DECREASING K_d UNCERTAINTIES THROUGH THE APPLICATION OF THERMODYNAMIC SORPTION MODELS

Cristina Domènech[a,1], David García[a,*], and Marek Pękala[a]

[a] Amphos 21, Passeig de Garcia i Fària 49-51, 08019, Barcelona (ES)

Abstract

Radionuclide retardation processes during transport are expected to play an important role in the safety assessment of subsurface disposal facilities for radioactive waste. The linear distribution coefficient (K_d) is often used to represent radionuclide retention because analytical solutions to the classic advection-diffusion-retardation equation under simple boundary conditions are readily obtainable, and because numerical implementation of this approach is relatively straightforward. For these reasons, the K_d approach lends itself to probabilistic calculations required by Performance Assessment (PA) calculations. However, it is widely recognised that K_d values derived from laboratory experiments generally have a narrow field of validity, and that the uncertainty of the K_d outside this field increases significantly. Mechanistic multicomponent geochemical simulators can be used to calculate K_d values under a wide range of conditions. This approach is powerful and flexible, but requires expert knowledge on the part of the user.

The work presented in this paper aims to develop a simplified approach of estimating K_d values whose level of accuracy would be comparable with those obtained by fully-fledged geochemical simulators. The proposed approach consists in deriving simplified algebraic expressions by combining relevant mass action equations. This approach was applied to three distinct geochemical systems involving surface complexation and ion-exchange processes. Within bounds imposed by model simplifications, the presented approach allows radionuclide K_d values to be estimated as a function of key system-controlling parameters, such as the pH and mineralogy.

It is hoped that this approach could be used by PA professionals to assess the impact of key geochemical parameters on the variability of radionuclide K_d values. Moreover, the presented approach could be relatively easily implemented in existing codes to represent the influence of temporal and spatial changes in geochemistry on the K_d values.

Keywords

[*] Corresponding author: David García, Ph.D Candidate in a collaborative project between Amphos 21, Ondraf-Niras and UPC. E-mail: david.garcia@amphos21.com. +34 935 830 500

[1] Present address: Grup de Mineralogia Aplicada i Geoquímica de Fluids MAG, Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona (UB), Martí i Franquès s/n, 08028 Barcelona, Spain

1. Introduction

Deep and near-surface underground disposal of nuclear waste is currently being considered in several countries worldwide (NEA 2005). Performance Assessment studies, known as PA, must be done to demonstrate in a quantitative manner the safety of this disposal concept (IAEA 1994, 1995). This type of studies must consider the evolution of groundwater over long periods of time (often hundreds of thousands of years) (Glynn 2003).The long term safety of a sub-surface repository for nuclear waste is affected by the transport of radionuclides in the engineered barriers system (EBS, the near-field) and in the geosphere (far-field).

Retention onto mineral surfaces (e.g. by ion exchange or surface complexation) is a factor that affects radionuclide transport in both the near- and far-field and can have significant consequences for the PA (NEA 2005, Payne et al. 2013).

Radionuclide retention due to surface reactions is typically represented in PA calculation by the equilibrium distribution coefficient (K_d) (Glynn 2003; Payne et al. 2013). The K_d for a given radionuclide is defined as the ratio between the adsorbed concentration of radionuclide (mass of radionuclide per unit mass of solid) and the aqueous concentration of radionuclide (mass of radionuclide per unit volume of solution). K_d represents therefore a linear relationship between radionuclide retention and its concentration in the solution. Due to this linearity, the use of K_d makes it easy to represent radionuclide retention in transport models (including analytical models for simple boundary conditions) and decreases the computational burden of the calculation (Glynn 2003). For this reason K_d has been the preferred approach to representing radionuclide sorption in PA.

PA radionuclide transport calculations often handle uncertainty by employing probabilistic methods, such as Monte Carlo approach (Nirex 2003), perturbation approach (Liu et al. 1986) or polynomial chaos (Hagues et al. 2010), that in general, require a large number of transport calculations.

The K_d values for a given radionuclide for various materials are typically derived from batch and/or column laboratory experiments (Ochs et al. 2001, 2012; Glynn 2003; Tachi et al. 2010), where the material (e.g. host-rock, concrete, bentonite, etc.) is brought in contact with an aqueous solution containing various concentrations of the radionuclide of interest. The concentration of the radionuclide in the aqueous solution is monitored in time and it is often assumed that the distribution of the radionuclide between the solution and solid surface achieves equilibrium once the aqueous concentration reaches a steady value. Multiple batch experiments of this type are performed under a variety of conditions (e.g. pH, redox values, ionic strength, solid-liquid ratio or presence of other dissolved constituents) relevant for the PA. Consequently, the derived K_d values lump together various processes (e.g. surface complexation, ion-exchange, precipitation, co-precipitation, etc.) and do not provide appreciable insight into the mechanism of retention processes at work (Glynn 2003; Gil-García et al. 2011, Payne et al. 2013). Derived K_d coefficients present a large range of values covering 2-3 orders of magnitude, given their high dependency on several factors such as pH, soil texture, or microbial activity (IAEA 1994; Gil-García et al. 2011). Importantly, the K_d values derived from

Suprimit: :

laboratory experiments are conditional in the sense that their applicability is restricted to conditions sufficiently close to those under which they were derived (Payne et al. 2013). However, these conditions are not always described in detail in literature and this, together with the fact that some other factors traditionally not controlled (e.g mineral reactive surface, fresh/weathered surface) may also have an important effect on the measured K_d, limit the validity of K_d (Glynn 2003). Therefore, it is difficult to choose the best estimate value with a narrow range of uncertainty for the K_d of a given element useful for PA studies (Sheppard and Thibault 1990; Gil-García et al. 2009). K_d has been identified as a critical parameter in the evaluation of radionuclide mobility (Viswanathan et al. 1998; Nair and Krishnamoorthy 1999). K_d approach is useful to describe the migration of contaminants in aquifers with groundwater chemical and mineralogical composition uniform over time and space, but it is not a good approach in heterogeneous or transient systems (Glynn 2003; De Windt et al. 2004). Alternatively, radionuclide retention data obtained with the experimental methodology explained above (i.e. from batch and/or column laboratory experiments where the adsorbent is brought in contact with an aqueous solution containing various concentrations of the radionuclide of interest) can be assessed through the use of thermodynamic sorption modelling (TSM). Such approach, based on the definition on a mechanistic reaction model (Davis and Kent 1990; Geckeis et al., 2013), can represent a variety of retention reactions (equilibrium and kinetic), and in principle can be implemented directly into reactive transport models (Goldberg et al. 2007). This has the advantage that complex, non-linear effects (e.g. aqueous speciation, competition, non-equilibrium kinetics, etc.) associated with coupled phenomena can be represented explicitly and that chemical composition of groundwater is specifically taken into account (Payne et al. 2013). This approach relies on the use of thermochemical calculations which can quantify retention processes in a generic matter that is not site specific (Wang et al. 2001; Geckeis et al. 2013; Romanchuk and Kalmykov 2014). Until recently, TSM have been largely limited to well-controlled laboratory experiments on single-mineral phases (Davis et al. 1998).

TSM application to rocks, soils and sediments has been hindered due to the complexity of these natural systems. Two general approaches for applying TSM to complex natural mineral assemblages exist: (1) the Component Additivity and (2) the Generalized Composite (Davis et al. 1998; NEA 2005; Davis 2008, Payne et al. 2013). In the Component Additivity approach it is assumed that the mineral assemblage is composed of a number of individual mineral phases whose respective surface properties are known from previous studies. Moreover, the assumption is made that the sorption behavior of the mineral assemblage as a whole can be represented by the sum of sorption behavior of its components (sorption is additive). A model for each single-mineral phase must be developed, and then, these single-mineral components are combined in an additive fashion according to their measured (or estimated) relative amounts or surface areas for each mineral in the mineral assemblage. In contrast, in the Generalized Composite approach the sorption properties of a complex mineral assemblage are considered to be inherently too complex to be adequately represented by a simple sum of the properties of

its individual components. In this case, the presence of "generic" surface functional sites are assumed, whose properties (stoichiometry and equilibrium constants) are fitted using experimental data. For complex mineral assemblages, the General Composite approach requires less experimental information than the Component Additivity approach, and may be preferred for immediate and practical applications (Davis et al. 1998). However, the limitation of the General Composite approach is that the properties of these "generic" functional sites are valid only for the specific mineral assemblage studied (are not transferrable to other mineral assemblages). Despite this limitation, the Generalized Composite approach is still considered superior to simplified empirical approaches (e.g. the linear distribution coefficient) as it offers (through the mass-action equations) a more mechanistic representation of the linkage between the dissolved and adsorbed species (Davis et al. 1998). On the other hand, the Component Additivity approach requires good detailed characterization of the mineral surface composition (e.g. the presence of mineral coating), including on molecular level. The advantage of the Component Additivity approach is however that it offers more flexibility and transferability once the necessary information is available, e.g. predictive modeling of sorption properties of complex mineral assemblages can be performed without the necessity for experimental investigation.

In general, the TSM approach offers the possibility to quantitatively understand the role and significance of every retention process considered, which adds valuable insight to system understanding and to interpolate or extrapolate from studied sites to other hypothetical or future conditions (Payne et al. 2013). Important aspects of TSM as applied to radionuclide retardation processes were studied under the auspices of the Integration Group for the Safety Case (IGSC) of the OECD/NEA Radioactive Waste Management Committee (RWMC), and are summarized in NEA (2005) and NEA (2012). Moreover, efforts are continuously made to create open-access internally consistent data sets for sorption modeling (see for example: https://www.hzdr.de/db/RES3T.login).

However, the use mechanistic reactive transport models can become cumbersome or impractical if the calculations must consider large spatial/temporal scales and complex chemical systems (Glynn 2003). Sensitivity analyses and/or probabilistic calculations are required to account for the quality of the results (Glynn 2003).

Another way of using geochemical retention models is to simulate (batch) retention processes in order to calculate a K_d value that can then be implemented in a PA model (e.g. Duro et al. 2001; NEA 2005; Payne et al. 2013). The advantage of this approach is that numerical simulations are typically very rapid in comparison with laboratory experiments, hence a large number of conditions can be considered and the derived K_d values can be described statistically. This is particularly useful for probabilistic PA calculations. Mechanistic geochemical models are powerful, but their proper use requires expert knowledge.

In this paper we investigate the possibility of using simplified analytic expressions for the K_d that could represent the dependence of K_d on geochemical conditions with sufficient accuracy avoiding the need of using geochemical codes to quantify radionuclide mobility. This TSM

based approach could provide an easy to use tool for PA scientists to obtain reliable and robust estimates of the effect of varying geochemical conditions (e.g. water chemistry or system mineralogy) on the radionuclide K_d.

2. Mathematical Formulation

The model presented in this paper is based on a previous work performed by Duro et al. (2001). The model of Duro et al. (2001) is further developed in this paper to include cation exchange and electrostatic effects for surface complexation reactions. Sorption coefficient (K_d) for a Radionuclide (Rn) is defined in eq. 1, where $\{Rn\}_{ads}$ and $[Rn]_{aq}$ stand for the total concentration of the Rn retained on the solid and the Rn total aqueous concentration, respectively.
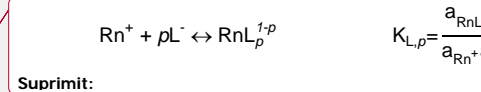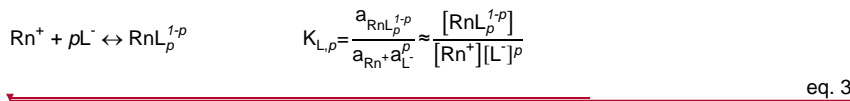
$$K_d = \frac{\{Rn\}_{ads}}{[Rn]_{aq}}$$

eq.1

Total aqueous concentration of Rn, $[Rn]_{aq}$, is the sum of all aqueous species of the Rn as shown in eq. 2, where L stands for the different ligands (hydroxyl ion, chloride ion, etc.) present in solution. For simplicity, the example given below is for a monovalent radionuclide cation but a similar derivation can easily be obtained for radionuclides of any charge. The aqueous complexes are cast in terms of complexation constants ($K_{L,p}$, eq. 3) associated with the equilibrium reactions of the different ligands present in the solution, which after substituting in eq. 2 leads to eq. 4. p stands for the corresponding ligand (L) stoichiometry coefficient. Activities of solutes are assumed equal to their aqueous concentrations.

$$[Rn]_{aq} = [Rn^+] + [RnL] + [RnL_2^-] + \ldots$$

eq. 2

$$Rn^+ + pL^- \leftrightarrow RnL_p^{1-p} \qquad K_{L,p} = \frac{a_{RnL_p^{1-p}}}{a_{Rn^+} a_L^p} \approx \frac{[RnL_p^{1-p}]}{[Rn^+][L^-]^p}$$

eq. 3

$$[Rn]_{aq} = [Rn^+] \times \{1 + K_{L,1}[L^-] + K_{L,2}[L^-]^2 + \ldots\}$$

eq.4

Eq. 4 could be re-written in a more general form (eq.5).

$$[Rn]_{aq} = [Rn^+] \times \left\{ 1 + \sum_{L,p} K_{L,p}[L^-]^p \right\}$$

eq.5

Similarly, $\{Rn\}_{ads}$ is defined in terms of the sum of all surface complexes of Rn, and hence depends on the solid surface properties (i.e. acidity and/or site density) and on the surface

complexation or exchange equilibrium of Rn with the solid surface. Eq. 6 shows an example for a case where sorption occurs on a single site ($>SO^-$) and no exchange reaction occurs.
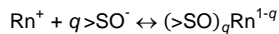
$$\{Rn\}_{ads}=\{>SORn\} + \{(>SO)_2Rn^-\} +\dots \qquad \text{eq.6}$$

As in the case of the aqueous speciation complexes, one can re-arrange eq.6 in terms of surface complexation constants ($K_{S,q}$). At this moment of the model development a decision on the TSM governing the sorption and/or exchange reactions occurring in the system under study must be taken. In this case, and for the sake of conciseness a non-electrostatic surface complexation is considered. Therefore, equations developed from this moment on would only apply to non-electrostatic surface complexation models, as in the first verification exercise shown in section 3. The sorption of $Rn^{\pm}$ on a surface site $>SO^-$ and the corresponding expression of $K_{S,q}$ can be written as in Eq.7, where q stands for the corresponding site $>SO^-$ stoichiometry coefficient. Assuming this, eq.6 may be rewritten as eq.8, and generalizing as eq.9.
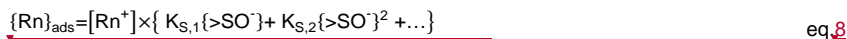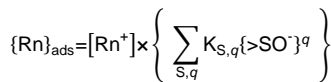
$$Rn^+ + q >SO^- \leftrightarrow (>SO)_q Rn^{1-q}$$

$$K_{S,q}=\frac{a_{(>SO)_qRn^{1-q}}}{a_{Rn^+}a_{>SO^-}^q}\approx\frac{\{(>SO)_qRn^{1-q}\}}{[Rn^+]\{>SO^-\}^q} \qquad \text{eq. 7}$$

$$\{Rn\}_{ads}=[Rn^+]\times\{\ K_{S,1}\{>SO^-\}+ K_{S,2}\{>SO^-\}^2 +\dots\} \qquad \text{eq.8}$$

$$\{Rn\}_{ads}=[Rn^+]\times\left\{\ \sum_{S,q} K_{S,q}\{>SO^-\}^q\right\} \qquad \text{eq.9}$$

Combining eq.1, eq.5 and eq.9, a new expression for calculating the K_d is obtained (eq.10), where $\{>SO^-\}$ and $[L^-]$ stand for the concentration of solid surface sites (mol×kg^{-1}) and the concentration of aqueous ligands (mol×dm^{-3}), respectively.
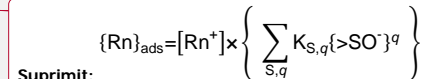
$$K_d=\frac{\sum_{S,q}K_{S,q}\{>SO^-\}^q}{1+ \sum_{L,p}K_{L,p}[L^-]^p} \qquad \text{eq.10}$$

Eq. 10 depends on the thermodynamic constants of the system under study ($K_{L,p}$), values that can be found in a thermodynamic database and implemented in the equation. It also depends on the sorption constants of the reactions considered in the mechanistic model from which the equation is derived ($K_{S,q}$). These values are also known and can be implemented in the equation.

{>SO$^-$} must be determined from the rock properties, the amount of mineral in the host rock and the number of coordination (or exchange) sites on the mineral surface. Combining this information with the surface equilibria of the proposed solid surface and re-arranging terms, eq.11 is obtained, where W_S is the amount of mineral (kg$_{of\ mineral}$ $\times$ kg$_{host\ rock}^{-1}$) and A_S is the number of coordination (or exchange) sites (mol$_{sites}$ $\times$ kg$_{mineral}^{-1}$). The number of coordination or exchange sites, A_S, has a constant value once the system is defined. The amount of mineral (W_S) can also be considered constant most of time if the mineral does not dissolve nor precipitate significantly. $K_{S,a}$ stands for the surface deprotonation constant.

$$K_d = \frac{\sum_{S,q}\left(K_{S,q}\dfrac{A_S W_S}{1+\dfrac{[H^+]}{K_{S,a}}}\right)^q}{1+\sum_{L,\,p}K_{L,p}[L^-]^p} \qquad\qquad eq.11$$

As seen in eq.11, the calculation of the variation of K_d with pH and the concentration of key ligands can be easily implemented in most of the codes used to work with K_d approach. Therefore, if we know how a radionuclide or trace element is sorbed onto a mineral surface and the mechanistic model for this process is well stablished, eq.11 allows to find a K_d supported by this mechanistic model and adequate to the properties of the system under study.

In the following section the application of this model to some cases of interest is presented alongside a general discussion of the applicability of the model in more complex situations. The test cases include the use of electrostatic models and exchange models, which need some additional terms in eq.11.

3. Model Verification

The above-described approach was applied to three different geochemical systems. The validity of this approach was tested against both the K_d values derived from experimental data and the K_d values calculated after reproducing the experimental results with a mechanistic sorption or exchange model (TSM).

The selected systems were: 1) Eu sorption onto illite; 2) Cs sorption onto iron-hydroxide phases, and; 3) Cs exchange within illite. Data for these systems were selected from literature after verifying the confidence on the chemical analysis performed. In all these cases, radionuclide retention is due to sorption/exchange processes. Therefore, non-other retention phenomena (i.e. surface precipitation, solid-solution formation) have been considered. Thermodynamic data other than surface sorption constants or selectivity coefficients (i.e. aqueous complexation) used in the calculations were selected from www.thermochimie-tdb.com (Giffaut et al. 2014) whose quality and consistency is detailed in the documentation available in the same webpage.

3.1 Test cases and input data

3.1.1 Case 1: Eu sorption onto illite

Illite is a clay-type mineral commonly found in most of the clays that are being studied within the frame of nuclear waste repositories, e.g. Callovo-Oxfordian or Boom clays in France and Belgium respectively (Bradbury and Baeyens 2005). The reason is that clay minerals are considered suitable components of the geological barriers because of their high capacity for sorbing radioelements, their swelling properties and their low water permeability (Schnurr et al. 2013). Eu(III) is considered a chemical analogue of Am(III) (Catalette et al. 1998).

Sorption of Eu onto illite has been studied by several authors. Poinssot et al. (1999a) studied the sorption behaviour of Cs, Sr, Ni and Eu on the Na-(homo-ionic) Illite du Puy as a function of $NaClO_4$ background electrolyte concentration (0.1 and 0.01 M), radionuclide concentration and pH. In the case of Eu, they determined sorption edges at trace concentrations (2.1×10^{-9} – 4.3×10^{-9} M) in 0.1 and 0.01M $NaClO_4$ and pH in the range 2 -10. They also obtained a sorption isotherm of Eu at pH 7 in 0.1 M $NaClO_4$.

Bradbury and Baeyens (2005) presented the results of some batch sorption experiments of Sr, Ni, Eu and U on the same Na-illite. In the case of Eu, they studied its sorption behaviour as a function of the background electrolyte concentration (0.01, 0.1 and 0.5 M $NaClO_4$), pH (2.7 - 11.1) and sorbate concentrations, at Eu trace concentration (3×10^{-9} M). Besides reporting experimental results, the authors also proposed two processes governing the behaviour of Eu in that system: sorption of Eu onto two different types of illite sites (called strong and weak sorption sites), and exchange of Eu with the Na cation originally present in the illite exchange positions. They considered that the electrostatic term was not required to account for the sorption of Eu onto illite surface sites and proposed a set of surface and exchange reactions of Eu onto illite with their corresponding log K values, as well as data for the protolysis of illite surface sites.

More recently, Schnurr et al. (2013) continued with the study of the sorption of Eu, but also of Cm(III) and U(VI), onto clay minerals under saline conditions with no CO_2. They carried out batch sorption edge experiments of Eu onto the Illite du Puy at different ionic strengths (0.1 M, 1.0 and 4.0 M NaCl), with an initial concentration of Eu of 2×10^{-7} M and at pH in the range 3 - 11. They applied the non-electrostatic surface protonation model of Bradbury and Baeyens (2005) to successfully describe their results.

Subsets of data sets from Poinssot et al. (1999a), Bradbury and Baeyens (2005) and Schnurr et al. (2013) were selected for this validation exercise. The selection was done based on availability of experimental information, such as sorption sites densities, pH, initial and final Eu aqueous concentration and S:L ratio, which is necessary to validate the K_d approach model described in chapter 2.

Selected data were:

- Data from Poinssot et al. (1999a), $[Eu]_o = 3.2 \times 10^{-9}$ M, I = 0.01 M $NaClO_4$, pH 2.7-11 Illite du Puy.
- Data from Bradbury and Baeyens (2005), $[Eu]_o = 3 \times 10^{-9}$ M, I = 0.01M, 0.1M and 0.5 M $NaClO_4$, pH 2.7-11, Illite du Puy.
- Data from Schnurr et al. (2013), $[Eu]_o = 2 \times 10^{-7}$ M, I = 0.1 M NaCl, pH 4.5-11.5, Illite du Puy.

The model reported by Bradbury and Baeyens (2005) was chosen in this work for an overall and accurate representation of Eu retention onto illite. The model is summarised in Table 1. In this model, the authors also considered the exchange of Eu with Na, resulting relevant at acidic conditions (pH < ~4.0). As the majority of experimental data selected for this test case validation exercise was obtained at pH values higher than ~4.0, we neglected Eu exchange for simplification purposes.

Table 1. Surface complexation model of Eu sorption onto illite as proposed by Bradbury and Baeyens (2005).

Reaction	log K^o
$>S^sOH + H^+ = >S^sOH_2^+$	5.50
$>S^sOH = >S^sO^- + H^+$	-6.20
$>S^wOH + H^+ = >S^wOH_2^+$	5.50
$>S^wOH = >S^wO^- + H^+$	-6.20
$Eu^{3+} + >S^sOH = >S^sOEu^{2+} + H^+$	3.10
$Eu^{3+} + >S^sOH + H_2O = >S^sOEu(OH)^+ + 2H^+$	-4.40
$Eu^{3+} + >S^sOH + 2H_2O = >S^sOEu(OH)_2^+ + 3H^+$	-12.70
$Eu^{3+} + >S^wOH = >S^wOEu^{2+} + H^+$	0.30
$Eu^{3+} + >S^wOH + H_2O = >S^wOEu(OH)^+ + 2H^+$	-6.20
S^s sites (mol×kg^{-1} mineral)	2.0×10^{-3}
S^w sites (mol×kg^{-1} mineral)	4.5×10^{-2}

3.1.2 Case 2: Cs sorption onto iron-oxide/hydroxide phases

[137]Cs is a monovalent radionuclide, a fission product of spent fuel, commonly found in almost all of the radioactively contaminated places (Marmier et al. 1999, Ebner et al. 2001). Although it is soluble its mobility might be retarded by sorption onto minerals or suspended particles (Comans et al. 1991). It is important to quantify this retention due to sorption processes in order to not only avoiding the transport of ^{137}Cs to the environment but also recovering Cs because of their important applications in medicine, science and industry (Ebner et al. 2001). It is also a long-lived radionuclide that is easily assimilated by terrestrial and aquatic organisms (Poinssot et al. 1999b).

Although very low in comparison to the retention of Cs in clays, the retention of Cs onto iron oxide phases (i.e. magnetite, Fe_3O_4,) has been studied by several authors (Catalette et al. 1998, Marmier et al. 1999, Ebner et al. 2001, Rovira et al. 2004, Granizo and Missana 2006). Magnetite is a corrosion product of carbon steel that may play a significant role in sequestering radionuclides by sorption and/or (co)precipitation phenomena and although not being as selective as other materials, it is relatively inexpensive and available (Ebner et al. 2001).

Catalette et al. (1998) studied the adsorption of Cs, Ba and Eu onto magnetite. They performed batch experiments at 25ºC, in 0.01 and 0.1 M $NaClO_4$, and in the pH range 3.1 - 9.2 and observed that although Ba and Eu were strongly sorbed onto magnetite, Cs was not sorbed except if magnetite contained some silica impurities. They checked this behaviour by doing also sorption batch experiments with a natural magnetite with some silica impurities ($2.4\pm0.5\%$ wt SiO_2). The authors fitted the experimental data using a diffuse layer model with the FITEQL code (Westall 1982). Nevertheless they could not obtain a good model for the sorption of Cs onto magnetite, given that poor experimental results obtained with this element.

Marmier et al. (1999) studied the sorption of Cs, Ni and Yb onto a pure magnetite in batch experiments at pH 3.5-8.5 and at 0.01 M $NaNO_3$. Cs initial concentration was 4×10^{-5} M. They observed that Cs onto magnetite was very low. They modelled their experimental results by using three different complexation models, the constant capacity model (CCM), the non-electrostatic model (NEM) and the diffuse layer model (DLM). But in the case of Cs, as no significant sorption was observed in the experiments, they could derive neither surface reactions stoichiometry nor reaction constants.

Later, Ebner et al. (2001) studied the adsorption of Cs, Sr and Co on pure magnetite and on a magnetite-silica composite (80-20%) through the use of constant pH adsorption isotherms at 25ºC. The authors obtained data at four different pH values (6, 7, 8 and 9) with initial Cs concentrations ranging from 10^{-5} to 10^{-4} M in 0.01 N $NaNO_3$. They observed that Cs sorption increased with pH and that the addition of silica enhanced it as was previously described by Catalette et al. (1998). They explained their results by the Langmuir adsorption isotherm model.

Rovira et al. (2004) studied the sorption of Cs onto magnetite at high S:L ratios using a synthetic magnetite (0.031% wt silica) at pH between 5 and 9 and at 0.01 and 0.1 m NaCl, and with an initial concentration of Cs of 10^{-5} M. They observed a slight increase in the sorption of Cs with a decrease in pH. They also observed that increasing ionic strength decreased Cs sorption due to the competition with the counter ion (Na in this case). The authors concluded that silica impurities played an important role in Cs sorption. According to Rovira et al. (2004) and references therein, this could be explained by the high surface area of silica and its affinity for Cs, that may help in the formation of ternary sorption complexes of magnetite-Si-Cs. They modelled their results with FITEQL (Westall 1982) assuming four reactions: the hydrolysis of magnetite surface sites, the adsorption of silica onto the surface of magnetite and the formation of the ternary complex $>SSiO_4H_3Cs^+$.

Granizo and Missana (2006) studied the sorption of ^{137}Cs on a pure magnetite synthesized in the laboratory as a function of pH (3-13.5), ionic strength (0.001, 0.01 and 0.1 M $NaClO_4$), Cs concentration (1×10^{-10} - 1×10^{-6} M) and sorbent concentration (2-10 g/L). They observed that maximum sorption occurred at pH around 12 and that sorption increased when decreasing the ionic strength, as did Rovira et al. (2004). They fit the experimental data assuming a diffusion layer model in which Cs^+ formed the complexes $>SOCs$ and $>SOHCs^+$ at the surface of magnetite. They applied this model to reproduce the results of the experiments of sorption of Cs onto magnetite in synthetic and cement porewater that they also presented in the paper.

Suprimit: But

Suprimit:

Selected data sets for the model verification were:

- Data from Catalette et al. (1998), $[Cs]_o = (2-8) \times 10^{-5}$ M, I = 0.01 - 0.1 M NaClO$_4$, pH 3 – 9.2, natural magnetite.
- Data from Marmier et al. (1999), $[Cs]_o = (2-4) \times 10^{-5}$ M, I =0.01 M NaNO$_3$, pH 3.5 – 8.5, pure commercial magnetite.
- Data from Ebner et al. (2001), $[Cs]_o = 1 \times 10^{-5} - 1 \times 10^{-4}$ M, I =0.01 N NaNO$_3$, pH 6.0 - 9.0, synthetic magnetite.
- Data from Rovira et al. (2004), $[Cs]_o = 1 \times 10^{-5}$ M, I = 0.1 m NaCl, pH 5.5 – 9.0, synthetic magnetite.
- Data from Granizo and Missana (2006), $[Cs]_o = 1 \times 10^{-10} - 1 \times 10^{-6}$ M, I = 0.001 - 0.1 M NaClO$_4$, pH 4 – 13.7, synthetic magnetite.

The model of Granizo and Missana (2006) with the sorption reactions of silica and silica and caesium onto magnetite provided in Rovira et al. (2004), was selected for the calculations presented in this study. Table 2 summarises these reactions.

Table 2. Equilibrium reaction input data used in case 2.

Reaction	log K^o	Reference
>SOH + H$^+$ = >SOH$_2$$^+$	5.10	Granizo and Missana (2006)
>SOH = >SO$^-$ + H$^+$	-9.10	Granizo and Missana (2006)
>SOH + Cs$^+$ = >SOHCs$^+$	1.05	Granizo and Missana (2006)
>SOH + Cs$^+$ = >SOCs + H$^+$	-10.5	Granizo and Missana (2006)
>SOH + H$_4$SiO$_4$ = >SSiO$_4$H$_3$ + H$_2$O	4.10	Rovira et al. (2004)
>SOH + H$_4$SiO$_4$ + Cs$^+$ = >SSiO$_4$H$_3$Cs$^+$ + H$_2$O	6.09	Rovira et al. (2004)
Surface (m$^2 \cdot$g^{-1})	8.5	Granizo and Missana (2006)
Sites·(site nm^{-2})	3.54	Granizo and Missana (2006)

3.1.3 Case 3: Cs exchange onto illite

The exchange of Cs in clay minerals has been identified as one of the most important process causing Cs retardation (Comans et al. 1991, Staunton and Roubaud 1997).
Comans et al. (1991) studied the adsorption and desorption of Cs on K- and Ca-illite. Experimental data were obtained at pH 8 and at variable Cs initial concentration (1 to 20 μg L^{-1}). They observed a fast initial sorption followed by a period in which Cs uptake occurred slowly.
Staunton and Roubaud (1997) studied the adsorption of Cs on two reference clays (Wyoming and Illite du Puy) under controlled conditions and as a function of charge compensating cations (Ca-, Na- or K-), Cs and K concentration, ionic strength and the presence of fulvic acid. The authors concluded that increasing ionic strength caused a decrease in the relative affinity for a trace amount of Cs on both minerals. They provided distribution coefficients and isotherms.
Poinssot et al. (1999b) measured the sorption of Cs onto illite as a function of NaClO$_4$ background electrolyte concentration (1.0, 0.1 and 0.01 M NaClO$_4$), Cs concentration and pH (3 – 10). They proposed a two-site cation exchange model in which Cs exchanged in the Frayed Edge Sites (FES) (high affinity and low capacity) and in the type II sites (low affinity and high capacity) of illite. They also proposed site capacities and selectivity coefficients for both sites.

In the year 2000, Bradbury and Baeyens proposed a generalised model for the exchange of Cs in illite. This model stated that sorption of Cs takes place in three different sites (planar sites, FES and type II), each one having its own site density and selectivity coefficient for Cs (Bradbury and Baeyens 2000) and was able to predict the uptake of Cs at equilibrium concentrations below ~10^{-3} M.

In this case, the data sets used in the validation exercise were:

- Data from Comans et al. (1991), $[Cs]_o = 1 \times 10^{-9} - 4 \times 10^{-8}$ M, pH 8.0, I not reported, Fithian Illite.

- Data from Staunton and Roubaud (1997), $[Cs]_o = 2 \times 10^{-9} - 6 \times 10^{-4}$ M, I and pH not reported, Wyoming clay and Illite du Puy.

- Data from Poinssot et al. (1999b), $[Cs]_o = 1 \times 10^{-8}$ M, I of 0.01 M $NaClO_4$, pH 3.0 – 11.5, Illite du Puy.

Finally, the model of Bradbury and Baeyens (2000) was selected for the calculations in this study (Table 3). It assumes Cs-K exchange to be the most important exchange reaction controlling Cs behaviour and sufficient to represent the overall system behaviour.

Table 3. Exchange reactions and selectivity coefficients according to Gaines-Thomas convention of Cs exchange on illite. Data from Bradbury and Baeyens (2000).

Reaction	log K^{ex}_{Ki}
$KX^* + Cs^+ = CsX + K^+$	4.6
$KY^* + Cs^+ = CsY + K^+$	1.5
$KZ^* + Cs^+ = CsZ + K^+$	0.5

*Illite site distribution according with Bradbury and Baeyens (2000):
Frayed edge site (FES) represented as X is 0.25% of total CEC,
Type II sites represented as Y is 79.75% of total CEC, and Planar
sites represented as Z is 20% of total CEC.

3.2 Comparison of results obtained with the proposed K_d derivation model with experimental and Phreeqc calculated K_d values

The verification of the proposed K_d derivation model was carried out in three steps for each of the test cases described above. First step consisted on the modelling of the selected experimental data sets with the selected TSM by the use of the geochemical code PhreeqC (Parkhurst and Appelo 1999) – a K_d value was calculated from the results of this geochemical model. Second step consisted on applying the K_d derivation model (chapter 2) to find the proper equation of K_d corresponding to each test case and on using it to estimate the K_d values corresponding to the conditions of the selected datasets. Third step consisted on comparing the experimental K_d values with those K_d calculated with the application of the TSM (step 1) and those K_d calculated with the K_d model described in chapter 2 (step 2). This comparison was done in order to understand the qualitative effect of the simplifying assumption made in the latter.

3.2.1 Case 1: Eu sorption onto illite

In this case, the model of Bradbury and Baeyens (2005) shown in Table 1 was implemented in PhreeqC to reproduce experimental datasets of Poinssot et al. (1999a), Bradbury and Baeyens (2005) and Schnurr et al. (2013). The corresponding K_d values were obtained. Results were compared with the experimental K_d in Figure 1, where continuous black line indicating a perfect match between calculated (PhreeqC or our K_d model) and experimental K_d values is also shown. As can be seen, values were consistent assuming an uncertainty value of 1 $\log_{10}$ unit in K_d. This uncertainty is below the 2-3 orders of magnitude of variability that K_d values usually present (IAEA 1994; Gil-García et al. 2011).

Figure 1. Comparison of K_d values for the Eu-illite system calculated using PhreeqC and obtained from experiments. Continuous line represents equivalence (ideal 1:1 match) between calculated and experimental K_d values. Dashed lines delimit a K_d deviation of ± 1 $\log_{10}$ unit. Experimental error bars are within data point symbols. Experimental data from Poinssot et al. (1999a), Bradbury and Baeyens (2005) and Schnurr et al. (2013).

K_d values were calculated for the same experimental datasets using the K_d derivation model presented in eq. 11. The value of density sites (A_s) was selected according to the model of Bradbury and Baeyens (2005) and the value of W_s was considered 1 $kg_{of\ mineral}$ × $kg_{host\ rock}^{-1}$. [H^+] depended on the pH of each data point. $K_{S,q}$ and $K_{S,a}$ are those listed in Table 1. Five aqueous species of Eu were considered in the calculations (Eu^{3+}, $Eu(OH)^{2+}$, $Eu(OH)_2^+$, $Eu(OH)_3(aq)$, $Eu(OH)_4^-$) (Thermodynamic data from www.thermochimie-tdb.com, Giffaut et al. (2014)). Figure 2 presents the comparison between the K_d's calculated with the K_d derivation model and the K_d calculated from experimental measures. It can be seen from Figure 2 that the analytical K_d model calculated K_d values which were relatively close to the measured (experimental) ones over a range of conditions (pH between 4.5-12.0 and I between 0.01 - 0.5 M). It is also observed that in this example the analytical model resulted in a small, but consistent, K_d overestimation.
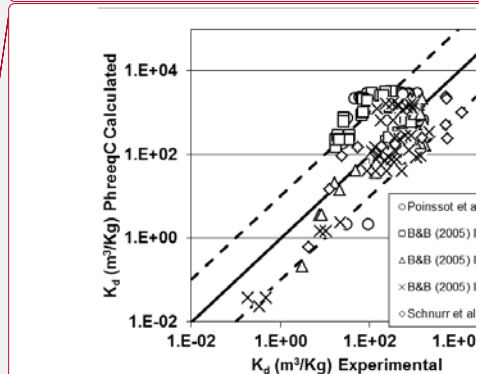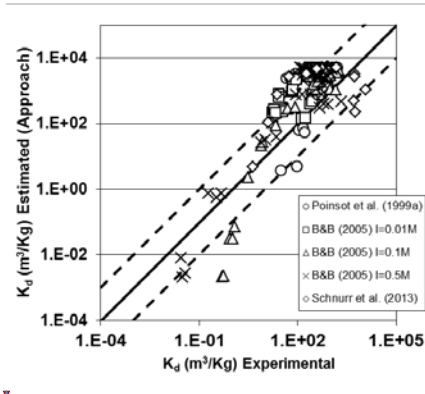
Figure 2. Comparison of K_d values for the Eu-illite system calculated using the K_d derivation model and those obtained from experiments. Continuous line represents equivalence (ideal 1:1 match) between calculated and experimental K_d values. Dashed lines delimit a K_d deviation of ± 1 $\log_{10}$ unit. Experimental error bars are within data point symbols. Experimental data from: Poinssot et al. (1999a), Bradbury and Baeyens (2005), Schnurr et al. (2013).

3.2.2 Case 2: Cs sorption onto iron-oxide/hydroxide phases

The model shown in Table 2 was implemented in the geochemical code PhreeqC to reproduce the selected datasets from Catalette et al. (1998), Marmier et al. (1999), Ebner et al. (2001), Rovira et al. (2004) and Granizo and Missana (2006). K_d values obtained with this model are shown in Figure 3 and compared with K_d derived from experimental data. Except for some values of Ebner et al. (2001), values were very consistent.

Figure 3. Experimental K_d values for the Cs-magnetite system compared to values calculated with PhreeqC using the model shown in Table 2. Continuous line represents equivalence (ideal 1:1 match) between calculated and experimental K_d values. Dashed lines delimit a K_d deviation of ± 1 $\log_{10}$ unit. The error bars of each value are within data point symbols. Experimental data

from Catalette et al. (1998), Marmier et al. (1999), Ebner et al. (2001), Rovira et al. (2004) and Granizo and Missana (2006).

Following the methodology described in Chapter 2 and according to the TSM model of Table 2, equation 12 was derived. As in the test case 1, the values of density sites (A_s) and [H^+], were obtained from the experimental conditions. The value of W_s was considered 1 kg of mineral × kg host rock $^{-1}$. Four aqueous species of Cs were considered in the calculations (Cs^+, CsI, CsCl, CsF). Thermodynamic data were selected from www.thermochimie-tdb.com (Giffaut et al. 2014).
In this case, however, and as discussed in section 3.2.2, this TSM is a diffuse layer model (Granizo and Missana 2006), which considers the formation of two charged layers next to solid surface (Dzombak and Morel 1990). In order to account for the effect of these charged layers onto surface complexation the electrostatic or coulombic correction factor $exp(\Delta ZF\psi/RT)$, where ΔZ is the change in the charge of the surface species due to sorption reaction, ψ the surface potential (V) and F, the Faraday constant, must be considered in the calculations. When deriving eq.12 after applying the K_d derivation model, a term CT appears in the equation. This term groups the effects of the electrostatic interactions between charged layers in the system.

$$K_d = \frac{\sum_{S,q} K_{S,q}\, CT\, \dfrac{A_S W_S}{1+\dfrac{[H^+]}{K_{S,a}CT}}}{1+ \sum_{L,\,p} K_{L,p}[L^-]^p} \qquad \text{eq.12}$$

The Coulombic term depends on several factors such as the ionic strength of solution, pH and the charge on the solid surfaces, and it is not easy to calculate directly from system properties. In this test case, however, the value of CT calculated with the code PhreeqC presented a linear correlation with pH at different ionic strengths (Figure 4). These correlations were used to estimate the CT for each experimental point.
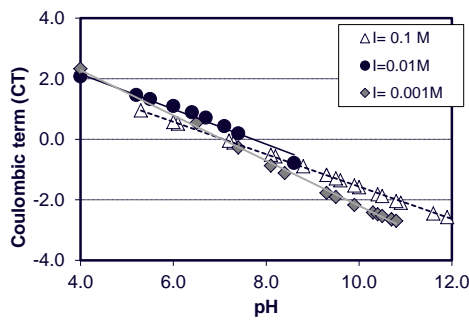

Figure 4. Coulombic Term calculated assuming the TSM of Table 2 with the code Phreeqc as a function of pH at three different ionic strengths.

Figure 5 shows the results calculated using eq. 12. As can be seen, the analytical K_d model (eq. 12) can reproduce experimental K_d values with reasonable accuracy. Although scattering in K_d is higher when using the analytical model than when the calculation is made with TSM in PhreeqC, it is important to highlight that the application of this equation gives K_d values more adapted to the studied system.
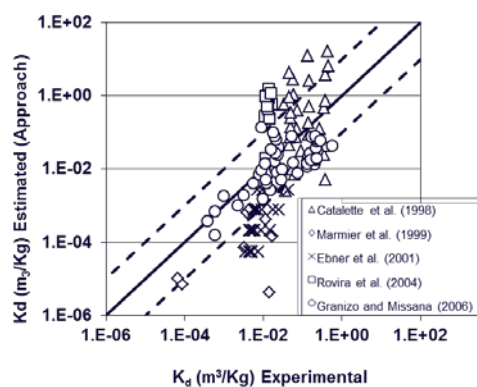
Figure 5. K_d calculated by using the K_d derivation model compared to experimental K_d values for the Cs-magnetite system. Experimental data from Catalette et al. (1998), Marmier et al. (1999), Ebner et al. (2001), Rovira et al. (2004) and Granizo and Missana (2006). Continuous line represents equivalence (ideal 1:1 match) between calculated and experimental K_d values. Dashed lines delimit a K_d deviation of $\pm 1 \log_{10}$ unit. The error bars of each value are within data point symbols.

Suprimit: equality between values

3.2.3 Case 3: Cs exchange onto illite

The exchange reaction model of Bradbury and Baeyens (2000) presented in Table 3 was implemented in PhreeqC to reproduce the selected experimental data sets of Cs exchange onto illite provided by Comans et al. (1991), Staunton and Roubaud (1997) and Poinssot et al. (1999b). As can be seen in Figure 6, the model of Bradbury and Baeyens (2000) is able to reproduce the experimental datasets, within the uncertainty.
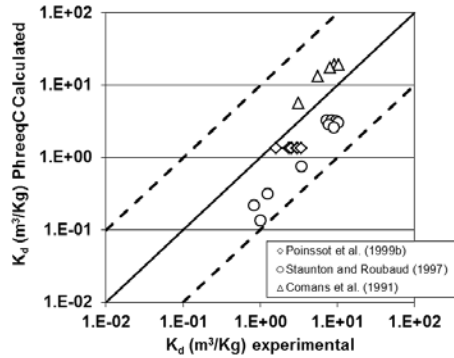
Figure 6. Experimental K_d values for the Cs-illite system compared to values calculated with PhreeqC using the model of Bradbury and Baeyens (2000) (Table 3). Continuous line represents equivalence (ideal 1:1 match) between calculated and experimental K_d values. Dashed lines delimit a K_d deviation of $\pm$ 1 $\log_{10}$ unit. The error bars of each value are within data point symbols. Experimental data from Comans et al. (1991), Staunton and Roubaud (1997) and Poinssot et al. (1999b).

Following the methodology provided in Chapter 2, and accordingly to the model of Bradbury and Baeyens (2000) that provides the selectivity coefficients of the exchange reactions of Cs in three different positions of illite (Frayed edge site, Type II sites and Planar sites, Table 3), equation 13 was derived. In this equation K^{ex}_{Ki} is the selectivity coefficient according to the Gaines-Thomas convention of the different exchange positions (KX, KY and KZ, of Table 3). Q_i is the exchange capacity of each of the sites and is also a known value. As in the case of the Cs sorption onto Fe-oxides, four aqueous species of Cs^+ were considered (Cs^+, CsI, CsCl, CsF) (thermodynamic data from www.thermochimie-tdb.com, Giffaut et al. (2014)).

$$K_d = \frac{\sum_{i=X,Y,Z}\left(\frac{K^{ex}_{Ki}Q_i}{[K^+]+K^{ex}_{Ki}[Cs^+]}\right)}{\left(1+ \sum_{L,\,p}K_{L,p}[L^-]^p\right)}$$

eq. 13

Results obtained with the K_d derivation model of eq. 13 are also shown in Figure 7. As can be seen the results calculated with the derived analytical K_d model are close to the values calculated with PhreeqC, and both agree fairly well with the experimental data.
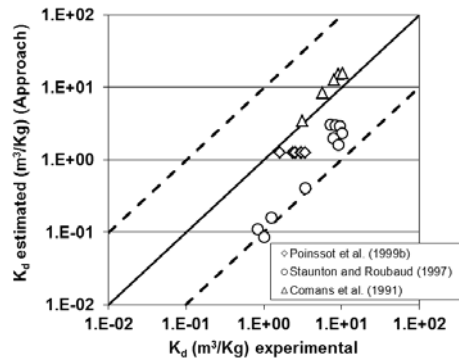
Figure 7. K_d calculated by using K_d derivation model vs experimental K_d values for the Cs-illite system. Continuous line represents equivalence (ideal 1:1 match) between calculated and experimental K_d values. Dashed lines delimit a K_d deviation of ± 1 log_{10} unit. The error bars of each value are within data point symbols. Experimental data from Comans et al. (1991), Staunton and Roubaud (1997) and Poinssot et al. (1999b).

3.3 Major Model Assumptions – Impact on results

As can be seen from Figure 1 to Figure 7, the K_d derivation model is capable of reproducing measured values with a reasonable accuracy. Also, in most cases the values calculated using a fully-coupled model (PhreeqC) and those estimated from the K_d derivation model are in fair agreement.

Nevertheless, some mismatch between the values calculated by PhreeqC and the K_d derivation model exist. This is due to some of the simplifying assumptions that were made in the derivation of the latter. In all cases, activities of aqueous species were considered equal to their aqueous concentrations. This assumption, although critical at high ionic strength solutions, is understandable considering the final destiny of the type of K_d equations that were derived in this paper. They are thought to be used in codes where no geochemical reactions are expected to be carried out, that is, where no speciation, neither ionic strength corrections will be implemented. Another important simplifying assumption that was made in test cases 1 and 2, is that it was considered that sorption sites were far from saturation with respect to the radionuclide of interest. That is, that the concentration of Eu in test case 1 and Cs in test case 2 in occupied sites was negligible in comparison with the concentration of un-complexed sites. This assumption can result in a systematic overestimation of the calculated K_d value, as can be seen in Figure 2 and Figure 5.

Moreover, in the case of Cs exchange with illite (test case 3) the simplifying assumption was made that the equilibrium Cs concentration in solution was equal to the initial Cs concentration. It is noteworthy that this assumption results in a systematic overestimation of both the Cs in
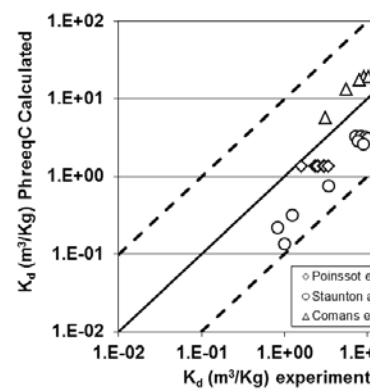
solution and on the exchanger, but these roughly cancel out in the K_d calculation, and therefore the impact of this assumption is limited.

In all these cases, radionuclide retention was only due to sorption or exchange processes. Therefore, K_d values calculated by PhreeqC (considering a TSM model) and with the K_d derivation model only account for retention due to these phenomena. Additionally non-redox sensitive radionuclides have been studied in the present work and thus redox reactions were not considered. On more complex systems those processes could be relevant to understand radionuclide behaviour.

4. Conclusions

A simplified model to calculate K_d values of selected radionuclides for distinct geochemical systems was developed and its results were compared with those obtained using the geochemical code PhreeqC (Parkhurst and Appelo 1999).

In the three test cases studied here, the K_d values estimated using the simplified and analytical K_d derivation model compared quite well with both the experimental values and with the modelling results obtained with a TSM and the fully-coupled approach of PhreeqC. K_d values obtained with the K_d derivation model produced some additional scattering (due to the simplifications made), whose magnitude depended on the particular experimental conditions of each dataset.

Specifically, it was observed that:

a) When studying sorption, the simplified assumption that sorption sites never reach radionuclide saturation leads to a systematic K_d overestimation.

b) In the case of exchange reactions, assuming that equilibrium radionuclide concentration is equal to the initial one does not affect calculated K_d values as the overestimation is done in both solution and exchange (which cancel out in the final calculation of the K_d).

Nevertheless, the proposed approach is considered to be a useful technique of obtaining K_d values estimations in an easy way and with a reasonable accuracy. Due to its linearity and to the nature of the parameters that the equation considers, it can be easily implemented in (not reactive) transport models. K_d values can be then recalculated if system conditions change, thus decreasing the uncertainty of the results. This will be useful in PA studies where the use of K_d values is of utmost importance for a proper radionuclide behaviour description without losing accuracy in the models, and where the calculation may need to be repeated many times as it the case for probabilistic simulations.

It is envisaged that the approach presented here could be extended to more complicated mineral assemblages (e.g., a combination of two or more minerals at the same time) in the future by using the additivity principle.

Formatat: Subíndex

Suprimit: ¶
Finally, the reader must notice that in this study apart from, sorption or exchange processes, non-other retention phenomena have been considered (i.e. surface precipitation, solid-solution formation) to calculate K_d values

Formatat: Subíndex

Formatat: Subíndex

References

Bradbury, M.H., Baeyens, B., 2000.A generalised sorption model for the concentration dependent uptake of caesium by argillaceous rocks. J. Contam. Hydrol., 42, 141-163. DOI: 10.1016/S0169-7722(99)00094-7.

Bradbury, M.H., Baeyens, B., 2005. Experimental and modelling Investigations on Na-Illite: Acid-Base Behaviour and the Sorption of Strontium, nickel, Europium and Uranyl. Nagra Technical Report, NTB-04-02.

Catalette, H., Dumonceau, J., Ollar, P.,1998. Sorption of caesium, barium and europium on magnetite. J. Contam. Hydrol., 35, 151-159. DOI: 10.1016/S0169-7722(98)00123-5.

Comans, R.N.J.; Haller, M.; De Preter, P., 1991. Sorption of Caesium on Illite: non-Equilibrium behaviour and reversibility. Geochimica et Cosmochimica Acta, 55, 433-440. DOI: 10.1016/0016-7037(91)90002-M.

Davis, J. A., Coston, J. A., Kent, D. B and Fuller, C. C.,1998. Application of the Surface Complexation Concept to Complex Mineral Assemblages. Environmental Science and Technology, 32, 2820-2828.

Davis, J.A., Kent, D.B.,1990. Surface complexation modelling in aqueous geochemistry. Reviews in Mineralogy and Geochemistry, 23(1), 177-260.

Davis, J. A., 2008. Application of Surface Complexation Modelling to Selected Radionuclides and Aquifer Sediments. U. S. Geological Survey report to United States Nuclear Regulatory Commision, NRC Job Code Y6462.

De Windt, L., Pellegrini, D., Van der Lee, J., 2004. Coupled modelling of cement/claystone interactions and radionuclide migration. Journal of Contaminant Hydrology, 68, 165-182.

Duro, L., Bruno, J., Honeyman, B., 2001. Proposal for the development of predictive surface complexation models (SCM) to be used as a supporting tool to K_d parameters in PA. In "Using thermodynamics sorption models for guiding radioelement distribution coefficient (K_d) investigations", OECD-NEA Report. DOI: 10.1787/9789264192935-en.

Dzombak, D. A., Morel, F.M.N., 1990. Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons,Ebner, A.D., Ritter, J.A., Navratil, J.D., 2001. Adsorption of Caesium, Strontium, and Cobalt Ions on Magnetite and a Magnetite-Silica Composite. Ind. Eng. Chem. Res., 40, 1615-1623. DOI: 10.1021/ie000695c.

Geckeis, H., Lützenkirchen, J., Polly, R., Rabung, Th., Schmidt, M., 2013. Mineral-Water interface reactions of actinides. Chemical Reviews, 113, 1016-1062. DOI: 10.1021/cr300370h.

Suprimit: ;
Suprimit: 2000,
Suprimit: ;
Suprimit: , 2005.
Suprimit: ;
Suprimit: ;
Suprimit: 1998,
Suprimit: 1991,
Suprimit: . (1998)
Suprimit: k
Suprimit:
Suprimit: and
Suprimit:
Suprimit: 1990
Suprimit:
Suprimit: . (2008)
Suprimit: Modeling
Suprimit: 2004,
Suprimit: ;
Suprimit: ;
Suprimit: , 2001.
Suprimit: and
Suprimit: 1990,
Suprimit: ¶
Suprimit: ;
Suprimit: ;
Suprimit: , 2001
Suprimit: 2013,

Giffaut, E., Grivé, M., Blanc, Ph., Vieillard, Ph., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé, B., Duro, L., 2014. Andra thermodynamic database for performance assessment: ThermoChimie, Applied Geochemistry, 49, 225-236, DOI:10.1016/j.apgeochem.2014.05.007.

Goldberg, S., Criscenti, L.J., Turner, D.R., Davis, J.A., Cantrell, K.J., 2007. Adsorption–desorption processes in subsurface reactive transport modeling. Vadose Zone Journal, 6(3), 407-435. DOI:10.2136/vzj2006.0085.

Gil-García, C., Rigol, A., Vidal, M., 2009. New best estimates for radionuclide solid–liquid distribution coefficient in soils. Part 1: radiostrontium and radiocaesium. J. Environ. Radioact. 100, 690–696.

Gil-García, C.J., Rigol, A., Vidal, M., 2011. The use of hard- and soft-modelling to predict radiostrontium solid-liquid distribution coefficients in soils. Chemosphere, 85, 1400-1405.

Glynn, P., 2003. Modelling Np and Pu transport with a surface complexation model and spatially variant sorption capacities: implications for reactive transport modelling and performance assessments of nuclear waste disposal sites. Computers and Sciences, 29, 331-349.

Granizo, N., Missana, T., 2006. Mechanisms of caesium sorption onto magnetite. Radiochim. Acta, 94, 671-677. DOI: 10.1524/ract.2006.94.9-11.671.

Hagues, A.W., Williams, M.M.R., Eaton, M.D., 2010. A probabilistic study of the effect of retardation factor uncertainty using a compartment model for radionuclide release into biosphere. Annals of Nuclear Energy, 37, 1197-1207.

International Atomic Energy Agency, 1994. Safety Indicators in Different Time Frames for the Safety Assessment of Underground Radioactive Waste Repositories. IAEA TECDOC-767, Vienna, Austria.

International Atomic Energy Agency, 1995. The Principles of Radioactive Waste Management. A Publication within the RADWASS Programme. Safety Series No. 111-F, Vienna, Austria.

Liu, W.K., Belytschko, T., Mani, A., 1986. Random field finite elements. Int. J. Numer. Meth. Eng., 23, 1831–1845.

Marmier, N., Delisée, A., Fromage, F., 1999. Surface Complexation Modelling of Yb(III), Ni(II), and Cs(I) Sorption on Magnetite. J. Colloid Interf. Sci., 211, 54-60. DOI: 10.1006/jcis.1998.5968.

Nair, R.N., Krishnamoorthy, T.M., 1999. Probabilistic safety assessment model for near surface radioactive waste disposal facilities. Environmental Modelling & Software, 14 (5), 447-460.

NEA, 2005. NEA Sorption Project Phase II: Interpretation and Prediction of Radionuclide Sorption onto Substrates Relevant for Radioactive Waste Disposal Using Thermodynamic Sorption Models. Organisation for Economic Co-Operation and Development (OECD), Nuclear Energy Agency (NEA) report No. 5992.

NEA, 2012. NEA Sorption Project Phase III: Thermodynamic Sorption Modelling in Support of Radioactive Waste Disposal Safety Cases. Organisation for Economic Co-Operation and Development (OECD), Nuclear Energy Agency (NEA) report No. 6914.

Nirex, United Kingdom Nirex Limited, 2003. Generic Repository Studies: Generic Postclosure Performance Assessment. Nirex Report No. N/080, Harwell, UK.

Ochs, M., Lothenbach, B.,Wanner, H., Sato, H., Yui, M. 2001. An integrated sorption-diffusion model for the calculation of consistent distribution and diffusion coefficients in compacted bentonite. Journal of Contaminant Hydrology, 47 (2-4), 283-296.

Ochs, M., Payne, T.E., Brendler, V., 2012. Thermodynamic Sorption Modelling in Support of Radioactive Waste Disposal Safety Cases. A Guideline Document. Nuclear Energy Agency, Paris.

Parkhurst, D., Appelo, T., (1999). User's guide to PhreeqC (Version 2). USGS Report 99-4259.

Payne, T. E., Brendler, V., Ochs, M., Baeyens, B., Brown, P. L., Davis, J. A., Ekberg, C., Kulik, D. A., Lutzenkirchen, J., Missana, T., Tachi, Y., Van Loon, L. R., Altmann, S., 2013.Guidelines for thermodynamic sorption modelling in the context of radioactive waste disposal. Environmental Modelling & Software, 42, 143-156.

Poinssot, C., Baeyens, B., Bradbury, M. H., 1999a.Experimental studies of Cs, Sr, Ni, and Eu sorption on Na-illite and the modelling of Cs sorption. PSI Nr. 99-06.

Poinssot, C., Baeyens, B., Bradbury, M.H., 1999b. Experimental and modelling studies of caesium sorption on illite. Geochimica et Cosmochimica Acta, 63, 3217-3227. DOI: 10.1016/S0016-7037(99)00246-X.

Romanchuk, A.Y., Kalmykov, S.N., 2014. Actinides sorption onto hematite: experimental data, surface complexation modeling and linear free energy relationship. Radiochimica Acta, 102(4), 303-310. DOI: 10.1515/ract-2014-2108.

Rovira, M., de Pablo, J., Casas, I., Giménez, J., Clarens, F., 2004. Sorption of Caesium on Commercial Magnetite with low Silica Content: Experimental and Modelling. Mat. Res. Soc. Symp. Proc., 807, 677-682. DOI: http://dx.doi.org/10.1557/PROC-807-677.

Schnurr, A., Marsac, R., Rabung, Th., Lützenkirchen, J., Geckeis, H., 2013. Investigations of actinide and lanthanide sorption on clay minerals under saline conditions. Proceedings of the ABC-Salt Workshop III, Santa Fe, USA.

Sheppard, M.I., Thibault, D.H., 1990. Default soil solid/liquid partition coefficients, Kds, for 11 four major soil types: a compendium. Health Phys. 59, 471–482.

Staunton, S., Roubaud, M., 1997. Adsorption of ^{137}Cs on montmorillonite and illite: Effect of charge compensating cation, ionic strength, concentration of Cs, K and fulvic acid. Clays and Clay Minerals, 45, 251-260.

Tachi, Y., Nakazawa, T., Ochs, M., Yotsuji, K., Suyama, T., Seida, Y., Yamada, N., Yui, M., 2010. Diffusion and sorption of neptunium (V) in compacted montmorillonite: effects of carbonate and salinity. Radiochimica Acta, 98 (9-11), 711-718.

Viswanathan, H.S., Robinson, B.A., Valocchi, A.J., Triay, I.R., 1998. A reactive transport model of neptunium migration from the potential repository at Yucca Mountain. Journal of Hydrology, 209 (1-4), 251-280.

Wang, P., Anderko, A., Turner, D. R., 2001. Thermodynamic modeling of the adsorption of radionuclides on selected minerals. I: Cations. Industrial & engineering chemistry research, 40(20), 4428-4443. DOI:10.1021/ie000991p.

Westall, J.C. FITEQL: A computer program for determination of chemical equilibrium constants from experimental data. Department of Chemistry, Oregon State University, 1982.