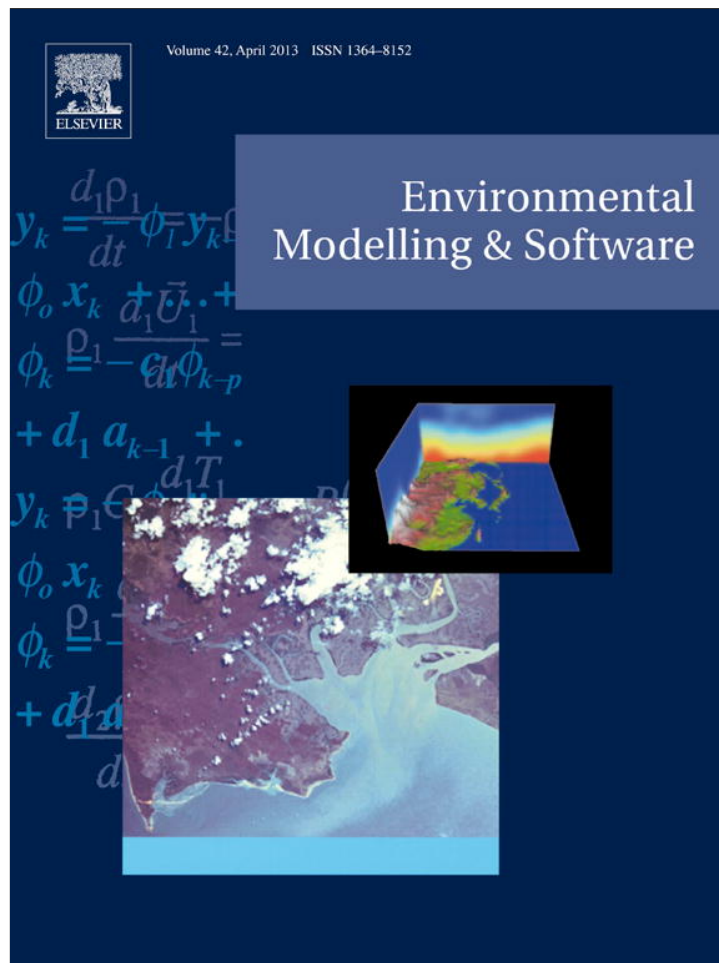


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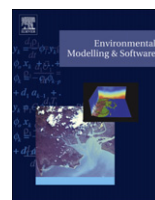
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## Guidelines for thermodynamic sorption modelling in the context of radioactive waste disposal

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### ARTICLE INFO

#### Article history:

Received 11 July 2012

Received in revised form

18 December 2012

Accepted 8 January 2013

Available online 9 February 2013

#### Keywords:

Sorption

Modelling

Radioactive waste

Repository

Distribution coefficient

### ABSTRACT

Thermodynamic sorption models (TSMs) offer the potential to improve the incorporation of sorption in environmental modelling of contaminant migration. One specific application is safety cases for radioactive waste repositories, in which radionuclide sorption on mineral surfaces is usually described using distribution coefficients ( $K_d$  values). TSMs can be utilised to provide a scientific basis for the range of  $K_d$  values included in the repository safety case, and for assessing the response of  $K_d$  to changes in chemical conditions. The development of a TSM involves a series of decisions on model features such as numbers and types of surface sites, sorption reactions and electrostatic correction factors. There has been a lack of consensus on the best ways to develop such models, and on the methods of determination of associated parameter values. The present paper therefore presents recommendations on a number of aspects of model development, which are applicable both to radioactive waste disposal and broader environmental applications.

The TSM should be calibrated using a comprehensive sorption data set for the contaminant of interest, showing the impact of major geochemical parameters including pH, ionic strength, contaminant concentration, the effect of ligands, and major competing ions. Complex natural materials should be thoroughly characterised in terms of mineralogy, surface area, cation exchange capacity, and presence of impurities. During the application of numerical optimisation programs to simulate sorption data, it is often preferable that the TSM should be fitted to the experimentally determined  $K_d$  parameter, rather than to the frequently used percentage sorbed. Two different modelling approaches, the component additivity and generalised composite, can be used for modelling sorption data for complex materials such as soils. Both approaches may be coupled to the same critically reviewed aqueous thermodynamic data sets, and may incorporate the same, or similar, surface reactions and surface species. The quality of the final 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, and capability of simulating independent data sets. Key recommendations for the process of TSM development include: definition of modelling objectives, identification of major decision points, a clear decision-making rationale with reference to experimental or theoretical evidence, utilisation of a suitable consultative and iterative model development process, testing to the maximum practicable extent, and thorough documentation of key decisions. These recommendations are consistent with international benchmarks for environmental modelling.

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## 1. Introduction

The prediction of the behaviour of contaminants that may be released in surface and subsurface environments is a major challenge to environmental scientists worldwide. Such contamination may arise from accidents or from the disposal of waste materials. A significant issue in this context is radioactive wastes, which have accumulated in the past few decades from activities related to the nuclear fuel cycle. The development of an appropriate strategy for safe disposal of radioactive waste is one of the most important problems facing many industrialised countries. A common central safety feature of underground radioactive waste repositories is the prevention, or sufficient retardation, of radionuclide migration to the biosphere. To evaluate the risks that are associated with potential releases along the groundwater pathway, particular attention must be given to the extent of sorption (uptake) of radionuclides on the surfaces of the various solid phases encountered along the migration path. Performance assessment calculations for radioactive waste disposal typically use equilibrium distribution coefficients ( $K_d$ ) to represent sorption, and it is therefore necessary to have scientifically robust arguments for supporting the selected  $K_d$  values and associated uncertainty management. Thermodynamic sorption models (TSMs), which are based on mechanistic chemical models of the sorption process, offer the potential to improve the incorporation of sorption in the overall safety case. However, a comparative modelling exercise has found that, while the TSM approach is highly promising for this purpose, further development and standardisation is desirable to apply TSMs in a scientifically defensible and consistent fashion (Davis et al., 2005).

This paper presents guidelines derived from the most recent phase of the international Sorption Project of the Nuclear Energy Agency (NEA), which aimed to establish a consensus of recommendations for developing TSMs to improve the representation

$$K_d = \frac{\text{amount of element "X" sorbed per unit mass of substrate}}{\text{amount of element "X" dissolved per unit volume of solution}} \quad (1)$$

of radionuclide sorption in the context of radioactive waste disposal (Ochs et al., 2012). The scope of the project included surveying the most appropriate methods for determining parameter values, the impact of individual model components and decisions on the estimated  $K_d$  values, and the effects of uncertainty on the quality of the model outputs. In particular, the project aimed to develop a scientific foundation for applying TSMs to complex and intact geological materials of relevance to safety cases for radioactive waste repositories. The specific aims of the present paper are to:

- (i) introduce the main features of TSMs;
- (ii) discuss the role of the TSM approach for the specific application to radioactive waste disposal;
- (iii) identify and address the key issues relevant to applications of TSMs in repository assessment and broader environmental applications; and
- (iv) assess the proposed modelling approach against international modelling guidelines, specifically the iterative modelling steps developed by Jakeman et al. (2006) and subsequently applied to diverse situations including sediment and nutrient transport in estuaries (Robson et al., 2008) and simulations of environmental fluid mechanics (Blocken and Gualtieri, 2012).

The emphasis of the paper will be on aspects of TSMs relevant to repository performance, particularly radionuclide sorption

reactions and the modelling of the sorption behaviour of complex natural materials. However, the recommendations are applicable to the general problems associated with modelling solute migration in a range of environmental situations.

## 2. Thermodynamic sorption models

### 2.1. Distribution coefficients ( $K_d$ values) and TSMs

Calculations relating to the migration of contaminants in the environment, and in particular the future performance of radioactive waste repositories typically rely on selected key parameters for quantifying contaminant migration. The chemical processes most relevant for the transport of contaminants are often described by the following two parameters:

- the maximum solubility of the contaminant in the various geochemical environments, which is typically assessed using reviewed thermodynamic data and models (e.g. Grenthe et al., 1992); and
- a  $K_d$  value, which quantifies the distribution of a dissolved element between the solution and the solid phases present along relevant transport pathways.

The  $K_d$  value thus represents the sorption process, encapsulating both adsorption and desorption of the contaminant between the solid surface and the aqueous phase. It combines the effects of various processes determining the reversible partitioning between the solid and liquid phases, including surface complexation and ion-exchange (discussed further below). The distribution coefficient ( $K_d$ ) is defined as the ratio of the mass-normalized sorbed concentration of an element "X" to its dissolved concentration:

and typically has units such as mL/g, L/kg or m<sup>3</sup>/kg. The amount of contaminant (in both the numerator and denominator) can be expressed in convenient units (such as moles, milligrams, or, for a radioactive isotope, Bq).

One of the attributes of a  $K_d$  value is that it can be incorporated into transport models, including those used for migration predictions associated with the deep disposal of high level radioactive waste, as well as near-surface repositories for low-level waste. However, in almost all applications  $K_d$  values are considered as constant in time and space, thus lacking any account for heterogeneity and dynamics of environmental conditions.

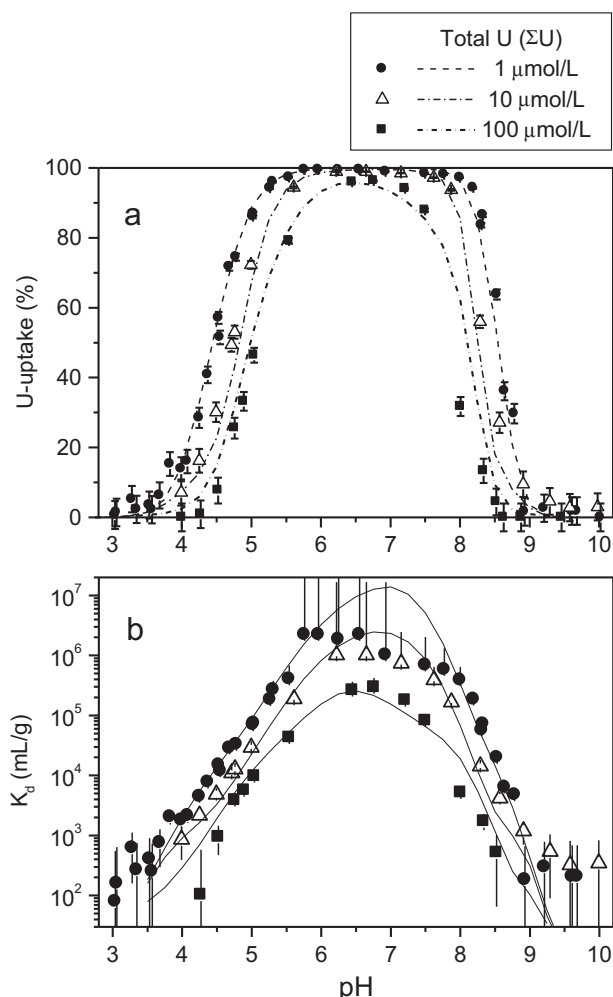
The sensitivity analysis of Nair and Krishnamoorthy (1999) showed that  $K_d$  is among the most critical parameters for the assessment of a shallow waste repository, together with seepage velocity in the unsaturated zone between the facility and the water table, dispersivity in groundwater and the thickness of the unsaturated zone. Similar studies have shown that sorption is a critical process reducing the mobility of radionuclides in the vicinity of high level repositories. For example, the extent of sorption was identified as being one of the geochemical processes that strongly affected the rate of migration of <sup>237</sup>Np from the proposed Yucca Mountain repository (Viswanathan et al., 1998).

The  $K_d$  values for contaminants can be determined in laboratory experiments. In a typical batch sorption experiment, a measured mass of a geological material of interest (such as a clay mineral or a sample of host rock formation material) is shaken with a solution containing a known quantity of a contaminant under well-

controlled conditions. The raw experimental data comprises the amount of the added contaminant remaining in solution, from which the amount sorbed under the conditions of each experiment can be calculated from a material balance. The experimental results can be converted to a  $K_d$  value using the following equation

$$K_d = \left( \frac{C_{\text{init}} - C_{\text{equil}}}{C_{\text{equil}}} \right) \cdot \frac{V}{m} \quad (2)$$

where  $C_{\text{init}}$  and  $C_{\text{equil}}$  denote the initial and equilibrium concentrations of a sorbing element, and  $V$  and  $m$  are the volume of the aqueous phase and the mass of the sorbent, respectively. Other types of experiments which can yield radionuclide retardation factors include flow-through experiments (column tests) as well as static diffusion type tests. Such tests typically involve a higher mass/volume ratio than batch experiments and are therefore a better representation of in situ geological environments. 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 column and diffusion experiments (Ochs et al., 2001, 2012; Tachi et al., 2010).



**Fig. 1.** Experimental data for U(VI) sorption on the amorphous iron mineral ferrihydrite, showing both (a) percentage sorbed and (b)  $K_d$  (calculated using Eq. (2)). Experiments were undertaken in 0.1 M NaNO<sub>3</sub> in equilibrium with air. Error estimates in  $K_d$  were propagated from the experimental sorption data and reflect the greater uncertainty when sorption is close to zero or 100%. Model curves were calculated using a TSM approach (using the sorption reactions and equilibrium constants in Waite et al., 1994).

The sorption of uranium has been extensively studied, and is relevant to a range of environmental problems, including low and high level radioactive waste repositories, mine tailings and environmental dispersion, such as depleted uranium projectiles fired in various conflicts (Eisenbud and Gesell, 1997). Fig. 1(a) shows experimental data for the percentage of uranium adsorbed on ferrihydrite (an iron oxide) as a function of pH for a range of uranium concentrations. The same data have been converted into  $K_d$  values in Fig. 1(b). The experimental  $K_d$  values cover a range of several orders of magnitude, thus demonstrating that the mobility of uranium is very sensitive to the pH and, in this case, affected by the total uranium concentration. In this representative example, both the type and amount of mineral surfaces available for sorption; and the composition of the aqueous solution (including pH, radionuclide concentration, ligands such as carbonate or natural organic substances) play an important role in determining the extent of sorption. Fig. 1 demonstrates that the factors leading to the range of  $K_d$  values need to be understood to derive an adequate model for the environmental mobility of uranium, and the same is true for other contaminants.

The importance of  $K_d$  in describing radionuclide migration has led to the compilation of a number of  $K_d$  databases intended for nuclear waste applications (Jung et al., 2001; Sheppard and Thibault, 1990). While these compilations are useful for demonstrating the range of  $K_d$  values for a specific radionuclide and, in some cases the factors affecting the extent of sorption, the data cannot be extrapolated to a wide range of conditions. Thus,  $K_d$  values are conditional parameters which are specific to a limited range of experimental data. This limits the potential value of collections of  $K_d$  values.

As will be shown throughout this paper, a fundamental underlying model of sorption phenomena, such as a TSM, in which all relevant sorption reactions are described by chemical equations with associated equilibrium constants, can be used to enable:

- direct estimation of contaminant  $K_d$  values for a wide range of scenarios and chemical conditions, thus reducing the number of experimental measurements;
- support or explanation of experimentally measured  $K_d$  values;
- sensitivity and uncertainty analyses regarding the influence of variability and uncertainties in geochemical conditions on  $K_d$ ;
- interpolation or extrapolation from existing data sets to other conditions; and
- scoping calculations to estimate the possible effect of different scenarios on  $K_d$  values.

Thus, the TSM approach enables a more fundamental understanding of sorption processes, compared to sets of  $K_d$  values, and therefore may enable a decrease in the number of conditional parameters incorporated in transport models.

## 2.2. Mineral surfaces and sites

A basic fundamental component of all TSMs is the conceptualisation of the mineral surface as being made up of chemical functional groups with which dissolved species interact through sorption, ion exchange, or hydrogen bonding. The surfaces of the minerals can be considered to fall into two major classes – variable charge and permanent charge types (Sposito, 1989).

The variable charge surfaces exhibit acid–base properties and surface complexation type reactions, which involve direct chemical bonding with surface site atoms. Most oxides, including the iron oxides which are ubiquitous in many environments, exhibit variable charge surfaces, and may have several distinct site types on their different surface planes.

A permanent charge surface is exhibited by many clays. Clay minerals are comprised of composite sheets consisting of layers of aluminium–oxygen octahedra and silicate tetrahedra. Substitution of lower-charged cations (for  $\text{Al}^{3+}$  or  $\text{Si}^{4+}$ ) gives rise to fixed structural charge that is compensated by binding of cations in cavities between the layers and on the outer planes (Sposito, 1989). These cations are exchangeable with others in the aqueous phase through ion exchange reactions (discussed further below). Binding is predominantly electrostatic in nature and relatively weak bonds are formed without a change in surface charge. A single mineral can exhibit different site types on its surface; for example, clays exhibit ion exchange interlayer sites, planar face sites and variable charge surface complexation edge sites.

The identification of site types and estimation of their concentrations are extremely important in the development of TSMs. Structural models for specific mineral phases can be used to estimate the number of functional groups per unit area of surface. 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 often in the range of 4–30 sites/nm<sup>2</sup>. In natural systems, which are the focus of this paper, sorption is often controlled by trace or mixed phases, therefore structural models are unlikely to be useful, although advanced methods may be applied to identify the key phases (Stubbs et al., 2009).

For both simple and complex materials, the number of surface sites can be estimated from the specific surface area (SSA) of the solid phase (which, as discussed in Section 4.1, can be measured by various methods). Some authors have proposed adopting a single constant total site density of 3.84  $\mu\text{mol}/\text{m}^2$  (2.31 sites/nm<sup>2</sup>) for all oxide solids to develop a uniform modelling approach across a wide range of adsorbing materials and facilitate comparison of derived log  $K$  values (Davis and Kent, 1990). The number of ion exchange sites (cation exchange capacity or CEC) can be estimated by chemical methods which involve replacing all exchangeable ions with a particular index cation (Sposito, 1989).

### 2.3. Chemical basis of TSMs

TSMs share the same basic principles as the widely accepted equilibrium models for solution chemistry (Morel and Hering, 1993), which are based upon mass action laws (MALs) representing chemical reactions. The fundamental concepts within such a framework are:

- The selection of the chemical components, which are a set of fundamental building blocks that can be combined to form all the chemical species in the system. Chemical elements or simple ions are often selected as components (e.g.  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{UO}_2^{2+}$ ). Other choices are possible, so long as they meet the requirement that no component can be expressed as a combination of other components.
- The identification of all chemical species which can be formed by combining one or more components. The definition of each species depends on the selected set of components.
- The charge neutrality requirement and the mass balance, by which the combined concentrations of all species containing a given component are governed by the fixed total quantity of that component.
- The MAL for each species, in which the activities of all chemical species and components involved in a chemical reaction are related by a thermodynamic stability constant (log  $K$  value).
- An underlying thermodynamic database containing the stability constants for all relevant dissolved (and solid) species.

- A model for calculating the thermodynamic activity coefficients of dissolved species (as well as solid solution members or non-ideal gases if relevant).

The basic concepts presented above are applicable for the models relying on the MAL approach, which have constituted the vast majority of TSMs developed thus far.

The TSM approach is based on a set of adsorption reactions on the relevant surfaces, each with an associated equilibrium constant. Thus, surface sites are visualised as taking part in reactions in a similar way to any other entity in the system. In the most commonly applied types of TSMs (known as the “2 pK” models), some of the surface atoms ( $>S$ ) can react with water to form surface hydroxyl groups, which can be depicted as having zero charge ( $>SOH^0$ ). These groups undergo acid–base reactions similar to ligands or metal ions in aqueous electrolyte solution. These reactions can be assigned equilibrium constants. For example, the deprotonation reaction of an acidic surface site is represented by:



with an acidity constant given by:

$$K_{al}^{app} = \frac{[>SOH^0]\{H^+\}}{[>SOH_2^+]} \quad (4)$$

Here the square brackets denote concentrations and the round brackets activities.  $K_{al}^{app}$  is an apparent equilibrium constant because it is dependent on the surface charge (Dzombak and Morel, 1990; Morel and Hering, 1993). There are analogous equations for the removal of the second proton:

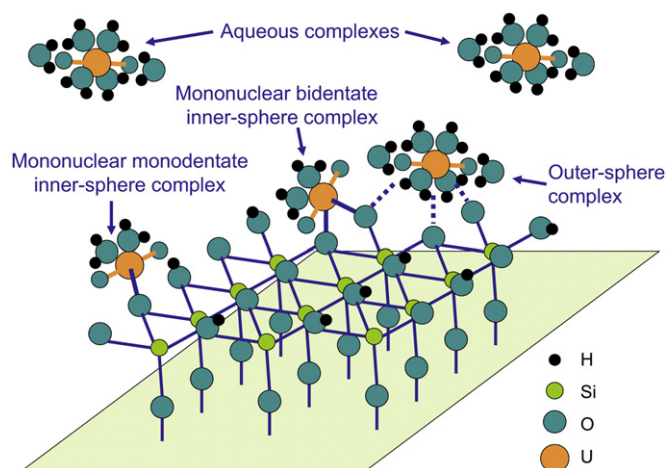


$$K_{a2}^{app} = \frac{[>SO^-]\{H^+\}}{[>SOH^0]} \quad (6)$$

The uptake of ions at a mineral surface changes the surface charge, which means an electrostatic interface layer (EIL) model is often a component of the overall TSM, to correct for the effects of surface charge on equilibrium constants. A number of EIL models for the interface have been developed and applied to modelling sorption, such as the diffuse layer, triple layer, and constant capacitance models (Davis and Kent, 1990; Marmier and Fromage, 1999). The main differences between the various EIL models are the number of adsorption planes, and how the relationships between the charge density and the electrostatic potential at these planes are defined. Multi-site surface complexation models, with the charge distributed between surface planes have also been developed (Hiemstra and van Riemsdijk, 1996; Hiemstra et al., 1989). In cases where the chemical contribution to the free energy of adsorption dominates over the electrostatic contribution, a non-electrostatic model (NEM) can be an acceptable simple alternative to using an EIL model (Davis et al., 1998). The NEM is often applied in modelling natural materials where the electrostatic effects are difficult to quantify (Bradbury and Baeyens, 1997; Stoliker et al., 2011), and, in effect, the EIL term becomes incorporated within equilibrium constants for sorption reactions (discussed further below).

### 2.4. Radionuclide surface complexation and ion exchange reactions

The distinguishing feature of TSMs is the explicit representation of sorption by one or more chemical reactions involving



**Fig. 2.** Inner sphere and outer sphere surface complexes on a metal oxide–water interface are distinguished by the types of chemical bonding between the aqueous ion and the surface site. In the outer sphere complex, the ion retains its hydration sphere and attaches to the surface via electrostatic forces, whereas the inner sphere complex is partially dehydrated and directly bound to the surface. U(VI) sorption onto a silica surface is used here as illustrative example.

radionuclides and the surface sites. One of the key issues is how to describe and model these surface reactions. While a number of interactions of radionuclides with surface groups are possible, 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 at a greater distance from the surface (Fig. 2). As a result, this species is associated with the surface mainly by electrostatic forces, which are weaker than inner sphere type bonds.

There are several important types of radionuclide adsorption reactions (Table 1), including simple adsorption reactions, reactions involving simultaneous ligand sorption (to form ternary surface complexes), and reactions involving multiple surface sites (multidentate sorption). Multiple sorbing species may attach to each site (polynuclear adsorption) at relatively high dissolved radionuclide concentrations (this is analogous to the formation of polynuclear solution complexes). Cations, such as uranyl ( $\text{UO}_2^{2+}$ ), are known to bind to two or more surface oxygens, which can be represented as a bidentate reaction. In a TSM, an equilibrium constant ( $\log K$  value) is associated with each reaction, typically defined analogously to equilibrium constants in aqueous chemistry (Davis and Kent, 1990; Dzombak and Morel, 1990) although some surface reactions (such as multidentate adsorption) require specific formulation of the associated equilibrium constants (Benjamin, 2002). While the details of the modelling are described elsewhere (Ochs et al., 2012), the key feature of the TSM approach is incorporation of a range of realistic and relevant surface reactions.

Ion exchange reactions are another important surface process affecting the migration of contaminants in aqueous systems. In an ion exchange reaction, there is no formation of covalent bonds with an atom contained in the solid matrix (i.e. only outer sphere complexes are formed). The classical ion exchange models assume that all permanent charges are balanced by exchangeable ions. For monovalent ions, such reactions can be represented as:



Here  $\text{X}^-$  represents the negatively charged cation exchange site. In most cases, there is some preference (selectivity) of one ion over another by the exchanging surface (Sposito, 1989). This can be expressed by the selectivity constant:

$${}^M_{\text{Na}}K_{\text{ex}} = \frac{[\text{X}^- \text{M}]\{\text{Na}^+\}}{[\text{X}^- \text{Na}]\{\text{M}^+\}} \quad (8)$$

representing the selectivity of the ion-exchange site for  $\text{M}^+$  with regard to  $\text{Na}^+$ . Ion exchange may also involve the exchange of a divalent cation for two singly charged ions:



It follows that a TSM for describing radionuclide sorption in oxide and clay materials should include the equilibrium constants for deprotonation reactions (equations (3) and (5)), surface complexation parameters ( $\log K$  values for reactions in Table 1) and ion exchange parameters for the radionuclide (e.g. reactions (7) and (9)), plus the ion exchange coefficients for all exchange reactions involving major cations, and surface complexation reactions of these species if relevant. The equilibrium constants ( $\log K$  values) for surface reactions are critical components of TSMs, and there is an extensive literature on methods of deriving  $\log K$  values for key reactions from experimental data as well as determining the associated uncertainties in these parameters (Dzombak and Morel, 1990; Herbelin and Westall, 1999; Stoulikar et al., 2011).

In recent years, advanced techniques, particularly the synchrotron-based technique of extended X-ray absorption fine structure (EXAFS) spectroscopy, have provided valuable information about surface speciation. EXAFS spectroscopy probes the coordination environment (i.e. type of neighbouring atoms, bond length and coordination number) of adsorbed species (Brown and Sturchio, 2002). For example, EXAFS spectroscopy of radionuclides on clay mineral surfaces can be used to distinguish between sorption on ion exchange and edge sites (Papelis and Hayes, 1996). Similarly, EXAFS can be used to differentiate various forms of adsorbed and precipitated species. The radionuclide surface coverage and total contaminant concentration are often unrealistically high in EXAFS studies, which may limit the applicability of the results. A recent EXAFS study of Zn sorption on montmorillonite demonstrated distinct crystallographic differences between sorption complexes formed at weak and strong sites (Dähn et al., 2011).

**Table 1**

Surface complexation reactions typical of oxide surfaces (here cationic radionuclides are represented as  $\text{M}^{z+}$  and anions (ligands) as  $\text{L}^{y-}$ ).

Reaction type	Representative equations
Adsorption of a z-valent cation ( $\text{M}^{z+}$ ) on a surface	$>\text{SOH}^0 + \text{M}^{z+} \rightleftharpoons >\text{SOM}^{z-1} + \text{H}^+$
Adsorption accompanied by hydrolysis	$>\text{SOH}^0 + \text{M}^{z+} + \text{H}_2\text{O} \rightleftharpoons >\text{SOMOH}^{z-2} + 2\text{H}^+$
Adsorption of anions $\text{L}^{y-}$ (e.g. $\text{SeO}_4^{2-}$ , $\text{SeO}_3^{2-}$ , $\text{CrO}_4^{2-}$ , $\text{SO}_4^{2-}$ ), usually represented as a ligand exchange or a ligand attachment reaction	$>\text{SOH}^0 + \text{L}^{y-} + \text{H}^+ \rightleftharpoons >\text{SL}^{-y+1} + \text{H}_2\text{O}$ $>\text{SOH}^0 + \text{L}^{y-} \rightleftharpoons >\text{SOHL}^{y-}$
Formation of polynuclear (e.g. binuclear) surface complexes	$>\text{SOH}^0 + 2\text{M}^{z+} \rightleftharpoons >\text{SOM}_2^{z-1} + \text{H}^+$
Cations binding to two or more surface oxygens, represented as a bi- or multidentate reaction	$2 >\text{SOH}^0 + \text{M}^{z+} \rightleftharpoons (>\text{SO})_2\text{M}^{z-2} + 2\text{H}^+$
Formation of ‘ternary’ surface complexes involving both cations ( $\text{M}^{z+}$ ) and anions ( $\text{L}^{y-}$ ) such as $\text{CO}_3^{2-}$	$>\text{SOH}^0 + \text{M}^{z+} + \text{L}^{y-} \rightleftharpoons >\text{SOML}^{z-1-y} + \text{H}^+$

Another technique that has found increasing applications in surface structural studies is infrared spectroscopy, in particular the surface-sensitive technique of ATR–FTIR (attenuated total reflectance–Fourier transform infrared) spectroscopy. This enables the surface speciation of a contaminant to be studied in real-time and can enable the kinetics and formation of outer and inner sphere complexes to be investigated (Muller et al., 2012). Although spectroscopic studies can provide useful constraints for the suite of

reactions to be included in TSMs, they rarely give unambiguous information relevant to the trace concentration conditions typical of radionuclide migration in repository contexts.

2.5. Overall model synthesis

TSM development requires decisions to be made on several key issues that have been discussed above. A representative

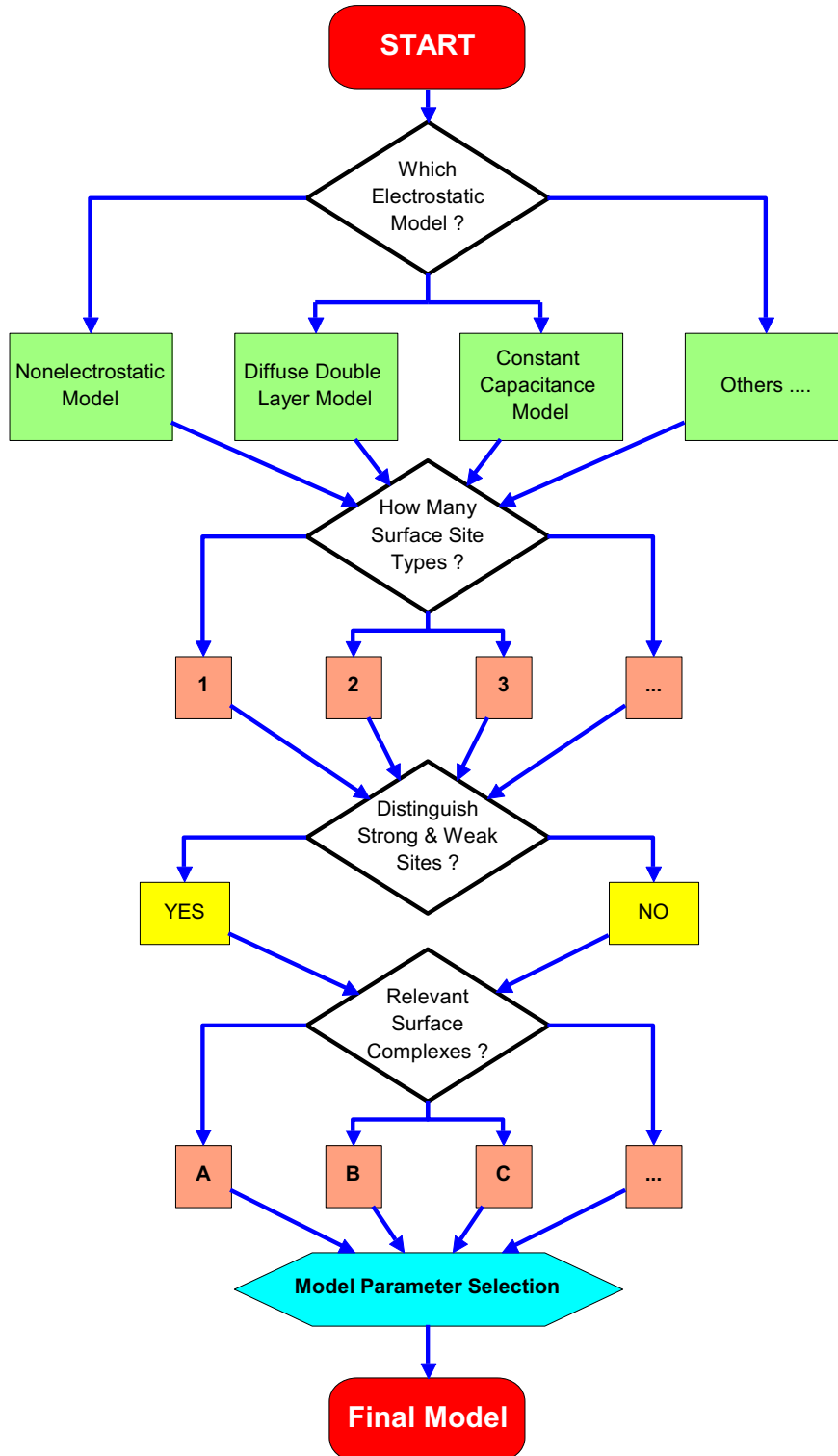


Fig. 3. Generalised decision tree for TSM development choices.

sequence of decision-making is summarised in Fig. 3. The typical strategy (which can be adapted to specific needs) is firstly to determine the specific surface area of the sorbent, then to define an initial set of relevant binding site types (which can later be refined) and to estimate the respective site concentrations. If the structure of surface complexes has been established (for example by EXAFS), the decision on the relevant surface complexes may precede the selection of site types (Waite et al., 1994), whereas in other cases, particularly those involving complex natural materials, it is more common to estimate the site populations and types and then select suitable surface reactions (Davis et al., 1998).

An EIL model (or NEM) is typically selected at an early stage, because the data processing depends on the type of model (Marmier and Fromage, 1999). It is usually difficult to estimate EIL parameters and/or surface protolysis constants independently of site densities, so these parameters may be determined simultaneously. The next step is to simulate data from radionuclide sorption experiments and derive surface complexation constants, using plausible reactions (such as those represented in Table 1). As these simulations 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) which can assist in optimizing experiments or can be used as a first approximation for parameter values (Ochs et al., 2012).

There are various approaches for allocating the total surface site concentration between different possible binding site types. As discussed above, specific sites might relate to distinct crystallographic planes on mineral surfaces, or specific elemental sites on a surface (for example silanol (Si–OH) and aluminol (Al–OH) on the surfaces of aluminosilicate minerals). This selection can facilitate estimates for certain reactions on the basis of outcomes for similar materials (such as deprotonation reactions, Eqs. (3) and (5)).

In many models, generic sites (e.g. surface hydroxyl groups denoted  $>\text{SOH}^0$ ) are incorporated in the absence of specific information on surface site types. A generic site is not associated with a specific type of surface site (such as a silanol or iron oxide site) and, at the commencement of modelling, has undefined properties (e.g. protonation constants or  $\log K$  values for sorption reactions). In most cases, these associated parameters will be assigned optimised numerical values during the modelling process. The number of such sites may range from a single type of sorption binding site, or two sites (e.g. generic weak and strong sites), or multiple sites. Adsorption across a range of sorbate 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 optimization techniques (Davis et al., 1998), and to define the weak sites as the difference relative to the total site concentration. In many cases, EXAFS data only provides the structure of one, or a limited number of surface complexes on specific minerals, and the weak and strong sites on these minerals are differentiated only by the values of the equilibrium constants (rather than different surface complexes). Different surface complexes may occur on the various minerals in complex materials and their structures will depend on the coordination environment at each surface.

If experimental sorption data are collected over a wide enough range of sorbate concentration, a three-site model may be justified (Davis et al., 2004). Often the final model is arrived at by a compromise between model complexity (number of sites and

reactions) against goodness of fit to the experimental data (Kohler et al., 1996). 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.

### 3. Considerations in TSM development

#### 3.1. Modelling objectives and degree of detail

The role of TSMs in describing the environmental behaviour of a contaminant depends on the specific application, which can range from quantitative estimation of  $K_d$  values as a function of chemical conditions, to qualitative support for radionuclide migration models (as reviewed in Section 2.1). A TSM can provide a scientific basis for the range of  $K_d$  values in a transport model, and a means of assessing future changes in  $K_d$  values resulting from alternative scenarios of the evolution of the repository system.

The complexity of natural and engineered repository systems makes it impossible to experimentally determine radionuclide sorption systematically for all conceivable sets of conditions. Therefore, experiments with site-specific conditions may be supplemented by a much larger set of data for representative, or model, systems. Because TSMs provide a consistent and quantitative framework for linking geochemistry with radionuclide sorption, they represent an ideal tool for integrating all available types of sorption information. Therefore, TSMs can serve as guidance of experimental  $K_d$  acquisition programmes, for example through the:

- selection of parameter spaces to be covered using sensitivity analyses;
- optimisation of experimental design through screening calculations (for example, identifying the most critical conditions for experimental measurements);
- interpretation and consistent combination of sets of laboratory data and data obtained on site-specific samples, using TSMs calibrated on the basis of laboratory data;
- detection of gaps in the database for experimental study, accompanied by a (partial) filling of such gaps with estimates based on TSMs, possibly complemented by the application of thermodynamic relationships and chemical reasoning.

The amount of detail in a TSM is dependent on the modelling objectives. If the aim is to describe quantitatively only the available experimental sorption data as closely as possible, then scientific rigour (e.g. incorporation of surface structural data from EXAFS) is less important than a convenient mathematical form. 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, and it is improbable that such a fundamental approach can be readily applied to the complex real world systems of interest to performance assessment for radioactive waste disposal.

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 give a simplified representation of reality implies that the associated parameter values (which represent measurable properties of the system) must lie within reasonable ranges. Such a constraint does not apply to optimised variables which have been extracted by simply fitting experimental data.



An intermediate objective between a purely fitted approach and a fully mechanistic model may therefore be 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 type of TSM approach for modelling sorption is more complex than empirical approaches (such as  $K_d$  values). However, it offers a method for directly coupling all relevant sorption and geochemical equilibria in a common thermodynamic framework.

### 3.2. Defining model quality

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. A previous international project showed that the TSMs constructed by various independent teams were able to reproduce trends, and in most cases magnitudes, of  $K_d$  values for a variety of mineral substrates and aqueous chemical conditions for a number of sorption data sets (Davis et al., 2005). This demonstrated the fundamental benefits of the TSM approach in its ability to handle geochemical variability. However, the individual models diverged substantially in important features, such as incorporation of highly dissimilar sets of chemical sorption reactions, site densities or electrostatic correction terms. It was also demonstrated that the number of fitted model parameters was a major factor in determining the final model performance. It was concluded that sorption modelling was not adequately standardised, particularly for complex materials.

The features and characteristics contributing to the overall quality of a sorption model may be summarised in the following list.

#### 3.2.1. An appropriate level of complexity

Complexity here refers to the number of parameters (not necessarily fitted) in a model. A high level of complexity is not always a negative model feature, as it may reflect a detailed fundamental understanding. However, the presence of a large number of adjustable parameters in a TSM may indicate a poor representation of the system. Therefore, a simple TSM with a small number of parameters may be preferable to a model having numerous fitted parameters, which cannot be properly constrained. On the other hand, a complex model having several derived parameters (including some which have been optimized) may be more reasonable than one with a smaller number of adjustable and chemically (or physically) meaningless parameters. As observed by Kohler et al. (1996) the best models represent a trade-off between model complexity and goodness of fit.

#### 3.2.2. A limited number of adjustable parameters

While fitting the experimental sorption 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 fitted parameters. A previous TSM intercomparison exercise showed modellers incorporated from zero to 15 adjustable parameters in a sorption model (Davis et al., 2005; Payne et al., 2004b), but the models with more fitted parameters did not always provide the best simulations of the data. 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).

#### 3.2.3. Documented and traceable decisions

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 has not been made clear why a certain choice has been made, or which alternatives were considered (Davis et al., 2005). Thus, traceability of the TSM components is necessary and the rationale for selecting model parameters should be documented.

#### 3.2.4. Internal consistency

There is a fundamental requirement for internal consistency. One reason for this is the dependence of the numerical values of derived parameters (such as  $\log K$  values for sorption reactions) on the specific aqueous reactions and associated equilibrium constants which are present in the thermodynamic database which was used during their derivation. It is therefore not appropriate to combine  $\log K$  values from different sources (without recalculation) unless the associated thermodynamic data are the same. In addition, there is a documented interdependence of TSM parameters within a given sorption model framework (Lutzenkirchen, 1999). For example, there is an apparent negative correlation between site density and equilibrium constants (Goldberg, 1991). Thus, selected parameter values (including aqueous thermodynamic data) must be taken from compatible sources or alternatively re-fitted to the experimental data within a self-consistent TSM framework (Davis et al., 2005; Dzombak and Morel, 1990).

#### 3.2.5. An adequate fit to a comprehensive calibration data set

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. 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.

#### 3.2.6. Capability of simulating independent data sets

An important test of a TSM is its ability to model independent data sets measured for a different set of conditions, by different methods, or for another mineral preparation or mixed mineral assemblage. 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 derived by different experimental protocols may reveal the importance of experimental error in sorption data sets, or be attributable to differences in methods for directly measurable model parameters (for example, surface area, as discussed in Section 4.1).

### 3.3. Determination of parameter values and target functions

A central part of the modelling is the fitting of the TSM to the experimental sorption data (calibration data set). This requires both a geochemical speciation code capable of handling the relevant type of TSM as well as a numerical engine providing robust optimization schemes and detailed statistical output. The computer code FITEQL has been designed to address these requirements simultaneously within one program and thus has been extensively used (Herbelin and Westall, 1999). These types of programs enable the estimation of TSM parameters from experimental data (such as acid–base surface titration data, or data for radionuclide sorbed as a function of pH in Fig. 1). This type of inverse modelling program optimises the various adjustable parameters, typically including the equilibrium constants ( $\log K$  values) for the formation of surface

species, as well as some parameters of the chosen electrostatic model (e.g. capacitance). This process is dependent on the chemical model (e.g. aqueous speciation, complexation constants, activity coefficients, site density, selection of surface complexes and double layer corrections). Uncertainties in the final model may originate from errors in experimental measurements and conditions (pH, mineral surface area, temperature, redox potential, etc) as well as from the model development and numerical fitting process (Ochs et al., 2012). These lead to uncertainties in derived parameters such as site densities, protolysis constants, EIL terms (e.g. layer capacitances) and log  $K$  values. Therefore, all measured and optimised parameters in a TSM should have an associated error estimate (Herbelin and Westall, 1999; Stoliker et al., 2011).

In such an optimisation process it is important to define the correct target function (i.e. the data (sub)set which is being simulated). An improper choice of the target function may bias the outcome of the fitting exercise. Presentation of sorption data as percentage sorbed values is common in the environmental sciences

literature, where pH sorption edges usually provide the main part of the data sets used in modelling. However the numerical fitting of the raw data for radionuclide adsorbed will emphasise the pH range of the sorption edge (where sorption increases rapidly from near-zero towards 100%) and gives much less weight to the pH region where higher sorption occurs (>95% sorbed).

An example of the differences in quality of fit obtained with different target functions is demonstrated in Fig. 4. Here, the model was fitted to the sorption edge data expressed in terms of percentage sorbed (Fig. 4(i)). Whilst appearing to be an adequate representation of the sorption edge, it actually provides a poor fit to the experimental  $K_d$  data, as shown in Fig. 4(ii). Thus, direct fitting to the  $K_d$  data (or possibly log  $K_d$ ) is often preferred for derivation of TSM parameters.

### 3.4. Requirement for a comprehensive calibration data set

The predictive capability of TSMs is limited if the experimental sorption data are only obtained over a limited range of conditions, or by varying only a small number of experimental parameters. For example, a model derived from a sorption 'isotherm' (where sorption is studied as a function of total radionuclide concentration with all other chemical conditions, including temperature, fixed) may not provide any predictive capability if another parameter, such as the pH, is varied. To adequately constrain sorption models, large data sets, showing the dependence of sorption on numerous experimental parameters, are required. These parameters should include pH, ionic strength and radionuclide concentration, and preferably other variables such as the concentration of competing and complexing ligands or the redox potential. These various types of data can help to understand the importance of various types of surface species, including inner and outer sphere complexes, or ternary surface complexes (Table 1).

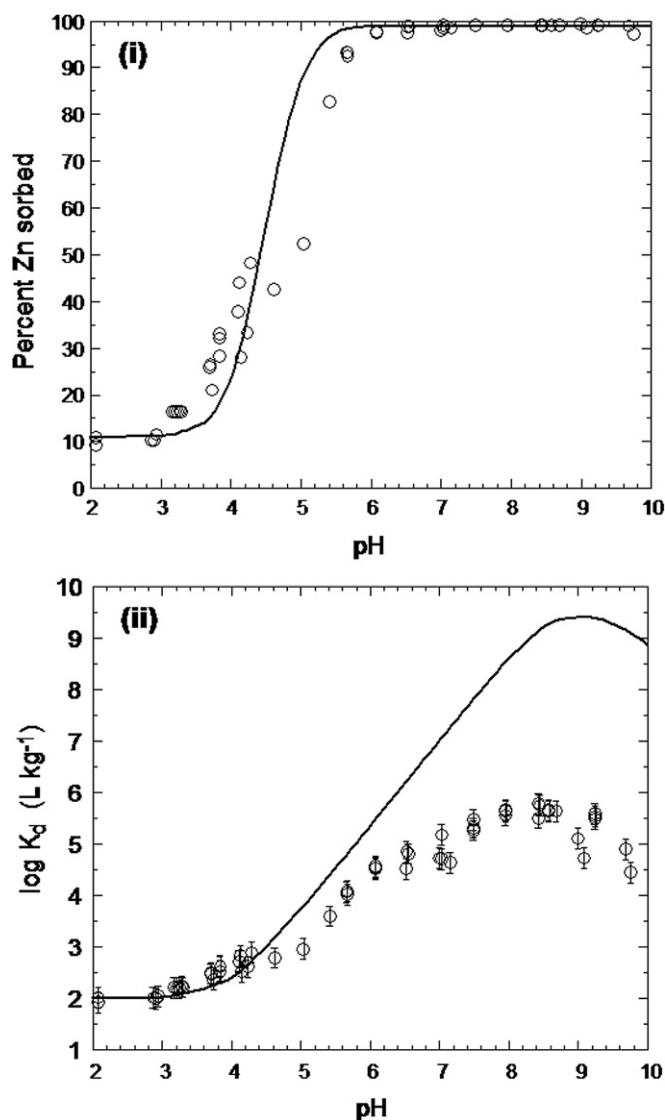
The dependence on radionuclide concentration can be particularly important in identifying any possible precipitation reactions which may occur at high radionuclide concentrations. While modern solid-phase analytical techniques can often distinguish between sorption and precipitation processes, the complex mixture of solid phases and the low concentrations of the radionuclide may prevent characterisation of the mode of retention of the radionuclide. Therefore, modelling must be guided by inferences drawn from experiments in which several parameters are systematically varied. A controlled set of experiments with systematic variation of conditions and with different sorbing materials can be very useful in developing models for radionuclide sorption. Systematic variation of total metal and ligand concentrations can enable the different mechanisms of sorption and precipitation to be distinguished (Payne et al., 2001).

The use of this type of reasoning is particularly valuable when direct experimental evidence for the structure of surface complexes or trace phases is not available. This remains the case for many examples of mobility of trace contaminants in the environment. However, when it is possible to apply multi-parameter sorption data sets in combination with advanced analytical techniques (such as EXAFS), model results can be very convincing. The parallel use of sorption databases and structural studies is a promising way towards improved models of interactions at mineral–water interfaces.

## 4. Complex natural materials

### 4.1. Characterisation of site densities of complex materials

When TSM approaches are applied to complex natural materials, such as soils and sediments, it is important to determine both the total amount of sorbing sites and the abundance of the



**Fig. 4.** Sorption edge data for Zn measured on Na-montmorillonite in 0.1 M NaClO<sub>4</sub>. (i) Data presented as % sorbed versus pH; (ii) Data presented as experimental distribution coefficient (log  $K_d$ ) versus pH. The curve is the best fit of the data presented in (i) obtained with a TSM (Bradbury and Baeyens, 1997). Solid liquid ratio was 1.2 g l<sup>-1</sup>, total Zinc inventory was 1 mmol kg<sup>-1</sup>.

individual component phases which may have an impact on radionuclide adsorption. The specific surface area is often measured to characterise a natural material for sorption modelling (Davis and Kent, 1990; Payne et al., 2011). The surface area can serve as an indication of the total number of sorbing sites, using conversion factors such as 2.31 sites/nm<sup>2</sup>, as recommended by Davis and Kent (1990). Most of the methods of surface area measurement involve the adsorption of molecules of known dimensions from either the gas or liquid phases, with interpretation by various mechanistic models. The commonly used BET method, named after its originators (Brunauer et al., 1938), involves measurement of adsorption of a gas such as nitrogen on a dried solid, while other methods involve the uptake of organic molecules such as ethylene glycol monoethyl ether (EGME) (Yukselen and Kaya, 2006). The surface areas of soils vary across an extremely wide range, with reported values ranging from approximately 1 m<sup>2</sup>/g to over 1000 m<sup>2</sup>/g (Payne et al., 2011). Soils containing large fractions of amorphous or clay minerals can have very large surface areas, particularly those containing a significant proportion of expanding clay minerals, such as montmorillonite. Unlike the BET method, the EGME measurement includes the internal surfaces of swelling clays, hence for some soils, the BET and EGME measurements can differ by an order of magnitude or more (Yukselen and Kaya, 2006). Determining the surface area of consolidated materials such as rocks can be problematic because the sorption properties of crystalline materials can be dominated by fracture surfaces, and crushing can create new surfaces (Bradbury and Baeyens, 1998).

As well as having a range of SSA, various natural materials also differ in their cation exchange capacity (CEC) (Section 2.2). The CEC is related to the layer charge of clays, and is expected to have a significant effect on radionuclide sorption, particularly where ion exchange is the dominant sorption mechanism (Sposito, 1989). Thus, one of the key requirements in characterising natural materials is to estimate the CEC as well as the total number of sorption sites as determined by the surface area.

#### 4.2. Abundance and role of different site types

Once the total number of sorption sites has been determined, one of the key issues in applying the TSM approach to sediments and soils is determining (or estimating) the specific type and relative abundance of mineral functional groups on the adsorbing surfaces. 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 microscopic analysis. Considerable progress has been made in identifying key minerals retaining radioactive contaminants, for example identifying host phases for uranium using electron microscopy (Stubbs et al., 2009).

While the implementation of a TSM approach based on a full characterisation of component minerals remains difficult for a complex mixture, it may be possible to assume that there are preferential sorbing phases that dominate its behaviour. TSM predictions are sometimes made by assuming that a single mineral component dominates adsorption (Waite et al., 2000), 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. Demonstrating that one mineral component dominates adsorption can be difficult, however, and may have to be justified by multiple lines of qualitative evidence. One method of achieving this is to use sequential extractions (Davis et al., 2004, 2005; Yanase et al., 1991). Such

methods can be used to determine the amounts of amorphous or crystalline oxides, which may dominate sorption of radionuclides. In some cases, individual minerals and their contribution to sorption cannot be identified, in which case modelling must proceed by a general approach, as discussed below.

Materials which are finely dispersed such as soils and unconsolidated sediments can, in some cases, be considered to behave as simple mixtures. Therefore, the sorption properties of the complex assemblage may be arrived at by considering the properties of the individual minerals. In many systems, the components do interact to some extent, for example, silica and aluminium derived from dissolution of alumina-silicates can be adsorbed onto iron oxyhydroxides, or amorphous iron minerals may coat clay minerals. Such coatings can significantly alter the sorption properties of the bulk material (Payne et al., 2004b; Stubbs et al., 2009).

In one intercomparison exercise which involved modelling uranium sorption data on weathered schists (Payne et al., 2004b), ten teams of modellers adopted a range of approaches to simulate the complex sorption behaviour of the materials. The simplest approach involved a single type of surface site on an iron mineral surface (based on sequential extraction data), whereas the most complex model assumed that kaolinite, muscovite and iron-oxides all played a role. Most modellers estimated the total number of sites from the BET surface area and the relative number of other sites from available data including sequential extraction and bulk mineralogy data. In some cases, the total site density was fitted to the uranium sorption data (Payne et al., 2004b).

The complexity of modelling is even greater where the materials cannot be conceptualised as mixtures of dispersed materials but are physically different forms, such as intact rocks or compacted clay materials (see Fig. 5). Crystalline rock (saturated sparsely fractured rock) presents suitable properties to host a deep geological repository for different types of radioactive waste (Ochs et al., 2012). Crystalline rock is generally composed of a variety of different primary minerals (mainly quartz, feldspars, 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. Crystalline rock is heterogeneous on a variety of scales. The use of TSMs for predicting radionuclide sorption in (intact) crystalline rock presents challenges in obtaining relevant sorption data needed for the testing/validation of sorption models.

Clay formations have been selected in many waste management programmes as potential host rocks for the deep geological disposal of radioactive waste, and nearly all disposal concepts for high-level radioactive waste involve engineered clay-rich barriers (such as compacted bentonite) as an important part of the repository system. A common feature of these systems is that radionuclide behaviour is influenced 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. Whilst these types of materials present many challenges relating to non-sorption phenomena it is still possible to address the sorption aspects using the TSM approach. 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. In the case of cations that sorb via an ion exchange mechanism (Na, Sr and Cs), there are several examples of successful applications of batch-derived TSM parameters to intact Opalinus clay and compacted bentonite (Ochs et al., 2001; Van Loon et al., 2005, 2009). In the case of elements where surface complexation is the dominating sorption process, there is less evidence available. Recent results by Tachi et al. (2010) suggest that the migration

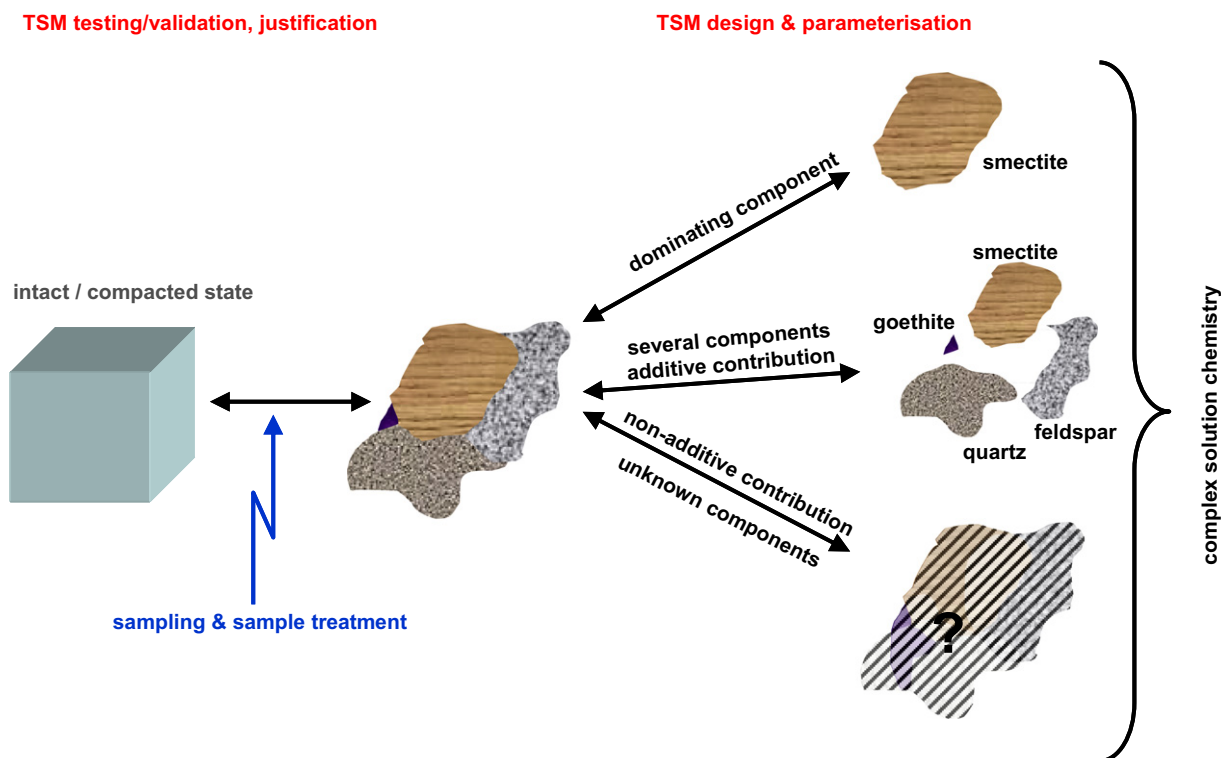


Fig. 5. Illustration of various aspects of complexity within a hypothetical substrate (Ochs et al., 2012).

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 TSM derived from batch experiments.

#### 4.3. Modelling approaches for complex materials

Due to the complexity of natural systems, TSMs and the associated model parameters often have to be based (fully or partly) on simplified representations. 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.

For modelling sorption in mineral assemblages, two major alternative approaches have emerged. These are the component additivity and generalised composite approaches (Arnold et al., 2001; Davis et al., 1998, 2005), and are illustrated in Fig. 5.

The most direct passage from the TSM modelling approaches for individual minerals 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 (Davis et al., 2004; Landry et al., 2009). 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) has been applied for this modelling approach (Davis et al., 1998, 2005). Adsorption by the mixture of mineral components can then be predicted in an equilibrium calculation, without any fitting of experimental data for the mixture.

CA model predictions are greatly simplified when it can be assumed that one mineral component dominates adsorption (Payne et al., 2004a). As described above, this allows a straightforward equilibrium calculation, based on the exposed surface area of

that mineral component in the soil or sediment. An estimate of total surface area and of the distribution of individual mineral surface areas can be made by multiplying the bulk weight abundance of various mineral phases with their known surface area. The summation of these contributions can be compared with the measured total surface area.

However, it is generally 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 Generalized Composite (GC) approach (Davis et al., 1998, 2005; Payne et al., 2004b) 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 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 in terms of generic surface functional groups. The number of functional groups may be estimated from the measured total surface area of the mineral assemblage (Section 2.2) or other experimental estimates. 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 (Bond et al., 2008; Hyun et al., 2009; Payne et al., 2004a). 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; Kent et al., 2000; Van Benschoten et al., 1998). While the fitted mass action equations may not provide accurate

representations of the stoichiometry of the reactions at the molecular scale, 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 the 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 surface complexes (coordinative 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 ionization 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 ionization 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 between 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). 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, double layer 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 (Ochs et al., 2012).

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.

## 5. General recommendations

The TSM approach has significantly matured during recent decades, to the extent that TSMs have potential applicability for radioactive waste disposal, and in other environmental contexts. Previous efforts to apply TSM approaches to estimate  $K_d$  values have highlighted that the same sorption data sets could be modelled in several different ways. There has been a lack of consensus on the appropriate methods of model development, particularly for complex natural materials.

A key finding presented in this paper is that the target function for sorption modelling should be correctly chosen, and the fit and applicability of the model is impacted by this choice. In many cases relevant to radioactive waste disposal, the  $K_d$  value should be the preferred target function. Models should be based on

comprehensive sorption data sets, which demonstrate the effects of key chemical variables (such as pH, radionuclide concentration, ionic strength, and the effects of competing and/or complexing ions). Solid phases of interest in natural environments must be thoroughly characterised, particularly in terms of the surfaces available for radionuclide adsorption. Models can be tailored to the desired degree of detail, ranging from a detailed description of the structural, coordinative, and electrostatic features of a mineral–solution interface to a more generalised model with generic sites and without explicit EIL terms. The latter type of simplified model may be used to demonstrate system understanding at a broader level.

While it is not possible to specify a single 'preferred' modelling sequence for developing a TSM, modelling must proceed in a systematic and defensible way, based on the following key recommendations:

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 documentation of key decisions.

These recommendations resemble those published in the environmental modelling literature. For example, Jakeman et al. (2006) recommended a set of minimum standards, including clear statement of the modelling objectives, full model documentation, a strong rationale for model features, justification of calibration methods, testing of model performance, a statement of model attributes and limitations, and a high level of reporting. These steps have been demonstrated and applied in subsequent papers in diverse fields including estuarine dynamics and fluid mechanics (Blocken and Gualtieri, 2012; Robson et al., 2008), and most of these aspects are covered in the above list.

However, the thorough testing of model performance is a challenge for TSMs associated with radioactive waste disposal, given that the predictive modelling needs to be applicable over geological timescales – far beyond the timescales of any laboratory or field experiments. One approach to this problem is to apply the results of the modelling in field situations such as uranium ore-bodies, which exhibit the results of radionuclide migration processes over long timescales (these are often referred to as 'natural analogue studies'). There have been some reviews of the collective results of natural analogues and their applicability to repository programs (Smellie and Karlsson, 1999), the most well-known being the Oklo site in central Africa which functioned as a natural reactor, and therefore produced a similar suite of radionuclides as a nuclear power reactor (Bruno and Ewing, 2006). At this site, the migration of radionuclides can be studied in the natural environment, although much of the evidence is inferential rather than direct because the Oklo reactors were active in the remote geological past. Some TSMs have been derived for laboratory data reported for samples from the Koongarra natural analogue site in Northern Australia (Payne et al., 2004b). Further testing along these lines may assist in demonstrating the robustness of the TSM approach.

## 6. Conclusions

One of the challenges in radioactive waste management is the necessity to make predictions about the evolution of geochemical systems, and the related behaviour of radionuclides, over very long timescales. The ability to do this is partly dependent on robust thermodynamic sorption models that can simulate radionuclide behaviour across a wide range of chemical conditions. A TSM provides a fundamental model of surface sorption processes and can be systematically embedded in an overall geochemical modelling framework. It can be used to estimate the effects of changes in conditions which may not be accessible by in situ investigations or laboratory experiments (and may occur in both time and space). Therefore thermodynamic sorption models can be directly coupled to transport codes, or alternatively, they may be utilised to generate or support deduced  $K_d$  values for incorporation in the repository performance safety case. It is hoped that the recommendations summarised in this paper will facilitate the development of such models.

## Acknowledgements

The authors thank three anonymous reviewers for numerous constructive suggestions. We also thank the organisations which supported the NEA sorption project (Phase III), and acknowledge the extensive input from members of the management board of this project. The text of this paper does not necessarily reflect the views of the NEA or the participating organisations.

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