5.14 | -1.12 ± 0.61 | 4.06 ± 0.97 |
| Manganese oxides*[e] | 33 ± 13 | 13.7 ± 0.8 | 0.89 ± 0.71 | 7.34 ± 2.00 |

a: Lepidocrocite, Schwertmannite, and Akageneite.
b: Anatase and Rutile.
c: Albite, Orthoclase, Microcline and Anorthite.
d: Biotite and Muscovite.
e: Pyrolusite, Ramsdelite, Hausmannite, Manganite and Birnessite.
f: Mainly BET measurements.
g: Mainly EGME measurements.
h: See text above for explanation of the large uncertainty.

## 3.5 Parameter uncertainty

### *3.5.1 Identification of relevant parameters and associated errors*

The importance of uncertainty analysis (UA) and sensitivity analysis (SA) has become increasingly recognised, in particular regarding their potential for environmental modelling (Criscenti *et al.*, 2006; Nicholson *et al.*, 2003). Despite this fact, both methodologies have been rarely used in TSM-based sorption studies. To date, there have been only a very few papers published on the application of sensitivity analysis in the context of TSM, the most relevant being Westall and Hohl (1980), Hayes *et al.* (1991), Goldberg (1991), Puigdomenech and Bergström (1994), Richter *et al.* (2005a) and Richter and Brendler (2008).

The objective of UA is to quantify the overall uncertainty associated with the final output of a model resulting from all of the uncertainties in model input. In simple terms, UA can be considered analogous to error propagation, and is closely related (but not identical) to sensitivity analysis (SA). According to Saltelli *et al.* (2000), SA is defined as "the study of how the variation in the output of a model can be apportioned, qualitatively or quantitatively, to different sources of variation, and of how the given model depends upon the information fed into it." SA therefore provides a methodology for identifying key model parameters.

The various input parameters for a TSM calculation can be categorised into the following principal groups, according to their origin or the information source from which they are derived (see also Figure 2.5):

- thermodynamic TSM parameters including binding site types and densities, surface protolysis constants, and surface complex formation constants, as well as the TDB for all aqueous species;
- system-specific characterisation data for the physico-chemical environment that the TSM is applied to, typically comprising pH value, redox state, and concentrations of all relevant chemical compounds, and also specific surface area.

In terms of system-specific data, the concentrations of the target sorbing components (radionuclides) have to be considered together with all major solids and solutes governing the overall chemical speciation. The uncertainty of this second category is determined not only by the associated chemical analysis procedures but – when natural/geological systems are concerned – by uncertainties associated with the physico-chemical characteristics of the geochemical system of interest. Such uncertainty can be greater than analytical uncertainty, due to difficult sampling procedures and spatial heterogeneities. As these parameters have large variations, they will not be dealt with in a generic way here, but we rather focus on a few selected test cases. Also, the variability of any auxiliary data, such as thermodynamic equilibrium constants for aqueous species, was not considered for the present illustration. Note that in actual TSM applications to complex systems, uncertainty concerning the TDB is not restricted to the numerical values of the equilibrium constants, but includes more fundamental uncertainties, such as missing species.

The following list summarises the parameters taken into account for the present analysis:

- mineral specific TSM parameters (surface site densities SSD, protolysis constants of the binding sites pK, capacitance C, point of zero charge PZC);
- surface complex formation constants, log K;
- formation constants (log K) for all reactions in aqueous solution;
- mineral specific surface area (SSA);
- solid-liquid ratio/porosity (SLR);
- aqueous phase composition and concentrations (most important: complexing ligands and ions competing for surface binding sites);
- gas phase partial pressures;
- pH;
- redox potential, $E_H$;
- temperature, T.

The aim of the present SA and UA can be briefly summarised as identifying which of the above derived and measured parameters has the greatest influence on the final calculated $K_d$ value.

### 3.5.2 *Quantification of uncertainties*

For characterising and quantifying the uncertainty ranges of the parameter values, error distribution functions (EDF) are used. Different EDFs can be assigned based on the amount and quality of *a priori* information about each parameter.

Most often Gaussians are used as EDFs. If only a very limited amount of data is available, to such an extent that only minimum and maximum values (and maybe the most probable value) can be derived, more robust approaches are required, e.g. triangular or uniform distributions. In cases where still less data are available, for instance only one generic or default value, experts in the specific area should be asked to give their advice and a conservative approach should be adopted. In general, linear distributions are used for all the above cases. However, logarithmic distributions (log-uniform, log-triangular, log-normal) are preferred when the ranges between the minimum and maximum values, or over four standard deviations, cover substantially more than one order of magnitude.

The problem with non-Gaussian EDFs is illustrated by taking the specific surface areas (SSA) of several common minerals as an example. The evaluation is based on more than 1 000 SSA records from the open literature, stored in the RES$^3$T mineral-specific sorption database (Brendler *et al.*, 2003). The following minerals were selected for a distribution analysis, due to both being representative of systems relevant to radioactive waste treatment and comprising enough data records: goethite, amorphous silica, kaolinite, ferrihydrite, montmorillonite, quartz, illite, gibbsite, rutile/anatase (the two $TiO_2$ varieties were merged due to their similar SSA value ranges).

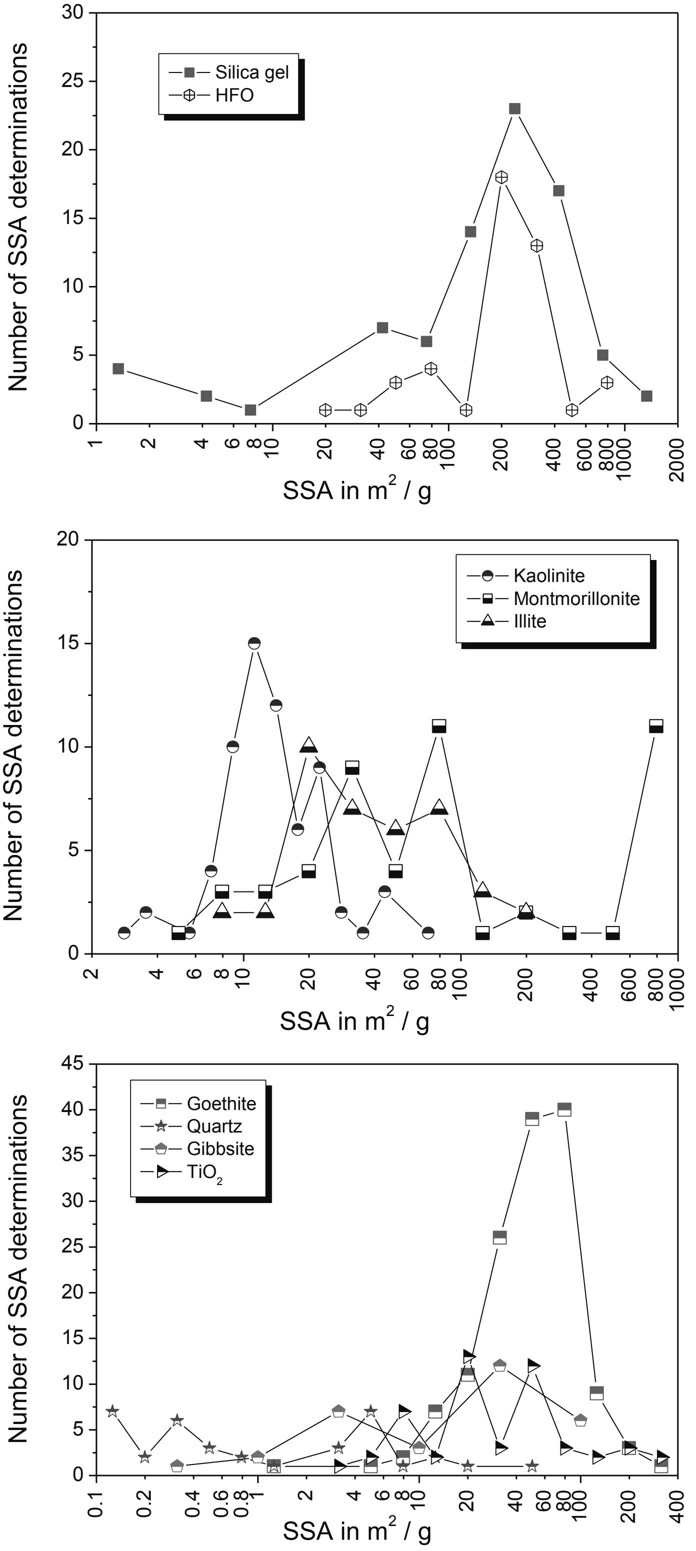
The following figure shows the SSA distribution for the various selected minerals, grouped into three categories. The presentations use logarithmic x-scales for better visibility. The first category (upper panel of Figure 3.6) contains two important amorphous materials, hydrous ferric oxide (HFO/ferrihydrite) and amorphous silica gel. The mean is clearly situated around 200 – 400 m$^2$/g, with a broad tailing towards lower values, especially for $SiO_2$. Here a log-trigonal EDF seems most appropriate.

The central panel of Figure 3.6 depicts the SSA value histogram for three clay minerals. Compared to the previous figure, the picture is much more scattered, with a broad peak around 10 m$^2$/g, and another one around 80 m$^2$/g. In addition, some SSA values for montmorillonite are extraordinarily high. Here, the multi-modal distribution is due to different analytical methods. For example, it is known that the EGME method tends to include the internal surfaces of swelling clays, whereas the BET method does not and, consequently, provides smaller SSA values (cf. Section 3.1.1).

Finally, the reported SSA values for four oxides are given in the lower part of Figure 3.6. The pattern resembles that obtained for the amorphous materials, albeit shifted to lower values with maxima between 40 and 80m$^2$/g, so a log-trigonal EDF would be recommended. Only quartz does not exhibit a clear peak and has on average the lowest SSA values, with a log-uniform EDF as the best approximation.

Note that recently the PAMINA project (Performance Assessment Methodologies in Application to Guide the Development of the Safety Case) has developed procedures to systematically derive EDFs (for PA in general, but they can also be adapted to TSM needs), as reported in Becker *et al.* (2009).

**Figure 3.6: SSA histogram for amorphous mineral coatings (upper), clay minerals (central) and for crystalline oxides (lower)**



Comments on utilising error distribution functions (EDFs) to describe data scatter patterns:

- Most often a Gaussian or a Log-Gaussian distribution can be used as an estimation.
- Alternatives in case of very limited information are a triangular or a uniform distribution, which can also occur in logarithmic form.
- Observed multi-modal distributions are a strong indicator of either different measuring techniques (analytical models) or systematic errors.

### *3.5.3 Parameter correlation: importance and derivation*

To the knowledge of the authors, no investigation of the effect of correlation of fitted parameters on uncertainties has been discussed in the open literature to date. Such correlation matrices will allow incorporation of the interdependencies between parameters when examining sensitivity within the modelling system. Correlations are usually observed (but rarely published) as a result of a simultaneous fit of multiple parameters to the same experimental data. There may also be other reasons, in particular the characterisation of the physico-chemical environment, which defines important variables such as solution composition, temperature or redox potential.

At present, it is not clear whether such correlation matrices always reduce the overall uncertainty of the target function values (which would be favourable for any conservative approach used in PA) or if there are correlation patterns that would actually increase the overall uncertainty. To progress towards a solution of this problem, the following approach has been chosen here:

- determination of a reference correlation matrix;
- sensitivity analyses of the same system with and without taking the correlation matrix into consideration;
- analysis and discussion of observed differences in model output.

Usually, a set of TSM parameters derived simultaneously by numeric optimisation codes from experimental results exhibits a certain degree of correlation. Respective correlation matrices may be obtained parallel to the fit results when using advanced optimisation codes in combination with geochemical speciation programs.

## 3.6 Illustration of parameter sensitivity and uncertainty analysis

### *3.6.1 Selection and design of test cases for illustration*

During the preparation of this guideline document, a variety of test cases were performed to examine and illustrate the effects of parameter uncertainty and the benefits of sensitivity analysis. The selected test cases covered a wide application range with respect to stoichiometry, oxidation states and complexing behaviour, including both oxides and layer silicates, cationic and anionic sorbates, redox inert and redox sensitive systems. In addition, the respective TSM submodels (i.e. differences in the EDL representation) associated with the different test cases also varied. Finally, a test case specifically addressing the issue of parameter correlation was constructed. A compilation of all test cases, together with a full tracking of their origin or derivation is provided in a separate NEA report (Brendler *et al.*, 2011). This report includes all auxiliary data that were used, such as thermodynamic data for the aqueous speciation.

Here, the test case of Np(V) sorption onto hematite (one type of surface site, two protolysis steps, diffuse double layer) is given in more detail to illustrate how such a sensitivity analysis can be prepared and performed.

### *3.6.2 Derivation of test case parameter sets*

Based on the previous sections, the necessary model input (namely the TSM parameterisation) is defined here. This includes respective numerical ranges, error distribution functions and problems associated with them. A challenge for the sensitivity analysis performed in the context of this project is that the uncertainty of the various input parameters is represented both by their experimental error (for experimentally determined parameters) and fitting uncertainty (for parameters derived indirectly by fitting procedures to model assumptions). It is, however, also necessary to account for the sampling variability of physico-chemical conditions in a geological context (spatial and temporal), which often is much larger than the errors introduced by imperfect measurements and fittings. The real complexity of the different geochemical environments may span even wider ranges.

The sorbent concentration is fixed between test cases to allow a better comparison of different environments, and to illustrate element-specific behaviour in a uniform manner. As the contaminant content will usually be in the tracer range, a value of $1.0 \cdot 10^{-7}$ mol/L has been selected. The solid-liquid ratio is set to a generic estimate of $C_S = 10$ g/L. This value is directly combined with the specific surface area and the site density (both being mineral-specific values) to yield a binding site concentration as required by the geochemical speciation code. Concerning the gas phase composition, two representative choices have been made: either an inert atmosphere is assumed, or a $CO_2$ content equal to ambient air is used, which will then in turn govern the carbonate content of the aqueous phase as a function of pH. Finally, a representative solution composition has to be chosen. To keep matters simple, we take a simple electrolyte with an ionic strength of 0.1 mol/L as a default value.

The parameters to be taken into account are summarised below (cf. Table 3.4) for the first test case, together with their numerical values, the assigned error distribution function and respective uncertainties. Depending on the assigned error distribution function (EDF), the columns marked with "EDF parameter" have varying meanings:

| | |
|---|---|
| Fixed | no extra EDF parameter (i.e. no uncertainty considered) |
| Normal | 1st EDF parameter equals the standard error (i.e. standard deviation $\sigma$ divided by the square root of the number of samples $n$) |
| Trigonal | 1st EDF parameter equals the minimum and 2nd EDF parameter equals the maximum |

A special case is the surface binding site concentration (SSD) usually given as $\Gamma_N$ in sites/nm². However, SSD is required here as the molar binding site concentration $\Gamma_M$ (with the unit mol/L). The necessary conversion from $\Gamma_N$ to $\Gamma_M$ follows the equation:

$$\Gamma_M = \Gamma_N \cdot S_A \cdot C_S / (F_C \cdot N_A) \tag{3.17}$$

where $C_S$ is the solid concentration (derived from the site-specific solid-liquid ratio, given in g/L), $S_A$ being the specific surface area (SSA) given in m²/g, $F_C$ being the conversion factor from nm² to m² ($10^{-18}$) and $N_A$ being Avogadro's number ($6.022045 \cdot 10^{23}$ mol$^{-1}$). This leads to the simplified equation:

$$\Gamma_M = \Gamma_N \cdot S_A \cdot C_S / 602204.5 \tag{3.18}$$

The SSD $\Gamma_N$ is set to 2.31 nm$^{-2}$ following Turner and Sassman (1996), whereas the SSA is a mineral-specific measure with the respective data selection (discussed in Brendler *et al.*, 2011).

The collection of the input parameter set for the test case of Np(V) sorption onto hematite followed the strategy outlined here. Namely, all published independent DLM data records for the hematite surface protolysis were normalised to the reference binding site density of 2.31 sites/nm². None showed obvious errors or differed significantly from the other values. Hence, averaging seemed to be appropriate, leading to the values $pK1^n = 7.23 \pm 0.40$ and $pK2^n = 9.49 \pm 0.44$ (the error represents one sigma).

RES³T (Brendler *et al.*, 2003) provided 74 independent SSA determinations for hematite. Excluding the four values below 1 m²/g and two values above 100 m²/g (considered non-representative extremes), the remaining 68 values were averaged. The mean value for the specific surface area of hematite, also used for the modelling, was derived to be 22.5 ± 1.9 m²/g. Setting the SSD to 2.31 sites/nm², a binding site concentration of $(8.63 \pm 0.73)\cdot10^{-4}$ mol/L can be derived for a given solid-liquid ratio of 10 g/L.

Concerning the surface site types to be considered, the vast majority of papers agree on the presence of only one Fe surface hydroxyl group, i.e. =Fe-OH [only applications using the CD-MUSIC model (Hiemstra and van Riemsdijk, 1996; see Section 2.3.3) differ, which is inherent to this type of model]. To keep the model simple, strong and weak binding sites were not distinguished.

The next step was to define a set of reasonable surface species. As there are very few TSM investigations reported for Np sorption on hematite, data for Np sorption on similar iron(hydr)oxide phases (goethite, lepidocrocite, and ferrihydrite) were also screened. It turned out that the minimal species set required to account for Np(V) sorption onto iron(hydr)oxides consisted of $>FeO\text{-}NpO_2$, >FeO-COOH, $>FeO\text{-}COO^-$ and $>FeO\text{-}NpO_2(HCO_3)_2^{2-}$.

Below, their normalised formation constants $\log K^n$, taken from literature included in the RES³T database, are given. The numbers appended in parenthesis refer to the number (n) of literature values used for the averaging. In the case of the ternary Np(V)-carbonate surface complex there was no DLM-based information available. Hence the only way to account for the clear spectroscopic evidence for the existence of this particular species was to apply data based on the TLM given by Kohler *et al.* (1999). As there is no uncertainty for this reaction, the error was estimated to be three times of the largest uncertainty of the other reactions (giving 3×0.28 = 0.84, which then was rounded to 0.9). In the case of the adsorption of carbonate, the reaction constants refer to equations based on $H_2CO_3$(aq) as the master species for carbonate.

| | | |
|---|---|---|
| $> FeO - NpO_2$ | $\log K^n = -2.61 \pm 0.21$ | (n=7) |
| $> FeO - CO_2^-$ | $\log K^n = 4.57 \pm 0.18$ | (n=6) |
| $> FeO - HCO_2$ | $\log K^n = 3.64 \pm 0.28$ | (n=7) |
| $> FeO - NpO_2(HCO_3)_2^{2-}$ | $\log K^n = 10.53 \pm 0.9$ | (n=1) |

Here, it should be emphasised that the uncertainties derived above originate from an averaging of different fits of different primary data sets obtained by different teams. Of course, a fit of a single homogeneous data set would give smaller errors, but would be much less representative.

The aqueous chemistry of Np(V), as well as auxiliary data for the carbonate equilibria, is dealt with in a manner consistent with the most recent NEA TDB recommendations (Guillaumont *et al.*, 2003).

**Table 3.4: Illustrative example – parameter set**

| TSM | 1 site 2 pK DLM | | | |
|---|---|---|---|---|
| Quantity | Value | EDF | 1st EDF parameter | 2nd EDF parameter |
| SSD / nm$^{-2}$ | 2.31 | Fixed | | |
| pK$_1$ | 7.23 | Normal | 0.40 | |
| pK$_2$ | 9.49 | Normal | 0.44 | |
| $\log K_{=FeO-NpO_2}$ | -2.61 | Normal | 0.21 | |
| (reaction) | $> Fe - OH + NpO_2^+ \Leftrightarrow > Fe - O - NpO_2 + H^+$ | | | |
| $\log K_{=FeO-COO^-}$ | -4.57 | Normal | 0.18 | |
| (reaction) | $> Fe - OH + H_2CO_3 \Leftrightarrow > Fe - O - COO^- + H_2O + H^+$ | | | |
| $\log K_{=FeO-COOH}$ | 3.64 | Normal | 0.28 | |
| (reaction) | $> Fe - OH + H_2CO_3 \Leftrightarrow > Fe - O - COOH + H_2O$ | | | |
| $\log K_{=FeO-NpO_2(HCO_3)_2^{2-}}$ | -10.53 | Normal | 0.9 | |
| (reaction) | $> Fe - OH + NpO_2^+ + 2H_2CO_3 \Leftrightarrow > Fe - O - NpO_2(HCO_3)_2^{2-} + 3H^+$ | | | |
| SSA / m$^2$g$^{-1}$ | 22.5 | Fixed | | |
| Scenario | | | | |
| pH | 4..(1)..9 a) | Stepped | | |
| SLR / gL$^{-1}$ | 1..10 | Stepped | | |
| $C_{Np}$ / molL$^{-1}$ | $1.0 \times 10^{-7}$ | Fixed | | |
| $E_H$ / mV | +800 | Fixed | | |
| $p_{CO2}$ / atm | $10^{-3.5}$ | Fixed | | |
| T / °C | 25 | Fixed | | |

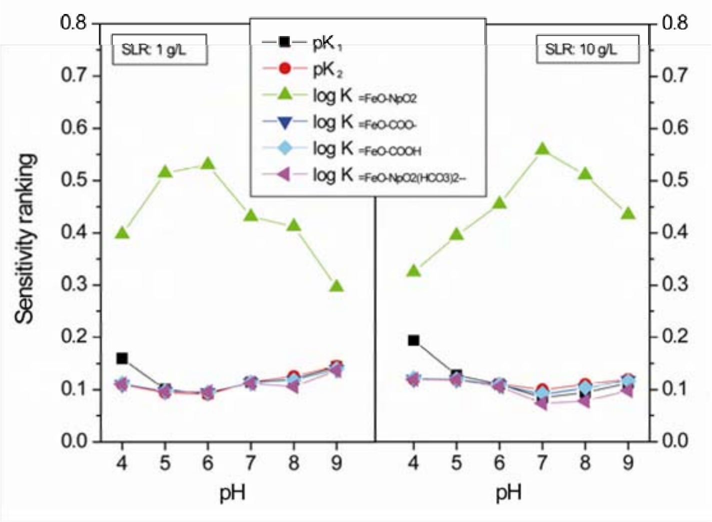
a) A parameter range specified as #1..(#2)..#3 means that the respective parameter is varied between #1 and #3 with a step size of #2. If #2 is not given, calculations are performed only for the two levels at #1 and #3.

### *3.6.3 Identified key TSM and geochemical parameters*

Based on the sensitivity and uncertainty analysis, those parameters that most significantly affect the distribution coefficients ($K_d$) were determined. These parameters may differ depending on RN, sorbent, and major environmental parameters determining the overall geochemical system behaviour. If possible, the main reasons for the original parameter scatter will be discussed below, to support strategies to reduce these uncertainties.

The SA computations were performed on six different pH levels and for two different values for the solid-liquid ratio (SLR) to account for the geochemical variability of these parameters. Figure 3.7 summarised the ranking of the various input parameters as a function of the pH. While the absolute value of the sensitivity ranking varies with pH and SLR, in all cases the stability constant for the surface complex >FeO-NpO$_2$ is the most sensitive input parameter. Even at the highest pH value, the log K for the ternary complex $> FeO - NpO_2(HCO_3)_3^{2-}$ is only second in ranking, despite its rather large uncertainty compared to the other stability constants in this test case.

**Figure 3.7: Normalised ranking of the sensitivity of input parameters as a function of pH, for two different solid-liquid ratios**



### 3.6.4 *Effects of key TSM or geochemical parameter uncertainties*

In this section, the effects of the given uncertainties (i.e. the propagation of errors) in key TSM or geochemical parameters on the calculated log $K_d$ values are investigated. The respective error in $K_d$ is roughly between 16% and 38% of the value itself for all computed combinations of pH and solid-liquid ratio (Table 3.5). Obviously, the associated uncertainties of the six varied input parameters (cf. Table 3.4) are rather high. Having identified the log K for the formation of =FeO-$NpO_2$ (see previous section) as being the most critical parameter, further efforts should be targeted towards a more precise determination of that parameter to reduce the uncertainty in $K_d$ most efficiently.

**Table 3.5: $K_d$ distributions (logarithmic) of Np (mean value and uncertainties) as a function of pH and solid-liquid ratio (SLR)**

| pH | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|
| SLR in g/L | 1 | | | | | |
| Mean log $K_d$ in L/kg | -0.52 | 0.89 | 2.07 | 3.15 | 4.08 | 3.69 |
| Log $K_d$ uncertainty in L/kg | 0.14 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 |
| SLR in g/L | 10 | | | | | |
| Mean log $K_d$ in L/kg | -0.56 | 0.89 | 2.09 | 3.17 | 4.11 | 3.73 |
| Log $K_d$ uncertainty in L/kg | 0.13 | 0.10 | 0.09 | 0.08 | 0.08 | 0.08 |

### 3.6.5 *Synthesis of results and discussion of relevance*

This summary section analyses the relevance of the key TSM parameters with respect to model performance. The test cases investigated in detail during the compilation of this document are primarily illustrative examples of the potential of sensitivity analysis and uncertainty analysis in the context of sorption. Despite the limited amount of parameter variation that could be explored within this project, several conclusions can be drawn.

Most striking is the finding that the stability constant for the formation of the surface complex is consistently the most sensitive parameter. Though this has been assumed before, it has not been previously proven numerically for a broad variety of geochemical systems. In connection with this result, it was demonstrated here that pK values (i.e. surface acidity constants) are not sensitive parameters. Thus, a parameter transfer between data sets derived for the same chemical system but fitted to different EDL representations (namely CCM, DLM, TLM or NEM) seems not to be critical, although sacrificing internal consistency to a certain degree. This generalises the findings of Richter *et al.* (2005b). To probe if these conclusions can be applied to the wide variety of systems encountered in geochemical and reactive transport modelling for PA, further numerical tests would be necessary.

Furthermore, it can be generalised that the variability in geochemical conditions is at least equally important for the overall $K_d$ uncertainty as uncertainties in model parameters. Thus, it is strongly recommended to perform specific SA and UA computations for site-dependent scenarios. Of the various geochemical parameters, pH turns out to be the most sensitive. Next in order of importance is the redox potential (at least for those systems where the ligand can occur in different oxidation states) as this may change the aqueous speciation and subsequently surface species equilibria to be considered. In third position comes the concentration of the contaminant and the solid-liquid ratio. These two parameters are (of course) related to each other, as they define the ratio between the amount of surface binding sites and the amount of dissolved ligand.

It could also be demonstrated that parameter correlation matrices can be very helpful for reducing the $K_d$ uncertainty, but they may also improve the sensitivity ranking for the various input parameters, and even change the actual value of a computed $K_d$. Thus the authors encourage the derivation and subsequent application of respective correlation matrices. Often they are not directly available, thus some robust estimates may serve as a rapid approach. For example, a negative correlation between the two protolysis constants within 2pK TSM applications can be assumed, as these parameters cannot vary independently but must be symmetric to the point of zero charge: $(pK_1 + pK_2) / 2 = PZC$.

The relative error derived for $K_d$ values by applying a TSM has to be compared with the spread of the underlying sorption data. It is also illustrative to consider the (sometimes very large) range of $K_d$ values for a given system documented in databases such as the EPA or JAEA sorption databases (Wilhelm and Beam, 1999; JAEA, 2008a; Suyama and Sasamoto, 2004). Within the overall framework of uncertainty in $K_d$, the application of SA and UA can provide errors that are statistically meaningful.

It is significant that these statistical techniques provide numerical estimates of likely uncertainties in $K_d$ values derived from TSMs. However, the most important conclusion is that the approach improves basic process understanding and allows a ranking of influential parameters, and thereby enables further optimisation steps to be undertaken.

A comprehensive sensitivity and uncertainty analysis provides various benefits, enabling:

- scoping calculations to assess the effect of various hypothetical scenarios on $K_d$ values;
- improved choice of conditions and procedures for sorption experiments focused on the most sensitive input parameters for TSM applications, leading to more efficient use of resources;
- estimation of applicability limits for $K_d$ values extrapolated beyond the original range of experimental conditions, and checking of interpolations;
- underpinning the paradigm of conservatism to quantify errors and thereby avoid over-conservatism;
- identification of the most sensitive parameters within a TSM, which, based on the cases investigated so far, are the stability constants for surface complexes;
- assessment of the importance of various geochemical parameters, among which the pH value typically influences RN sorption to the greatest extent.

# 4. Approaches for applying TSMs to intact and complex materials

## 4.1 Introduction

The previous chapters introduced the TSM approach and described the key TSM parameters, their interrelations and methods for their estimation for simplified laboratory systems. However, while these systems are useful for exploring trends of radionuclide sorption and for demonstrating various aspects of system understanding, the value of TSMs in the context of radioactive waste disposal is tied to their ability to interpret and predict radionuclide sorption by "real" or intact materials having a greater degree of chemical and/or physical complexity and associated uncertainties.

The present chapter is concerned with the issues arising when TSMs are developed for, and applied to, the complex and/or intact "real world" systems that are of specific interest to radioactive waste disposal. These include different types of natural host rock materials, as well as engineered clay barriers that are expected to be employed in various repository concepts.

As will be discussed in more detail, the implications of the greater complexity of real systems with regard to sorption modelling are twofold, affecting both the parameterisation as well as the application of TSMs:

- The determination of TSM parameters is more complex for nearly all real-world substrates due to the chemical complexity of the solid substrate and/or the corresponding aqueous solution. In some cases, additional challenges are presented by the limited experimental accessibility of the system. A wider range of approaches for the determination of TSM parameters must be considered.
- In the case of typical simple systems, the challenge of sorption modelling (in practical terms) is largely restricted to the determination of all relevant TSM parameters. Once that is achieved, model application is more or less straightforward. On the other hand, for complex systems there are additional, often substrate-specific difficulties of TSM application. For example, there are cases where the main challenge to sorption modelling is the need to justify the application of TSM parameters to the intact materials, even in case of well-calibrated TSMs.

## 4.2 Real substrates (What makes them complex?)

Real substrates relevant in the context of radioactive waste disposal can be defined as the solid phases that host the representative reactive surfaces with regard to the migration pathway of radionuclides in geological and other natural environments. The respective sorption phenomena are of direct relevance for safety analyses of radioactive waste disposal systems and related safety cases. As will be explained, the various substrates of interest in the context of radioactive waste disposal pose entirely different problems and require different modelling approaches.

In the present context, the following types of intact solid materials are seen as most relevant on the basis of the strategies of many countries for future disposal of radioactive waste and for the remediation of existing radioactive environmental contamination (ANDRA, 2005; ONDRAF/NIRAS 2001; JAEA, 2000; NAGRA, 2002; SKB, 2006; USDOE, 2008):[1]

- compacted clays in argillaceous and other sedimentary host rock formations as well as in engineered barriers;
- crystalline rock environments, including the bulk rock matrix as well as fractures with secondary minerals;
- near-surface sediments typically characterised by a high degree of chemical complexity.

A detailed discussion of these substrates and their main features regarding radionuclide sorption is given in Sections 4.4 to 4.6 below.

From the viewpoint of sorption modelling, these substrates are significantly more complex than the laboratory systems discussed in Chapters 2 and 3. Depending on the substrate and geological setting, the increase in complexity may arise from one or more of the following typical features:

- complex mineralogy;
- complex solution chemistry;
- intact/compacted state.

The challenges in terms of determining TSM parameters and applying models that arise from these features are addressed below. A schematic illustration is given in Figure 4.1.

**Complex mineralogy:** In case of most real substrates, the greater complexity relative to simplified laboratory systems means that the substrate likely contains a greater number of solid phases. Simplified or model substrates typically comprise only one solid phase; in a few cases, binary systems (involving two different sorbing solids) have been used. In contrast, real substrates typically consist of many solid phases. In terms of defining the values and the exact meaning of TSM parameters, the presence of multiple solids has several possible implications:

- Most fundamentally, it implies the presence of several types of surface sites.
- In some simple cases, sorption is dominated by one component (e.g. smectite clays in the case of bentonite, see further below).
- In most cases, more than one, or all, of the components making up the substrate contribute to sorption. Therefore a TSM either:
  - needs to consider all relevant surface site types, allowing calculating sorption by adding up the contributions by the individual sites (component additivity approach, Davis *et al.*, 1998, see Section 4.3.2 for details), or
  - has to approximate the overall effect of the various surface site types by lumping their behaviour into a small number (possibly one or two) of generic sites (generalised composite approach, Davis *et al.*, 1998, see Section 4.3.2 for details).

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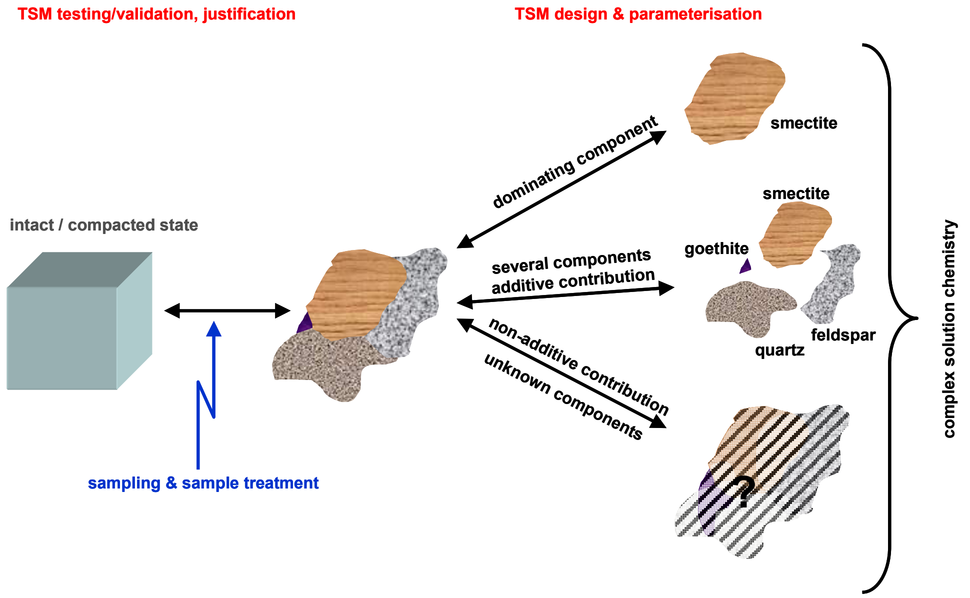
[1] For repositories in evaporites, e.g. salt domes, radionuclide retention by salt rocks is usually not considered in the long-term safety assessment, because of the very low sorption of radionuclides on salt minerals. Safety cases (e.g. in Germany) are much more based on showing the safe containment of the waste in the salt rock formation (demonstrating the integrity of the geotechnical and geological barriers and as a result an insignificant flow of solution and radionuclides out of the host formation), rather than on the retention of radionuclides.

- Depending on the complexity of the substrate, and on the reactivity of the individual solids, it may not be possible to identify all or any of the components determining sorption.
- An additional and significant complication arises when the contributions by the different solids are not additive or simply competitive. This means that the contribution to sorption of the individual solids cannot be modelled by combining TSMs for the individual components. Non-additivity may arise from electrostatic interactions among different types of surfaces that are in close proximity, modification of surfaces by mineral coatings, as well as other effects that are not completely understood. Presumably, a frequent reason behind an apparent non-additivity is the neglect of the influence of sorbing species (aqueous Al- and silica-species, etc.) originating from the dissolution of various mineral phases.

**Figure 4.1: Illustration of various aspects of complexity using a hypothetical substrate**



**Complex solution chemistry:** Almost invariably, real-world systems are characterised by a complex aqueous chemistry. Typical ground- or pore waters contain a range of major cations and anions, such as alkali and alkali earth elements, chloride, sulphate, and carbonate. Further relevant ligands such as phosphate, silica and dissolved natural organic substances are also often present.

One of the implications for sorption modelling is that, for any given surface (or type of surface site), radionuclide behaviour must be modelled in the presence of a range of other solution constituents. For the reasons detailed below, this may present a significant challenge to sorption modelling, even in cases where the sorption properties of the solid can be approximated by a single model mineral.

- An adequate description of the aqueous chemistry of the radionuclide of concern in complex solutions is required. Where the solution chemistry is well constrained and a reliable and complete thermodynamic database (TDB) for aqueous radionuclide species is available, this is straightforward. However, this is seldom the case in reality. Where the radionuclide TDB does not contain all relevant species or is not reliable, the application or development of a TSM may fail due to lacking or erroneous aqueous radionuclide species.

- In many situations, some or most of the solution constituents will also be involved in sorption (surface complexation or ion exchange) reactions. This results often in competition between radionuclide and other solution constituents for available sorption sites. Thus, a given radionuclide-TSM needs to be expanded to include the surface equilibria for all relevant competing sorbents (an example is documented in Test Case 4 in NEA, 2005).
- In some cases, a radionuclide bound to a surface complexation site can react further with a dissolved ligand to form a ternary surface complex (Equation 2.28). Such surface species need to be included in a TSM (an example is documented in Test Case 5 in NEA, 2005).
- In addition, the sorption of solution constituents can modify the surface properties of oxide-type surfaces and change their affinity towards radionuclides. This is an area where relatively little experimental data are available, and the significance of these effects is not clear.

**Intact/compacted state:** The degree to which the intact or compacted state of rocks or other natural materials presents a complicating factor in terms of sorption modelling will depend on the type of substrate. Important issues for all substrates are heterogeneity and often limited accessibility of the solid material. While these have no influence on sorption modelling *per se*, they are extremely important with respect to calibrating TSMs and defining the boundary conditions for model application:

- As pointed out in Chapter 1, the present report is concerned with the application of TSMs to representative volume elements (RVE). Within such a domain, heterogeneity is assumed to be small enough that a constant (average) solid composition can be used. Methods of handling spatial and temporal heterogeneity (meshing, scenario-specific $K_d$ values, reactive transport modelling) are beyond the scope of this report.
- Heterogeneity and ability to recover representative samples of the solid material needs to be considered when representative samples of the solid substrate and of the pore water are to be obtained for sorption experiments. Further, due to the limited experimental accessibility of many intact substrates, there is a lack of sorption data that can be used for TSM calibration and testing. Challenges related to heterogeneity and accessibility differ strongly among the various substrates and are discussed in more detail in Sections 4.4 to 4.6.
- Further important aspects, which are outside the scope of sorption modelling, include issues such as the estimation of the relative amount of flow-wetted surface available for sorption.

An important feature specific to compacted clays is the influence of the permanent structural charge on the distribution of charged solution species (i.e. effective concentrations or activities) as a function of pore size. On the other hand, the chemical composition of the substrate does not change significantly when moving from simple laboratory to real systems. This is discussed in more detail in Section 4.5. In terms of sorption modelling, the challenge lies in:

- accounting for the effects of compaction (electrostatic effects due to closely approaching surfaces) and/or justifying the use of TSM parameters determined in disperse systems;
- the non-accessibility for representative pore water sampling, which needs to be compensated by exchange experiments and detailed geochemical (including ion exchange) modelling.

In case of crystalline rocks, two different situations need to be considered, according to their specific environment:

- The complex mineral assembly typically making up the infill of fractures can be considered as a case of chemically complex material (see above).
- In the case of the crystalline rock matrix, the main challenge of sorption modelling appears to be the acquisition of relevant and reliable experimental sorption data (due to inaccessibility of surfaces in intact rock, lack of sorption data in non-crushed systems, and absence of consensus on methods for testing sorption on intact solids).

The higher complexity of real substrates in comparison to simple systems generally can be attributed to one or more of the following features:

- Complex mineralogy: Real substrates often are composed of several solid phases and expose a larger number of surfaces and site types. Contributions by the different solids may not be additive.
- Complex solution chemistry: Pore solutions in contact with real substrates nearly always have a complex composition, which typically affects not only the aqueous radionuclide speciation but also the surface chemistry of sorbing solids.
- Intact/compacted state: While not directly influencing sorption, the acquisition of data on sorption and geochemistry for such materials is often made difficult by the limited accessibility to representative samples and heterogeneity. In the narrow pores of clays, electrostatic effects need to be considered.

## 4.3 Determination and estimation of TSM parameters in real systems

### 4.3.1 *Overview of aspects specific to real substrates*

The fundamentals of determining and estimating the required model parameters for a TSM for simple systems were reviewed and discussed in Chapter 3, and related recommendations were given. This chapter will not repeat the material presented earlier, but focuses on the additional challenges encountered when TSM parameters need to be determined for real systems.

For better overview, this chapter is oriented along the same sequence of TSM parameterisation described in Chapter 3 (surface sites – surface protolysis – radionuclide surface equilibria – EDL correction terms). Before the determination of individual TSM parameters is addressed in Sections 4.3.4 to 4.3.8, general modelling approaches and sample characterisation are discussed in Sections 4.3.2 and 4.3.3, respectively, because the framework given by these issues largely determines TSM parameterisation.

While a range of approaches is available for measuring or estimating the key properties of complex substrates, the suggestions given in this chapter should be viewed as a basis for a suite of characterisation options.

The discussion in Section 4.2 indicates that many of the characteristics of complex systems that need to be represented in a TSM are difficult to constrain, due to various possible reasons (such as inherent complexity, limited experimental accessibility). This has several important implications for sorption modelling and requires that in comparison to typical laboratory systems (simplified mineralogy and solution chemistry, disperse suspensions), TSM parameterisation must be placed within a broader framework:

- Due to the complexity of real systems, TSMs and the associated model parameters often have to be based (fully or partly) on an approximated or simplified representation of the systems of concern. For modelling purposes, the system complexity must be reduced to a level where all processes influencing sorption can either be parameterised within the framework of a TSM or can be neglected.

- Depending on the modelling approach and on the specific system, the parameterisation of a TSM will, to some degree, depend on data from simplified laboratory systems, as will be discussed in more detail for selected substrates (Sections 4.4 to 4.6). Therefore, modelling choices and selected parameters for the intact substrate must be justified with scientific arguments in order to be defensible.
- A successful and transparent TSM development will critically depend on an adequate understanding of the actual *in situ* geochemical conditions of a system and of their variability. Such an understanding often can be achieved only through detailed geochemical modelling.
- As mentioned in Section 4.2, careful attention has to be given to representative sampling of the substrate in question to allow appropriate characterisation and experimentation.

The complexity of real-world systems has important implications for sorption modelling:

- TSMs have to be based on simplified representations of the complex reality.
- TSM development will critically depend on an adequate understanding and constraint of the actual geochemical conditions.
- Sampling and characterisation of solid and aqueous phase of real systems need sufficient attention to ensure that they are adequate and representative.
- Use of data from simplified systems for modelling sorption in real substrates needs to be justified.

### *4.3.2 Modelling sorption in mineral assemblages: component additivity and generalised composite approach*

For the application of TSM models to real substrates consisting of an assemblage of various minerals, two major alternative approaches have emerged (Davis *et al.*, 1998; NEA, 2005):

- component additivity (CA) approach;
- generalised composite (GC) approach.

The most direct passage from the TSM modelling approaches for individual minerals (described in the foregoing sections) to analogous approaches applicable to mineral assemblages is to consider a substrate that is composed of a mixture of identifiable minerals. In this case, surface chemical reactions are known from independent studies of each mineral component (Landry *et al.*, 2009; Davis *et al.*, 2004a, b; Arnold *et al.*, 2001). These single-mineral component TSMs can be combined in an additive fashion according to the measurement or estimate of the relative amounts or surface area of each mineral (i.e. site concentration of each component) present in the substrate. Hence the term component additivity (CA) for this modelling approach (Davis *et al.*, 1998; NEA, 2005) arose. Adsorption by the mixture of mineral components can then be predicted in an equilibrium calculation, without any fitting of experimental data for the mixture (Honeyman, 1984).

CA model predictions are greatly simplified when it can be assumed that one mineral component dominates adsorption (Zhang *et al.*, 2009; Davis *et al.*, 2004a; Payne *et al.*, 2004; Barnett *et al.*, 2002; Schmeide *et al.*, 2000). This allows a straightforward equilibrium calculation if the exposed surface area of that mineral component in the soil or sediment can be estimated. This approach is particularly successful in case of clays and clay rocks (see the examples given in Section 4.5 and e.g. Maes *et al.*, 2008).

However, as pointed out above, it is often not possible to identify all (sorbing) solids in real substrates, or to ascertain whether the different solids in the mineral assemblage retain their original surface chemical properties. This has led to the development of the generalised composite (GC) approach (Davis *et al.*, 1998; NEA, 2005) wherein the surface of the mineral assemblage is considered to be too complex to be quantified in terms of the contributions of individual phases to adsorption and/or that the contribution of individual components is not simply additive. Such complexity is caused, in part, by the difficulties in quantifying the electrical field and proportions of surface functional groups at the mineral-water interface in mixtures of (partly) amorphous mineral phases and associated surface coatings.

In such cases, adsorption on the whole substrate can often be described by mass laws written with generic surface functional groups. The stoichiometries and formation constants for each mass law are determined by fitting experimental sorption data (*macroscopic* dependence of adsorption as a function of pH and other relevant conditions) for the mineral assemblage as a whole (Hyun *et al.*, 2009; Bond *et al.*, 2008; Davis *et al.*, 2004b; Payne *et al.*, 2004). The GC modelling approach has generally been applied using a non-electrostatic model (NEM), which considers surface equilibria strictly as chemical reactions without explicit correction for electrostatic attraction or repulsion (Davis *et al.*, 1998, 2002; Kent *et al.*, 2000; Westall *et al.*, 1998; van Benschoten *et al.*, 1998). Because of the exclusion of electrical double layer terms, the mass action equations are not expected to provide accurate representations of the stoichiometry of the reactions *at the molecular scale*. However, the surface reactions can still be coupled with aqueous complexation reactions to provide TSM simulations of macroscopic adsorption as a function of aqueous chemical conditions.

Apart from these differences between the GC and CA approaches, they are very similar with respect to their underlying scientific basis. The following concepts form the basic tenets of both GC and CA modelling approaches (Davis *et al.*, 1998):

1) Mineral surfaces are host to chemical functional groups that can react with dissolved solutes to form inner- or outer-sphere surface complexes (co-ordinative complexes or ion pairs) in a manner analogous to aqueous complexation reactions in homogeneous solutions. Permanently charged but chemically relatively inert surfaces occur on layer silicates and lead to ion exchange.

2) The equilibria of surface complexation and ionisation reactions can be described via mass law equations, either with or without correction factors applied for electrostatic attraction to or repulsion from the surface. Ion exchange can be modelled with classical exchange equilibria.

3) The apparent binding constants determined for the mass law equations of surface complexation and ionisation reactions are semi-empirical parameters related to thermodynamic constants via activity coefficients for surface species. Similarly, empirical selectivity coefficients can be converted to thermodynamic constants using the mole- or equivalent-fraction formalisms.

The differences among the CA and GC approaches lie primarily in the manner in which a TSM is calibrated, and assumptions about various model parameters (in particular, whether the contributions of the various mineral phases to sorption and electrostatic fields can be considered as additive). Traditionally, CA models have often been applied using mass laws with electrostatic correction factors, while GC models have usually not used these factors (i.e. are NEM models).

It follows from the above that the values of TSM parameters (site densities; protolysis and radionuclide binding constants and related reaction stoichiometry; EDL term, if any) may vary as a function of the chosen modelling approach. However, the distribution of TSM parameter values for real substrates often falls within the range of values found for TSMs calibrated for single minerals.

GC and CA modelling approaches are end members in a spectrum of TSM approaches that can be used for complex materials. Indeed, many of the TSMs developed recently for complex materials combine both GC and CA aspects.

Both CA and GC models may: 1) be coupled to the same critically reviewed aqueous thermodynamic data, 2) use spectroscopic data to constrain and/or determine surface complex chemical composition and stoichiometry, and 3) use the same mass laws and surface species.

The determination of TSM parameters for real substrates will depend on whether a GC or CA approach is being followed:

- In a CA approach, TSM parameters need to be defined for the models associated with the individual mineral components. Where adequate literature data are available, it is most efficient to take parameters directly from compilations or from the original literature. If this is not possible, parameters can be determined based on experiments with mineral separates or representative model minerals, or by re-interpreting published experimental sorption data.
- In a GC approach, TSM parameters have to be defined for the whole substrate and must be based on experimental data obtained directly for representative samples of the substrate.

### *4.3.3 Sensitivity analysis for complex systems: CA vs. GC*

In order to explore the capabilities of sensitivity analysis when investigating complex systems, an analysis of two alternative modeling approaches was carried out, namely the GC and CA approaches (as described in the previous section). Test Case 7 ($Co^{II}$ sorption on soil, based on the experiments reported by Zachara *et al*., 1994) taken from the NEA Sorption Project Phase II report (NEA, 2005) was identified as a suitable test case. There, $NaClO_4$ of various concentrations is specified as background electrolyte, with nitrogen as the gas phase. To keep the system simple, all computations were performed for an ionic strength of 0.1 mol/L $NaClO_4$ and a solid-liquid-ratio of 1 g/L. As with all the previous illustrative calculations in this report, a reference SSD of 2.31 $nm^{-2}$ was used for all minerals. The aqueous Co(II) speciation was handled identically for both approaches, the respective complexation constants are those published by Markich and Brown (1999). Similarly to the previous sensitivity analysis (Section 3.6.1) the general objective was to identify the model components to which the calculated $K_d$ value for $Co^{2+}$ was the most sensitive, and to compare this between the GC and CA approaches.

To be consistent with the approach used for the illustrations in Section 3.6, the ***CA model*** for the present purpose was also built in a purely predictive fashion from literature data (instead of adopting one of the CA models developed for phase II, which used the provided system-specific information). The CA model was built based on the mineralogical composition of the soil (BET surface areas given in parentheses) with 70% kaolinite (11.4 $m^2/g$), 10% gibbsite (4 $m^2/g$), 6% goethite (186 $m^2/g$) and 14% 2-1 layer silicates (68.2 $m^2/g$) following Zachara *et al*. (1994). Here, montmorillonite is used as typical representative for the latter minerals. The TSM parameters for the Co interactions with kaolinite, gibbsite, goethite, and montmorillonite mineral surfaces are summarised in Table 4.1 (upper), details on how they were derived from a literature survey are found in Brendler *et al.* (2011). The CCM was selected to represent the EDL, with a capacitance value C = 2.1 ± 0.2 F/m² used uniformly for all minerals. The sensitivity analysis covered the specific surface areas of two major soil components (equivalent to a 10% uncertainty in mineral composition) and log K values of the six selected surface species formations, i.e. eight variable input parameters in total.

**Table 4.1: Parameter set for test case of the component additivity (CA) approach (upper) and for the test case of the generalised composite (GC) approach (lower)**

| Mineral | Site conc. (in mol/L) | $pK_1$ | $pK_2$ | Surface species | Log K |
|---|---|---|---|---|---|
| Kaolinite (Si) | $1.53\times10^{-5}$ | -0.77 | 7.58 | $>Si\text{-}O\text{-}Co^+$ | -7.06 |
| Kaolinite (Al) | $1.53\times10^{-5}$ | 3.64 | 8.36 | $(>Al\text{-}O)_2\text{-}Co$ | -7.03 |
| Gibbsite | $1.53\times10^{-6}$ | 6.93 | 10.97 | $>Al\text{-}O\text{-}CoOH$ | -9.92 |
| Goethite | $4.28\times10^{-5}$ | 7.04 | 9.41 | $>Fe\text{-}O\text{-}Co^+$ | -4.11 |
| | | | | $>Fe\text{-}O\text{-}CoOH$ | -12.25 |
| Montmorillonite | $3.66\times10^{-5}$ | 5.73 | 8.66 | $X(s)\text{-}O\text{-}Co^+$ | -0.90 |

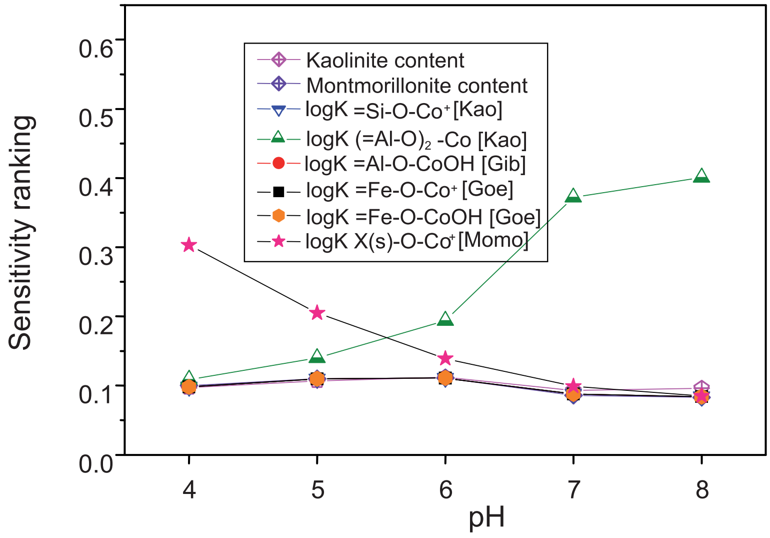
| Generalised reaction | Log K |
|---|---|
| $>S\text{-}OH+Co^{2+} \Leftrightarrow >S\text{-}O\text{-}Co^{+}+H^{+}$ | -3.47 ± 0.40 |
| $>S\text{-}OH+ Co^{2+}+H_2O\ >S\text{-}O\text{-}CoOH + 2\ H^{+}$ | -10.69 ± 0.40 |
| $XH+Na^{+} \Leftrightarrow XNa+H^{+}$ | 3.76 ± 0.40 |
| $2\ XNa+ Co^{2+} \Leftrightarrow (X)_2Co+ 2\ Na^{+}$ | 0.633 ± 0.40 |

For the ***GC model***, an overall specific surface area of 68.2 m²/g was used (Zachara *et al.*, 1994), giving a binding site concentration of $2.616\times10^{-4}$ mol/L. The generic surface reactions follow an approach successfully applied within the NEA Sorption Project Phase II (GC-3 of the test case 7, see NEA, 2005). It provides the minimum set of reactions required to model the system [see Table 4.1(lower) for reactions and log K values] and thus best exploits the advantages of the GC approach. The model is based on one generic surface binding site >S-OH (with a non-electrostatic EDL) and a cation exchange site XH. The cation exchange capacity CEC was determined to be 0.0596 mol/kg, yielding a site concentration [XNa] for ion exchange of $5.96\times10^{-5}$ mol/L. The generic reactions, which subsume a variety of real surface reactions, were assigned an uncertainty of 0.4 [Table 4.1(lower)], whereas in analogy to the CA version the specific surface area (and the CEC) was assigned an uncertainty of 10%. Thus, a total of six variable input parameters were examined during the sensitivity analysis.

In the case of the CA approach, the most sensitive TSM input parameter (see Figure 4.2) turned out to be the formation constant for the ion exchange associated with the montmorillonite component for pH values below 5 – which is an expected result as ion exchange is typically the dominant process in complex materials at lower pH. At higher pH values the computed $K_d$ is most sensitive to the formation of the bidentate Co-surface complex on the aluminol sites of the kaolinite component.

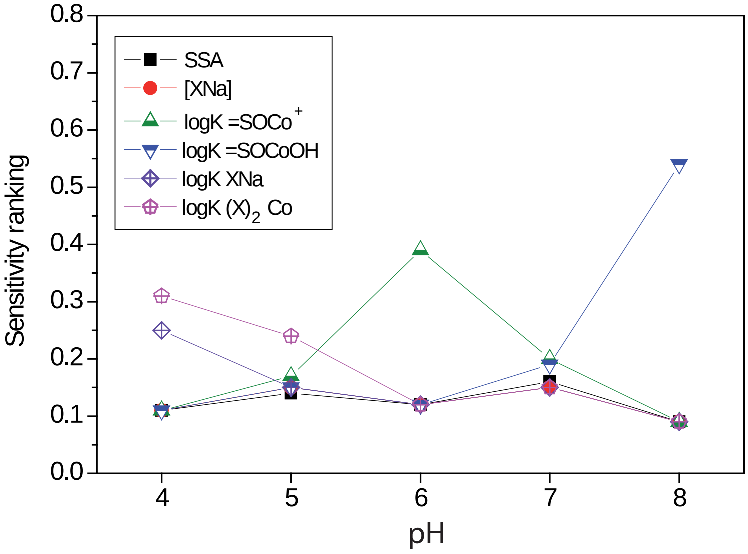
**Figure 4.2: Normalised ranking of the sensitivity of input parameters for the CA approach test case as a function of pH**

Here the minerals are abbreviated as follows: Kao (kaolinite), Gib (Gibbsite), Goe (Goethite) and Momo (Montmorillonite)



The sensitivity analysis for the GC case showed that a sequence of parameters governs the overall sensitivity in log $K_d$ with increasing pH. Whereas at acidic pH values the ion exchange reaction exhibits the strongest sensitivity with respect to the distribution coefficient of $Co^{2+}$, this role is taken over by the generic deprotonated surface complex of $Co^{2+}$ in the neutral pH region, and finally by the hydrolysed complex for pH values of 8 and beyond (see Figure 4.3) for illustration. The high sensitivity of the ion exchange reaction and of a deprotonated surface complex is thus similar in both (CA and GC) approaches whereas the second surface complex governing the GC $K_d$ computation at higher pH values is not matched by a respective surface species in the CA framework.

**Figure 4.3: Normalised ranking of the sensitivity of input parameters for the GC approach test case as a function of pH**



The identification of very few relevant surface reactions by means of sensitivity analysis for the CA approach is also an argument for the validity of GC models with a restricted set of generic surface sites and species. Actually, sensitivity analysis starting from a scoping-level CA model (using e.g. published parameters for model minerals rather than fitting models to data for mineral separates) may even serve as a building block to derive sensible GC setups, thereby linking CA and GC.

When comparing magnitude and total uncertainty of the various $K_d$ values computed from the two different approaches (Table 4.2) the present CA approach based on model minerals generates higher $K_d$ values than the GC calibrated to the specific experimental data (up to two orders of magnitude different). It should be pointed out that the GC and CA approaches developed in phase II for this test case (TC7, see Part II, Chapter 5 and related pages in Appendix I of NEA 2005) were in good agreement, and the CA models did not tend to over/underestimate the data more systematically than GC models. On the other hand, similar tendencies of over-prediction by CA models were observed during the NEA Sorption Project Phase II in the case of the Koongarra weathered schist (TC5, see Part II, Chapter 4.4 of NEA 2005). The main difference between the two test cases is that the information available for the soil case (TC7) allowed a more "educated" CA approach, whereas the CA models in the Koongarra case (TC5) relied more on a-priori assumptions. In fact, most over-predictions can be traced back to inappropriate choices of model mineral sorbents (i.e. the CA models were constructed from unsuitable component models). It appears that estimating $K_d$ by utilising solely a CA approach based on *a priori* assumptions (purely predictive modelling) can lead to overly high, therefore non conservative, $K_d$ values. This clearly indicates that CA approaches should be supported by system-specific sorption data.

**Table 4.2: $K_d$ distributions (logarithmic) of Co (mean value and uncertainties) as a function of pH for both the GC and the CA approach**

| pH | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|
| General composite (GC) | | | | | |
| Mean log $K_d$ in L/kg | 0.44 | 1.20 | 1.90 | 3.01 | 4.60 |
| Log $K_d$ uncertainty in L/kg | 0.08 | 0.07 | 0.06 | 0.06 | 0.07 |
| Component additivity (CA) | | | | | |
| Mean log $K_d$ in L/kg | -0.22 | 1.60 | 3.28 | 5.01 | 6.67 |
| Log $K_d$ uncertainty in L/kg | 0.06 | 0.06 | 0.06 | 0.07 | 0.05 |

$K_d$ values computed using the CA approach based on model minerals tend to generate higher $K_d$ values than the GC calibrated to the specific experimental data (up to two orders of magnitude different). This indicates that estimating $K_d$ based solely on the CA approach can lead to overly high, therefore non conservative, $K_d$ values.

### 4.3.4 *Sample characterisation*

#### 4.3.4.1 *Environmental variability and representative sampling*

The present discussion regarding TSM application to complex substrates focuses on RN sorption on samples that constitute a representative volume element of the subsurface material in question (i.e. complexity is only considered as far as chemical complexity within such a sample is concerned). Treatment of additional complexity arising from (medium- to large-scale) spatial heterogeneity is not within the present scope.

Nevertheless, these issues are briefly discussed below, as they are an integral part of obtaining appropriate samples for sorption experiments and TSM development.

In practice, one of the most difficult and uncertain aspects of TSM development for a complex system is the collection of representative and appropriate samples of the materials to be characterised. In this context, it is important to keep in mind that sampling and characterisation need to be representative of the potential pathways for radionuclide migration. This ultimately determines the range of materials and chemical conditions that need to be considered.

Decisions on the collection, treatment, and handling of samples will depend to a great extent on site-specific characteristics, and typically require careful evaluation of hydrogeological and (bio)geochemical aspects. An overview of important issues is given below, a more detailed substrate-specific discussion is provided in Sections 4.4 to 4.6.

- Compact/intact materials typically allow only very limited access to the substrate in question (i.e. to mineral surfaces and the aqueous phase in pore spaces relevant for RN migration). How, and the extent to which, this affects sample characterisation depends strongly on the specific substrate.
    - For example, the characterisation of the solid substrate is relatively straightforward in the case of bentonite, because it can be used in powdered form for experiments and the compacted material can be assumed to be homogeneous. On the other hand, the solution composition in the compacted state needs to be constrained by geochemical modelling, because the solution composition in the pore space is not accessible by direct measurements.
    - Fractured granitic rocks potentially expose different surfaces to radionuclides. Due to the artefacts often introduced by crushing solid rock (see Section 4.6), it is difficult to demonstrate that the material used for characterisation and experimentation is indeed representative for the potential transport pathways.
- Whenever the sorption behaviour of radionuclides (or other dissolved substances) in a geological formation is to be described, it is important to adapt sampling to the heterogeneity of this formation. As indicated in Chapter 1, the present report is concerned only with modelling sorption within a representative volume element. When a formation shows significant heterogeneity even within small spatial units, it needs to be decided whether a TSM should be derived for a single composite of samples collected at various locations or whether individual TSMs must be derived even for small sub-domains.
- Organic materials form an important component of many soils, sediments and clayrocks, a large proportion of which are humic substances comprising a variety of compounds derived from the degradation of natural organic matter. Humic materials can have a significant impact on radionuclide sorption. For example, it has been reported that actinide sorption at low pH tends to be enhanced by the presence of humic acids (e.g. Payne *et al.*, 1996). Because the GC approach fits model curves to experimental data using generic surface sites, any organic solid phase binding sites are implicitly included in the model calibration. CA model applications can consider the organic materials as a specific component of the system (e.g. Test Case 7 in NEA, 2005).
- Another key issue is the redox state of the system under investigation:
    - The simplest cases are oxic systems, where solid material and the corresponding aqueous phase can be sampled by drilling or other methods without undue concern about changes caused by exposure to air. In such cases, the sediments can be collected, composited, and either

air-dried or stored cold or frozen in a moist state. Air-drying can cause experimental problems for sediments with a high clay content and leaves a small salt accumulation that needs to be addressed subsequently during experiments.

- The collection and handling of samples from chemically reducing conditions is much more complex. In general it is necessary to transfer such material very quickly after collection into an inert atmosphere for any further processing. Samples can then be preserved by packing in gas impermeable containers and keeping them frozen until use.

#### *4.3.4.2 Solid and aqueous phase characterisation*

This section gives a general overview on the characterisation of the bulk solid and aqueous phase composition. The characterisation of the surface properties of a substrate is discussed in Section 4.3.5, further substrate-specific details are given in Sections 4.4 to 4.6.

*Mineralogical distribution:* The qualitative mineralogy and relative weight percentage of sufficiently crystalline minerals (e.g. quartz and other oxides, feldspars, carbonates, clays) in intact materials can be determined by bulk X-ray diffraction and thin section analysis (conventional optical polariser microscope). The clay mineral fraction should be characterised by X-ray diffraction after separation of the clay-sized fraction by grain separation techniques. Other techniques include XPS spectroscopy, electron spectroscopy, and chemical extractions described below (Davis *et al.*, 2004b; Coston *et al.*, 1995). SEM, FTIR and thermal analysis are also used in some cases.

*Identification of preferential sorbing phases:* TSM predictions are sometimes made by assuming that one mineral component dominates adsorption (Barnett *et al.*, 2002; Waite *et al.*, 2000; Schmeide *et al.*, 2000; Davis *et al.*, 2004a), permitting a straightforward equilibrium calculation if the exposed surface area of that mineral component in the soil or sediment can be quantified. This is a typical approach for clay-dominated substrates, because the surface areas of clays can be estimated and the clay mineral content by mass can be determined. Proof that one mineral component dominates adsorption can be difficult, however, and may have to be justified by multiple lines of qualitative evidence.

*Surface functional groups:* One of the most difficult issues in applying the CA modelling approach to sediments and soils is determining (or estimating) the type and relative abundance of mineral functional groups on the adsorbing surfaces. One method of doing this is to use sequential extractions (Chao and Zhou, 1983; Yanase *et al.*, 1991). Such methods can be used to determine the amounts of amorphous or crystalline oxides which may dominate sorption of some radionuclides. This approach can sometimes be facilitated by isolating quartz grains of the sediment before extraction so that the composition of poorly crystalline mineral coatings can be estimated (Coston *et al.*, 1995; Davis *et al.*, 2004a, b). Determinations of the masses of iron oxide mineral phases in a sediment by extractions are useful, but calculation of site concentrations then requires that the surface area of those phases be known.

*Elemental analysis:* The concentration of total carbon, inorganic carbon and total sulphur can be determined by an element analyser (a detailed description is given by Fernández, 2001). Organic carbon is calculated from the difference between the total carbon and the inorganic carbon, or is determined using a selective extraction technique (e.g. Walkley-Black method).

To develop meaningful sorption data and TSMs for real materials, and to sufficiently constrain the chemical conditions for model applications:

- representative samples of the solid material and corresponding liquid phase should be obtained as much as practicable;
- solid and liquid phase samples should be thoroughly characterised.

### 4.3.5 *Surface site density and surface area*

Knowledge of these parameters is central to all TSM applications. There are several points of general importance that modellers need to be aware of with regard to the definition of values for surface site density (concentration of sorption sites per unit mass or per unit surface area) and surface area:

- The way in which these parameters can be obtained for a real substrate depends on the complexity of the material and whether a CA or GC approach is being followed.
- The surface site density and specific surface area represent basic properties of the substrate which are largely independent of conditions; and they influence the values for protolysis and radionuclide binding constants determined by interpretation of experimental data.
- Surface area is not only an important TSM parameter, but can also be critical for applying a calculated $K_d$ to a field situation. Some types of real substrates contain a range of grain sizes, and TSMs are often developed for the fine fraction (e.g. materials with grain size less than 2 mm) only, while larger grains are not used for experimentation. In such cases, the specific surface area for different fractions of the substrate can be used to calculate surface area-corrected $K_d$ values that are applicable to the field site.

#### *4.3.5.1 Surface site density*

In many situations, the *total site density* of a mixed mineral assemblage is composed of contributions from surface hydroxo groups and cation exchange sites (i.e. the CEC). Depending on the relative abundance of each type of site, measurements of the total site density can be very difficult.

- When all individual minerals can be identified and additive contributions can be assumed (as for a CA approach), the concentration of surface complexation groups and the CEC (see Section 2.3.6) can be determined on mineral separates, assuming that the individual mineral phases can be isolated. An alternative is to use site density values for comparable solids given in the literature (e.g. the RES$^3$T database, Brendler *et al.*, 2003). Great care must be taken in using data from appropriate mineral components, especially in case of amorphous phases such as Fe-(hydr)oxides. Chapter 5.2.3 in NEA (2005) describes an example where modellers overestimated site densities by assuming the presence of HFO and using literature data by Dzombak and Morel (1990) and Waite *et al.*, (1994).
- In cases where the individual minerals and their contribution to sorption cannot be identified, a GC approach must be adopted and sorption site density must be determined or estimated for the substrate as a whole. Available options are further described below.

The total *cation exchange capacity* should be measured when layer silicates (clay minerals, micas) are present (e.g. in weight abundance greater than 1%). The CEC can be measured as in the case of single clay minerals; i.e. by the different methods cited in Section 2.3.6. Due to the presence of accessory minerals and impurities in natural clays, the displaced cation concentrations have to be corrected for contributions from the pore water and dissolution reactions (calcite, dolomite) that occur during the exchange experiment. When cation exchange sites make up only a small fraction of total sites, there may also be a contribution by cations located as outer-sphere complexes at oxide-type surfaces. Determining the CEC of a mineral assemblage may therefore require iterative experimental extractions and ion exchange modelling runs.

In contrast, the density of surface functional groups responsible for surface complexation ("SOH groups") cannot be determined by direct analytical measurements. Methods for determining this parameter for single minerals are described in Chapter 3. Possible approaches for complex mineral assemblages include:

- measurement of maximum metal ion sorption or hydrogen exchangeable density by isotope dilution techniques, assuming that one can saturate all surface sites with either metal ions or exchangeable protons;
- estimating the concentration of total surface functional groups from measurements of the specific surface area, using simplified surface area/site density relationships such as 2.31 sites/nm$^2$ (NEA, 2005; Davis and Kent, 1990);
- fitting the density of surface functional groups together with radionuclide binding constants on the basis of (sufficiently detailed) radionuclide sorption data.

Acid-base titrations could also be used in principle (see Chapter 3), but this is difficult and cannot be recommended in the case of mineral assemblages because of dissolution/precipitation reactions with mineral such as carbonates.

#### *4.3.5.2 Specific surface area*

Typically, a mixed mineral assemblage is characterised by BET analyses of nitrogen or noble gas adsorption. Adjustments may need to be made for samples that contain high abundances of clay minerals, depending on whether a modeller is interested in estimating both the surface area related to surface functional groups as well as the surface area of the basal planes of clay mineral particles (giving rise to ion exchange). Since the permanent structural charge associated with the basal planes is involved in ion exchange only (and is therefore not relevant with regard to surface complexation), the surface area of basal planes needs to be separated from the surface area attributable to the oxide-type edge surfaces, which may be included in surface complexation models. See Section 3.1.1 for a discussion of methods for estimating the specific edge surface area of clay minerals.

In the GC approach, the measured total surface area of a sample is used in a straightforward fashion. For the CA modelling approach, the surface area may also be estimated (instead of, or in addition to, being measured). After the sediment mineralogy is known, an estimate of total surface area and of the distribution of individual mineral surface areas can be made by simply multiplying the bulk weight abundance of various mineral phases with their known surface area and summing up over all mineral components. When the distribution of surface area among different minerals is of interest, additional experimental approaches may also be used, including chemical extractions (NEA, 2005; Davis *et al*., 2004a, b).

For most substrates (except when the presence of layer silicates such as clay and mica minerals can be excluded), both the concentration of surface complexation sites and the CEC have to be determined:

- Analytical CEC measurements are straightforward, whereas different methods need to be evaluated for the determination of the concentration of surface complexation sites.
- In cases when all individual minerals can be identified (CA approach, typical examples see Section 4.5), the component mineral surface areas can be taken from the literature and combined in an additive fashion. Alternatively, surface areas can be determined for mineral separates or model minerals using the methods discussed in Chapter 3.
- For a substrate with greater complexity (GC approach), surface complexation site density can be estimated from the measured specific surface area, evaluated by isotope dilution, or fitted to tracer sorption data.

The specific surface area of a real substrate can be obtained by the same methods that are available for single minerals (see Chapter 3).

### 4.3.6 *Surface protolysis*

In principle, potentiometric surface acid-base titration data can be used to determine the surface proton balance of complex mineral assemblages (Charlet and Sposito, 1987), as is commonly done to determine surface charge on pure, insoluble mineral phases, such as goethite (Lützenkirchen *et al.*, 2002, see also Chapter 3). However, the interpretation of the titration data in the case of complex materials is nearly always complicated, and often made impossible, because the consumption of titrant is often dominated by the dissolution of mineral phases, the release of organic acids, or other adsorption/desorption reactions [e.g. Al(III)]. Alternatively, surface acidity constants can be assumed as "reasonable values" centred around a measured isoelectric point.

Because of these difficulties, protolysis constants are often not directly determined for a complex substrate. Rather, the consideration of protolysis constants in TSMs for real-world materials usually depends on whether a GC or CA modelling approach is being followed.

- For CA models, the protolysis constants are already known for the mineral phases to be considered in the sediment/rock materials (either from experiments with mineral separates or model minerals, from re-interpreting original published titration data, or directly from the literature), and are thus applied in a straightforward manner in the calculations.
- In the GC model, an explicit representation of surface protolysis is not needed, because the proton stoichiometry can be built into the radionuclide surface equilibria and a non-electrostatic (NEM) EDL-model is typically assumed. Indeed, explicitly considering surface protolysis in a GC model would unnecessarily increase the number of adjustable parameters.

As discussed below, these different modelling approaches have important implications for how electrical double layer corrections are considered, usually implicitly in GC models and sometimes explicitly in CA approaches.

### *4.3.7 Radionuclide surface equilibria*

As in case of the protolysis constants (see previous section), the derivation or determination of radionuclide binding constants for real materials depends on the overall modelling approach (GC *vs* CA).

Again, model predictions with the CA approach are based on combining TSMs for single mineral components. The respective radionuclide surface equilibria and corresponding equilibrium constants for the component minerals can be taken from the literature or from compilations such as RES$^3$T (Brendler *et al.*, 2003). In practice, there are several reasons why this approach cannot always be followed, and additional sorption experiments become necessary.

- All sorption-relevant minerals must be identifiable, which is often not the case.
- While protolysis constants are available for most relevant minerals, radionuclide sorption often has been studied for only a few elements. The required literature information may not be available, especially for less-common minerals and elements.
- As discussed in Chapters 2 and 3, TSMs should be internally consistent. However, it is often the case that the protolysis constants for a given mineral are based on a certain site density and EDL parameters, whereas for the selected radionuclide, only log K values based on a different site density and a different EDL model can be found. While scaling methods are available to deal with the different site densities (see Chapter 3), there is no solution available for bringing the different EDL-models to consistency. This type of inconsistency may be acceptable for scoping calculations, but it would be detrimental to a model applied for PA-purposes.
- There may be shortcomings in the available literature data. This issue was identified in Phase II (NEA, 2005) as one of the biggest limitations to further TSM development, since most radionuclide sorption data have been measured primarily for pure minerals in simple/inert 1:1 background electrolytes. On the other hand, radionuclide sorption in real systems will take place in the presence of important ligands and major ions that may sorb and alter surface properties and/or form ternary radionuclide surface complexes. Thus, appropriate component models for a CA approach need to be calibrated in the presence of such major solution constituents. NEA (2005) identifies the lack of relevant component models as a likely reason for observed failures of the CA approach.

These issues are mainly relevant in case of surface complexation. Ion exchange selectivity coefficients with respect to $Na^+$ can normally be found for all major ions and a range of trace elements. Conversion to the preferred representation (e.g. Gaines-Thomas convention) can then be done (see Chapters 2 and 3).

To overcome the obstacles and limitations discussed above, several alternatives are possible:

- Where consistency is an issue, radionuclide binding constants can be determined by fitting the model of choice to original experimental sorption data from the literature (instead of using the published binding constants). See Section 3.1.7.
- When basic information (such as the influence of carbonate or Ca-ions on the sorption of a given radioelement) is lacking, the generation of further data becomes unavoidable. In some cases, LFERs (see Chapter 3) or simple analogy considerations may help to fill data gaps. In other cases, the lacking experimental data can be measured using mineral separates or model minerals. In the latter case, care has to be taken to select appropriate minerals.

Depending on the foreseen use of the TSM, the GC approach can represent a valuable alternative. In this approach, laboratory experiments are conducted with the substrate across the range of relevant chemical conditions. Then, mass law relationships are derived that describe the change in radionuclide adsorption with variations in the aqueous chemical conditions (Davis *et al*., 2004a, b).

- This is done by comparing various plausible surface reaction stoichiometries for the radionuclide under consideration and fitting the experimental data with the fewest number of reactions possible (also see description in Chapter 3).
- The number of surface site types and the number and stoichiometry of surface binding reactions is a practical modelling decision based on the goodness-of-fit of different modelling trials and the acceptable number of adjustable TSM parameters.

In terms of (radionuclide) surface species, GC and CA approaches typically differ for a given model application. In the future, as spectroscopic methods further improve, it may be possible to match model surface species with spectroscopic results. So far, this has only been achieved in a limited number of cases (e.g. Arai *et al*., 2006). Still, spectroscopic results can be used to indicate the presence of a certain type of species, such as ternary surface-RN-carbonato complexes (Bargar *et al*., 2000).

Surface binding constants for a given application may have a significant range of values because of variations in the compositions of complex materials, the spread of literature values for a given sorption reaction on a component mineral, and differences in fundamental model properties such as densities and types of sites or the inclusion or exclusion of coulombic (EDL) terms.

In the CA approach, RN surface equilibria and the related stability constants can in principle be taken from the literature. However, adequate TSMs for mineral components are in many cases not yet available, because RN sorption on single minerals has only been measured in simple electrolytes but not under relevant solution conditions. This indicates a need for system-specific sorption data.

In the GC approach, RN surface equilibria are developed on the basis of sorption experiments conducted with representative substrates for the entire range of relevant chemical conditions.

### *4.3.8 Surface charging behaviour and EDL correction term*

Basic relations between the surface charge of a substrate, its influence on surface protolysis and radionuclide binding constants, and the available correction terms (EDL models) are described in Section 2.3.4. The difficulties in determining the pH-charge behaviour of a mineral assemblage by potentiometric surface titrations is discussed in Section 4.3.6. In some cases, it is possible to measure surface charge using the methods of Charlet and Sposito (1987, 1989). In these methods, the concentrations of counterions in the electrical double layer of the mineral assemblage are measured directly. Because of the principle of electroneutrality, the net surface charge is then known from the measured counterion charge. Even more than in the case of single minerals, there is no best *a priori* method for the selection of an EDL model and the estimation of the required parameters (if any) for a complex substrate.

For illustration, the following examples may be considered:

- When a GC approach is being followed, it is often because the substrate is considered too complex to completely characterise and to perform acid-base titrations, and/or because the behaviour of the whole substrate cannot be approximated sufficiently well by a combination of TSMs for individual components. In such a situation, the acid-base behaviour is typically included directly in the radionuclide equilibria. It then makes little sense to explicitly account for electrostatic effects and a NEM is the natural choice.

- Even when CA approaches are used, most modellers try to minimise the number of adjustable TSM parameters. As shown in Table 3.1, NEM and DLM do not introduce any additional adjustable parameters. Therefore, the acid-base equilibria in the underlying component models are often described using NEM or DLM.
- To be used in a meaningful way, the more sophisticated EDL models require surface chemical information that is generally not available for complex materials. Further, in generalised models (either GC, or CA based on simplified component models) there is normally no convincing argument for using a detailed EDL model. For example, if all possible sorption sites on a clay mineral edge (up to 27 different sites, cf. Tournassat *et al.*, 2004) are approximated using one or two generic SOH sites, it would be consistent with this approach to use no or only a simple EDL term.
- One reason to use a triple-layer type model (TLM) would be to model competition between a relatively weakly sorbing radionuclide, whose surface species likely include outer-sphere complexes (e.g. Se oxo-anions), and other ions of similar charge. Again, it needs to be remembered that the TLM-type model variants require electrolyte ion-specific parameters (Lützenkirchen, 1998), which makes them nearly impossible to calibrate for a complex aqueous solution. Further, such competition can also be modelled by explicitly including it as inner-sphere surface complexes (possibly at the cost of additional fitted parameters).

No *a priori* method exists to select the most adequate EDL model for complex substrates. In view of the complexities of TSMs for such materials, and the challenges in determining their surface charging behaviour, it is reasonable to initially consider EDL models that introduce no adjustable parameters.

## 4.4 TSM application for $K_d$ estimation on chemically complex substrates

Since the original framework of CA and GC models was described (Davis *et al.*, 1998; Honeyman, 1984), there have been numerous applications of each approach to complex mineral assemblages for adsorbing radionuclides. In many cases, the GC and CA modelling approaches were compared in the same report. Most of the CA applications to complex mineral assemblages may be classified as *simplified* CA models (Payne *et al.*, 2006; NEA, 2005; Payne *et al.*, 2004), which recognises that the mineral assemblage was not fully characterised, or that a single mineral component in the mixture was assumed to dominate the adsorptive reactivity. For example, it is often assumed that adsorption in an assemblage is dominated by the iron oxide minerals (see model calculations in Zhang *et al.*, 2009; Payne *et al.*, 2004; Davis *et al.*, 2004a; Barnett *et al.*, 2002; Davis *et al.*, 1998) or by the clay fraction (see examples in Section 4.5). In the following sections, these issues are illustrated through the discussion of case studies.

### 4.4.1 *Uranium(VI) sorption on weathered schist (Koongarra, Australia)*

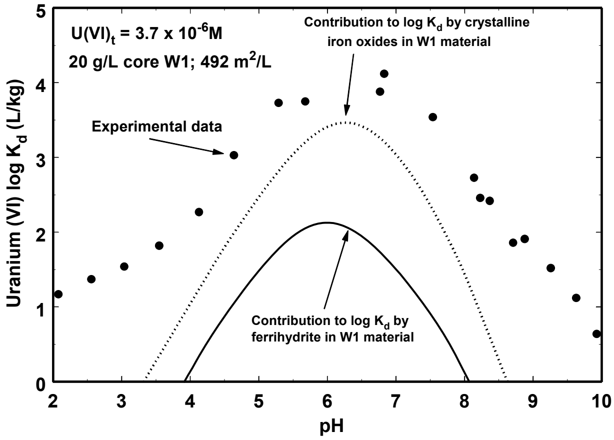
Here we examine the modelling results of Davis *et al.* (2002) to illustrate some points about CA and GC modelling approaches and their comparison. The adsorption data considered are for adsorption of U(VI) on the Koongarra weathered schist, and were used for Test Case 6 in the Phase II Sorption Project (NEA, 2005; Payne *et al.*, 2004). Surface area, mineralogical composition, and labile adsorbed U(VI) were determined for several samples from the Koongarra site (Payne, 1999; Payne and Airey, 2006). High-resolution TEM studies indicated that U present on the surfaces of the schist materials was principally associated with iron oxide phases (Lumpkin *et al.*, 1999). The results of chemical extractions were used by Davis *et al.* (2002) to estimate the abundances of poorly crystalline and crystalline iron oxides present in the weathered schist. Then, using published TSM model parameters for ferrihydrite, goethite, and hematite, predictive surface complexation DLM model calculations for U(VI) adsorption by the iron oxides in the weathered schist were made.

The predicted U(VI) adsorption on the iron oxide components was less than that observed experimentally for the weathered schist (Figure 4.4). Waite *et al.* (2000) made a CA modelling calculation with the assumption that the entire surface area of the weathered schist had U(VI) binding constants and site densities identical to those observed for ferrihydrite. In other words, Waite *et al.* (2000) made the simplifying assumption that all minerals in the schist adsorbed U(VI) in exactly the same way as ferrihydrite. The results yielded an adsorption curve similar in shape to that shown for crystalline iron oxides in Figure 4.4, but with the adsorption edges displaced to lower and higher pH values because of the greater surface area, and with model predictions in reasonably good agreement with the experimental data at pH values in the range 4-9.

These results illustrate that CA models often should be re-calibrated in order to accurately represent experimental data for complex mineral assemblages. The best way to ensure the CA approach is properly calibrated is to collect experimental radionuclide adsorption data for the mineral assemblage, as is done for the GC approach. This approach works well when adequate experimental data are collected for the specific mineral assemblage (Payne *et al.*, 2004). Generally, the results of CA modelling in the literature show that the pure predictive capabilities of this approach seldom match experimental data perfectly (Davis *et al.*, 2004a), but this is perceived as being due to a lack of sample characterisation (including methodological issues) and lack of adequate mineral component models, rather than being a fault of the modelling approach (NEA, 2005).

**Figure 4.4: Experimental data (circles) for adsorption of uranium(VI) on a weathered schist as a function of pH**

Curves represent component additivity (CA) model predictions of uranium(VI) adsorption on the ferrihydrite mineral (solid curve) and goethite and hematite minerals (dotted curve) in the weathered schist



Source: Davis *et al.*, 2002.

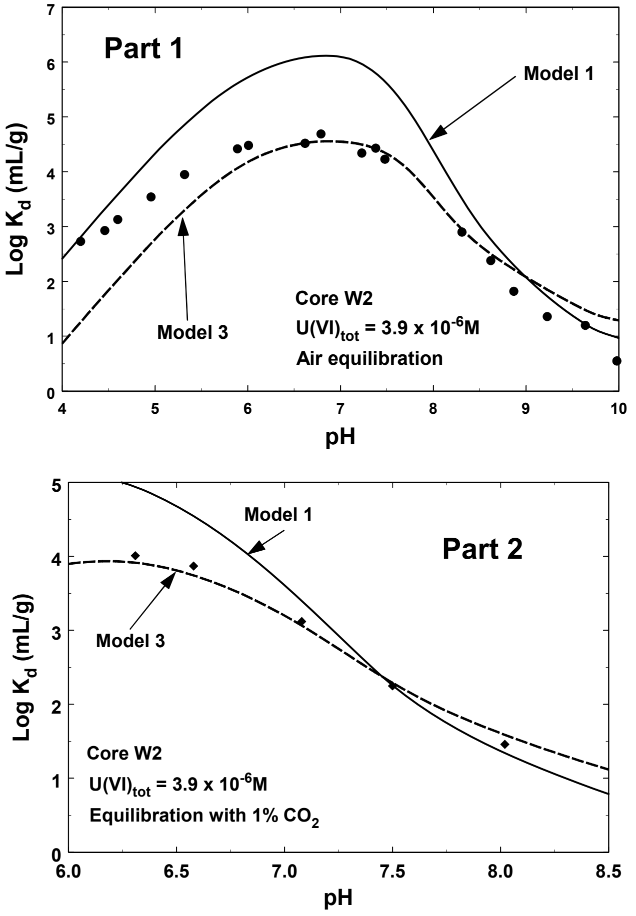
Davis *et al.* (2002) also calibrated GC models to the weathered schist data and compared model characteristics with CA models. In addition, these authors investigated the impact of the amount and parameter range of experimental data on model calibration.

Figure 4.5 compares experimental data and model results for two different GC models: Model 1 used all experimental data (samples W1 and W2; pH 4-10; air and 1% $CO_2$) to calibrate the model; Model 3 used only data in the pH range 6 to 8.6. Note that Model 3 simulations of the data in the pH range 6 to 8.6 were superior to that of Model 1, including the simulations under ambient air (Figure 4.5: Part 1) and 1% $CO_2$ (Part 2).

Another way to describe the results is that the model calibrated with data over the entire pH range significantly overestimated $K_d$ values in the neutral pH range. Model 3 obviously works better because it was calibrated with data only in the near-neutral pH range, but the point of the comparison is to show that weighting of experimental data during model calibration can have significant results. A GC model calibrated with data weighted significantly towards the parameter range of an application (e.g. the pH range of relevance for a specific PA) could improve model performance. Davis *et al.* (2002) also calibrated a GC Model 2 that only used the experimental data in the pH range 6 to 8.6 under ambient air. This model did a poor job of simulating the data at 1% $CO_2$, indicating the importance of collecting data as a function of the partial pressure of $CO_2$ if sorption of U(VI) under varying $CO_2$ concentrations is relevant to PA.

**Figure 4.5: Experimental data (circles and diamonds) for adsorption of uranium(VI) on a weathered schist as a function of pH**

Generalised composite (GC) model simulations of uranium(VI) adsorption on schist (curves) are shown. Model 1 was calibrated with all experimental data available while Model 3 was calibrated with all data in the pH range 6 to 8.6 under ambient air (Part 1) and 1% $CO_2$ (Part 2)



Source: Davis *et al.*, 2002.

These CA and GC model simulations also illustrate that another typical difference between the two model approaches is surface speciation. The simplified CA model of Waite *et al.* (2000) simulated the experimental data fairly well in the pH range 4 to 9 with surface species $(\equiv O_2UO_2)^0$ and $(\equiv O_2UO_2CO_3)^{2-}$, where $\equiv O_2$ refers to a bidentate surface site. In contrast, the GC Model 3 of Davis *et al.* (2002) simulated the data equally well with surface species $(\equiv O_2UO_2)^0$, $(\equiv O_2UO_2HCO_3)^{-}$, and $(\equiv O_2UO_2HCO_3CO_3)^{3-}$. The difference in surface speciation in the two modelling approaches arises primarily from the fact that the CA model corrects for electrostatic energy in surface complex formation assuming the mineral assemblage has the charging characteristics of ferrihydrite (using a diffuse double layer EDL), whereas the GC model calculations used no electrostatic correction terms. In this case, the change in surface speciation in the GC model compensates for the pH dependence of the EDL term in the CA model.

The dataset underlying this modelling example was also used as test case (TC 6) for a range of modelling exercises in Phase II of the NEA Sorption Project; further details are given in NEA (2005). In summary, the modelling discussed above, as well as in NEA (2005), shows that either a GC or CA approach can give a good description of the data. In addition to the fit to the experimental data, the quality of the modelling approach also depends on further factors, such as plausibility of TSM parameters and overall justification.

### 4.4.2 *Uranium sorption on alluvial sediments (Naturita, USA)*

Another major comparison of CA and GC approaches was reported by Davis *et al.* (2004a, b) for U(VI) adsorption on aquifer sediments from an alluvial aquifer next to a river in Naturita, Colorado (United States). The major minerals in the sediments were quartz, feldspars, and calcite, with minor amounts of magnetite and clay minerals. Quartz grains commonly exhibited coatings that were greater than 10 nm in thickness and composed of an illite-smectite clay with occluded ferrihydrite and goethite nanoparticles. Chemical extractions of selected quartz grains from the sediments were used to estimate the masses of iron and aluminum present in the coatings. U(VI) adsorption was measured on the sediments as a function of the partial pressure of $CO_2$, but the calcite present in the sediments meant that pH and $pCO_2$ could not be varied independently.

Published models for U(VI) adsorption on reference minerals were applied to predict U(VI) adsorption in various CA models, based on assumptions about the sediment assemblage surface composition and physical properties (e.g. surface area and electrical double layer). Figure 4.6 (Part 1) shows a CA model prediction of U(VI) adsorption on the Naturita sediment, assuming that 30% of the sediment surface area was due to quartz, and that the sediment contained 20 µmoles/g of both ferrihydrite and goethite, and using a triple layer model for electrostatic correction. Adsorption was overpredicted at low $pCO_2$ values, due to strong adsorption predicted on the goethite component (Davis *et al.*, 2004a, b), even though the component models were appropriately calibrated in the presence of $CO_2$. Agreement between the experimental data and model predictions was good at the intermediate and high $pCO_2$ values.

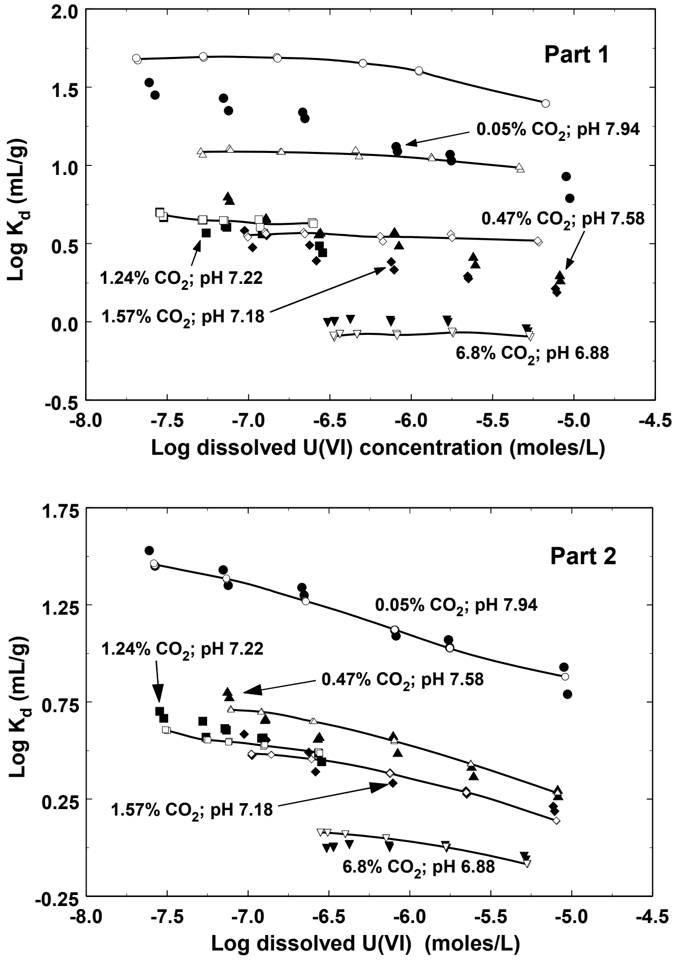
In general, predictions with the CA models were variable, with results over-predicting or under-predicting the experimental data, depending on the assumptions used for each model (Davis *et al.*, 2004a, b). Although the models for reference minerals were supported by detailed experimental studies (and in a few cases, surface spectroscopy), the results suggested that errors in applying the CA modelling approach directly to the sediments were caused by uncertain knowledge of:

- the proportion and types of surface functional groups available for adsorption in the surface coatings;
- the electric field at the mineral-water interface; and
- surface reactions of major ions in the aqueous phase, such as $Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, H_4SiO_4$, and organic acids (Davis *et al.*, 2004a, b).

Figure 4.6 (Part 2) shows a GC simulation of the experimental data with no electrostatic correction terms to the mass laws for surface complexation formation. As can be seen, the semi-empirical GC surface complexation modelling approach was able to describe the U(VI) experimental data more precisely than the CA approach as a function of aqueous chemical conditions, as was also observed in Test Case 6 in the NEA Sorption Project Phase II (NEA, 2005). Also, there were different surface species in each case. In the CA model simulation, surface species were $(\equiv O_2HUO_2)^+$, $(\equiv O_2UO_2)^0$, and $(\equiv O_2UO_2CO_3)^{2-}$ on quartz, $(\equiv O_2UO_2)^0$ and $(\equiv O_2UO_2CO_3)^{2-}$ on ferrihydrite, and $(\equiv O_2UO_2)^0$, and $(\equiv O_2UO_2(CO_3)_2)^{4-}$ on goethite. In the GC model simulation, surface species were $(\equiv O_2HUO_2)^+$ and $(\equiv O_2UO_2)^0$. Again, this demonstrates that the experimental data can be simulated with different surface species, but the species chosen are a result of the assumptions of each modelling approach, particularly the use of electrostatic correction terms to the mass laws for surface complex formation.

**Figure 4.6: Experimental data (filled symbols) for adsorption of uranium(VI) on an alluvial aquifer sediment as a function of U(VI) concentration and partial pressure of $CO_2$ gas equilibrated with synthetic groundwater solutions**

Part 1) CA model predictions of U(VI) adsorption with quartz, ferrihydrite, and goethite mineral components. Open symbols represent the CA model prediction for each experimental data point with the corresponding filled symbol; the solid curves are splines drawn through the open symbols to represent the CA model. Part 2) GC model simulations are shown as smoothed solid curves drawn through the open symbols



Source: Davis *et al.*, 2004a.

Although the surface species differ between the GC and CA models, an important point in the comparison of the modelling approaches is that the surface species do not differ greatly (NEA, 2005). Among a range of modelling teams and approaches, very similar surface species were chosen to represent the adsorption process in all the models, meaning the chemical similarity of these models is significant. This is a characteristic of the TSM approach and highlights that the chemical foundation of the various modelling approaches is the same.

To apply the GC modelling approach in reactive transport modelling, emphasis must be placed on site-specific characterisation of natural mineral assemblages and groundwater compositions expected to be encountered along major flowpaths away from contamination sources. Because of their relative simplicity, GC models have been incorporated more frequently into complex multi-component reactive transport models of field-scale systems than CA models (Ma *et al.*, 2010; Yabusaki *et al.*, 2008; Curtis *et al.*, 2006; Kent *et al.*, 2000).

### 4.4.3 *Further experimental and modelling issues associated with chemically complex substrates*

At present, a critical point in the development of TSMs for chemically complex materials is the determination of the distribution of mineral surface areas in a mixed mineral assemblage. Extractions, X-ray diffraction, and surface spectroscopic methods have been used by various investigators, but each of these methods provides estimates that are difficult to confirm independently. This uncertainty is circumvented in the GC approach by assuming that the distribution of site types is an unknowable quantity, and only generic sites are used. However, this requires that experimental data for the radionuclide sorption on the sediment sample are collected, whereas these additional experiments are not needed for the CA modelling approach

Many (unconsolidated) near-surface sediments are heterogeneous, regardless of the scale of observation. Materials range by orders of magnitude in size and surface area per unit mass, from colloidal particles (<0.1 micron) to clays, silt, sand, gravel, and larger rocks. Deposition and mixing of biological material within near-surface sediments is often more recent than for other geological deposits, and thus the weight abundance of organic carbon may be greater. Organic carbon may be present both as detrital organic particles or as deposits on the surfaces of inorganic mineral particles. Bacterial processes may be important, and in recent years have been increasingly considered in modelling radionuclide transport (Yabusaki *et al.*, 2007).

The variability of radionuclide adsorptive properties within a relatively homogeneous geologic formation has not been well studied. The two following studies dealt with relatively homogeneous aquifer materials in a single geologic formation:

- Curtis *et al.* (2006) compared uranium(VI) $K_d$ values in a 2 km reach of an alluvial aquifer. These authors found that $K_d$ values for 14 samples of aquifer sediments varied only by a factor of three when exposed to the same artificial groundwater composition. Much greater variation in uranium(VI) $K_d$ values was observed when groundwater compositions were varied within the range actually observed in the alluvial aquifer.
- Fuller *et al.* (1996) determined zinc adsorptive variability in a sand and gravel aquifer on a spatial scale of 200 m and found that $K_d$ values varied by a factor of about three for similar groundwater compositions.

This points to an issue which has already been discussed in Chapter 5.3 of NEA (2005):

> Probably the biggest hindrance to the application of TSMs to real substrates is the lack of RN sorption data obtained in the presence of relevant ground- or pore water constituents. The sorption of certain radionuclides on a given substrate may differ significantly not only as function of pH, but also as a function of the concentration of Ca, Mg, carbonate, etc. This uncertainty is minimised in a GC approach, because sorption data have to be measured for the actual solid and aqueous composition. In case of CA approaches, it cannot be assumed that an available TSM for a RN is actually applicable to a system with a typical natural water composition. This type of application actually represents an extrapolation in terms of chemical conditions, which is always potentially problematic.

## 4.5 Sorption modelling in clay rocks and compacted clay systems

This section illustrates the present state of the art of using TSMs for deriving $K_d$ for compacted clay systems, such as compacted bentonite and argillaceous (clay rock) formations. Some examples are also discussed for clay-dominated siliceous sedimentary rocks (mudstone).

### *4.5.1 Background, typical features and challenges regarding TSM applications to compacted clay systems*

#### *4.5.1.1 Overview*

Clay formations are selected in many waste management programmes as (potentially) suitable host rocks for the deep geological disposal of radioactive waste:

- Boom and Ypresian Clays, Belgium (ONDRAF/NIRAS, 2001);
- Callovo-Oxfordian argillite, France (ANDRA, 2005);
- Boda Clay Formations, Hungary (Arkai *et al*., 2000);
- Opalinus Clay, Switzerland (NAGRA, 2002).

In nearly all disposal concepts for high-level radioactive waste, engineered barriers (buffer and backfill) form an important part of the repository system. In many countries, the most likely candidate materials for these barriers are compacted swelling clays, in particular bentonite.

Typical examples of bentonites foreseen in waste disposal programmes are:

- MX-80 bentonite (Switzerland, France, Sweden, Finland);
- FEBEX bentonite (Spain);
- Kunigel-V1 (Japan).

Before compaction/emplacement, bentonites are handled in powdered and homogenised form, which means that a spatially homogeneous distribution of mineral composition and porosity can also be assumed for the compacted material.

#### *4.5.1.2 Composition and total porosity*

A common characteristic of the materials indicated above is that they contain only a limited number of sorption-relevant solid phases, typically well-crystallised clay minerals (mainly smectite, kaolinite, illite). While clay rocks and compacted clays used in engineered barriers (bentonite) share many common features, there are important differences in clay mineralogy that are relevant for applying TSMs to intact samples. Whereas swelling clays such as bentonite contain montmorillonite as dominant clay mineral and have plastic properties, non-swelling clay rocks mainly contain illite, kaolinite and mixed-layered illite/smectites and feature a lower plasticity. Mudstones are non-plastic siliceous rocks where clay minerals are embedded in an amorphous silica matrix. Amorphous or microcrystalline (hydr)oxides or other coatings are not common. Accessory minerals are mostly relevant with regard to the pore water composition.

In argillaceous rocks, clay minerals such as illite, smectite, illite/smectite mixed layers and kaolinite are important components and can often make up 50 or more wt.% (see Table 4.3). Typical accessory minerals include quartz, carbonates and smaller amounts of pyrite, gypsum, and feldspars. The content of Fe-/Al-oxides is typically insignificant compared to the reactive surfaces provided by clay minerals. Typical for clay rocks is the presence of organic matter. Depending on the type of clay rocks, this material is humic-like and consequently may have an important effect on the sorption/migration behaviour of radionuclides (e.g. Boom Clay: Aoki, 2002; Maes *et al.*, 2009). In clay rocks such as Opalinus Clay and Callovo-Oxfordian, the organic matter is not humic-like and the effect on the sorption/migration of radionuclide is likely to be small or even absent. An overview of methods for determining the composition of rocks and other natural substrates is given in Section 4.3.4.

Bentonites owe their relevant properties (low permeability, high swelling capacity, high plasticity and high sorption) to the high content (typically about 50% to 90%) of expandable 2:1 smectite clays (see Table 4.3). Hence for compacted bentonite, the interlayer is the dominant type of pore space (see Section 4.5.2.1). The remaining minerals are largely carbonates and silica (amorphous or crystalline); other clay minerals and metal oxides are typically only present in traces or not at all. Some bentonites may also contain small amounts of pyrite. Clay rocks on the other hand tend to have a higher proportion of non-expandable clay minerals, which means that the pore distribution is less homogeneous and that the interlayer pore space is of minor importance as transport path.

The total porosity is small in clay rocks (10-20%) compared to bentonite, due to the high bulk dry density of 2.300-2.400 kg m$^{-3}$ (an exception is the more plastic Boom Clay with a bulk dry density of 1.650 kg m$^{-3}$ and a porosity of ca. 37%, Maes *et al.*, 2008). In comparison, the total porosity of compacted bentonite is larger (35-40%), whereas the bulk dry density is lower: typical values for a buffer in a HLW or spent fuel disposal concept are in the range of 1.600-1.800 kg m$^{-3}$.

**Table 4.3: Overview of some major characteristics of clay rich rock types and bentonite**

| Parameter (unit) | Boom Clay[1] | Opalinus Clay[2] | Callovo Oxfordian[3, 4] | Horonobe mudstone[5, 6] | Boda Clay[7, 8] | MX-80 bentonite[2, 9] |
|---|---|---|---|---|---|---|
| *Mineralogy* | | | | | | |
| Clay minerals (%) | 30 - 60 | 54 | 25 - 55 | 18 - 26 | 30 - 50 | 75 |
| *Physical characteristics* | - | - | - | - | - | - |
| Water content (%) | 19 - 24 | 4.0 | 6 - 9 | - | - | 7.1 |
| Physical porosity (-) | 0.37 | 0.12 | 0.12 - 0.19 | 0.38 | 0.6 - 1.4 | *0.36 |
| Anion-accessible porosity (-) | 0.16 | 0.06 | 0.06 - 0.09 | - | - | - |
| CEC (meq/kg) | - | 106 | 110 - 220 | 200 | - | 787 |
| Total SA (EGME) (m$^2$/g) | - | 90 | 56 - 78 | 192 | - | 30 |
| External SA (BET)(m$^2$/g) | 44 | 28 | 20 - 40 | 71 | - | 562 |
| *Pore water features* | | | | | | |
| pH/pCO$_2$(bar) | 8.5/10$^{-2.62}$ | 7.24/10$^{-2.2}$ | 7.3/10$^{-2.5}$ | 6.7 - 8.5/- | 8.0/- | 7.25/10$^{-2.2}$ |
| Ionic strength (M) | 0.016 | 0.3 | 0.08 | 0.24 | 0.02 | 0.39 |
| Pore water type | Na-HCO$_3$ | Na-Cl-SO$_4$ | Na-Cl-SO$_4$ | Na-Cl | Na-HCO$_3$ | Na-Cl-SO$_4$ |

1) Boom Clay (location Mol): De Craen *et al*. (2004); 2) Opalinus Clay: NAGRA (2002); 3, 4) Callovo-Oxfordian, Bure: ANDRA (2005); 5, 6) Horonobe Sediments (mudstone, Wakkanai Formation): JAEA (2005, 2008b); 7, 8) Boda Clay Formations: Arkai *et al*. (2000), Lázár *et al*. (2008); 9) MX-80 Bentonite: Curti and Wersin (2002); *re-saturated at 2 150 kg/m$^3$.

#### *4.5.1.3 TSM applications to compact clays: typical sorption properties and challenges*

An important characteristic of the materials discussed in this chapter is that sorption of most RNs is dominated by clay minerals, due to their high surface area and advantageous surface properties (see also Chapter 3):

- The planar siloxane surface is crystallographically well defined and chemically relatively inert. Sorption on this surface is by ion exchange which refers to the exchange of counterions.
- The edges of the clay platelets feature exposed Al, Si and O atoms with broken bonds, forming amphoteric hydroxyl surface functional groups similar to a typical metal oxide surface. Here sorption takes place by surface complexation.

It has been shown in the past that the sorption of RNs on the mineral assemblage making up clay barriers and host rocks can be described by TSMs for pure clay minerals (see NEA, 2005). The dominant influence of the clay minerals on sorption has important implications with regard to the experimental constraint of the system and the development of TSMs:

- all sorption-relevant phases can be characterised by standard mineralogical methods (in contrast to many near-surface materials);
- the sorption-relevant phases can be isolated (as mineral separates) and purified for performing surface titrations, RN sorption measurements and spectroscopic investigations;
- site-specific studies using whole substrates can be supplemented with sorption data (newly generated or literature values) for model minerals (e.g. montmorillonite, kaolinite, illite);
- TSMs for describing RN sorption in clay materials need to include the surface complexation and ion exchange parameters for the RN, plus the ion exchange coefficients for all exchange reactions involving major cations.

On the other hand, there are significant experimental difficulties in obtaining pore water and actual sorption data in the intact (compacted) material, especially as a function of pH and other conditions. This normally prevents the parameterisation of TSMs on the basis of data directly corresponding to compacted conditions, thus TSM parameters have to be obtained on the basis of dispersed systems.

The principal challenge of sorption modelling for compacted clay systems therefore is the prediction of radionuclide surface complexation and ion exchange based on information obtained from dispersed systems/batch experiments while maintaining consistency with concepts of narrow pore space and electrostatic effects. Confidence in calculated $K_d$ values will therefore require their justification on the basis of good scientific arguments.

- The most fundamental question relates to the influence of compaction and the resulting physico-chemical characteristics of pore space in a charged porous medium such as compact clay on aqueous and surface chemical equilibria. It needs to be assessed whether, and to which degree, TSM and other thermodynamic parameters (surface equilibrium and protolysis constants, site densities, etc., but also thermodynamic constants for aqueous species) obtained from disperse batch experiments are applicable in an intact/compacted system. The key issue is whether the thermodynamic relationships derived in bulk water are applicable to the pore water in compacted systems. A basic question is centred around the (steric) accessibility of surface sites in dispersed vs. compacted material.

- From a more pragmatic point of view, the definition of pore water composition in compact clays is an important issue, since it is extremely difficult to obtain representative samples of the aqueous phase in compact clay systems. On the other hand, the ability to sufficiently constrain pore water chemistry is a prerequisite for any successful sorption modelling. The experimental hindrances to directly determining pore water composition require the development of reliable thermodynamic models for the main water-clay interactions.

Note that all above issues will affect both sorption and aqueous reactions of RNs as well as all major elements and ions.

Important support can often be drawn from RN transport (typically diffusion) experiments performed with intact material. To keep experimental efforts as well as time frames at a reasonable level, such experiments are primarily performed with mobile (i.e. weakly or non-sorbing) tracers and under a limited range of conditions. Nevertheless, such experiments can allow an assessment of radionuclide $K_d$ values that is independent from sorption measurements and directly related to the compacted state.

### 4.5.2 Compaction, pore space characteristics and relevance for sorption modelling

The compacted state (in comparison to dispersed material) can influence sorption in clay substrates in different ways (as pointed out above):

First, compaction could directly reduce the accessibility of surface sites due to steric reasons (Oscarson *et al.*, 1994). This issue can be addressed comparatively easily and unambiguously. None of the available evidence from sorption experiments in both crushed and intact clay rock (see Section 4.5.3 on model applications below) and diffusion experiments in compacted clay (Kato *et al.*, 1995; Jakob *et al.*, 2009) indicates any decrease in the concentration of available sorption sites.

Second, compaction leads to narrow pores strongly influenced by the permanent negative charge of the clay platelets, and the resulting pore space characteristics are important for sorption modelling in several ways:

- Pore size and electrostatic effects have an important influence on pore water composition and limit the possibility to extract and directly analyse pore water. At the same time, knowledge on pore water composition (and thus, RN speciation) is essential for any TSM application.
- Because the determination of TSM parameters is based on dispersed systems, validation of models and justification of TSM parameters for the compact state receive an important role:
    - Validation through TSM predictions for the compacted state can be made by comparing predicted and measured sorption values. In many cases, experimental sorption values for the compacted state can only be estimated through interpreting diffusion experiments, which should take into account the characteristics of the pore space.
    - In narrow pore spaces, the influence of electrostatic effects from the permanently charged clay surfaces is much more important than in disperse systems. Therefore, the application of TSM parameters to compact clay systems also must be supported from a more fundamental scientific viewpoint.

#### 4.5.2.1 *Concepts of pore space in clay rocks and compacted bentonite*

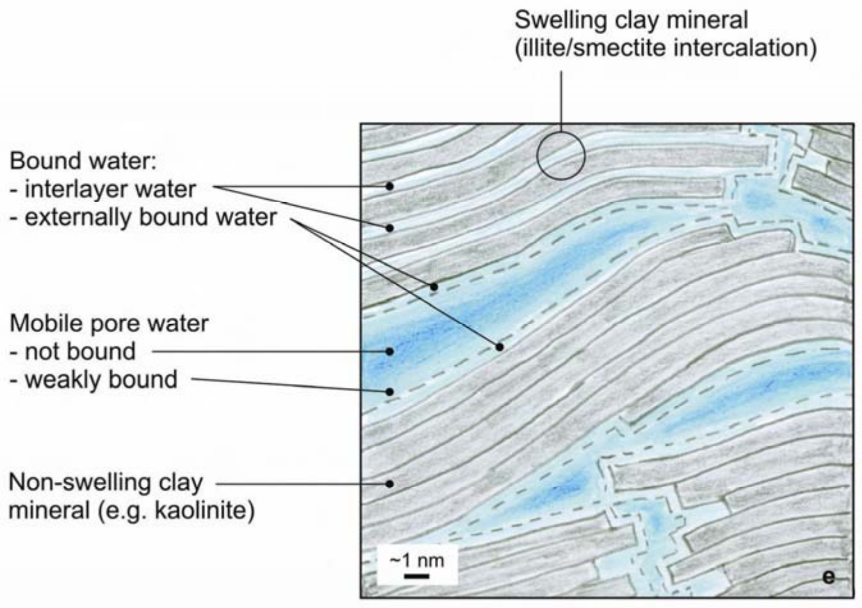
In charged porous media (such as argillaceous rocks and compacted bentonite), the transport pathways, where radionuclide sorption takes place, are formed by the water-filled pore space, which may also be influenced by electrostatic effects. However, the properties of the respective pore space differ significantly between compacted bentonite and clay rocks, due to the difference in mineralogy and related swelling properties. This has implications with regard to the applicability of TSMs to these materials, as will be explained below.

In typical clay rocks, different types of pores can be distinguished. In general, the pore space in argillaceous rocks can be subdivided into the interlayer pore space and the interparticle pore space. Depending on the density of the clay and the solution conditions, the latter can be further sub-divided into the pore space influenced by the diffuse layer extending from the charged pore wall (diffuse layer pore space) and the free pore space. For illustration, Figure 4.7 schematically represents the different types of pores (or types of water) present in Opalinus Clay.

In case of compacted bentonite, only few studies are available that address pore characteristics in the compacted state. Kozaki *et al.* (1998, 2001) investigated the basal spacing of Na-montmorillonite in compacted systems by X-ray diffraction methods, and calculated the fraction of interlayer water based on interlayer spacing. They also applied X-ray micro computer-tomography to compacted montmorillonite, indicating the presence of different types of porosity as a function of compaction.

**Figure 4.7: Simplified sketch of the Opalinus Clay structure at the micrometre scale**

The pore water-filled void space is composed of the "interlayer" and a complex 3D pore-network with "double layer water" and "free water" surrounding the clay platelets and the mineral grains



Source: NAGRA, 2002, p. 82.

Because the experimental evidence for the description of pore space (and diffusive/sorptive transport, see Section 4.5.3.1) in compacted bentonite is very scarce, and not free of contradictions, various model concepts were developed. These can be categorised into two groups. One group is formed by models that treat the pore space as a homogeneous charged porous medium as a first approximation:

- The "traditional" pore water modelling approach makes no provision for electrostatic effects in the pore space; i.e. compacted clay is simply treated like a dispersed system with an extremely high solid/liquid ratio. When applied to compacted bentonite, these models yield $K_d$ values that are significantly larger than $K_d$ values derived from diffusion experiments (e.g. Wanner *et al.*, 1996). On the other hand, this type of approach can be expected to be suitable in case of clay rocks, based on the results of Van Loon *et al.* (2005, 2009) as discussed below.

- Donnan-equilibrium models (Birgersson and Karnland, 2009) treat compacted bentonite like a homogeneous solution containing immobile negative charges (clay platelets) contained inside a semi-permeable membrane. Such models successfully describe cation and anion diffusion using the same underlying process, as well as swelling pressure development as a function of compaction and salinity.
- The model developed by Sato *et al.* (1995) and Ochs *et al.* (1998, 2001) explicitly considers the distribution of ions between bulk solution, diffuse layer (extending from planar surfaces) and ion exchange (or surface complexation) sites. The model is able to describe sorption as well as enhanced cation diffusion and anion exclusion effects in compacted bentonite, using the same underlying process (cation excess and anion deficit in the diffuse layer) and only one type of porosity (i.e. different diffusion pathways are not assumed for cations and anions). This model used several simplifications which are partly remedied in the modified version used by Tachi *et al.* (2009a, 2010).

In contrast to the above models based on a single porosity, several approaches exist where different diffusion pathways are assigned to anions and cations (e.g. Van Loon *et al.*, 2007; Bourg *et al.*, 2007). While these models differ in several details, the effects of cation and anion diffusion are described on the basis of different processes and corresponding different types of pores (interlayer pores and interparticle pores). Cations diffuse (at least partly) through the interlayer pores, whereas anions cannot access the interlayer pores. In line with this concept, the different types of pores in compacted bentonite could also contain different pore waters with different composition (Bradbury and Baeyens, 2003a; Wersin, 2003). In their microstructural description of compacted bentonite, these models are approximately consistent with the microscopic evidence presented by Kozaki *et al.* (2008) and molecular dynamics simulation data (Kosakowski *et al.*, 2008).

These concepts are also relevant for evaluating the mobility of “sorbed” species in compacted clays. More precisely, this refers to the distinction between the following types of “surface” species:

- A radionuclide that is part of an inner-sphere surface complex (i.e. bound to the clay edge surface via coordinative bonds) can be assumed to be immobilised by sorption. With regard to RN mobility, the resulting $K_d$ has the same meaning in dispersed and compacted systems, namely that the sorbing RN is retained with the solid (i.e. is not available to the dissolved phase after phase separation and is not available to diffusive transport, respectively).
- In case of ions accumulated in the EDL near the clay surface by ion exchange (and possibly also by outer-sphere surface complexation), the concept of mobile vs. immobile differs from the dispersed to the compacted state. During phase separation in a dispersed-state experiment, ions accumulated in the EDL will be separated with the clay, for reasons of electroneutrality. In a clay pore with overlapping EDLs, transport by diffusion takes place along the clay surface, and it must be assumed that at least part of the ions retain their mobility in this direction.
- Ultimately, these concepts of mobility in pores feed into the calculation of $K_d$ values for safety analyses, which are assumed to be a measure of the partitioning of a RN into mobile vs. immobilised (by sorption) fractions.

In view of the challenges discussed above, it is worthwhile considering at which degree of compaction bulk water may no longer exist. There are several indications that the border between dilute and compact systems is at ca. 1300 kg $m^{-3}$. The number of water layers in the interlayer of a compacted bentonite starts to decrease for a bulk dry density above 1300 kg $m^{-3}$ (Kozaki *et al.*, 1998). The swelling pressure of compacted bentonite starts to increase dramatically above a bulk dry density of 1300 kg $m^{-3}$ (Birgersson and Karnland, 2009).

### *4.5.2.2 Estimation of pore water composition*

As pointed out above, the definition of the pore water composition in compacted clay is a critical prerequisite for the derivation of valid $K_d$ values (by TSMs or any other method). Compact clay systems exert an important influence (pH and ion buffering) on the pore water, due to the high surface area and the presence of exchangeable ions as well as fairly soluble impurities. It is therefore not possible to infer the pore water composition from the composition of the contacting groundwater. Because of the various contributions to the dissolved content of pore water (soluble impurities such as NaCl, $CaSO_4$, exchangeable ions, constituents of residual pore water and/or contacting groundwater), its composition can be only be sufficiently constrained by a combination of aqueous extractions at different solid-to-liquid ratios, cation exchange measurements, as well as detailed geochemical/ion exchange calculations (Baeyens and Bradbury, 1991, 1994; Bradbury and Baeyens, 2003a).

The pore water chemistry can be experimentally obtained by two different techniques:

- Water for chemical analyses can be extracted directly from samples in the compacted state using squeezing techniques (Pearson *et al.*, 2003). The volume of water extracted depends on the water content of the rock sample, the rock properties (e.g. dry density, the relative contents of easily-squeezed clays or stiffer materials like quartz and calcite), and the experimental conditions, e.g. the pressure applied, the duration of squeezing and size of the squeezing cell (Fernández *et al.*, 2004). Whenever pore water is extracted from compacted clay, questions arise as to which fraction of the total porosity and of the pore water are actually being sampled (such as total porosity, anion-accessible porosity, etc., see Pearson, 1998). Alternative experimental methods are radial out-diffusion measurements (van der Kamp, 1996; Savoye *et al.*, 2006; Appelo *et al.*, 2008), ultra-centrifugation and immiscible displacement. A good overview is given in NEA (2000). In principle, squeezing techniques allow a comparatively direct determination of pore water composition (all other methods rely significantly on geochemical modelling). However, the composition of the squeezed water depends on many factors: possible modifications of water/rock equilibria due to the pressure/temperature regime; out-gassing from squeezed water; oxidation during squeezing; contamination; fractionation processes; uncertainty arising from the small volumes of squeezed water. In spite of these problems, the squeezing technique has been successfully adopted in different argillaceous formations (Opalinus Clay, Boom Clay, Callovo-Oxfordian).
- Water composition in compacted material can also be inferred from aqueous extracts prepared at different solid to liquid ratios. The chemical composition of the respective aqueous extracts reflects the clay-water interactions and resulting chemical reactions. It is useful to extrapolate the pore water composition when the squeezing technique cannot be used, or to develop clay-water interaction models. When squeezing cannot be used (i.e. for highly compacted bentonite), geochemical modelling represents the main (or unique) solution for deriving pore water characteristics.

There are some fundamental uncertainties regarding the volume and type of pore water sampled in the different experiments (total porosity vs. anion accessible porosity, see Pearson, 1998), which depends on compaction and ionic strength of the pore water. That is, the initial model interpretation of experimental results already implies a particular concept of the clay pore structure (such as homogeneous pore distribution or double-porous medium where interlayer water, adsorbed water and free water with different physico-chemical properties coexist).

Oda *et al.* (2001) conducted *in situ* measurements of pH in compacted bentonite using resin particles doped with pH indicator. The pH trend as a function of liquid-to-solid ratio could be reproduced reasonably well by a simple TSM (bentonite-water reaction model for $H^+$ and major cations).

In clay rock formations where underground research laboratories have been installed [Mont Terri (Switzerland), Mol (Belgium), Bure (France)], representative pore water can be sampled under well-controlled field conditions.

### 4.5.3 Validation of TSM application: comparison of data from disperse and compacted systems

While there are different approaches for describing sorption on clays (single vs. two- or multi-site models, types of surface species and EDL correction terms), it has been shown that the sorption of a variety of radionuclides and other elements in dispersed systems can be satisfactorily described by TSMs. For selected cases, supporting spectroscopic data are also available (e.g. NEA, 2005). In the case of argillaceous rocks, TSMs for individual clay minerals have been successfully applied in a CA approach (assuming additivity of the sorption properties of the different clay minerals) to describe radionuclide sorption by the whole rock (Tachi *et al.*, 2009b; 2010). Thus, while certain model details still warrant further development, it can be concluded that the sorption of radionuclides on various clay-dominated substrates can be modelled satisfactorily by TSMs.

The key question for a successful application of TSMs in a disposal context is whether these models (or the underlying batch-type sorption data) are able to explain the experimentally observed (macroscopic) sorption behaviour of relevant radionuclides in intact/compacted clay systems.

Accordingly, the confidence in applying batch-derived TSMs to compacted systems could be substantially increased by an independent verification of the predicted $K_d$ values.

#### 4.5.3.1 *Diffusion in compact clays*

Due to the small average pore size and low hydraulic conductivity ($K_h<10^{-10}$ m/s) of compacted bentonite and clay rocks, diffusion is the dominant process for RN transport (at least for hydraulic gradients relevant for waste disposal).

Because of the electrostatic fields extending from the clay surfaces into the narrow pores, cations, anions and neutral species display different diffusion behaviour (anion exclusion, enhanced cation diffusion).

To describe RN migration, it is necessary to know the diffusion-available porosity and the apparent diffusion coefficient ($D_a$) valid for repository conditions. In PA calculations, $D_a$ for most (sorbing) RNs is typically derived from a combination of effective diffusion coefficients ($D_e$) and a sorption value ($K_d$) which has to be derived for repository conditions, using the following equation:

$$D_a = \frac{D_e}{\varepsilon + \rho \cdot K_d} \tag{4.1}$$

where $\varepsilon$ represents the transport porosity and $\rho$ the bulk dry density of the porous medium. The effective diffusion coefficient is defined as:

$$D_e = \varepsilon \cdot \frac{\delta}{\tau^2} \cdot D_w \tag{4.2}$$

where $\delta$ represents the constrictivity (or pore narrowing), $\tau$ the tortuosity (or effective diffusion path lengthening) and $D_w$ is the diffusion coefficient in bulk water.

For reasons of pragmatism and data limitations, typically only $D_e$ values for a few reference tracers (e.g. HTO, $Cs^+$, $Cl^-$) are used to represent the diffusion behaviour of cations, neutral species and anions (see Wersin and Schwyn, 2004; JAEA, 2000). For strongly sorbing tracers, the contribution of sorption ($K_d$) to $D_a$ is much more relevant than the contribution of $D_e$. The apportionment of anion exclusion and cation diffusion to $D_e$ and diffusion-available porosity is not straightforward, and different programmes use different approaches.

#### 4.5.3.2 *Comparison of sorption values from diffusion-dominated and disperse systems*

It can be seen from Equation 4.1 that $K_d$ can be derived on the basis of diffusion data obtained on compacted or intact samples, given that density and (diffusion-available) porosity are known. Due to the experimental constraints of diffusion experiments with compacted clays (long timeframe required, very limited possibilities of systematically varying chemical conditions in pores), this approach can only be applied to a few selected cases. Therefore, $D_e$ for slowly diffusing elements often has to be approximated by $D_e$ measured for HTO. Further, the EDL existing in the pore space of compacted clays influences the diffusion of charged species (apparently enhanced cation diffusion, anion exclusion). The assignment of this effect to $\varepsilon$ and $D_e$ is a fundamental (and not yet resolved) uncertainty in the derivation of $K_d$ by coupling of $D_e$ and $D_a$.

Some comparisons of sorption behaviour as derived from batch vs. diffusion experiments have been made in the past to support the conventional evaluation of $K_d$ for compacted bentonite. Most discrepancies observed in such direct comparisons of experimental results are considered to be insignificant within overall experimental uncertainties, or can be shown to be the results of effectively comparing non-matching data from systems with different chemical conditions (Yu and Neretnieks; 1997; Ochs; 1997; JAEA, 2000; Bradbury and Baeyens, 2003b).

The different pore spaces have a direct influence on the mobility of radionuclides. The interlayer water and the diffuse double layer water are characterised by an anion deficit and cation excess (Bolt, 1979; Ochs *et al.* 2004; Birgesson and Karnland, 2009). This results in reduced anion diffusivity (Ochs *et al.*, 2001; Tachi *et al.*, 2009b) and/or reduced accessibility for anions (Van Loon *et al.*, 2007; Van Loon *et al.*, 2003a, b). On the other hand, cations can access the whole pore space in an argillaceous rock. In terms of diffusive transport, anions thus show anion exclusion behaviour in argillaceous rocks, whereas cations sometimes show enhanced diffusive transport ("surface diffusion"). For practical (PA) purposes, transport in clay rocks is described analogously to transport in compacted bentonite.

For weakly to moderately sorbing elements, the direct determination of $D_e$ and $K_d$ values by transient through-diffusion tests can give valuable results. In this method, the change in tracer concentrations in inlet and outlet reservoirs of a through-diffusion cell are monitored during transient diffusion, and the tracer depth profile in the solid is also obtained. $D_e$ and $K_d$ are determined by simultaneously fitting the tracer depletion, breakthrough, and in-depth concentration profiles (Tachi *et al.*, 2009a). Using this approach, Tachi *et al.* (2009b, 2010) obtained consistent $K_d$ values for intact and crushed mudstone samples (see case study 3 below).

### 4.5.4 *Case studies of TSM application for* $K_d$ *estimation: sorption on clay materials*

This section illustrates the present state of the art of using TSMs for deriving $K_d$ for compacted clay systems, such as compacted bentonite and clay rock formations. The following issues are addressed:

- The possibilities of characterising such systems in terms of sorption-relevant parameters (mineralogy/surface area and water chemistry), in particular with regard to the limited accessibility of pore characteristics and the difficulties of defining pore water chemistry.
- The basic problems of defining/justifying thermodynamic modelling (of sorption) in narrow pores where the entire pore space may be influenced by electrically charged mineral surfaces; and the conceptual models available to date.
- The possibilities of assessing radionuclide sorption by independent means (diffusion experiments).
- Selected cases of TSM application to intact clay rock and compacted bentonite.

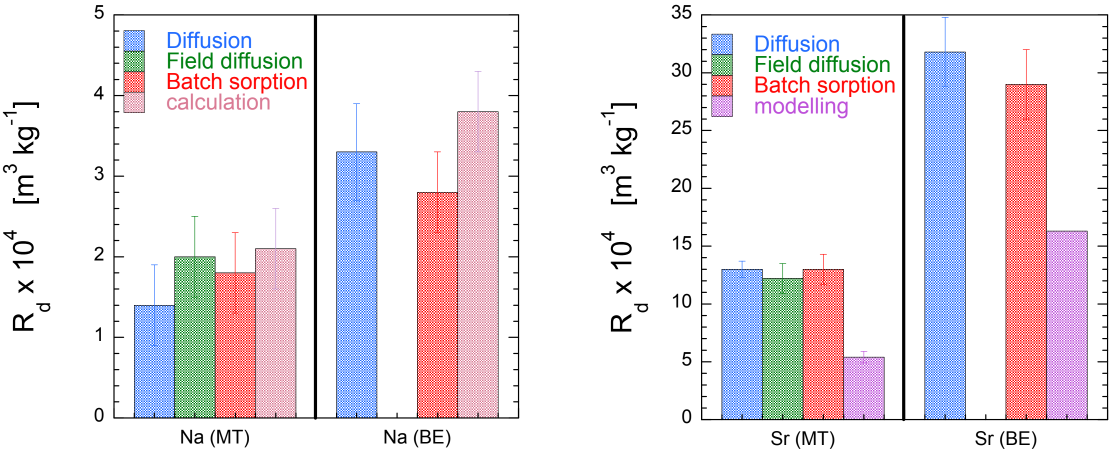
The great majority of publications that address the sorption behaviour in both dispersed and intact systems are carried out with weakly sorbing elements ($Na^+$, $Sr^{2+}$, $Cs^+$). As all these elements adsorb principally by ionic exchange, the available information on sorption processes in intact systems is limited.

### 4.5.4.1 *Case 1: sorption and modelling of Na and Sr on dispersed and compacted Opalinus Clay*

Van Loon *et al.* (2005) performed batch sorption and diffusion measurements for Na and Sr on Opalinus Clay in dispersed systems and intact rock, respectively. $K_d$ values measured in batch type experiments were compared with those obtained from diffusion tests on the intact rock in HTO experiments ($D_e$ and porosity values). They also applied TSMs developed originally on the basis of data from crushed clay rock (Bradbury and Baeyens, 1998) to these systems and compared the results of all three approaches.

As shown in Figure 4.8, the results from the through- and out-diffusion as well as the batch sorption experiments for Na and Sr in Opalinus Clay samples from Mont Terri and Benken present a very consistent internal picture. The $K_d$ values deduced from the two methods agree also very well with the modelled data for each case; they are effectively the same within typical experimental and modelling uncertainties.

**Figure 4.8: Comparison of $K_d$ ($R_d$) values of Na and Sr on Opalinus Clay [Mont Terri (MT) and Benken (BE)] obtained in diffusion measurements (in the laboratory and in the field), batch sorption experiments, and from geochemical calculations**



#### *4.5.4.2 Case 2: sorption experiments and modelling of Cs on clay rock and bentonite*

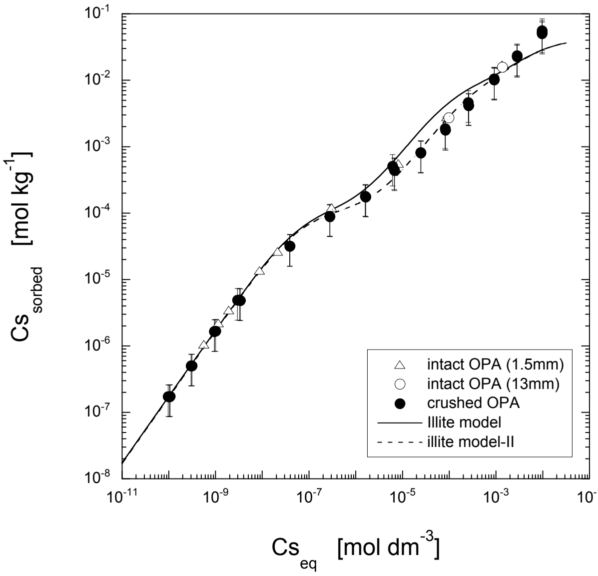
Van Loon *et al.* (2009) have carried out sorption measurements of Cs on both intact and crushed (particle size ≤ 63 µm) Opalinus Clay rock. All experiments were based on the same Opalinus Clay sample, and were carried out using similar pore water compositions. The sorption isotherm determined for the crushed sample was modelled using the TSM of Bradbury and Baeyens (2000) developed for Cs sorption on illite. All model parameters (site capacities and selectivity coefficients) had been derived from batch sorption measurements on dispersed illite suspensions. The only scaling factor for application to Opalinus Clay samples is the illite content; Cs sorption to other clay minerals is neglected.

The results of the measurements and modelling are shown in Figure 4.9. The experimental data clearly demonstrate that the sorption of Cs on crushed and on intact (compacted) Opalinus Clay are essentially identical. The data set could also be modelled successfully by the TSM for Cs sorption on illite. This demonstrates the following important points:

- The TSM for pure illite is applicable to whole argillaceous rock and illite content suffices as scaling factor; i.e. there are no effects of non-additivity.
- Compaction does not influence the accessibility of sorption/ion exchange sites on illite.
- Compaction does not influence the overall thermodynamics of the sorption process of Cs.

**Figure 4.9: Cs sorption isotherm on Opalinus Clay (OPA)**

The solid line is the calculated Cs isotherm using the generalised Cs sorption model, assuming an illite content of 21 wt.%.



In contrast to the above, Van Loon and Glaus (2008) present data suggesting that the selectivity of the exchanger for Cs dramatically increases above a bulk dry density of 1 300 kg m$^{-3}$. They attribute this to a reduction of the interlayer space, leading to a lower availability of the interlayer water for cation hydration. Cations with a low hydration tendency such as caesium therefore accumulate in the interlayer space, whereas highly hydrated cations such as sodium tend to accumulate in the bulk water where water is easily available for hydration.

Oscarson *et al.* (1994) reported a weaker sorption of Cs in compacted bentonite than in the dispersed state, using the same technique as Van Loon and Glaus (2008), whereas Suzuki *et al.* (2007) did not observe significant differences between dispersed and compacted state. Further, a comparison of in- and through-diffusion data for Cs on crude and purified bentonite (Sato, 1998) does not suggest a dramatic change in the sorption of Cs as a function of density. The measured $D_a$ values for Cs can also be interpreted by the same combined ion exchange/diffusion model up to high degrees of compaction (Ochs *et al.*, 2001) without introducing a change in the Cs sorption behaviour.

The diffusive transport and sorption-induced retardation of $Cs^+$ in Opalinus Clay, Callovo-Oxfordian Argillite and Boom Clay samples was investigated in several studies within the EC IP Funmig (Altmann *et al.*, 2011). Datasets for through- and out-diffusion of $Cs^+$ in Opalinus Clay were interpreted using a number of different modelling approaches (Jakob *et al.*, 2009). A satisfactory description of the data set could be achieved by modelling sorption of Cs using the TSM of Bradbury and Baeyens (2000), including the specific sorption site density determined for dispersed systems and fitting the $D_e$ value. The best-fit $D_e$ value, $1.8{\cdot}10^{-10}$ $m^2{\cdot}s^{-1}$, is roughly an order of magnitude higher than $D_e$(HTO), which is indicative of $Cs^+$ preferential diffusion in (interlayer and planar) double layer solutions.

A similar order of magnitude difference between $D_e(Cs^+)$ and $D_e$(HTO) was also measured by interpretation of steady state flux during through-diffusion for $Cs^+$ in Callovo-Oxfordian argillites (Melkior *et al.*, 2007), who obtained $D_e(Cs^+)$ values of $2(\pm 0.6){\cdot}10^{-10}$ $m^2{\cdot}s^{-1}$. This value was used along with Fick's second law to estimate the corresponding intact rock $K_d$ value, giving values in the same range as measured on dispersed material, i.e. 25-45 $L{\cdot}kg^{-1}$.

Maes *et al.* (2008, 2009) performed two types of in-diffusion experiments in Boom Clay samples. A coupled transport simulation of the $Cs^+$ diffusion profile [again using the model of Bradbury and Baeyens (2000)] showed that the data can be interpreted with a pore diffusion coefficient ($D_p$) which is about an order of magnitude higher than the $D_p$ value for HTO. Sorption experiments with Cs on compacted clay were also performed, and showed that compaction did not affect the accessibility of sorption sites.

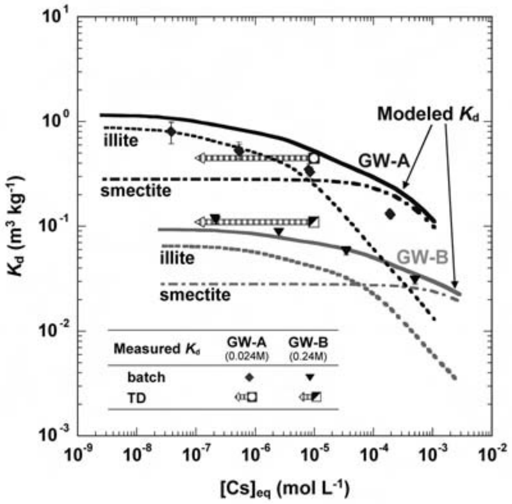
#### 4.5.4.3 *Case 3: sorption and diffusion of Cs in mudstone*

The previous section discussed Cs sorption on disperse vs. compact clay materials and diffusion effects. Here, this is extended to mudstone, since the sorption-relevant solids in mudstone are also clay minerals. On the other hand, mudstone is lithified (i.e. the clay minerals are embedded in a siliceous matrix) in contrast to clay rocks.

Using a transient diffusion method, Tachi *et al.* (2009b) measured $K_d$ values of Cs in intact mudstone from Horonobe (Japan). The obtained values as a function of ionic strength of synthetic groundwater were consistent with data obtained from batch tests using crushed rock. The sorption behaviour of Cs could be interpreted using a component-additive (CA) ion-exchange model for illite based on Bradbury and Baeyens (2000) and Wanner *et al.* (1996). The Cs sorption in argillaceous rock is sensitive to the relative concentrations of key clay minerals and geochemical conditions (Figure 4.10). In the case of Horonobe mudstone, both smectite and illite have important contributions to overall sorption.

**Figure 4.10: Cs sorption on Horonobe mudstone; comparison between $K_d$ values measured by batch sorption and transient diffusion (TD) experiments for GW-A (ionic strength; 0.024M) and GW-B (0.24M), and modelled by the clay-based CA model**

Solid lines are total $K_d$ values, and dotted and dashes lines are the contributions by illite and smectite, respectively.

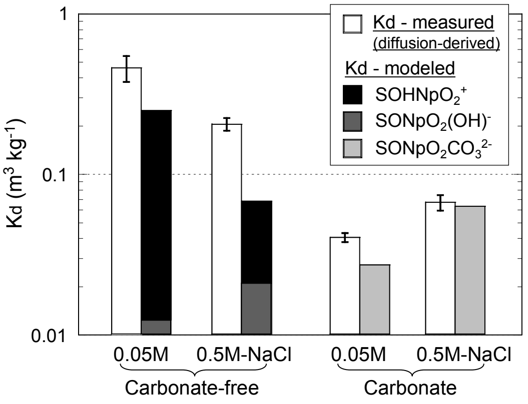


### 4.5.4.4 *Case 4: sorption and diffusion of Np(V) in bentonite*

Tachi *et al.* (2010) simultaneously measured the diffusion and sorption of Np(V) in moderately compacted montmorillonite under different salinity and carbonate concentrations, using transient diffusion. Sorption of Np(V) decreased with increasing carbonate concentration. At low-carbonate conditions, dissolved Np(V) exists mainly as cationic species and $D_e$ values decreased as salinity increased; at higher carbonate conditions dissolved Np(V) exists mainly as an anionic species and $D_e$ increased as a function of salinity. A sorption-diffusion model based on the approach by Sato *et al.* (1995) and Ochs *et al.* (2001) and parameterised for Np(V) sorption on the basis of experimental data from different dispersed clay systems (Turner *et al.*, 1998; Gorgeon, 1994) is able to describe the experimentally observed tendency of $D_e$ and $K_d$ in the moderately compacted material as a function of salinity and carbonate concentration (see Figure 4.11).

**Figure 4.11: Diffusion-derived $K_d$ values, modelled $K_d$ values, and surface speciation of Np(V) in compacted montmorillonite in different pore water solutions**

The shading approximately indicates the contribution of different surface species to overall sorption as represented by $K_d$.



### 4.5.5 *Summary and key messages*

A common feature of compact clay systems (including compacted bentonite as well as a variety of argillaceous rocks) is a RN migration path characterised by narrow pore space and influenced by electrostatic effects. In terms of sorption-relevant minerals, these substrates typically are dominated by clay minerals. The main challenge with respect to TSM applications may be caused by the narrow pore space and the presence of the permanent negative charge of the clay minerals, which imposes conditions on the aqueous phase that are different from those of bulk water. This may significantly affect the activities of dissolved and sorbed species, as well as EDL and surface properties.

Following these main features, a number of key issues with regard to sorption modelling in intact clay systems can be identified:

1. The task of sorption modelling *per se* is not the main problem in many cases (see examples in previous sections):
    - In the case of bentonite, sorption modelling can be reduced to the description of sorption on smectite minerals, which in turn can be well approximated by a TSM for pure montmorillonite. Generalised models (using generic "SOH" sites and a simplified EDL term) have proven successful for a range of situations.
    - While argillaceous rocks exhibit more complex clay mineralogy than bentonite, sorption often can be modelled adequately by considering additive contributions by the main clay components (such as smectite and illite).
2. From a more pragmatic point of view, it needs to be assured that a TSM application is based on representative conditions. It is difficult to obtain representative pore water samples from compacted clay systems, and the results from different investigations (including solid phase composition and exchange experiments) typically cannot be interpreted without the help of basic TSMs. Due to the high amounts of (charged) reactive surface area available, the solid phase in compacted clay systems exerts a significant buffering effect on the pore solution. In combination with the contribution of easily soluble accessory minerals and impurities, careful modelling is required to constrain the composition of the pore solution (Bradbury and Baeyens, 2003a; Wersin, 2003; Ochs *et al.*, 2004). If this preliminary step is not sufficiently precise, any subsequent sorption modelling may be based on erroneous conditions.
3. A valuable approach for evaluating the macroscopic applicability of TSM parameters derived from batch experiments to compacted conditions is to assess whether TSMs can predict diffusion-derived sorption data (within the uncertainties expected for an application to batch data). In the case of cations that sorb via an ion exchange mechanism (Na, Sr and Cs), examples of successful applications of batch-derived TSM parameters to intact Opalinus Clay and compacted bentonite can be found in the literature (Van Loon *et al.*, 2005, 2009; Ochs *et al.*, 2001; Tachi *et al.*, 2009a). In the case of elements where surface complexation is the dominant sorption process, less evidence is available. Recent results by Tachi *et al.* (2010) suggest that the migration behaviour of Np(V) in compacted bentonite as a function of salinity and in the presence and absence of dissolved carbonate can be interpreted by a batch-based sorption model.
4. Based on the macroscopic evidence (sorption data from batch and diffusion experiments) available to date, there seems to be no need to modify any of the TSM parameters derived from batch experiments for applications of these TSMs to compacted systems. The evidence suggests that (at least within the experimental uncertainties) TSMs are able to correctly predict the sorption of different radionuclides in compacted clay systems. While a direct demonstration of the consistency of TSM applications to disperse and to compacted systems is difficult, model applications are consistent with the available evidence.

5. At the same time, there is not enough information at the molecular-level to warrant modifications of TSM parameters.
6. There are no indications that sorption sites become inaccessible upon compaction. However, there are open questions on how sorption sites should be apportioned to different pore types in cases where several types of porosities are considered. In particular, there are questions regarding the mobility of ions (especially alkaline and alkaline earth elements) sorbed by accumulation in the EDL near the planar (possibly also edge) surface of clays. If we consider that $K_d$ should be a measure for the immobilisation (by sorption) of elements in diffusive transport, the contribution of weak (electrostatic) sorption to $K_d$ may have to be reconsidered.
7. From a more fundamental viewpoint, the justification of TSM applications to compacted systems with detailed scientific evidence is likely to remain elusive for the next years. In particular the possible existence of different types of pore water with different compositions will most likely be a matter of debate.
8. Direct experimental evidence for sorption in compacted systems has to be assessed by some type of migration experiments (typically in- and/or through-diffusion), which present a challenge to obtain reliable and reproducible results. This is especially true for elements that sorb appreciably.

## 4.6 TSM applications to crystalline host rocks

### *4.6.1 Overview*

Crystalline rock (saturated sparsely fractured rock) presents suitable properties to host a deep geological repository for different types of radioactive waste. For this reason, different European countries (Sweden, Finland, Switzerland, Spain, United Kingdom) as well as Canada, Japan and the United States analysed radionuclide migration in these systems for many years, including the use of underground research laboratories (URLs). Finland and Sweden have already approved the disposal of high-level radioactive waste in crystalline host formations (Olkiluoto and Forsmark, respectively).

Redox conditions at repository depth are expected to be reducing but a “typical crystalline” groundwater cannot be defined. As crystalline rock itself typically exerts no important influence on water composition (unlike clays), water composition can be very different from one formation to another. The groundwaters from the Grimsel test site in Switzerland are alkaline (pH 8-10) and have a low ionic strength ($1 \cdot 10^{-3}$ M), whereas waters from Äspö in Sweden have a more neutral pH and can reach much higher salinity due to seawater intrusion effects.

### *4.6.2 Characteristics of rocks and fracture filling*

Crystalline rock is generally composed of a variety of different primary minerals (mainly quartz, feldspars and micas and other accessory minerals such as hornblende) with typical grain sizes of the order of millimetres to centimetres. These mineral grains, with both inter-granular and intra-granular porosity, constitute the rock matrix. The porosity of the intact rock matrix is typically a few tenths of a percent; altered rocks may present porosity up to one order of magnitude higher.

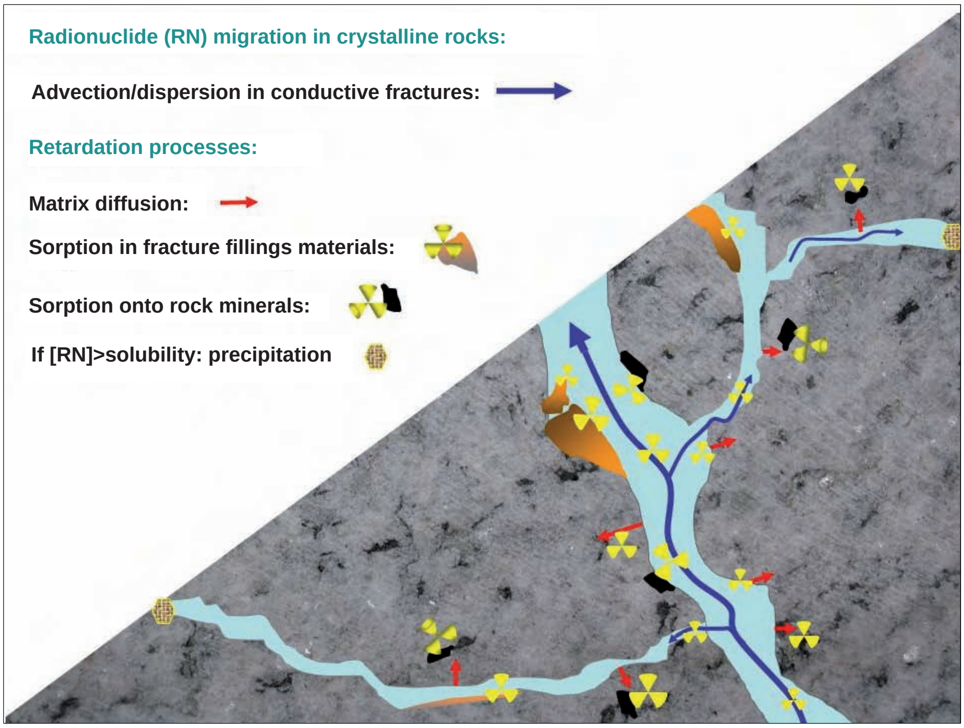
Crystalline rock is heterogeneous at a variety of scales. The smallest heterogeneities, relevant for sorption and solute transport within a representative volume element, are in the μm-cm scale, i.e. equivalent to the mineral grain or pore size (for PA, heterogeneities at much larger scales, m-km, are also of importance). Due to the physico-chemical heterogeneity of the crystalline medium, the identification of the water flow and solute transport pathways is a critical issue for defining the relevant substrate for sorption and for performance assessment in general (Retrock, 2005).

A common simplified way to describe solute transport in crystalline rock is the dual-porosity medium (Neretnieks, 2006) approach (Figure 4.12). It considers the rock matrix as a low-conductivity domain where advection is assumed to be negligible, and where solute transport is restricted to matrix diffusion (Jakob, 2004), whereas preferential water flow takes place in open water-conducting fractures where the dominant transport mechanism for solutes is advection. Fractures exist from mm to km scales in very complex configurations, which can be described by very different hydrological modelling approaches. Radionuclide migration takes place through both matrix and fractures, with their respective contribution depending on the site-specific hydrogeological conditions and rock properties.

Because crystalline rock consists of primary minerals prone to weathering and alteration, fractures may contain fillings consisting of various secondary minerals. The nature of the fracture fillings depends to a large extent on the nature of the primary rock, but minerals commonly found are iron oxy-hydroxides (magnetite, hematite, goethite, HFO…), other oxides (alumina, titanite, silica,..), calcite and other carbonates; clay minerals (montmorillonite, kaolinite,..), fluorite, secondary mica minerals, zeolites as well as residual (unaltered) quartz.

Fractures thus possess diverse physico-chemical properties with varying porosity (higher than the matrix and up to 10%) and a different mineralogy with higher specific surface area and CEC than the bulk rock.

**Figure 4.12: Schematic representation of RN migration pathways and sorption in crystalline rocks**



### 4.6.3 Retention mechanisms in the rock matrix and fractures

#### 4.6.3.1 Overview

Because of the mineralogical heterogeneity of both the bulk rock matrix and fracture fillings, retention processes comprise a variety of ion exchange (with constant-charge minerals like micas and clay minerals) and surface complexation (with minerals exhibiting pH-dependent surface charge: micas, oxides, clays…) reactions [which may lead to further (co)precipitation with e.g. carbonates, iron oxides…].

Sorption onto the (primary) fracture surface or the fracture filling materials is the main retardation process for solutes in the preferential fracture flow paths. However, the volume of the fractures represents only a small fraction of the total volume of a given rock. The pore system of the rock matrix, forming a water-filled heterogeneous network, includes the majority of the existing aqueous phase. This pore network provides a large solid/liquid interface area, larger than the surface area of fracture walls, so that diffusion into the rock matrix and sorption onto inner pore surfaces may significantly reduce the RN concentration in flowing groundwater (Neretnieks, 1980; Moreno *et al.*, 1997).

To understand retention processes in crystalline rock, the flow and rock structure (i.e. the hydrodynamic system) must be considered (Moreno and Neretnieks, 1993). Water residence time does not affect sorption directly, but it is very important for the physical processes of matrix diffusion. Consequently, it indirectly affects the extent of sorption into the pores within the rock matrix. Chemical and physical retention processes are difficult to separate and the applicability of some concepts related to retention in crystalline rock to other geologic media is limited.

The overall (apparent) interaction of radionuclides with fracture surfaces or with the rock matrix, and related retention processes, depends on different physical or "engineering" parameters (Crawford *et al.,* 2003): the amount of surface area in contact with the flowing water (flow wetted surface), water *flow rate* in the fractures, *porosity* of the matrix, *diffusion coefficients* and the *timescale* of interest. Sorption onto fracture surfaces and fillings may be the principal retention processes at short timescales, but at the larger timescales expected for a repository, bulk sorption is expected to dominate (Neretnieks, 1980).

As mentioned earlier, in crystalline rocks RN sorption may take place onto fracture walls, onto the materials filling the fractures and onto the inner pores of the matrix. In most PA exercises, the inner pore surface of the rock matrix is considered to dominate sorption, while the sorption on fracture surface or fillings is considered minor and is often (conservatively) neglected (Retrock, 2005). Fracture filling materials are expected to play an important role mainly when radionuclide transport occurs in preferential pathways (Failor *et al.*, 1982).

#### 4.6.3.2 Sorption processes and modelling approaches

Based on the indicated mineralogy of the bulk rock and fracture fillings, the modelling task will in most cases correspond to the issues already described in Section 4.4; i.e. the development and application of TSMs to a chemically complex substrate:

- Typically, the (unaltered) rock matrix will contain only feldspars, quartz and mica, in which case sorption will be dominated by mica. Sorption on mica can be modelled analogously to sorption on clay minerals (surface complexation on edge sites, ion exchange on siloxane layer surfaces); taking into account the surface complexation site density and CEC of mica.
- Weathered rock, and especially fracture fillings, are likely to contain phyllosilicates (clay/mica minerals) and (hydr)oxides in addition to quartz. In such cases, it can be expected that several mineral phases will contribute to sorption.

Additional complicating factors, such as the electrostatic effects in the pore space of clays, are not to be expected. Therefore, TSM development and application can be done following either CA or GC approach, as described in Section 4.4. As pointed out there:

- The CA approach would require the identification of the sorption-relevant minerals in fresh (and altered, if relevant) rock and fracture filling material, and the acquisition of TSM parameters by conducting experiments on mineral separates or by obtaining parameters from the literature (using scaling methods where needed, see also Chapter 3).
- Phyllite rock. Using the GC approach would require a representative sample of the solid material to be obtained for conducting sorption experiments.

In one of the few published case studies in which TSM concepts have been systematically applied to crystalline rocks, Arnold *et al.* (2001) analysed sorption of U(VI) onto phyllite. Applying a TSM, they attempted to model the properties of the main minerals constituting this rock sample (quartz, chlorite, muscovite, albite) and also considered contributions by minor constituents such as iron oxide or hydroxides on the overall sorption properties. As a first modelling step, the surface acidity constants for the main components of the rock and their surface site densities were determined. Next, the surface complex formation constants of U(VI) with the various minerals were evaluated, by studying the sorption properties of each individual mineral and using a TSM for interpreting the experimental data. Finally, an attempt was made to describe the sorption data obtained for the whole rock using a CA approach. They showed that the simple addition of the sorptive contribution of the main minerals could not simulate sorption on the whole rock. On the other hand, inclusion of ferrihydrite as secondary phase formed by chlorite dissolution improved the modelling.

The most critical point is probably the measurement of sorption data for the bulk rock matrix. Such $K_d$ values for crystalline rock are typically measured in static batch experiments with crushed and sieved material under approximated site-specific conditions (mineralogy and water chemistry). TSMs are sometimes used to provide support to expert judgement for $K_d$ selection, but their application is still very limited. While isolated model-oriented studies on several minerals existing in fillings materials or bulk rock (iron oxides, chlorite, biotite, quartz…) can be found in the literature, a convincing picture of modelling retention processes in crystalline rock is still missing.

The underlying problem is presumably not the actual sorption modelling for the complex mineralogy, but data acquisition and fundamental problems in treating the properties of intact rock:

- The difficulties of measuring relevant $K_d$ values in experiments using crushed rock is a critical limitation to the development of TSMs based on the GC approach, as well as to the validation of CA models. Recent critical reviews of sorption data in crystalline rock conclude that experimental problems are still significant (Crawford *et al.*, 2006; Missana *et al.*, 2008). The variability of $K_d$ values for various RNs obtained under reportedly similar experimental conditions often spans two to four orders of magnitude, and the values are not necessarily representative of the actual mineralogical or aqueous geochemical variability. Further, sorption on crushed rock depends not only on chemical conditions, but also on grain size. This can partly be explained by considering the specific surface area as a function of grain size, but a reliable method to derive surface site density from surface area measurements is currently not available. A further significant uncertainty is related to the creation of new surfaces during crushing, and to possible fractionation of different minerals.
- The extrapolation from laboratory systems to field conditions is complicated by the need to take into account the rock structure and its hydrodynamic properties as well as matrix diffusion effects. While such issues are outside the scope of sorption modelling and of this report, they are obviously relevant with respect to

model validation. Further factors in intact rock include diffusion-limitation of sorption (Papelis *et al.*, 1995; Trivedi and Axe, 2000; Skagius *et al.*, 1982) and the effects of weathering processes in certain pores (Wersin *et al.*, 1994; Nakata *et al.*, 2000, 2002; Jeon and Hoell, 2004). $K_d$ values obtained in crushed rocks always overestimate those obtained with the intact rock, and the reasons are not always clear (Vandergraaf *et al.*, 1993; Höltta *et al.*, 1997; Höltta *et al.*, 2008; Baik *et al.*, 2003). This situation is corroborated by the fact that only a few studies dealing with sorption onto intact rock coupons (including diffusion experiments with sorbing tracers) can be found in the literature.

The use of coupons of intact rocks instead of crushed material to study retention properties of crystalline rock is now more frequently proposed (Alonso *et al.*, 2009; André *et al.*, 2009). Such experiments can be expected to provide more realistic sorption values, and possibly other additional information useful for the development and validation of TSMs.

In summary, the state of the art in sorption modelling for crystalline rocks is still unsatisfactory. The reason is not the actual sorption modelling, which is not more difficult than for other complex materials, but rather the lack of reliable and interpretable sorption data in intact rock, which would be needed for model validation. In particular, a better process-level understanding of all retention mechanisms (sorption as opposed to additional, non-sorption processes) in crystalline rocks is needed before this situation can be improved.

## 4.7 Application of generalised TSMs to complex and intact materials: concluding remarks and key messages

### *4.7.1 Use of generalised models for real substrates*

The discussions and modelling examples presented in the preceding sections show that TSMs for real substrates are typically of a generalised type, where generalisation is understood as a synthesis of various details of a system into a more general expression. TSMs for complex and/or intact materials often need to be generalised in terms of treating

- the mineralogical composition of the solid;
- the types of surface sites available; and
- the EDL-term in the surface equilibria.

Typical examples of generalisations are:

- modelling the behaviour of many different surface sites which can be distinguished on a molecular level, using one or few generic sites (“SOH” groups);
- approximating the details of the EDL by using a simple electrostatic correction term without any adjustable parameters (DLM), or including the electrostatic correction implicitly in the surface equilibria (NEM).

Such generalisations are sometimes introduced by modellers to avoid making the models overly complex and unwieldy. Most often, generalisations are unavoidable because:

- the chemical-mineralogical complexity of the solid simply does not allow a detailed description, or even identification, of all surface sites and properties;

- even in cases where details of all surface sites could be described in principle, the experimental data for determining all the required TSM parameters are not available.

The level of generalisation required may differ significantly between substrates.

- For substrates with a high degree of chemical complexity (such as surface sediments or fracture infill containing a number of sorption-relevant minerals, possibly in the form of amorphous phases and/or coatings), the combined effect of all mineral phases on sorption is often synthesised into generic surface equilibria for the whole substrate (GC approach, see Sections 4.3.2 and 4.4).
- On the other hand, sorption in clay substrates is typically dominated by one or several well-defined clay minerals (such as montmorillonite and illite), and the sorption behaviour of the whole substrate often can be described using the surface equilibria for the pure components (CA approach, see Sections 4.3.2 and 4.5). Generalisations in such cases are largely restricted to a simplified treatment of clay edge functional groups (generic SOH groups instead of all possible silanol and aluminol groups) and of the associated EDL term.

It should be noted that the reduction of the level of detail brought about by these generalisations is not a simplification in the sense that parts of the system are simply ignored. Rather, various details of a system are treated by synthesising ("lumping") them into a more general expression.

### *4.7.2 Handling chemical complexity*

As discussed and illustrated in this chapter, generalised models (GC and simplified CA) are applicable to complex substrates, based on published examples. While different examples of GC and CA concepts have been discussed, it is pointed out that there is a degree of similarity between GC and (simplified) CA, and that these two concepts are not exclusive.

The main limitation of TSM applications to real systems is frequently the lack of experimental sorption data obtained in the presence of major solutes in ground- or pore water, such as calcium, magnesium, sulphate, and carbonate species. This is especially an issue when a CA approach is being followed and the TSMs for the component minerals are taken directly from the literature. Even though a very large amount of studies on single minerals is available, very few include the effects of geochemically relevant solutes.

In general, any TSM application to the real environment will be more robust when the range of ground- or pore water geochemical conditions is well understood. Thus, if there is a lack of information on the geochemical conditions (or the range is not well known), or too few samples of intact materials are characterised, model uncertainty is likely to be determined by a lack of input data rather than limitations inherent to the TSM modelling approach. For this reason, PA programs should give more emphasis and priority to geochemical characterisation and generation of sorption data for model calibration in order to apply TSM models.

### *4.7.3 Applicability of TSMs to compacted/intact systems*

The examples discussed in this chapter show that TSMs are able to describe the sorption of RN under a variety of conditions in compact clay systems, including intact clay rocks and compacted bentonite, as well as mudstone. From the relatively brief overview given here, as well as from the more extensive discussion that has evolved in the literature, the following important points emerge:

- First, a variety of experimental information and careful modelling is required to constrain the composition of the pore solution sufficiently well for the estimation of $K_d$ (by TSMs or conventional methods).
- There seems to be a difference between fully swelling and less or non-swelling clay systems. The latter comprise substrates that are dominated by illite (including illite/smectite mixed layer) and/or kaolinite as well as more consolidated materials, such as mudstone. Uncertainties related to the thermodynamics of the pore solution appear to be mainly an issue for compacted systems of fully expandable clays (mainly bentonite). In case of clay rocks and mudstone, all available evidence suggests that the thermodynamic relationships do not change from crushed to intact material.
- In compacted bentonite, the determination and modelling of pore water composition is complicated by uncertainties regarding the number and types of porosities to be considered. This issue still is a matter of debate; different types of single- and dual/multi-porosity models are in use at present.
- Further uncertainties exist regarding the mobility of cations accumulated at the planar surface. Such "sorbed" ions may be immobilised at the surface but may also be retained in the diffuse layer, partly or fully retaining their mobility within the pore space.
- Apparent uncertainties in sorption modelling may be driven by these issues, especially in case of compacted bentonite.
- While different concepts differ in their detailed descriptions, various examples cited above and discussed (e.g. NEA, 2005) show that at a macroscopic level (i.e. for calculating $K_d$), generalised CA models are applicable to a range of clay substrates in the dispersed and compacted state, and that sorption by different clay minerals appears to be additive.
- Based on the presently available macroscopic evidence, it appears that thermodynamic descriptions valid for bulk water can also be applied to the pore water in compacted clay systems, with the possible exception of ion exchange modelling for Cs.

While there is no indication that TSMs are applicable to both fresh crystalline rock and fracture infill, the use of TSMs for predicting radionuclide sorption in (intact) crystalline rock (see Section 4.6) is not considered feasible at present, for two reasons that are outside of the scope of sorption modelling:

- experimental difficulties in obtaining relevant sorption data needed for the testing/validation of sorption models;
- difficulties in describing boundary conditions relevant for radionuclide retention by intact rock, such as hydrodynamic effects.

# 5. General guidelines and recommendations

The preceding chapters have described the basic rationale for the application of TSMs:

- to explain the sorption behaviour of radionuclides as function of geochemical conditions;
- to evaluate trends of sorption with respect to changes in key chemical parameters and to assess related uncertainties;
- to directly support the selection of $K_d$ values for modelling radionuclide migration in engineered barriers and in the geosphere.

The main model components, steps in the development of a TSM, and methods to determine the various parameters have been described. The challenges inherent in applying TSMs to complex and intact/compacted systems have been discussed, and the state of the art in approaching these problems has been illustrated. Special attention has been given to the specific applications of TSM in the support of PA or building safety cases for radioactive waste disposal.

This final chapter aims to bring together the key issues and recommendations from the preceding chapters in the form of general guidelines for TSM development (but is not intended to serve as a stand-alone chapter). The central part of the chapter is built around the requirements needed to develop a TSM, basic issues to take into account, and decisions required in the model development. Prior to that, the general framework for TSM applications in the context of radioactive waste disposal is reviewed in the initial part of the chapter.

## 5.1 Framework for TSM applications in the context of radioactive waste disposal

Applications of TSMs to questions relevant in the context of radioactive waste disposal typically involve various types of complexities. This is obvious for model applications to complex substrates, such as rocks or sediments. However, even the use of TSMs for single mineral systems is placed in a complex overall framework whenever such a model application is directly linked to radioactive waste disposal issues.

To construct or apply a TSM in a meaningful way within a PA or safety case context, several requirements must be addressed. The TSM framework includes general considerations of model purpose, various prerequisites in terms of available data and geochemical conditions, and requirements regarding TSM performance, as follows:

- Model purpose: This needs to be clearly defined at the outset of any TSM development, as it influences the choice of systems to be considered as well as the type of TSM and overall modelling approach to be used.
- Geochemical conditions: A very fundamental and important prerequisite is a well-constrained geochemistry in terms of both pore water and major mineral phases. How well this can be achieved depends on the complexity of the system, the accessibility of the solid and liquid phases for sampling, the appropriateness of the sampling and characterisation programme, and the quality and detail of geochemical modelling. Here it is critical to appreciate the possible complexity of

conditions and the degree to which they can be constrained based on geochemical modelling and sampling/analyses.

- Thermodynamic databases of sufficient quality and completeness need to be available to describe the chemistry of a system with regard to all aqueous species and solid phases (major components and radionuclides).
- Measurements of sorption data of sufficient quality are needed to parameterise and/or to test the model quality and applicability. The amount of sorption data which needs to be accumulated depends strongly on the model purpose and the complexity and geochemical characteristics of the system. It also must be clarified whether the processes of surface sorption included in a TSM (surface complexation, ion exchange) are sufficient for describing all observable effects of RN retention, or whether additional (non-sorption, see Section 1.1.3) processes need to be considered.

## 5.2 Purposes and predictive capabilities of TSMs

The purpose and anticipated use of a TSM will be decisive with regard to the overall modelling approach and framework, but will also influence the detailed selection of the TSM type and strategy for its parameterisation, as well as the available resources for experimentation and model development. As discussed in Section 1.3.1, the range of intended applications can be very wide and may include:

- general scoping calculations in a screening phase (for example, to develop and guide a program for the acquisition of sorption data);
- the development of TSMs aimed at explaining selected macroscopic or mechanistic aspects of radionuclide sorption to support confidence building in safety analyses and safety cases;
- predictive applications for calculating $K_d$ values as well as for evaluating trends and uncertainties that will feed into PA calculations.

Where predictive model applications are expected, an important distinction can be made between interpolative and extrapolative predictions:

- In case of interpolations, the entire parameter space must be covered by the experimental data. This means that all relevant parameters must be identified, and that the TSM should be parameterised for all extremes of these parameters. Consequently, all model predictions will lie within calibrated points; i.e. all model predictions are within the validity range of the model.
- In case of extrapolations, the predictive application of a TSM (as of any other model) will be beyond the range of calibration, and therefore, outside the range of tested validity. Whether a model is suitable to make predictions beyond the calibrated range can only be critically assessed by evaluating and comparing the processes likely to be relevant in the prediction and those actually addressed by the model.

In many PA-related applications, it is likely that some type of extrapolative TSM application is required. In this context, it is important to distinguish the following types of extrapolations:

- Extension to other substrates. A TSM calibrated for the sorption of a radionuclide on a certain mineral (e.g. an iron oxide or clay) under a certain set of solution conditions (pH, chemical composition) may be applied to a different mineral with similar basic characteristics (a different iron oxide or a different clay mineral). In each case, a careful evaluation should be made with regard to which mineral surface properties need to be scaled (see Chapters 3 and 4 for appropriate methods).

- Extrapolation to different chemical conditions. Where chemical conditions are different in two systems, the governing sorption reactions may be significantly dissimilar. Thus extrapolations of TSMs over large ranges of chemical conditions are unlikely to be valid. However, extrapolation to different conditions may be possible in cases where no significant changes in the radionuclide aqueous and surface speciation (surface charge) are to be expected. For example, consider a radionuclide whose dominant hydrolysis species change between pH 5 and pH 10, but are well understood. It may then be acceptable to extend a model that has been calibrated between pH 3 and pH 8 to a higher pH of 9. However, the quality (or failure) of an extrapolation to pH 11 cannot be evaluated because important species may be missing in the model. In general, extrapolation is more likely to be acceptable if the model has been initially calibrated over a large range of conditions.
- As a special case of extrapolation, the estimation of log $K$ values for surface species through the application of LFERs (e.g. in case of completely lacking experimental data for a given radionuclide (cf. Dzombak and Morel, 1990) may be considered (see also Section 3.2.2). Again, well-parameterised TSMs for some radionuclides are the basis for the use of LFERs.

## 5.3 Strategies for building TSMs

Before considering complex materials, the development of models for simple systems can often be valuable. They can help to gain a detailed understanding of the fundamental sorption processes (thus increasing confidence in conclusions and data derived). Moreover, TSMs for single minerals can serve as components of models for complex systems, particularly when radionuclide sorption in complex systems is dominated by a few single mineral phases (e.g. montmorillonite and illite in a clay rock formation). Finally, knowledge acquired for simple systems can indicate plausible starting points for building models applicable to complex systems.

Typically, the construction and application of a TSM for a complex natural material will be an iterative process. Initially, the key system parameters (pH, concentration of aqueous components, characteristics of the solid) will be determined, followed by (aqueous) geochemical speciation computations and the experimental determination of a first set of sorption values. At this point, it may be possible to decide whether a CA or GC modelling approach (or some type of mixed approach) can be followed. Depending on the system under investigation:

- in a CA approach, it may be possible to apply and test the ability of existing TSMs to describe and explain the experimental data;
- in a GC approach, parameterisation of a new TSM on the basis of the obtained sorption data may be attempted.

The quality of the fits (or predictions) to the data by this first TSM application will indicate whether the main hypothesised sorption processes are pertinent and properly represented. Typical issues to be addressed at this point may include the following:

- Is the model able to reproduce the trend of sorption, for example as a function of pH?
- Is the model able to predict, at least qualitatively, the influence of changes in major solution components (such as major cations, ligands)?

- Is the model able to reproduce the magnitude of sorption, or is there a significant over/under–prediction (in the CA case)? Or do fitted site densities differ significantly from expectations (in the GC application)?

If the above exercise indicates that the main features of the sorption datasets are relatively well represented, these results can be used to design further experiments supplementing the existing data in the most critical areas. Otherwise, the experimental system may be revisited to obtain further information on the nature of the substrate, or to investigate the possibility of further (non-sorption) retention processes such as solid-solution formation.

Depending on the complexity of the system and on the questions to be addressed by the modelling effort, the number of iterative cycles (experimental data generation – model interpretation) and the degree to which pre-existing TSMs can be utilised may vary significantly.

During the iterative process described above, feedback between the modelling and the experimental investigations is crucial. If this is properly documented, it can become an essential element of the quality assurance. It is important to document all decisions taken, and alternatives considered for the various modelling steps; including the basic geochemical description, the physico-chemical processes identified to govern sorption, the decision about which TSM to be used, the establishment of a TSM parameter set and the details of the computations.

## 5.4 Recommendations

This section summarises important recommendations presented in the foregoing text, grouped on the basis of major stages to be passed in the course of TSM set-up and application (see Tables 5.1-5.3).

**Table 5.1: Generic recommendations**

| | Recommendation | Key section(s) of text |
|---|---|---|
| 1 | A focused and detailed programme is needed for TSM development, application and interpretation. | 1.2.2 |
| 2 | TSMs can be used to analyse only sorption phenomena that are governed by surface complexation and ion exchange. | 1.1.3, 1.2.3, 5.1 |
| 3 | The objectives of the TSM must be defined at the outset. This may influence the range and types of experiments required as well as the modelling approaches. | 1.2.2, 1.3.1,<br>5.1.1 |
| 4 | Model development should proceed according to a defined model framework (for example, following the flowcharts in Figures 5.1 and 5.2 below). | 1.3.2, 5.1, 5.2 |
| 5 | All modelling decisions should be properly documented, including justification for incorporated features and rationale for excluding alternatives. The key evidence relied on to derive the model should be clearly stated. | 1.3.2, 2.6<br>5.2 |
| 6 | The model-specificity and interdependence of model parameters should be recognised. | 1.3.2, 2.6, 3.1.7 |

## Table 5.2: Advice on an acquisition programme for sorption data and TSM parameterisation

| | Recommendation | Key section(s) of text |
|---|---|---|
| 7 | Modelling and experimental phases should be carried out in a complementary and continuous fashion. Preliminary modelling outcomes may indicate which further experiments are needed to develop the model. | 3.3, 4.4.1<br>5.2 |
| 8 | A comprehensive RN sorption data set should be obtained, showing the impact of all major geochemical parameters including as a minimum pH, ionic strength, RN concentration, carbonate, and major competing cations. Precipitation must be excluded, and experimental parameters such as redox state and $p\mathrm{CO_2}$ should be controlled. Aqueous chemistry must be well understood in sorption experiments. | 2.4, 3.3, 3.6 |
| 9 | Error estimates should be available; and ideally they should be associated with each experimental data point. | 3.1.2, 3.5.1, 3.1.6, 3.6 |
| 10 | Postulated surface reactions should be plausible in the sense that they do not contradict existing evidence. Ideally, they will be supported by spectroscopic information. | 2.4, 3.1.5<br>4.3.6 |
| 11 | Standard methods are available to estimate site density, surface protolysis behaviour, EDL parameters, etc., as well as for data reduction, at least for simple materials. Appropriate methods should be used for each parameter relevant to the system being studied. Certain limitations and experimental choices within these techniques must be recognised, as these can be a source of inconsistent results. | 4.3.4, 4.3.5 |
| 12 | Heterogeneous materials such as soils require thorough characterisation, through chemical and physical methods, as described in Section 4.2. The presence or absence of organic materials, and, if possible, their influence on sorption, should be investigated. | 4.3.3, 4.4.2 |

## Table 5.3: Advice on model development and application

| | Recommendation | Key section(s) of text |
|---|---|---|
| 13 | Modelling should take into account that the surfaces of minerals contain a variety of distinguishable sites with different sorption characteristics. In particular, complex materials such as soils contain a range of sites. | Table 3.3,<br>4.3.3, 4.4.2 |
| 14 | Sorption data for complex materials can be modelled using either CA or GC approaches. | 4.5.4, 4.3.2,<br>4.6.3 |
| 15 | Data should be fitted using a numerical optimisation routine with an appropriate choice for representation of sorption. | 3.1.6 |
| 16 | Parameters utilised in sorption models should be checked for consistency with the state of knowledge concerning their reasonable range. Parameter values based solely on data fitting are inherently uncertain. | 3.4 |
| 17 | Extrapolations to chemical conditions different from those of TSM parameterisation are associated with a high uncertainty (as in all model extrapolations). Extensions to other (but similar) substrates are often possible, but need to be done carefully. Interpolation within the parameter range considered in model parameterisation is expected to be more robust. | 4.6, 5.1.1 |
| 18 | Uncertainty analyses may help to identify those parameters having the greatest influence on calculated $K_d$ (as well as those that are insignificant). | 3.6 |
| 19 | The ability of the model to reproduce specific key aspects of the experimental data such titration curves, adsorption pH edges and isotherms should be tested as much as possible. | See various case studies, Figure 5.4 |
| 20 | Feedback between the modelling and the experimental investigations is crucial. This, if properly documented, is also an essential element of the quality assurance. | 3.3, 4.4.1 |

## 5.5 Building a scientifically defensible, calibrated TSM for radioactive waste applications

In Section 1.3 several requirements for building a TSM were defined. Starting with a clear definition of the model purpose, the level of complexity required of the TSM can be estimated. After analysing the geochemical conditions, the major aqueous components and mineral phases as well as basic physico-chemical processes can be identified. Then the parameterisation of the TSM model follows, with improvement by an iterative process. Model quality and applicability must be checked based on the criteria outlined in Section 1.3.2.

This section summarises the requirements to develop TSMs for complex systems as envisaged for deep geological radioactive waste disposal. Supporting illustrative material comprises four flow charts illustrating the major components required, and their connectivity (i.e. feedback paths). These flowcharts (Figures 5.1 to 5.4) build on the principles mentioned in the tables presented in the previous section.

Figure 5.1 provides a general overview of a TSM development framework, whereas Figures 5.2 to 5.4 focus on some more complex parts of this general overview. The flow charts presented in these figures may guide the developers, users and reviewers of TSM in PA. Though the flowcharts are generic (to avoid excessive complexity), the major paths in developing and applying TSMs within a PA framework are sketched out, as are important decision points.

The various major reasons for developing TSMs in a PA context, and the respective decision chains to implement these models, are shown in Figure 5.1. The flowchart illustrates the iterative approach usually required to refine a TSM. The circles on the right hand side (marked as A, B, and C) point to those parts of the general chart where more detailed information is provided in separate charts: A relates to Figure 5.2, B to Figure 5.3, and C to Figure 5.4.

The topic “Determination of the expected range of geochemical conditions” is expanded in Figure 5.2. The flowchart addresses the different questions arising from either a preliminary scoping stage involving a generic disposal site, or alternatively a more focused study where one (or more) specific locations are investigated. In the former case, one is limited to a review of literature data and generic geochemical modelling. In the latter case, with a specific site identified, a geochemical sampling program together with extensive radionuclide adsorption experiments and associated modelling will be undertaken.

Figure 5.3 focuses on the model-specific settings that eventually define a specific TSM as described in the present volume (EDL term, number and types of surface binding sizes, etc.). All the major questions are listed in a logical order that allows a proper parameterisation of the TSM selected. As indicated (by the notation B’) at the lower part of the flowchart, this is an iterative process and it is likely that more than one iteration of the decision-making process will be made, possibly choosing different options at various decision points.

Finally, Figure 5.4 gives guidance with respect to the way a selected TSM (and its parameterisation) can be assessed by investigating the results of geochemical speciation utilising this TSM. The scheme also covers issues of sensitivity analysis to allow further refinement of the model. The key issues in Figure 5.4 revolve around whether the model that has been developed is able to produce specific aspects of the experimental data such titration curves, adsorption pH edges and isotherms. Note that in this case a model failure leads to a re-examination of the model itself and returns the user to the flowchart in Figure 5.3.

**Figure 5.1: Overview flowchart of TSM modelling framework and resulting approaches**

The small circles on the right of the figure connect to other flowcharts.
"A" relates to Figure 5.2, "B" to Figure 5.3, and "C" to Figure 5.4.
See Section 5.4 for further discussion.

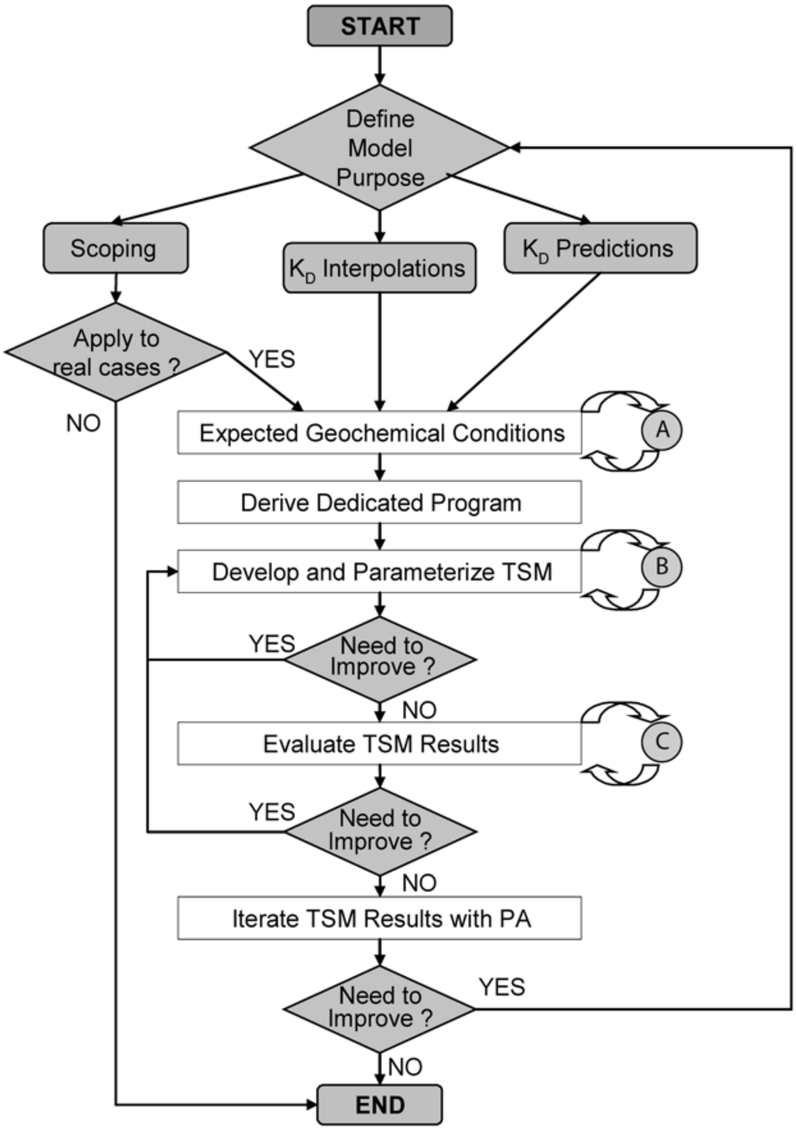


**Figure 5.2: Detailed flowchart to determine the expected range of geochemical conditions for TSM model setup**

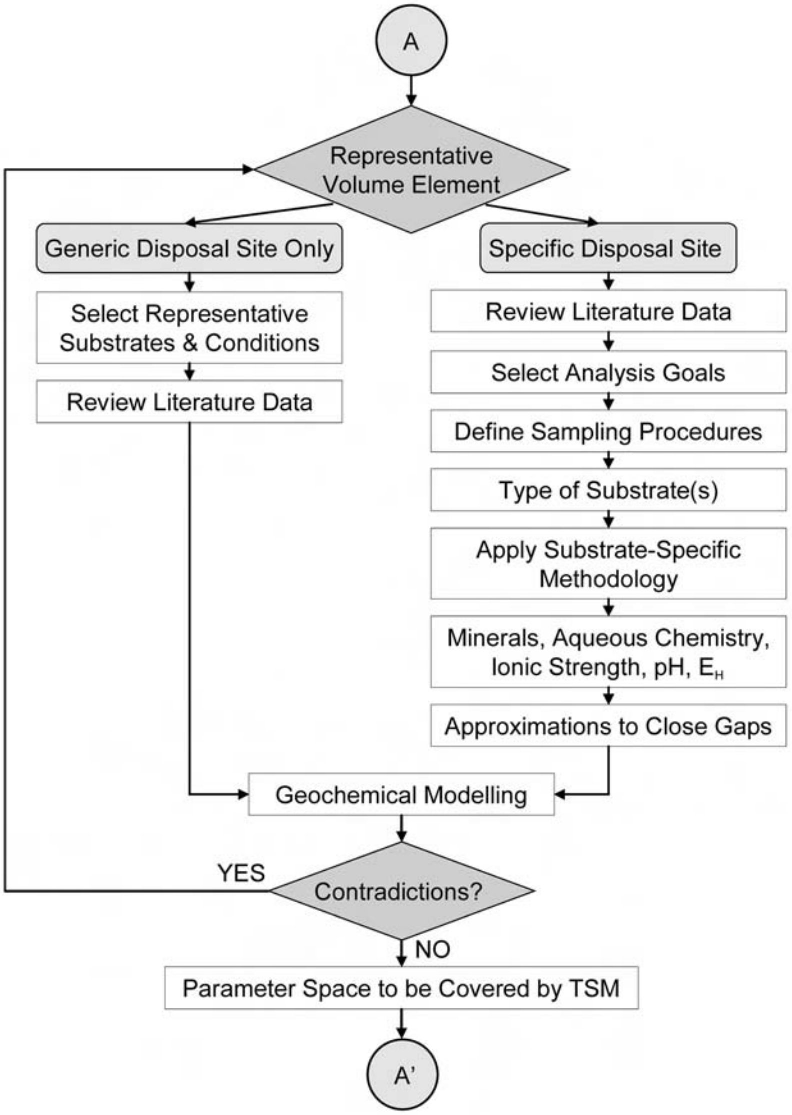


**Figure 5.3: Detailed flowchart to develop and parameterise a specific TSM**

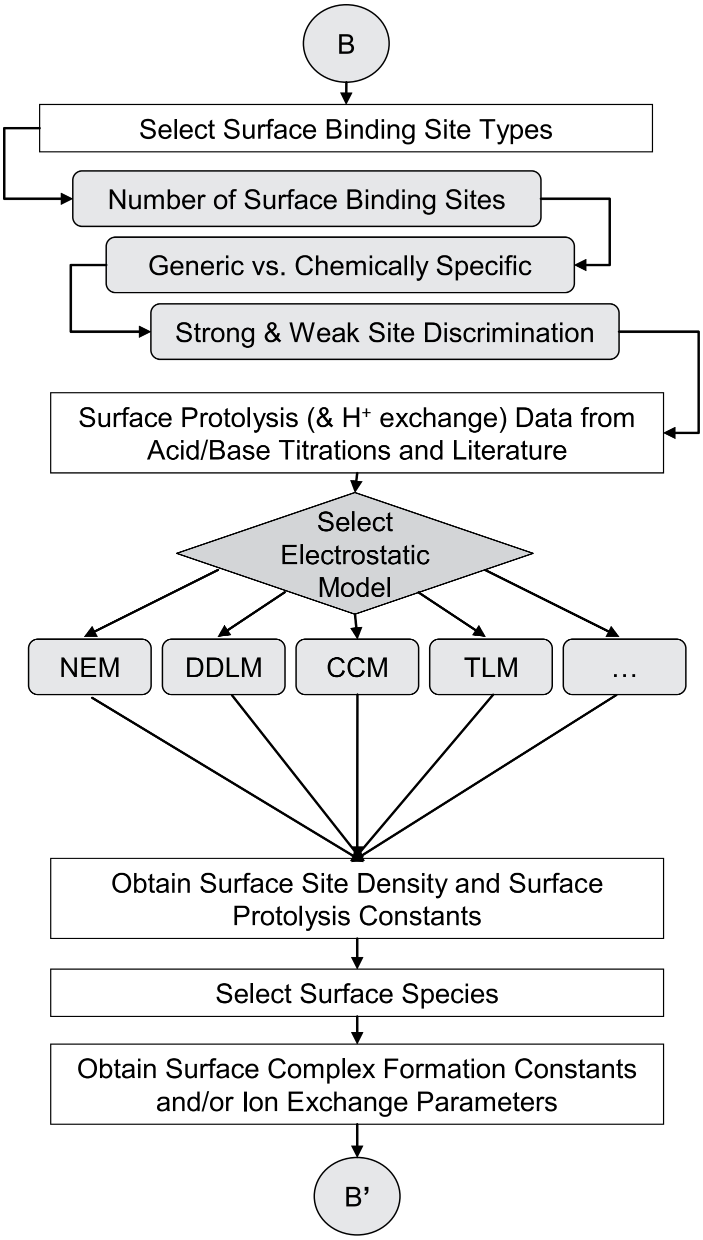
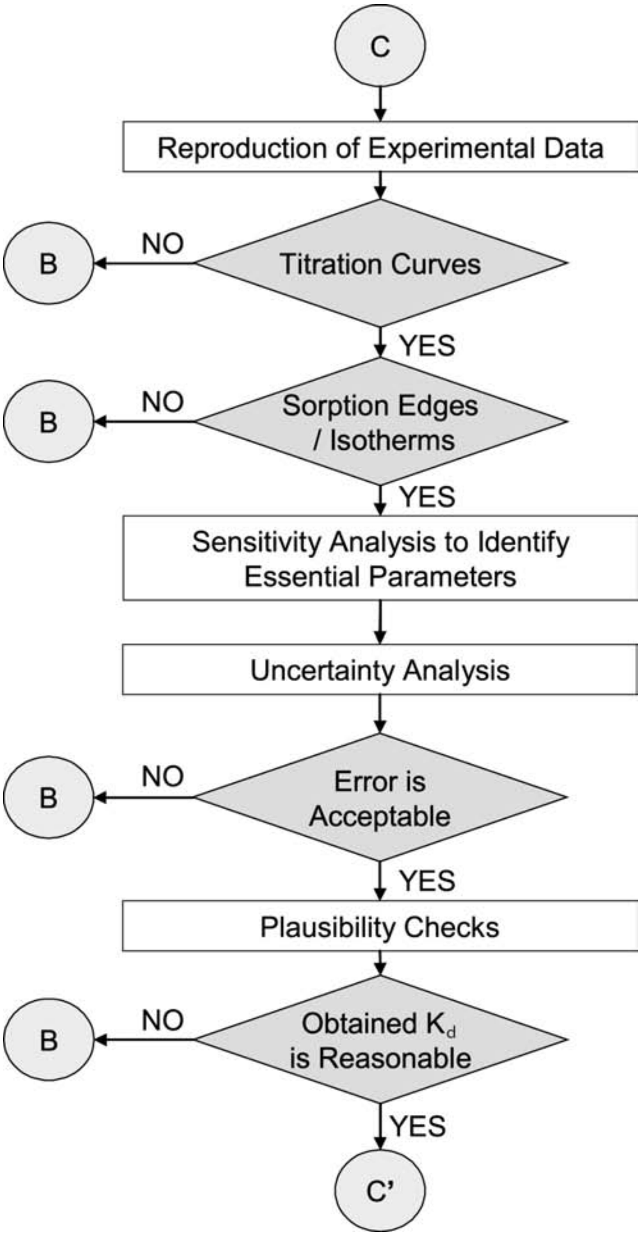


Figure 5.4: Detailed flowchart to evaluate a specific TSM



## 5.6 Concluding comments

The present report demonstrates that the TSM approach has significantly matured during recent decades, to the extent that TSMs can be used for predictive as well as interpretive/supporting purposes in the context of radioactive waste disposal. Some of the key benefits of TSMs are that they can estimate the effects of changes in physico-chemical conditions (that may occur in both time and space), with a degree of dimensionality that cannot be achieved by *in situ* investigations or lab experiments. In addition, a TSM-supported interpretation of sorption data can be systematically embedded in an overall (geo)chemical modelling framework, and therefore enables the experimental sorption data to be interpreted in the context of broader literature data and thermodynamic considerations. Models can be tailored to the desired degree of detail, ranging from a detailed description of the structural, co-ordinative and electrostatic features of a mineral-solution interface on one hand; to a more generalised model, for example, using generic sites and neglecting EDL terms. The latter type of simplified model may be used to demonstrate system understanding at a more generic level. To actually go through a comprehensive benchmark process for a defined real-world system would be a realistic and worthwhile challenge for a future international research effort.

The previous phase of the NEA sorption project (Phase II) showed the potential value of the TSM approach in simulating sorption data for a range of radionuclides and geochemical conditions. This outcome was clearly significant for PA applications. However, the previous phase also highlighted that the same sorption data could be modelled in a number of different ways, and there was a lack of clear guidance on the appropriate methods of model development.

The present Phase III has not specified a single "preferred" modelling sequence that can be applied in a recommended optimum approach. But it has shown that modelling can proceed in a systematic and defensible way, by following some key recommendations, in particular:

1. The objective of the modelling exercise should be carefully defined at the outset.
2. The key decision points in the modelling process at which critical modelling choices must be made should be clearly identified.
3. The range of choices can be reduced and decisions justified by reference to key pieces of experimental or theoretical evidence, and by chemical reasoning. The key evidence used to derive the model should be documented.
4. The modelling should utilise a suitable consultative and iterative model development process, during which it is tested as much as practicable.
5. Confidence in the resulting models can be increased by a decision-making rationale aimed at maintaining consistency with available evidence and by the documentation of key decisions.

Whereas it is still a challenging task to develop and apply an appropriate TSM for a specific case, the present guideline report delivers the essentials to solve this task, namely the basic strategies and tools, but also provides key references and discussions regarding the required input parameters. At the same time, there are ongoing efforts within the scientific community to increase the knowledge about TSMs and to extend the base of available experimental data and TSM parameters in terms of broadening their scope and improving their quality.

One of the challenges facing PA is the necessity to make predictions about the evolution of geochemical systems over very long timescales and about the related behaviour of radionuclides. The ability to do this is dependent, in part, on robust thermodynamic sorption models that can simulate radionuclide behaviour across a wide range of chemical conditions. The recommendations summarised in this volume will facilitate the development of such models.

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# 7. Annexes

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## 7.2 List of acronyms

| | |
|---|---|
| $A_s$ | Specific surface area (same as SSA) |
| ATR-FTIR | Attenuated total reflectance FTIR |
| BET | A method of determining surface area (see Section 3.1.1) |
| BSM | Basic Stern model (an EDL model) |
| $C_1$,$C_2$ | Capacitance(s) of double layer(s) |
| CA | Component additivity (a modeling approach for complex materials) |
| CCM | Constant capacitance model (an EDL model) |
| CD-MUSIC | Charge distribution – multi site complexation (an EDL model) |
| CEC | Cation exchange capacity |
| $C_{init}$, $C_{equil}$ | Initial and equilibrium concentration in a sorption experiment |
| $C_{sat}$ | Concentration at saturation (maximum solubility) |
| CSH | Calcium-silica-hydrate (component of cement paste) |
| $D_a$ | Apparent diffusion coefficient |
| $D_e$ | Effective diffusion coefficient |
| DLM | Diffuse (double) layer model (an EDL model) |
| EDF | Error distribution function |
| EDL | Electrostatic double layer |
| EGME | Ethylene glycol monoethyl ether |
| Eh | Redox potential |
| EXAFS | Extended X-ray absorption fine structure |
| FITEQL | A computer code, primarily used determining equilibrium constants |
| FTIR | Fourier transform infrared |
| GC | Generalised composite (a modeling approach for complex materials) |
| GIXAFS | Grazing incidence EXAFS |
| HFO | Hydrous ferric oxide |
| HLW | High level waste |
| IGSC | Integration Group for the Safety Case (NEA) |
| $K^{app}$ | Apparent equilibrium constant |
| $K_d$ | Distribution coefficient |
| $K_{int}$ | Intrinsic equilibrium constant |
| LFER | Linear free energy relationship |
| MAL | Mass action law |
| MINTEQA2 | A chemical speciation computer code |
| NEM | Non-electrostatic model (a TSM which does not contain an EDL model) |
| $N_S$ | Total number of surface sites |

| | |
|---|---|
| PA | Performance assessment |
| $pCO_2$ | Partial pressure of carbon dioxide (in equilibrium with aqueous phase) |
| PHREEQC | A chemical speciation computer code |
| pK values | Surface protolysis constants |
| PZC | Point of zero charge |
| $R_d$ | Distribution ratio (identical to $K_d$ except equilibrium is not assumed) |
| RES$^3$T | A sorption database |
| $R_f$ | Retardation factor |
| RN | Radionuclide |
| RVE | Representative volume element |
| RWMC | Radioactive Waste Management Committee (NEA) |
| SA | Sensitivity analysis |
| SEM | Scanning electron microscopy |
| SLR | Solid / liquid ratio |
| SSA | Specific surface area (also $A_s$) |
| SSD | Surface site density |
| TDB | Thermodynamic database |
| TLM | Triple layer model (an EDL model) |
| TRLFS | Time resolved laser fluorescence spectroscopy |
| TSM | Thermodynamic sorption model |
| UA | Uncertainty analysis |
| UCODE | An external parameter optimisation shell |
| URL | Underground research laboratory |
| XANES | X-ray absorption near edge spectroscopy |

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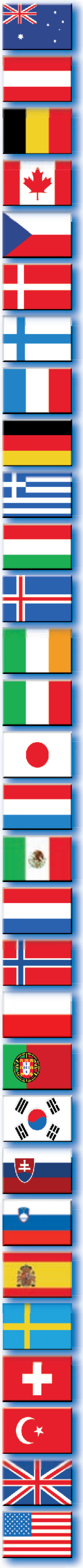

# Thermodynamic Sorption Modelling in Support of Radioactive Waste Disposal Safety Cases

A central safety function of radioactive waste disposal repositories is the prevention or sufficient retardation of radionuclide migration to the biosphere. Performance assessment exercises in various countries, and for a range of disposal scenarios, have demonstrated that one of the most important processes providing this safety function is the sorption of radionuclides along potential migration paths beyond the engineered barriers. Thermodynamic sorption models (TSMs) are key for improving confidence in assumptions made about such radionuclide sorption when preparing a repository's safety case. This report presents guidelines for TSM development as well as their application in repository performance assessments. They will be of particular interest to the sorption modelling community and radionuclide migration modellers in developing safety cases for radioactive waste disposal.

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