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Adaptation of Mechanistic Sorption Models for Performance Assessment Calculations

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Executive Summary

Sorption is considered in most predictive models of radionuclide transport in geologic systems. The majority of such models simulate the effects of sorption in terms of empirical parameters, such as distribution coefficients, which relate an element's concentration in solution to its concentration on the surfaces of coexisting minerals. An important advantage in using these empirical coefficients is that they can be easily incorporated into the governing mass-transport equations describing radionuclide migration.

The empirical approach has been criticized, however, because the data are only strictly valid under the experimental conditions at which they were measured, and extrapolation to other conditions is therefore not scientifically defensible. An alternative to the empirical approach is to adopt a more mechanistic modeling framework based on recent advances in understanding the electrical properties of oxide mineral-water interfaces.

It has recently been proposed that these "surface-complexation" models may be directly applicable to natural systems because the surfaces of minerals in such systems are typically coated with complex mixtures of thermodynamically metastable amorphous and microcrystalline oxides and hydroxides of Fe^{3+}, Mn^{4+}, Al^{3+}, and Si^{4+}. A possible approach for adapting mechanistic sorption models for use in performance assessments, using this *surface-film* concept, is described in this report.

Surface-acidity parameters in the Generalized Two-Layer (GTL) surface-complexation model are combined with surface-complexation constants for Np(V) sorption on hydrous ferric oxide to derive an analytical model enabling direct calculation of corresponding intrinsic distribution coefficients as a function of pH, and Ca^{2+}, Cl^-, and HCO_3^- concentrations. The surface-film concept is then used to calculate whole-rock distribution coefficients for Np(V) sorption by altered granitic rocks coexisting with a hypothetical, oxidized Äspö groundwater.

The calculated results suggest that distribution coefficients for Np adsorption on these rocks could range from approximately 10 to 100 ml g^{-1}. Independent estimates of K_d for Np sorption in similar systems, based on an extensive review of experimentally measured distribution coefficients, are consistent, though slightly conservative, with respect to the calculated values. These preliminary results suggest that analytical-mechanistic sorption models may be useful to constrain, and provide a scientific basis for, the selection of distribution coefficients used in performance assessment calculations.

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1 Introduction

1.1 Background

Sorption reactions are important constraints in predictive models of radionuclide transport in geologic systems. The majority of such models simulate the effects of sorption using distribution coefficients, which relate an element's concentration in solution to its concentration on the surfaces of coexisting minerals. Extensive databases of experimentally determined distribution coefficients for radionuclide sorption on minerals and rocks have been compiled by various international regulatory authorities and research organizations (e.g., McKinley and Hadermann, 1984; Andersson, 1991). An important advantage in using distribution coefficients is that they can be easily incorporated into the governing mass-transport equations describing radionuclide migration in geologic repositories for nuclear waste.

The empirical approach has been vigorously criticized, however, because the data are only strictly valid under the experimental conditions at which they were measured, and extrapolation to other conditions is therefore not scientifically defensible (Reardon, 1981; Serne and Muller, 1987; Serne et al., 1990). This may be an especially important limitation for models simulating radionuclide transport in nuclear-waste repositories, where the geochemical environment may vary significantly in both space and time.

An alternative to the empirical approach is to adopt a more mechanistic modeling framework based on recent advances in understanding the electrical properties of mineral-water interfaces. The electrical properties of the interfacial region have been incorporated into several modeling approaches, which have in common the treatment of sorption as a chemical reaction involving sorbate species and specific sites on the mineral's surface. Variants of these models, collectively referred to as surface-complexation models, are described by Davis et al. (1978), Davis and Leckie (1978), Davis and Leckie (1980), Westall (1986), Kent et al. (1988), Dzombak and Morel (1990), and Smith and Jenne (1991). They have proven to be useful in interpreting laboratory investigations of sorption onto oxide minerals of alkali and alkaline earth cations (e.g., Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+}), base metals (e.g., Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+}), oxyanions (e.g., SO_4^{2-}, SeO_4^{2-}, SeO_3^{2-}, CrO_4^{2-}, WO_4^{2-}, and MoO_4^{2-}), and a limited number of actinides (UO_2^{2+}, NpO_2^{2+}, NpO_2^+).

The laboratory applications of surface-complexation models have not been widely extended to geologic systems because such systems typically are comprised of non-oxide minerals, such as primary aluminosilicates and secondary clay minerals and zeolites. Bradbury and Baeyens (1993) have

proposed, however, that the surface-complexation models for oxide sorbents may be applicable with minimal modification to geologic systems, because the surfaces of minerals in natural systems are typically coated with complex mixtures of thermodynamically metastable amorphous and microcrystalline oxides and hydroxides of Fe^{3+}, Mn^{4+}, Al^{3+}, and Si^{4+}. As noted originally by Jenne (1977), these layers appear to be the important trace-element sorbents in natural systems. If so, the primary and secondary non-oxide minerals may only be important insofar as they act as substrates controlling the surface areas of the enveloping oxide layers.

Bradbury and Baeyens (1993) tested this possibility using the Generalized Two-Layer (GTL) model of Dzombak and Morel (1990), to interpret experimental data from Allard (1982) characterizing pentavalent Np sorption on 18 minerals commonly found in crystalline rocks in Sweden. They assumed that the surfaces of the minerals were coated with thin layers of amorphous Hydrous Ferric Oxide (HFO), which could not have been detected in the experimental investigation by x-ray diffraction. Experimental data from Girvin et al. (1991) on Np(V) sorption by HFO were re-interpreted to derive surface-complexation constants consistent with the GTL model. The surface areas of the minerals, determined by N_2-BET measurements (Allard et al., 1982), and characteristic site densities for HFO (Dzombak and Morel, 1990) were chosen as primary modeling constraints fixing the total concentration of sorption sites associated with the HFO layers coating the minerals.

The results of the GTL model calculations compared favorably in most instances with experimentally determined distribution coefficients reported by Allard (1982). Discrepancies were found in cases where the mineral substrate (quartz, fluorite, anhydrite, and apatite) may have been incompletely covered by HFO, and whose surfaces were suspected of containing additional Np-complexing sites. Even this general agreement is remarkable, however, because none of the parameters in the surface-complexation model were derived from the experimental data being modeled.

1.2   Objective

Although Bradbury and Baeyens (1993) alluded to the potential importance of this surface-film concept in simplifying sorption models and enhancing the credibility of radionuclide transport calculations, it is unclear how the concept could best be employed in actual performance assessment calculations supporting licensing of a high-level nuclear waste repository. Adaptation of mechanistic sorption models requires consideration of several possible technical and programmatic constraints on performance assessment.

First, it may be desirable to retain simplified treatments of sorption, such as

distribution coefficients, in mass-transport models. As noted by Allard (1991) and by Bradbury and Baeyens (1993), although the chemical environment in natural systems is complex and heterogeneous, in most cases only a few processes and subsystems actually control sorption. Moreover, uncertainties in the extent of sorption should be considered in relation to other uncertainties, such as variations in groundwater flow rates, porosity, and fracture properties, which affect the overall mobility of radionuclides. The latter uncertainties may prove to be far more significant than uncertainties introduced by the utilization of constant retardation coefficients in mass-transport models.

Second, preliminary scoping calculations using simplified mass-transport models and highly conservative distribution coefficients can identify a subset of radionuclides having the highest probability of posing a threat to public health. A more detailed mechanistic approach to refine the initial estimates of distribution coefficients for these "problem radionuclides" can then be justified on the basis of their disproportionate influence on the overall risk posed by the repository.

Third, performance assessment is an iterative process that should be closely coordinated with site characterization. A mechanistic basis in sorption models for key radionuclides considered in mass-transport calculations could be used to identify groundwater and mineralogic parameters that most significantly affect their mobility in the geosphere. This information is critical for prioritizing the properties of a given site that require the most detailed characterization. Conversely, site characterization may identify environmental conditions for which mechanistic sorption models have not been experimentally calibrated. This information could be used to prioritize experimental studies of mechanistic sorption models under conditions that are relevant for the site.

Fourth, distribution coefficients are not intrinsically less mechanistic than truly mechanistic models, such as surface-complexation models. The empirical nature of distribution coefficients is engendered by the experimental techniques used to measure them. Distribution coefficients simply relate the uptake of a trace component from aqueous solution to a solid phase or phases. Despite various notations, distribution coefficients (referred to here as K_d) are most commonly defined by the ratio, $c_{i,solid}/c_{i,solution}$, where $c_{i,solid}$ stands for the total analytical concentration of the sorbate, i, among all the solid phases in the system of interest, and $c_{i,solution}$ represents the sorbate's total analytical concentration in the coexisting solution. Implicit in this definition is that all relevant reactions are at equilibrium.

As such, there are no theoretical reasons why K_ds cannot be calculated as functions of mechanistic parameters and simplifying concepts such as the surface-film model discussed above. This would permit the appealing

simplicity of the distribution-coefficient concept to be retained in mass-transport models, and credibility in the results of the transport calculations would be enhanced by the mechanistic, rather than empirical, basis in determining K_ds. The mechanistic basis in this approach would enable a range in K_d values to be calculated relative to ranges in site-specific environmental parameters, such as pH and Eh.

The objective of this investigation is to demonstrate how a mechanistic sorption model can be adapted for use in performance assessments, given the constraints noted above. The approach is based on that described by Bradbury and Baeyens (1993), and a brief summary of the GTL surface-complexation model is therefore provided in Section 2.0. A method for calculating K_d for Np sorption by HFO as a function of corresponding GTL model parameters is outlined in Section 3.0. In Section 4.0, application of the analytical model is illustrated by using the surface-film concept to estimate whole-rock distribution coefficients for Np sorption on crystalline rocks in Sweden.

2 The Generalized Two-Layer Model

The Generalized Two-Layer (GTL) Model is a surface-complexation model developed by Dzombak and Morel (1990). The main appeal of the GTL model in comparison to other surface-complexation models is that it is the simplest model available that can account qualitatively and quantitatively for all available experimental data. The model is presently equipped with an internally consistent database of model parameters specifically for HFO (Dzombak and Morel, 1990). The GTL model has been incorporated in version 3.0 of MINTEQA2, a geochemical software package for modeling aqueous speciation, solubility and adsorption in natural waters (Allison et al., 1991). Bradbury and Baeyens (1993) also incorporated the GTL model in DSURF, which is based on a very similar software package [MINEQL, Westall et al. (1976)].

The GTL model, like all surface-complexation models, describes the sorption of solutes at oxide surfaces in terms of chemical reactions involving aqueous solute species and surface species. The surface reactions include acid-base reactions and coordination reactions among cationic and anionic sorbate species. Each reaction is governed by mass-action and mass-balance constraints. Corresponding equilibrium constants are controlled by the product of terms reflecting the change in intrinsic chemical free energy associated with the reaction, and the coulombic free energy of binding contributed by the electrostatically charged oxide surface. Surface charge is generated by ionization of surface sites. For oxides, the surface charge is controlled primarily by acid-base reactions involving surface hydroxyl groups. Coulombic interactions are described in the GTL model by the Gouy-Chapman theory of the electrical double layer, assuming an inner layer of surface charges and a diffuse outer layer of countercharge extending into the bulk aqueous phase (Figure 2.1).

2.1 Acid-Base Properties of Oxide Surfaces

Oxide surfaces display amphoteric behavior due to surface ionization reactions such as:

$$\equiv XOH_2^+ \rightleftharpoons \ \equiv XOH^\circ + H^+, \tag{2.1.1}$$

and

$$\equiv XOH^\circ \rightleftharpoons \ \equiv XO^- + H^+, \tag{2.1.2}$$
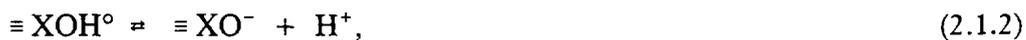
where $\equiv X$ stands for a structural metal ion of the oxide surface, $\equiv XOH_2^+$, XOH° and XO^- represent protonated, neutral, and deprotonated surface species,
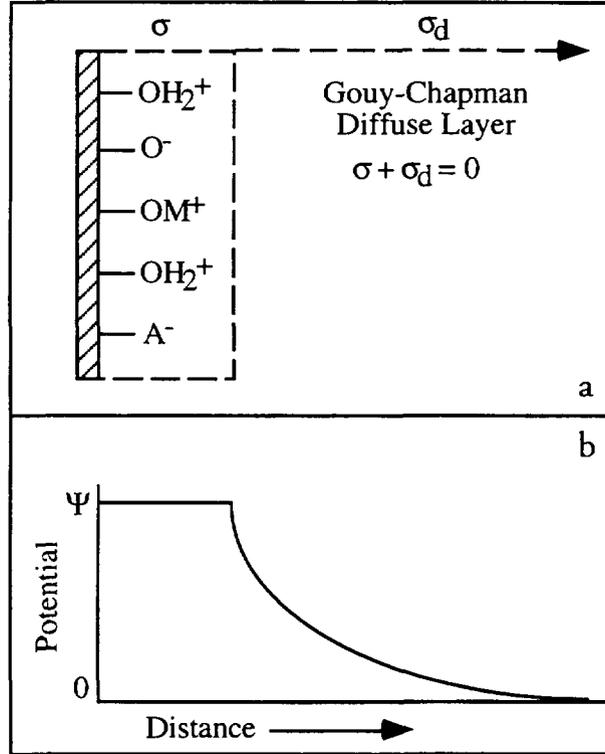
Figure 2.1. Schematic Diagram of Ion Binding at the Oxide-Water Interface (a), and Potential Decay in the Diffuse Layer (b). From Dzombak and Morel (1990).

respectively, and H^+ refers to protons in the bulk aqueous solution. Mass-action equations for reactions (2.1.1) and (2.1.2) are given by:

$$K_{a1}^{app} = \frac{\left(\equiv XOH^\circ\right)\left\{H^+\right\}}{\left(\equiv XOH_2^+\right)}, \text{ and}$$

$$K_{a2}^{app} = \frac{\left(\equiv XO^-\right)\left\{H^+\right\}}{\left(\equiv XOH^\circ\right)},$$

where the equilibrium constants, K_{a1}^{app} and K_{a2}^{app}, denote the first and second *apparent* acidity constants, respectively, and ( ) and { } denote concentrations and activities, respectively.

The apparent equilibrium constants include surface-charge effects, but do not account for the energy necessary to move ions from the bulk aqueous phase through potential gradients near the charged oxide surface (Figure 2.1). *Intrinsic* equilibrium constants do account for this energy, and are related to the

apparent equilibrium constants by (e.g., Dzombak and Morel, 1990):

$$K_{a1}^{int} = \frac{(\equiv XOH^\circ)\{H_s^+\}}{(\equiv XOH_2^+)} = K_{a1}^{app}\exp(-F\Psi/RT), \text{ and} \qquad (2.1.3)$$

$$K_{a2}^{int} = \frac{(\equiv XO^-)\{H_s^+\}}{(\equiv XOH^\circ)} = K_{a2}^{app}\exp(-F\Psi/RT). \qquad (2.1.4)$$

The intrinsic equilibrium constants thus pertain to reactions occurring on the oxide surface. Surface protons are related to the bulk aqueous proton concentration by the Boltzmann distribution, where F stands for the Faraday constant (C mol^{-1}), Ψ refers to the potential at the oxide surface (V), R represents the molar gas constant (J mol^{-1} K^{-1}), and T denotes temperature (K).

In the GTL model the activity coefficients of surface species are assumed to be equal. This is one of two extra-thermodynamic assumptions used in this model. The other is in the choice of the theoretical expression defining the mean surface potential, Ψ. The GTL model is based on the diffuse-layer model of the electrical double layer (Figure 2.1), from which the Gouy-Chapman theory (for a symmetrical electrolyte of valence Z) defines a relation between the surface potential and surface charge, σ (C m^{-2}), given by:

$$\sigma = (8RT\varepsilon\varepsilon_0 c \times 10^3)^{1/2} \cdot \sinh(Z\Psi F/2RT) \qquad (2.1.5)$$

where ε stands for the dimensionless dielectric constant of water, ε_0 represents the permittivity of free space (8.854 x 10^{-12} C V^{-1} mol^{-1}), and c refers to the molar electrolyte concentration. At constant surface charge and temperature, the surface potential is thus proportional to electrolyte valence and concentration, and thus depends on the ionic strength.

For sorption of trace constituents in natural waters, surface charge is controlled predominantly by the amphoteric properties of the oxide surface, and the charge-potential relation is therefore strongly pH dependent. Under such conditions, mass balance on the total concentration of surface sites, $(\equiv XO_{tot})$, is given by:

$$(\equiv XO_{tot}) = (\equiv XOH_2^+) + (\equiv XOH^\circ) + (\equiv XO^-) \qquad (2.1.6)$$

The net surface charge and surface potential must therefore both be zero when

$$(\equiv XOH_2^+) = (\equiv XO^-), \qquad (2.1.7)$$

a condition referred to as the pristine point of zero charge (PPZC). The pH of the bulk solution corresponding to the PPZC is given by:

$$pH_{PPZC} = 0.5 \left[pK_{a1}^{int} + pK_{a2}^{int} \right] \qquad (2.1.8)$$

(where p = -log). The surface charge and potential are positive when pH < pH$_{PPZC}$, and negative when pH > pH$_{PPZC}$. Oxides typically exhibit a transition in the sign of the surface charge in the pH range 0 to 14, which strongly influences the sorption behavior of cationic and anionic sorbates.
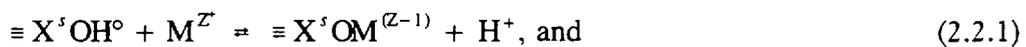
2.2 Surface Complexation

The GTL model, like other surface-complexation models, treats sorption in terms of specific reactions involving the surface hydroxyl groups discussed above, and cationic and anionic sorbate species. A distinction is made in the this model, however, between the types of sites available on oxide surfaces for cation and anion binding. From experience it is known that sorption densities are not generally proportional to the dissolved concentrations of cations, whereas sorption densities and dissolved anionic concentrations are proportional over a wide range of anion concentrations. For this reason a distinction is made among surface sites available for cation sorption. Two site-types are assumed:

- a large concentration of low-affinity sites, referred to as *weak* sites, and

- a small concentration of high-affinity sites, termed *strong* sites.

No distinction is made among these sites in terms of their acid-base behavior.

2.2.1 Cations

Surface complexation of cations on oxide surfaces involves the formation of bonds with surface oxygen atoms and the release of protons, e.g,:

$$\equiv X^s OH^\circ + M^{Z^+} \rightleftharpoons \equiv X^s OM^{(Z-1)} + H^+, \text{ and} \qquad (2.2.1)$$

$$\equiv X^w OH^\circ + M^{Z^+} \rightleftharpoons \equiv X^w OM^{(Z-1)} + H^+, \qquad (2.2.2)$$

where the superscripts, s and w, refer to the strong and weak surface sites, respectively. Typically, only one kind of surface complex stoichiometry is characteristic of cation (M^{z+}) binding on both the strong and weak sites. Moreover, for the vast majority of situations involving transport and sorption of radionuclides, only the behavior of the strong sites is important because the relative concentrations of the radionuclides is extremely small compared to the

total concentration of strong sites in a volume of host rock comprising a given flow path.

Under these conditions, the overall mass-action relation for sorption of cationic radionuclides can be expressed by a single equation for the strong sites:

$$K_{M^{Z+}}^{int} = \frac{\left(X^s OM^{(Z-1)}\right)\{H^+\}}{\left(X^s OH^\circ\right)\gamma_{M^{Z+}}\left(M^{Z+}\right)} \exp\left[\frac{\Delta ZF\Psi}{RT}\right] \qquad (2.2.3)$$

where $\gamma_{M^{Z+}}$ represents the solution activity coefficient, and ΔZ stands for the net change in valence of the surface species. Dzombak and Morel (1990) also consider wider applications of the GTL model for other conditions involving sorption onto both strong and weak sites, as well as transitional behavior between sorption and surface precipitation at high sorbate concentrations.

2.2.2 Anions

Sorption of anions at oxide-water interfaces involves ligand exchange between surface hydroxyl groups, i.e., reactions such as:

$$\equiv XOH^\circ + A^Z + H^+ \rightleftharpoons \equiv XA^{(1-Z)} + H_2O, \qquad (2.2.4)$$
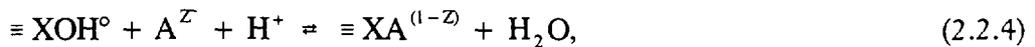
where A^{Z-} stands for the anion of charge z-. Anion sorption differs from cation sorption in two important respects. First, the distinction between strong and weak sites is unnecessary because, unlike cations, sorption densities for anions are typically proportional to total dissolved concentrations. In addition, sorption of anionic complexes usually entails consideration of from one to three surface complexation reactions in addition to the surface acidity reactions. The mass-action relations for the surface-complexation reactions are analogous to equation (2.2.3). In addition, Dzombak and Morel (1990) discuss application of the GTL model at high dissolved anion concentrations where surface-precipitation effects may be important.

2.3   Properties of Hydrous Ferric Oxide (HFO)

Although the GTL model is general and applicable to any oxide surface, the vast majority of experimental sorption data pertain to Hydrous Ferric Oxide (HFO), a term that is synonymous with amorphous ferric hydroxide, amorphous iron oxyhydroxide, and other terms applied to the product of rapid hydrolysis of ferric iron solutions at 20° to 30°C. This is a fortunate circumstance for repository investigations in Sweden, because the crystalline

rocks there are typically Fe-rich and contain relatively abundant hematite, magnetite, goethite, and/or HFO (e.g., Eliasson, 1993). In addition, Goldberg and Sposito (1984) and Schindler and Stumm (1987) have pointed out that the acid-base and surface-complexation behavior of HFO and Al oxides are very similar. Moreover, Goldberg and Glaubig (1986) successfully modeled the pH-dependent sorption of boron on kaolinite using surface-complexation data for Al-oxides, suggesting that the hydroxyl sites in some clays may behave similarly to hydroxyl sites on Al/Fe-oxides. Smith and Jenne (1991) have also noted that the calculated intrinsic sorption properties among Fe-oxide and hydroxide polymorphs appear to be very similar, provided uncertainties in experimental measurements of surface-site densities are minimized. Consequently, there is evidence suggesting that the properties of HFO can be applied in a much more general sense to model sorption behavior in natural systems (Bradbury and Baeyens, 1993).

The literature on HFO properties that are relevant to the GTL model are reviewed by Dzombak and Morel (1990). Their best estimates of parameter values and supporting data are summarized in the following sections.

2.3.1 Structure and composition

Freshly precipitated HFO particles are approximately spherical and range in size from 1 and 10 nm. On aging, the particles coagulate into aggregates resembling a highly porous gel rather than a homogeneous solid phase. The bulk structure of HFO gel is uncertain and its composition is therefore generally represented by $Fe_2O_3 \cdot nH_2O$, with n ranging between 1 and 3. A nominal formula weight for HFO = 90 g mol^{-1} Fe.

HFO is metastable relative to all other Fe(III) oxides and hydroxides, and with continued aging the gel therefore transforms into one of these crystalline counterparts, usually goethite (α-FeOOH). The rate of transformation apparently increases with increasing pH (when pH > 10), increasing total Fe^{3+} concentrations, and increasing temperature.

2.3.2 Surface area

The surface areas of laboratory-prepared HFO, determined usually by N_2-BET measurements, are generally on the order of 200-300 m^2 g^{-1}. These may represent minimum surface areas, however, because of suspected surface decomposition occurring during the drying procedure required in this analytical technique. A maximum surface area of 840 m^2 g^{-1} can be calculated assuming a spherical geometry and minimum diameter of 2 nm. Dzombak and Morel (1990) estimated a representative value of 600 m^2 g^{-1} for fully hydrated and aged HFO.

2.3.3 Site density

The density of weak sites is determined from observed sorption maxima, and represents the total concentration of reactive sites available for sorption of protons, cations, and anions. A median value of 0.2 mol mol^{-1} Fe is recommended by Dzombak and Morel (1990). The density of strong sites, applicable only for surface-complexation of cationic species, can be estimated from the maximum sorption density at which sorption is still proportional to total dissolved cation concentrations. Dzombak and Morel (1990) estimated a value of 0.005 mol mol^{-1} Fe for these sites.

2.3.4 Surface acidity constants

Weighted averages at the 95% confidence interval for log K_{a1}^{int} and log K_{a2}^{int} at 25°C among the best available acid-base titration data reported in the literature are -7.29 ± 0.10 and -8.93 ± 0.07, respectively (Dzombak and Morel, 1990). Thus, from Equation (2.1.8), pH$_{PPZC}$ = 8.1.

3 Calculated Distribution Coefficients for Np(V) Sorption on HFO

An analytical model is developed in this section in terms of the governing parameters in the GTL surface-complexation model for purposes of calculating distribution coefficients for Np(V) sorption on hydrous ferric oxide over the pH range 4 - 10. The intrinsic surface complexation constant for NpO_2^+ sorption on HFO retrieved by Bradbury and Baeyens (1993) from experimental data reported by Girvin et al. (1991) are used in conjunction with the intrinsic surface acidity constants recommended by Dzombak and Morel (1990).

3.1 Neptunium Speciation in Oxidized Reference Groundwater

The aqueous speciation of Np is an important control on the sorption behavior of this element. Although redox conditions at depths being considered in Sweden for the deep geologic disposal of nuclear wastes are normally reducing (e.g., Laaksoharju et al., 1993), relevant experimental data on Np sorption under such conditions are presently unavailable. Thus, the analytical modeling approach is illustrated in the present investigation by assuming oxidizing conditions at 25°C, for which experimental data characterizing Np sorption on HFO are reported by Girvin et al. (1991).

Bradbury and Baeyens (1993) used FITEQL (Westall, 1982) to infer that the sorption data of Girvin et al. (1991) can best be explained by the following surface-complexation reaction:

$$\equiv Fe^s OH^\circ + NpO_2^+ \rightleftharpoons \equiv Fe^s ONpO_2^\circ + H^+. \tag{3.1.1}$$
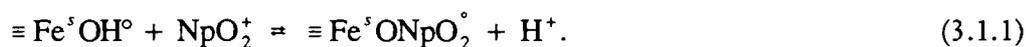
The experimental data pertain to oxidizing conditions at 25°C over a pH range of 4 to 9.

An oxidized variant of the reference groundwater composition defined by SKI (SKI SITE-94) on the basis of detailed geologic studies carried out by SKB at the Äspö Hard Rock Laboratory in southeastern Sweden is adopted to illustrate the analytical approach. Redox conditions in the variant groundwater are assumed to be controlled by equilibration with $O_2 (g)$ in ambient air (Table 3.1). Neptunium speciation in this groundwater is calculated using version 7.2 of the EQ3/6 geochemical software package (Wolery, 1992) and its supporting thermodynamic database (data0.com.R22).

Pentavalent Np species comprising greater than 1% of the total dissolved Np concentration in the oxidized reference groundwater over the pH range 4 - 9 include predominantly NpO_2^+, with subordinate amounts of NpO_2OH° and

Basis Species	Concentration[*]
Na^+	2100
K^+	8.1
Cl^-	6410
$SiO_2(aq)$	8.79
Mg^{2+}	42
SO_4^{2-}	560
F^-	1.5
Fe^{2+}	0.24
Al^{3+}	0.01[∞]
Ca^{2+}	1890
HCO_3^-	10
HPO_4^{2-}	0.005
Sr^{2+}	35
pH	8.1
Eh (V)[§]	0.758

¶- from SKI SITE-94 and Smellie and Laaksoharju (1992).
*- total concentration (mg kg^{-1}).
∞- estimated minimal concentration in natural waters (Hem, 1970).
§- calculated assuming $f_{O2\,(g)}$ = 0.69 bar.

Table 3.1. Reference Groundwater (oxidized)¶.

$NpO_2Cl°$. These species are therefore considered in this study. The calculated concentrations of Np(VI), Np(IV) and Np(III) species are extremely small under the assumed conditions, and are therefore not considered in the model.

3.2 Analytical Model for NpO_2^+ Sorption on HFO

The approach is based on three simplifying assumptions:

1) the aqueous speciation of Np is controlled by only the three Np(V) species noted in Section 3.1,

2) total dissolved Np concentrations are small compared to the total concentration of surface sites on hydrous ferric oxide, and

3) only Np(V) species and Ca^{2+} are sorbed by HFO.

The second assumption simplifies the problem because only the strong sites on

HFO require consideration. Although the assumption is generally applicable for sorption of trace constituents in natural systems, it is evaluated in more detail below for the specific case of Np release from a geologic repository for nuclear waste. Calcium cations sorb readily onto the strong sites of HFO (Dzombak and Morel, 1990), and the resultant competitive effects on Np sorption therefore also need to be considered. Bradbury and Baeyens (1993) note that similar competitive effects may be generated by other cations, such as Mg^{2+}, for which surface-complexation parameters are currently unavailable.

With these assumptions, the distribution coefficient for Np(V) sorption on HFO can be defined:

$$K_d = \frac{c_{Np,HFO}}{c_{Np,soln.}}, \tag{3.2.1}$$

where $c_{Np,HFO}$ stands for the total sorbed Np concentration (mol g^{-1}), and $c_{Np,soln.}$ represents the total concentration in solution (mol ml^{-1}). Expressing both the concentration terms in Equation (3.2.1) in units of molarity [indicated by ( )]:

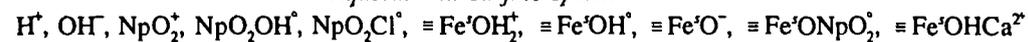$$K_d = 1000 \left[\frac{(Np)_{HFO}}{(Np)_{soln.}} \right] C_{HFO}^{-1}, \tag{3.2.2}$$

where the factor 1000 converts liters to milliliters, $(Np)_{HFO}$ represents the total amount of sorbed Np per liter of solution, and C_{HFO} stands for the sorbent's concentration (g l^{-1}).

The concentration terms in Equation (3.2.2) are expressed in terms of GTL parameters using the mass-action, mass-balance, and charge-potential relations shown in Table 3.2. This entails first deriving an equation for the concentration of the surface species, $Fe^sONpO_2^\circ$ (Table 3.3), using the mass-action equation for Reaction 1, Table 3.2. Because this species is assumed to be the only sorbed Np species (Section 3.1), its concentration is equivalent to $(Np)_{HFO}$.

The molar concentrations of $\equiv Fe^sOH^\circ$ and NpO_2^+ needed to calculate $(Fe^sONpO_2^\circ)$ are computed from speciation Equations (4) and (5) of Table 3.3, respectively. These equations are derived by substituting the relevant mass-action equations for Reactions 1 - 6 (Table 3.2) into the respective mass-balance equations (Table 3.2), and solving for $(\equiv Fe^sOH^\circ)$ and (NpO_2^+).

The concentration term, $(\equiv Fe^sONpO_2^\circ)$, appearing in the mass-balance equation for $\Sigma(Fe^s)$ (Table 3.2) is negligible compared to the concentrations of other surface species, in accordance with the second assumption noted in Section 3.1. Scoping calculations suggest this assumption is valid if $\Sigma(Np)$ is less than

Aqueous and Surface Species

H^+, OH^-, NpO_2^+, NpO_2OH°, NpO_2Cl°, $\equiv Fe^sOH_2^+$, $\equiv Fe^sOH^\circ$, $\equiv Fe^sO^-$, $\equiv Fe^sONpO_2^\circ$, $\equiv Fe^sOHCa^{2+}$

Mass-Action Constraints

Np Speciation   (ref.)§

1) $\equiv Fe^sOH^\circ + NpO_2^+ \rightleftharpoons \equiv Fe^sONpO_2^\circ + H^+$ $K^{int}_{NpO_2^+} = 10^{-0.98}$ (1)

2) $NpO_2^+ + H_2O \rightleftharpoons NpO_2OH^\circ + H^+$ $K_{NpO_2OH^\circ} = 10^{-8.9}$ (2)

3) $NpO_2^+ + Cl^- \rightleftharpoons NpO_2Cl^\circ$ $K_{NpO_2Cl^\circ} = 10^{-0.4}$ (2)

Fe Speciation*

4) $\equiv Fe^sOH^\circ + H^+ \rightleftharpoons \equiv Fe^sOH_2^+$ $[K^{int}_{a1}]^{-1} = 10^{7.29\pm0.1}$ (3)

5) $\equiv Fe^sOH^\circ \rightleftharpoons \equiv Fe^sO^- + H^+$ $K^{int}_{a2} = 10^{-8.93\pm0.07}$ (3)

6) $\equiv Fe^sOH^\circ + Ca^{2+} \rightleftharpoons \equiv Fe^sOHCa^{2+}$ $K^{int}_{Fe^sOHCa^{2+}} = 10^{4.97}$ (3)

Mass-Balance Constraints

$\Sigma(Np) = (NpO_2^+) + (NpO_2OH^\circ) + (NpO_2Cl^\circ) + (\equiv Fe^sONpO_2^\circ)$

$\Sigma(\equiv Fe^s) = (\equiv Fe^sOH_2^+) + (\equiv Fe^sOH^\circ) + (\equiv Fe^sO^-) + (\equiv Fe^sONpO_2^\circ) + (\equiv Fe^sOHCa^{2+})$

Charge-Potential Relation (25°C)

$\sigma = 0.1174c^{1/2}\sinh(19.46xZ\Psi)$

§_   (1)   Bradbury and Baeyens (1993)
      (2)   data0.com.R22
      (3)   Dzombak and Morel (1990)
*_ $\equiv Fe^s$ represents high-affinity sorption sites on HFO

Table 3.2   Model Constraints for Np(V) Sorption on HFO.

1) $K_d = 1000 \left[\dfrac{(Np)_{HFO}}{(Np)_{soln.}} \right] C_{HFO}^{-1}$

2) $(Np)_{soln.} = \Sigma(Np) - (Np)_{HFO}$

3) $(Np)_{HFO} = (\equiv Fe^rONpO_2^+) = \dfrac{K_{NpO_2^+}^{int}(\equiv Fe^rOH^s)(NpO_2^+)\gamma_{NpO_2^+}}{\{H^+\}}$

4) $(NpO_2^+) = \dfrac{\Sigma(Np)}{\left[1 + \dfrac{K_{NpO_2OH^+}\gamma_{NpO_2^+}}{\{H^+\}} + K_{NpO_2Cl^+}(Cl^-)\gamma_{NpO_2^+}\gamma_{Cl^-} + \dfrac{K_{NpO_2^+}^{int}(\equiv Fe^rOH^s)\gamma_{NpO_2^+}}{\{H^+\}} \right]}$

5)

$(\equiv Fe^rOH^s) = \dfrac{\Sigma(\equiv Fe^r)}{\left[1 + K_{a1}^{int}\{H^+\}\exp(-F\Psi/RT) + K_{Fe^rOHCa^{2+}}^{int}(Ca^{2+})\gamma_{Ca^{2+}}\exp(-2F\Psi/RT) + \dfrac{K_{a2}^{int}}{\{H^+\}\exp(-F\Psi/RT)} \right]}$

Table 3.3   Analytical Model for Calculation of Kd from GTL Surface-Complexation Parameters.

approximately 10^{-10} mol l^{-1}. A more comprehensive analytical approach, considering Np sorption on both the weak and strong sites of hydrous ferric oxide, would be required if total Np concentrations exceed this value.

The equations in Table 3.3 define the analytical model for Np(V) sorption on hydrous ferric oxide. Inspection of terms suggests that if variations in temperature, ionic strength, and Ca^{2+} and Cl^- concentrations are small, sorption will be primarily pH dependent. Under such conditions, the pH-sorption behavior can be readily calculated by the following procedure:

1) solve Equation (5),
2) solve Equation (4), using the value for $(\equiv Fe^sOH^o)$ from Step 1,
3) solve Equation (3), using (NpO_2^+) from Step 2 and $(\equiv Fe^sOH^o)$ from Step 1,
4) solve Equation 2, for a given initial $\Sigma(Np)$, and
5) solve for K_d using Equation (1).

Distribution coefficients calculated in this manner are independent of the total concentration of hydrous ferric oxide. This can be seen by noting that $\Sigma(Fe^s)$ in the equation for $(\equiv Fe^sOH^o)$ can be expressed as a function of C_{HFO}:

$$\Sigma\left(\equiv Fe^s\right) = \frac{C_{HFO}}{W_{HFO}}\ v_{HFO}^{Fe}\ \frac{\left(\equiv Fe^s\right)_{HFO}}{\left(\equiv Fe\right)_{HFO}}, \tag{3.2.3}$$

where W_{HFO} represents the molecular weight of hydrous ferric oxide (90 g mol^{-1}), v_{HFO}^{Fe} stands for the stoichiometric number of moles of Fe in one mole HFO (1 mol mol^{-1}), and the ratio, $(\equiv Fe^s)_{HFO}/(\equiv Fe)_{HFO}$, denotes the proportion of strong sorption sites on the HFO surface (0.005). The concentration term, C_{HFO}, in Equation 3.2.2 is canceled in calculation of K_d (Equation 1, Table 3.3), and K_d is therefore independent of the HFO concentration.

This means that although the amount of Np sorbed will increase with increasing HFO concentration, and the concentration of Np in solution will decrease accordingly, the _specific_ concentration of Np (per gram HFO) also decreases and K_d will therefore remain constant. This is an important feature of the model that enables, with the surface-film concept of Bradbury and Baeyens (1993), application of the model to estimate whole-rock distribution coefficients (Section 4.2).

3.3 Verification of the Analytical Model

The accuracy of the analytical model is tested using the experimental data of Girvin et al. (1991). Experimental constraints are summarized in Table 3.4. The objective of the calculations is to duplicate the sorption-edge (pH versus

Parameter	Value	$\exp(-F\Psi/RT)$ [‡]	$\exp(-2F\Psi/RT)$ [‡]
Temperature (°C)	25		
Ionic Strength (mol l^{-1})	0.1		
$\Sigma(Np)$ (mol l^{-1})	4.5×10^{-11}		
$\Sigma(\equiv Fe^s)^*$ (mol l^{-1})	5.0×10^{-5}		
$\Sigma(Ca^{2+})$ (mol l^{-1})	0		
$\Sigma(Cl^-)$ (mol l^{-1})	0		
pH	4	$10^{-2.45}$	$10^{-4.90}$
	5	$10^{-2.12}$	$10^{-4.24}$
	6	$10^{-1.57}$	$10^{-3.14}$
	7	$10^{-0.88}$	$10^{-1.76}$
	8	$10^{-0.09}$	$10^{-0.18}$
	9	$10^{0.71}$	$10^{1.42}$
$\gamma_{+/-}$ [§]	$10^{-0.11}$		

‡ - from Table 8.8, Dzombak and Morel (1990)

* - = total HFO concentration as Fe (0.01 mol l^{-1}) x ≡ Fe^s site density (0.005 mol ≡ Fe^s mol^{-1} Fe).

§ - solution activity coefficient for singly charged species at 25°C, I = 0.1 mol l^{-1} (Table 8.7, Dzombak and Morel, 1990).

Table 3.4 Experimental Data (Girvin et al., 1991) and Associated Parameters Used to Verify the Accuracy of the Analytical Model for Np(V) Sorption on Hydrous Ferric Oxide.

percentage Np sorbed) measured by Girvin et al. (1991).

The results for an initial Np concentration of 4.5×10^{-11} mol l^{-1} are shown in Figure 3.1, where it can be seen that the analytical sorption model accurately predicts the experimentally determined sorption edge over the pH range 4 - 9. Calculations for the other $\Sigma(Np)$ concentrations considered by Girvin et al. (1991) are virtually identical to the curve shown in Figure 3.1. Comparison of the results of the analytical model with similar calculations by Bradbury and Baeyens (1993) using the computer code DSURF reveal no perceptible differences in the predicted sorption edges.
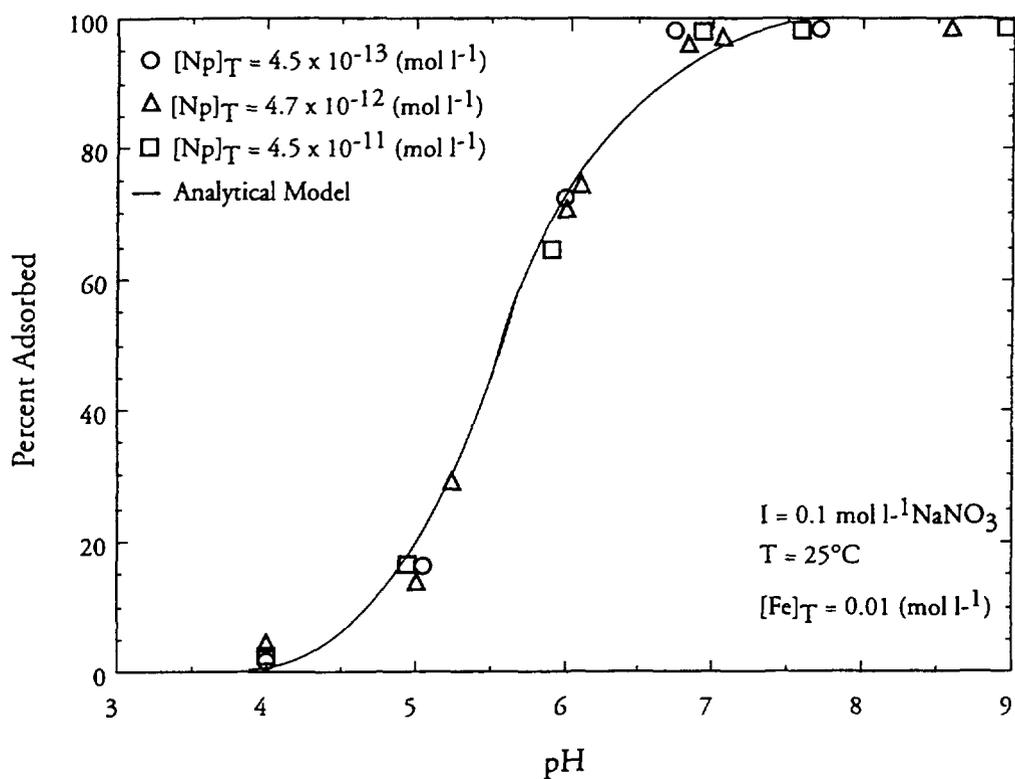
Figure 3.1. Adsorption of Np(V) on HFO. Symbols represent experimental data from Girvin et al. (1991). The curve is calculated using the analytical model. Total analytical concentrations are indicated for Np and Fe .

4 Application of the Surface-Film Model to Calculate Whole-Rock Distribution Coefficients

Application to geologic systems of the model discussed in Section 3 requires evaluation of possible competitive effects among sorbing species. Also, because the model K_d is intrinsic for hydrous ferric oxide, additional constraints are necessary to extend the model for purposes of calculating "whole-rock" distribution coefficients. Possible constraints that are consistent with the surface-film concept of Bradbury and Baeyens (1993) are evaluated in Section 4.2.

4.1 Competitive Sorption by Ca²⁺

To illustrate the effects of competitive sorption of Np(V) and Ca²⁺ on HFO it is assumed that calcite equilibrium controls $\Sigma(\text{Ca}^{2+})$. Mass-balance equations for $\Sigma(\text{Ca}^{2+})$ and $\Sigma(\text{CO}_3{}^{2-})$, and mass-action equations for the species $H_2CO_3{}^\circ$, $HCO_3{}^-$, $CO_3{}^{2-}$, and Ca^{2+} are then used to derive a modified form of the third term in the denominator of Equation 5 (Table 3.3):

$$\frac{K^{int}_{Fe^sOHCa^{2+}}\cdot\exp(-2F\Psi/RT)K_{calcite}}{\Sigma(CO_3^{2-})}\left[\frac{\{H^+\}}{K_{H_2CO_3^*}} + \frac{\{H^+\}}{\gamma_{HCO_3^-}} + \frac{K_{HCO_3^-}}{\gamma_{CO_3^{2-}}}\right].$$

In this term, $K_{calcite}$ represents the equilibrium constant for the reaction,

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \tag{4.1.1}$$

and $K_{H_2CO_3^*}$ and $K_{HCO_3^-}$ refer to equilibrium constants for the reactions

$$H_2CO_3^\circ \rightleftharpoons H^+ + HCO_3^-, \text{ and} \tag{4.1.2}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{4.1.3}$$

respectively. All other aspects of the analytical model are as given in Table 3.3.

The effects of competitive sorption by Ca²⁺ on Np(V) sorption on hydrous ferric oxide, assuming calcite equilibrium, are illustrated in Figure 4.1. The curves in the figure are calculated using the analytical model and the modified term in the equation for (Fe^{s}OH) discussed above. The curve representing the effects of no competitive sorption are calculated assuming $\Sigma(\text{Ca}^{2+})$ and $\Sigma(CO_3^{2-}) = 0$. Other compositional constraints, based on the oxidized variant of
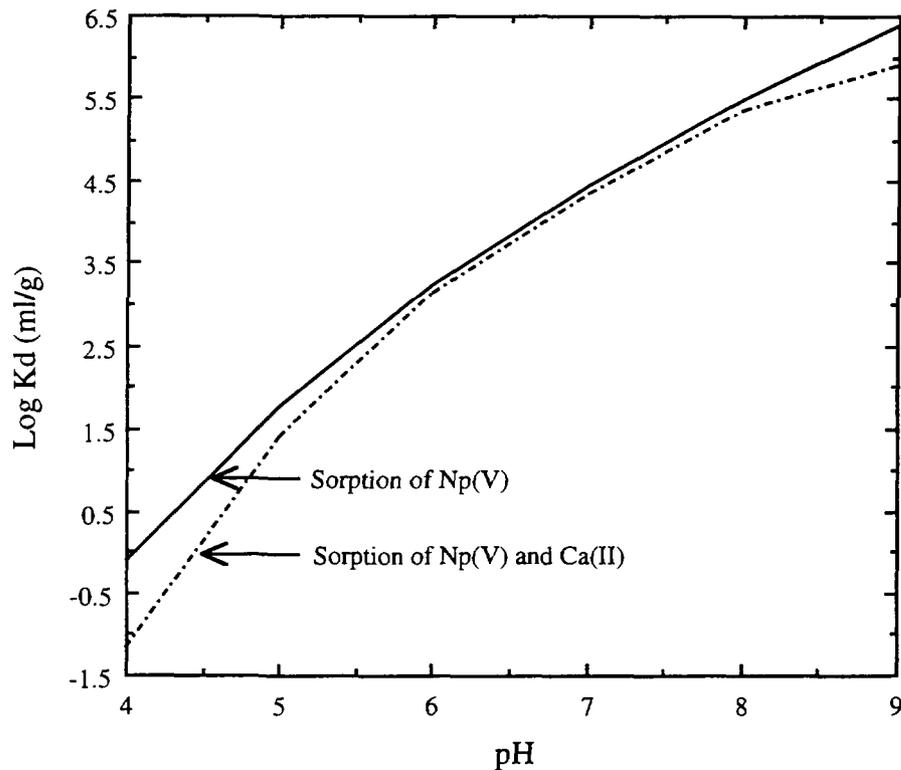
Figure 4.1.   The Effects of Competitive Sorption by Ca^{2+} on Np(V) Sorption on HFO.

the reference groundwater composition, are given in Table 4.1. The results in Figure 4.1 suggest the effects of competitive sorption will be minimal under these conditions, except at the lowest and highest extremes of the pH range considered. Even here, however, these effects are relatively unimportant.

4.2   Calculation of Whole-Rock Distribution Coefficients

The analytical K_d model is modified in this section to calculate corresponding whole-rock distribution coefficients using the surface-film concept of Bradbury and Baeyens (1993), combined with measurements (or estimates) of the total wetted surface area in a unit volume of rock.

The basis for this model is the assumption that hydrous ferric oxide is distributed as a thin layer over minerals in the host rock that are in contact with water. A whole-rock distribution coefficient can then be readily calculated as a

Parameter	Value	$\exp(-F\Psi/RT)$ [‡]	$\exp(-2F\Psi/RT)$ [‡]
Temperature (°C) [*]	25		
Ionic Strength (mol l^{-1})	1.0		
Σ(Np) (mol l^{-1})	10^{-11}		
$\Sigma(\equiv Fe^s)$ (mol l^{-1}) [**]	$10^{-5.3}$		
$\Sigma(Cl^-)$ (mol l^{-1})	$10^{-0.7}$		
$\Sigma(CO_3^{2-})$ (mol l^{-1})	$10^{-3.8}$		
pH	4	$10^{-1.58}$	$10^{-3.16}$
	5	$10^{-1.47}$	$10^{-2.94}$
	6	$10^{-1.15}$	$10^{-2.30}$
	7	$10^{-0.64}$	$10^{-1.28}$
	8	$10^{-0.06}$	$10^{-0.12}$
	9	$10^{0.52}$	$10^{1.04}$
	10	$10^{1.05}$	$10^{2.10}$
$\gamma_{+/-}$ [§]	$10^{-0.1}$		
$\gamma_{2+/2-}$ [§]	$10^{-0.8}$		
$K_{calcite}$	$10^{1.85}$		
$K_{H_2CO_3^*}$	$10^{-6.35}$		
$K_{HCO_3^-}$	$10^{-10.33}$		

‡ - from Table 8.8, Dzombak and Morel (1990)

* - the reference groundwater assumes T = 15°C, a temperature of 25°C is assumed here for consistency with surface acidity and surface-complexation thermodynamic data.

** - $\equiv$ total HFO concentration as Fe (0.001 mol l^{-1}) x $\equiv Fe^s$ site density (0.005 mol $\equiv Fe^s$ mol^{-1} Fe).

The total HFO concentration, 0.09 g l^1, is used to calculate K_d with Equation 1, Table 3.3.

§ - solution activity coefficient for singly and doubly charged species at 25°C, I = 1.0 mol/l (estimated from aqueous-speciation data calculated using EQ3/6).

Table 4.1. Parameter Values Used to Calculate K_d for Np(V) Sorption on HFO.

function of the intrinsic K_d for sorption of Np(V) on HFO:

$$K_d^{wr} = K_d \frac{S_r}{S_{HFO}}, \qquad (4.2.1)$$

where K_d^{wr} stands for the whole-rock distribution coefficient (ml g^{-1}), S_r denotes the total surface area per gram of rock contacted by water, and S_{HFO} represents the specific surface area (cm^2 g^{-1}) of hydrous ferric oxide. Data characterizing

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the in-situ specific surface areas of crystalline rocks are often unavailable. It is possible, however, to estimate S_r using the intrinsic surface area-to-volume ratio of idealized geometric pore spaces in a given rock volume, and representative data for the rock's porosity and density.

For example, the surface area-to-volume ratio of a spherical pore of radius r is equal to $3/r$. The total specific surface area is then given by:

$$S_r = \frac{3\phi_r}{\rho_r r} \tag{4.2.2}$$

where ϕ_r denotes porosity and ρ_r stands for density (g cm^{-3}).

To illustrate how such whole-rock distribution coefficients can be estimated for specific environments, a relation between density and porosity for altered rocks at the Äspö Hard Rock Laboratory can be used to constrain S_r for various assumed characteristic pore dimensions, together with K_d data as a function of pH for Np(V) sorption from the oxidized variant of the reference Äspö groundwater (Section 3). The density-porosity data are from Eliasson (1993), who determined that alteration of the Äspö granites involves, among other reactions, saussuritization of plagioclase and "staining" by HFO. A density for altered Äspö granite of 2.68 g cm^{-3} was assumed, for which the porosity = 20% (Eliasson, 1993). As noted in Section 2.4.2, S_{HFO} = 600 m^2 g^{-1} (Dzombak and Morel, 1993).

Calculated whole-rock distribution coefficients for Np(V) sorption on Äspö granites are given in Table 4.2 for the assumed spherical pores and three assumed mean pore radii: 1cm, 1mm and 0.1mm. The upper value in this

pH	K_d (ml g^{-1})	K_d^{wr} (ml g^{-1})		
		r = 1 cm	r = 1 mm	r = 0.1 mm
4	$10^{-1.18}$	$10^{-4.62}$	$10^{-3.62}$	$10^{-2.63}$
5	$10^{1.38}$	$10^{-2.06}$	$10^{-1.06}$	$10^{-0.06}$
6	$10^{3.12}$	$10^{-0.32}$	$10^{0.68}$	$10^{1.68}$
7	$10^{4.35}$	$10^{0.91}$	$10^{1.91}$	$10^{2.91}$
8	$10^{5.33}$	$10^{1.89}$	$10^{2.89}$	$10^{3.89}$
9	$10^{5.90}$	$10^{2.46}$	$10^{3.46}$	$10^{4.46}$
10	$10^{5.98}$	$10^{2.54}$	$10^{3.54}$	$10^{4.54}$

Table 4.2 Calculated Whole-Rock Distribution Coefficients for Np(V).

range is included for comparison and to approximate conditions possibly existing in fractures, which may be incompletely filled with alteration minerals. The data indicate that neptunium sorption will increase, at fixed porosity and density, with increasing pH and increasing S_r (i.e., decreasing pore radius). Whole-rock distribution coefficients in excess of about 10 to 100 ml g^{-1} generally indicate that radionuclide migration will be strongly attenuated by sorption.

Although there are no field data to verify the predicted whole-rock distribution coefficients for Np, it is noteworthy that a best-estimate value for this parameter under oxidizing conditions, based on an extensive review of experimentally determined sorption data (Andersson 1991), is approximately 10 ml g^{-1} (SKI, 1991). The data estimated in the present study suggest that this estimate is realistic, if not slightly conservative, except for unlikely conditions when the pH is less than about 6.

5   Conclusions

The advantages/disadvantages of the approach described in this report for adapting mechanistic sorption models for use in radionuclide-transport calculations is evaluated in terms of practical constraints on performance assessment calculations discussed in Section 1.2.

The key advantage of the approach is that a mechanistic understanding is explicitly incorporated into the predicted distribution coefficients. This is an improvement over alternative experimental methods, which have been criticized because they are too empirical. It may be desirable to retain the distribution coefficient approach in radionuclide-transport models because more comprehensive approaches, such as coupled reaction-sorption-transport models, may not be justified given the complexity and related uncertainties in natural systems. If so, analytical-mechanistic sorption models can be used to constrain, and defend, the selection of appropriate distribution coefficients.

If it can be shown, on the basis of scoping calculations or other means, that a limited number of "problem radionuclides" pose the greatest potential radiological risk to public health and safety, then development of analytical sorption models enabling more detailed and mechanistic evaluations of their migration behavior may be justified. However, an analytical approach may be impractical for some elements exhibiting complex aqueous- and surface-speciation properties. An alternative approach in such cases could involve using sorption models in existing computer programs, such as MINTEQA2.

A criticism of the mechanistic approach is that there are comparatively few experimental sorption studies that are relevant for radionuclides and for geochemical conditions in a deep geologic repository for nuclear waste. For example, virtually the entire surface-complexation database developed by Dzombak and Morel (1990) are for relatively oxidizing conditions at 25°C. Moreover, it is important to stress that the surface-film concept described by Bradbury and Baeyens (1993) is an hypothesis that has yet to be verified experimentally or by field investigation. However, given appropriate constraints derived from site characterization, and the probability that only a few radionuclides will warrant detailed investigations of their sorption behavior, a concerted experimental investigation can generate the necessary surface-acidity and surface-complexation data required to develop a limited number of mechanistic sorption models.

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