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Experimental measurements and modeling of sorption competition on montmorillonite

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Abstract—The source terms arising from radioactive/toxic metal waste repositories will contain a multitude of dissolved metal species, as do natural systems. The influence of sorption competition on the uptake of safety-relevant metals, and the effects this may have on transport rates to the biosphere, is an important repository performance assessment issue which has not, as yet, been resolved. The main aim of this work was to quantify the influence of competition between metals in different valence states on their individual sorption characteristics under conditions dominated by pH-dependent sorption. The sorption experiments were carried out on Na- and Ca-montmorillonites using various combinations and concentrations of Co(II), Ni(II), Zn(II), Eu(III), Nd(III), Am(III), Th(IV), and U(VI). For metals sorbing at trace concentrations in a background electrolyte containing a competing metal up to mmolar concentrations, and pH values generally greater than 6, all of the experimental results were consistent with the observation that metals with similar chemistries (valence state, hydrolysis behavior) compete with one another, but metals with dissimilar chemistries do not compete, i.e., competition is selective. For example Eu, Nd, and Am exhibit unambiguous sorption competition effects, as do Ni, Co, and Zn. On the basis of the above preliminary criteria, competition between divalent transition metals and trivalent lanthanides, Th(IV), and U(VI) and between Th(IV) and U(VI) would not be expected, and this is found experimentally. In general, neither single-fixed-site capacity models nor two-site (strong/weak) models with fixed capacities, whether with or without electrostatic terms, are capable of modeling the spectrum of experimental results presented here. To explain the competitive effects observed it is proposed that multiple sets of strong sites exist as subsets of the 40 mmol kg⁻¹ of weak sites present in the montmorillonite conceptual model. It is shown that if the 2SPNE SC/CE sorption model is extended to include multiple strong sites, and the average site capacity and protolysis constant values defined in previous publications are assigned to each of the sets of strong sites, then the model can be used to reproduce all of the experimental data, provided it can be specified which groups of metals are competitive and which are not. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

The uptake of metal sorbates by clay minerals is generally treated in terms of different mechanistic processes occurring at the solid-liquid interface. The main ones are cation exchange (outer sphere complexes) and surface complexation (inner sphere complexes). Models are being developed at various levels of complexity to describe these processes (e.g., Schindler et al., 1987; Fletcher and Sposito, 1989; Davis and Kent, 1990; Goldberg, 1992; Turner et al., 1996; Bradbury and Baeyens, 1997, 2002; Jenne, 1998; Prikryl et al., 2001; Kulik, 2002; Coppin et al., 2002; Payne et al., 2004). At the moment, such models can only be described as quasimechanistic because information concerning the nature of the sorbed surface species is generally lacking.

The majority of sorption data comes from batch-type experiments in which it is usual to measure the sorption behavior of a single metal at a time. In complex systems such as a deep underground radioactive waste repository many radionuclides and inactive metal contaminants are simultaneously present at different concentrations in the aqueous phase. Under such circumstances competitive sorption effects may be an important issue. Although competition has been addressed on oxides (e.g., Benjamin and Leckie, 1981a, b; Schulthess and Sparks, 1989; Christl and Kretzschmar, 1999), soils (Vulava, 1998;

Serrano et al., 2005), and some clay minerals (Saha et al., 2002; Heidmann et al., 2005), little attention has so far been paid to the possible effects of competition on the uptake characteristics of individual sorbates in the montmorillonite/bentonite systems and how this can influence rates of transport.

The porewater in a compacted Na-bentonite has a pH of ~8 and a Na content of ~0.2–0.3 M with much lower levels of Ca and Mg (~10 mM), so Na dominates the aqueous composition (Wanner, 1986; Curti, 1993; Muirinen and Lehtikoinen, 1999; Bruno et al., 1999; Pusch et al. 1999; Bradbury and Baeyens, 2003). Further, most radionuclides are present in the aqueous phase at trace concentrations, but there are circumstances in which certain metals, e.g., Fe(II), could be present in the repository at much higher levels (Tournassat, 2003). Thus the main interest lies in competitive sorption effects at near neutral pH in a Na background electrolyte at levels of a few tenths of molar and radionuclides at trace concentrations.

The influence of the background electrolyte type (NaClO₄, Ca(NO₃)₂) and their concentrations has been investigated in previous studies (Bradbury and Baeyens, 1999, 2002, 2005). The results from those studies have been included in the modeling reported here. For the experimental conditions used, competition will be taking place on all of the different site types simultaneously (cation exchange sites, strong and weak ≡SOH sites; see Appendix, section A1). However, because high sorption at trace levels is associated with the strong sites, and these have a low capacity (the capacities of the cation exchange sites and weak sites are much greater), any competitive effects will

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be most significant for these sites because they could become saturated. This work focuses on competitive effects taking place on the strong sites.

The main aim of the experimental work was to quantify the influence of competition between metals of different valence on their individual sorption characteristics. Competitive sorption experiments on Na- and Ca-montmorillonite at pH values generally >6 using various combinations and concentrations of Co(II), Ni(II), Zn(II), Eu(III), Nd(III), Am(III), Th(IV), and U(VI) are described. The concept behind the experiments was to measure the sorption of metals at trace concentrations (the "index metal") in the presence of high concentrations of a selection of metals having either the same or a different valence (the "blocking metal"). The sorption values obtained were compared with those determined in the absence of the blocking metal. A number of variations on this type of experiment were performed. Reductions in sorption values would indicate that competition was occurring.

A second aim was to test the capacity of a 2-site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model (Bradbury and Baeyens, 1997) to predict the sorption values in the competition experiments. This simple model, briefly described in the Appendix, has been used extensively to quantitatively describe the sorption edges and isotherms in single sorbate experiments (Bradbury and Baeyens, 1997, 1999, 2002, 2005). One of the assumptions in the model is that pH dependent uptake at trace concentrations occurs predominantly on a single set of high-affinity amphoteric edge sites ("strong sites"), having a capacity of 2 mmol kg⁻¹ for montmorillonite. The competition experiments were always arranged so that the concentration of the blocking metal was always more than sufficient to saturate these strong sites.

2. EXPERIMENTAL

2.1. Materials and Methods

SWy-1 Na-montmorillonite (Crook County, Wyoming, Source Clay Minerals Repository, University of Missouri, Columbia) was thoroughly washed three times in succession with 1 M NaClO₄ (solid to liquid (S:L) ratio ~25 g L⁻¹) to remove all soluble salts and/or sparingly soluble minerals such as calcite and to convert the clay into the homo-ionic Na-form. The <0.5- μ m fraction was separated by successive washing with deionized water preequilibrated with conditioned clay, combined with centrifugation (600g (max.), 7 min), decantation of the supernatant solution, and subsequent flocculation with 1 M NaClO₄. Soluble hydroxy-aluminium compounds were removed by an acid treatment (pH 3.5, 1 h) followed by phase separation (1800g (max.), 5 min), decantation of the supernatant solution, and neutralization with 1 M NaClO₄ (pH 7). Sub-batches of clay suspensions were prepared at appropriate NaClO₄ or Ca(NO₃)₂ concentrations using dialysis methods. The conditioned Na- and Ca-montmorillonite suspensions (10–20 g L⁻¹) were stored in the dark at 4°C. Details of the preparation procedures can be found in Baeyens and Bradbury (1995a).

Mineralogical analyses of the conditioned SWy-1 Na-montmorillonite were carried out by x-ray diffraction methods. Montmorillonite was present at ~97 wt%, illite and quartz at ~1 wt%, and other minerals such as albite, K-feldspar, calcite, dolomite, and kaolinite/chlorite were below 1 wt%. The cation exchange capacity, determined using the ²²Na isotopic dilution method (e.g., Cremers, 1968) was found to be 0.870 ± 0.035 eq. kg⁻¹ (Baeyens and Bradbury, 1997).

All experiments were carried out in controlled N₂ atmosphere glove boxes (CO₂ ~2 ppm, O₂ ~2 ppm) at ~24 ± 2°C where sampling and pH measurements on a WTW Microprocessor 535 pH meter using Orion 8103 combination pH electrodes were made. Source radiotracer solutions of ⁶⁰Co and ⁶³Ni were purchased from Amersham Interna-

Table 1. Buffers used in the sorption measurements (data from Perrin and Dempsey, 1974).

Buffer	pK _a	pH range
MES (2-(N-morpholino)ethane-sulphonic acid)	6.15	5.7–6.7
MOPS (3-(N-morpholino)propanesulphonic acid)	7.20	6.8–7.7
TRIS (Tris(hydroxymethyl)aminomethane)	8.06	7.5–8.5

tional, UK, and of ¹⁵²Eu, ²⁴¹Am, and ²²⁸Th from Isotope Products Europe, Blaseg, Germany. A 1000-ppm ²³³U source solution was used for the uranium sorption experiments. Each source tracer solution was diluted in 25 or 50 mL of deionized water to produce a stock solution having a pH of ~1, from which appropriate standard solutions were prepared, as described below. The standard solutions were always allowed to stand at least overnight before use to ensure equilibrium (wall sorption) and then used to label the sorption tests.

Aqueous activities were measured using either a Canberra Packard Tri-Carb 2250 CA liquid scintillation counter (⁶³Ni, ²⁴¹Am, ²²⁸Th, and ²³³U), or a Canberra Packard Cobra Quantum gamma counter (⁶⁰Co and ¹⁵²Eu). Reference-labeled solutions also were prepared and were always counted simultaneously with the solutions from the batch sorption tests.

Solutions were buffered with MES, MOPS, or TRIS at concentrations of ~2 × 10⁻³ M in the sorption experiments to maintain constant pH conditions, Table 1. A series of separate tests had previously shown that there was no significant influence of these buffers on sorption (e.g., Baeyens and Bradbury 1995b; Bradbury and Baeyens, 2002).

Batch sorption measurements at trace radionuclide concentrations (generally <10⁻⁷ M) were carried out at fixed ionic strengths and S:L ratios between 1 and 2 g L⁻¹ under inert atmosphere conditions in 40 mL polypropylene centrifuge tubes. After labeling with the chosen tracer, and shaking end over end for at least 3 days, the samples were centrifuged in a Beckman L7 Ultracentrifuge at 96000g (max.) for 1 h before returning them to the glove box for sampling of the supernatant solutions and pH measurements. Experiments were normally carried out in triplicate. Previous studies had shown that sorption kinetics are fast and equilibrium is reached within 3 days (Baeyens and Bradbury, 1995b).

Results from batch sorption tests are expressed throughout as R_d values defined in the usual manner as

$$R_d = \frac{C_{\text{init}} - C_{\text{eq}}}{C_{\text{eq}}} \cdot \frac{V}{m} \quad (1)$$

where C_{init} is total (active + inactive) initial aqueous nuclide concentration (M), C_{eq} is total (active + inactive) equilibrium aqueous nuclide concentration (M), V is volume of liquid phase (L), and m is mass of solid phase (kg).

Based on an assessment of wall sorption effects, as well as of the maximum absolute error calculated by considering the maximum error in each operation in batch sorption experiments, and on sets of repeat measurements, a realistic uncertainty in the measured sorption distribution ratio values (R_d) was estimated to be a factor of ~1.6 (Baeyens and Bradbury, 1995b). However, for very low sorption values (only a few % of the radiotracer sorbed) or where sorption was very high (~99% of the radiotracer sorbed), the variability in comparable data indicated that the uncertainties in the R_d values could be a factor of ~3.

The maximum concentrations used for the blocking metals, Table 2, were always well below the solubility of their respective hydroxides (Co(II): 6.8 × 10⁻² M, pH 7; Zn(II): 3.8 × 10⁻³ M, pH 7; Nd(III): 6.3 × 10⁻² M, pH 7 (thermodynamic data taken from Baes and Mesmer, 1976); and Eu(III): 4.9 × 10⁻³ M, pH 7; U(VI): 1.5 × 10⁻² M, pH 5 (thermodynamic data taken from Hummel et al., 2002))

2.2. Sorption Competition Experiments

Four types of competition experiments were carried out according to the procedures described below. The main aim of these tests was to investigate which metals compete with one another and which do not. The methodology was essentially the same in all cases. Batch-type

Table 2. Overview of competition experiments.

Exp. Nr.	Index metal		Blocking metal		Background electrolyte	pH	S:L ratio (g L ⁻¹)
	Metal	Conc. (M)	Metal	Conc. (M)			
Series A: single-point competition experiments							
1	⁶⁰ Co(II)	6.8 E - 9	Zn(II)	2.9 E-5	0.1 M NaClO ₄	7.1	2.24
2	⁶³ Ni(II)	2.2 E - 8	Zn(II)	2.9 E-5	0.1 M NaClO ₄	7.1	2.24
3	¹⁵² Eu(III)	4.1 E - 9	Nd(III)	1.25 E-5	0.1 M NaClO ₄	7.0	0.98
4	²⁴¹ Am(III)	1.4 E - 13	Eu(III)	5.0 E-6	0.1 M NaClO ₄	6.7	0.51
5	²⁴¹ Am(III)	1.4 E - 13	Eu(III)	1.0 E-4	0.1 M NaClO ₄	6.7	0.51
6	⁶⁰ Co(II)	6.8 E - 9	Eu(III)	2.3 E-5	0.1 M NaClO ₄	7.0	2.24
7	⁶³ Ni(II)	2.2 E - 8	Eu(III)	2.3 E-5	0.1 M NaClO ₄	7.1	2.24
8	⁶³ Ni(II)	1.4 E - 8	Nd(III)	2.9 E-5	0.1 M NaClO ₄	7.0	2.24
9	¹⁵² Eu(III)	2.4 E - 8	Zn(II)	1.25 E-5	0.1 M NaClO ₄	7.1	0.98
10	²²⁸ Th(IV)	2.0 E - 10	Zn(II)	1.25 E-5	0.1 M NaClO ₄	7.1	0.98
11	²²⁸ Th(IV)	2.0 E - 10	Eu(III)	1.0 E-5	0.1 M NaClO ₄	7.0	0.98
12	²²⁸ Th(IV)	2.6 E - 10	²³⁸ U(VI)	1.14 E-4	0.1 M NaClO ₄	5.1	0.85
13	²³³ U(VI)	1.6 E - 7	Co(II)	1.8 E-5	0.1 M NaClO ₄	7.1	1.42
Series B: competition experiments as a function of blocking metal concentration							
14	⁶³ Ni(II)	2.8 E - 8	Co(II)	0-1.0 E-3	0.066 M Ca(NO ₃) ₂	7.0	1.01
15	¹⁵² Eu(III)	1.8 E - 8	Co(II)	0-1.0 E-3	0.066 M Ca(NO ₃) ₂	7.0	1.01
Series C: competition experiments as a function of blocking metal concentration and pH							
16	⁶³ Ni(II)	1.1 E - 8	Co(II)	1.0 E-4	0.1 M NaClO ₄	6, 7, 8	1.42
17	⁶³ Ni(II)	1.1 E - 8	Co(II)	8.5 E-6	0.1 M NaClO ₄	6, 7, 8	1.42
18	¹⁵² Eu(III)	8.7 E - 9	Co(II)	1.0 E-4	0.1 M NaClO ₄	6, 7, 8	1.28
19	¹⁵² Eu(III)	8.7 E - 9	Co(II)	8.5 E-6	0.1 M NaClO ₄	6, 7, 8	1.28
20	¹⁵² Eu(III)	4.0 E - 7	Zn(II)	7.2 E-6	0.066 M Ca(NO ₃) ₂	3 to 8	1.28
Series D: competition isotherm experiment							
21	¹⁵² Eu(III)	2 E - 9 to 5 E-4	Zn(II)	4.3 E-5	0.066 M Ca(NO ₃) ₂	6.7	2.62

sorption experiments were carried out at trace concentrations with one metal (the "index metal") in the absence and presence of a different metal at relatively high concentrations, the "blocking metal." The concentration of the blocking metal was always more than sufficient to saturate the strong site capacity of the montmorillonite used in the tests (see Appendix). Where competition is occurring, significant reductions in sorption would be expected, whereas no reductions would be expected when the metals are not competitive.

2.2.1. Single-point competition experiments: Series A

Single-point scoping competition experiments were carried out using various combinations of index metals (⁶⁰Co(II), ⁶³Ni(II), ¹⁵²Eu(III), ²⁴¹Am(III), ²²⁸Th(IV), ²³³U(VI)) and blocking metals (Co(II), Zn(II), Eu(III), Nd(III), ²³⁸U(VI)) at near-neutral pH in 0.1 M NaClO₄ solutions. Weighed quantities of salts of the blocking element were added to 100 mL of a montmorillonite suspension (~10-20 g L⁻¹) and allowed to equilibrate for 1 day. Three- to five-mL aliquots were then pipetted from this strongly stirred suspension into polypropylene centrifuge tubes containing 30 mL of a buffered (pH 7) 0.1 M NaClO₄ solution labeled with the index metal. The tubes were closed with screw caps and shaken end over end for 3 days. Following centrifugation for 1 h at 96000g (max.), the pH was measured and samples taken for radioassay. Similar types of experiments in which no blocking metal was added were carried out in parallel.

2.2.2. Competition experiments as a function of blocking metal concentration: Series B

A second series of experiments was carried out with Co(II) as the blocking metal and ⁶³Ni(II) and ¹⁵²Eu(III) at trace concentrations as the index metals. The montmorillonite was conditioned to the Ca-form and the background electrolyte was 0.066 M Ca(NO₃)₂. The experimental procedure was the same as described above except that the sorption of ⁶³Ni(II) and ¹⁵²Eu(III) was determined as a function of Co(II) concentration up to 10⁻³ M.

2.2.3. Competition experiments as a function of blocking metal concentration and pH: Series C

Before the sorption experiments, Na-SWy-1 suspensions were pre-conditioned with Co(II) as blocking metal in the following manner. Approximately 40-mL aliquots of the clay suspension (~20 g L⁻¹, 0.1 M NaClO₄) were pipetted into dialysis bags. Three dialysis bags were placed in 500-mL bottles which were then filled with a buffered 0.1 M NaClO₄ solution set at pH ~6, ~7, or ~8 and containing Co(II) as blocking element at concentrations of 10⁻⁴ M or 8.5 × 10⁻⁶ M. The bottles were shaken end over end for at least six hours after which time the solution was sampled, analysed for Co(II), and then replaced by a fresh Co(II) solution. (Co(II) concentrations were determined by JCP-OES, Varian Vista AX CCD.) The process was repeated four times, which was sufficient for the system to reach equilibrium with Co(II) at the initial concentration. The contents of the dialysis bags were emptied into a container and vigorously stirred. Three-mL aliquots of this Co(II) conditioned suspension were added to 30 mL of the last conditioning solutions in polypropylene centrifuge tubes which had been previously labelled with trace levels (<5 × 10⁻⁷ M) of the index radionuclide ⁶³Ni(II) or ¹⁵²Eu(III). The tubes were closed with screw caps and shaken end over end for 3 days. Following centrifugation for 1 h at 96000g (max), the pH was measured and samples taken for radioassay.

Exactly the same preparation and experimental procedures were used for the measurement of a ¹⁵²Eu(III) sorption edge on Ca-SWy-1 from pH ~3 to pH ~8 in 0.066 M Ca(NO₃)₂ in the presence of 7.2 × 10⁻⁶ M Zn(II) as the blocking metal.

2.2.4. Competition isotherm experiments, series D

To further test the competitiveness of Eu(III) and Zn(II), a sorption isotherm for Eu on Ca-montmorillonite in 0.066 M Ca(NO₃)₂ at pH 6.7 was measured over an equilibrium concentration range from ~5 × 10⁻¹¹ M to ~3 × 10⁻⁴ M in the absence and presence of 4.3 × 10⁻⁵ M Zn(II). The S:L ratio used was 2.62 g L⁻¹ so that the concentration of Zn(II) in the experiments was more than sufficient to block the strong sites.

A summary of the different blocking-competition experiments carried out in series A, B, C, and D is given in Table 2.

Table 3. Series A: Measured distribution ratios on montmorillonite for trace concentrations of the index metals in the absence of any blocking metal (column 3), and in the presence of a blocking metal (column 4). The experimental conditions in the individual experiments can be read in Table 2 from the corresponding "Exp. Nr."

Exp. Nr.	Trace index/blocking metal	$\log R_d$: index metal alone ($L\ kg^{-1}$)*	$\log R_d$: index metal in the presence of a blocking metal ($L\ kg^{-1}$)*
1	$^{60}\text{Co(II)}/\text{Zn(II)}$	3.7 ± 0.1	2.3 ± 0.1 (2.3)
2	$^{63}\text{Ni(II)}/\text{Zn(II)}$	3.3 ± 0.3	2.2 ± 0.1 (2.2)
3	$^{152}\text{Eu(III)}/\text{Nd(III)}$	5.2 ± 0.3	4.2 ± 0.1 (4.1)
4	$^{241}\text{Am(III)}/\text{Eu(III)}$	5.0 ± 0.2	3.9 ± 0.1 (4.0)
5	$^{241}\text{Am(III)}/\text{Eu(III)}$	5.0 ± 0.2	3.3 ± 0.1 (3.1)
6	$^{60}\text{Co(II)}/\text{Eu(III)}$	3.9 ± 0.1	3.6 ± 0.2
7	$^{63}\text{Ni(II)}/\text{Eu(III)}$	3.3 ± 0.3	3.1 ± 0.1
8	$^{63}\text{Ni(II)}/\text{Nd(III)}$	3.3 ± 0.3	3.2 ± 0.1
9	$^{152}\text{Eu(III)}/\text{Zn(II)}$	5.2 ± 0.3	5.4 ± 0.2
10	$^{228}\text{Th(IV)}/\text{Zn(II)}$	5.4 ± 0.3	5.4 ± 0.1
11	$^{228}\text{Th(IV)}/\text{Eu(III)}$	5.4 ± 0.3	5.6 ± 0.1
12	$^{228}\text{Th(IV)}/^{238}\text{U(VI)}$	5.4 ± 0.3	5.1 ± 0.3
13	$^{233}\text{U(VI)}/\text{Co(II)}$	5.3 ± 0.3	5.0 ± 0.1

The values in parenthesis were calculated using the 2SPNE SC/CE model (see section 4). The error values given are from individual sets of experiments carried out at least in triplicate.

* This study, and Bradbury and Baeyens (2005) and references therein.

3. RESULTS

In Table 3 an overview of the results from the single-point measurements (series A) is given. These scoping experiments were carried out under the conditions listed in Table 2 and were designed to provide some first information on sorption competition effects. The sorption data are presented in two main groups. In the first group, column 3, the measured sorption values are those from batch-type experiments in which only a single metal tracer was used.

The second group of data in Table 3, column 4, relate to experiments in which the sorption of an index metal at trace concentrations was measured in the presence of relatively high concentrations of blocking metals (Table 2).

The data in Table 3 are further divided into 2 subgroups in which the trace index and blocking metals have either the same or different valencies. In the former case, for the combinations Co(II)/Zn(II), Ni(II)/Zn(II), Eu(III)/Nd(III), either Am(III)/Eu(III), the measured values in the presence of blocking metals are all significantly less than the corresponding ones in column 3. In the second subgroup, for the combinations Co(II)/Eu(III), Ni(II)/Eu(III), Ni(II)/Nd(III), Eu(III)/Zn(II), Th(IV)/Zn(II), Th(IV)/Eu(III), Th(IV)/U(VI), and U(IV)/Co(II), the measured values in the competition experiments are the same as the

results from the single index metal tracer experiments within the uncertainty ranges given.

Table 4 presents the results from the series B experiments (Table 2). The distribution coefficients for the index metals $^{63}\text{Ni(II)}$ and $^{152}\text{Eu(III)}$ measured as a function of Co(II) concentrations up to $\sim 10^{-3}$ M are given together with the corresponding Co(II) sorption isotherm values. The sorption of $^{63}\text{Ni(II)}$ at trace concentrations behaves essentially the same as Co(II) and follows the measured Co(II) isotherm closely, indicating that they compete with one another; $^{63}\text{Ni(II)}$ is effectively acting as a radiotracer for Co(II). In contrast, the sorption of $^{152}\text{Eu(III)}$ remains essentially constant over the whole range of Co(II) concentrations at a value close to that measured in conventional batch test, i.e., the presence of Co(II) has no influence on the uptake of Eu(III).

In a further series of tests (series C), $^{63}\text{Ni(II)}$ sorption onto Na-montmorillonite in 0.1 M NaClO₄ solution was measured at varying pH values (6–8) at two Co(II) concentrations of 8.8×10^{-6} M and 10^{-4} M (Table 5). As would be expected from the above, the sorption of $^{63}\text{Ni(II)}$ is smaller than the values measured in the absence of Co(II), and the reduction in $^{63}\text{Ni(II)}$ sorption increases with increasing Co(II) concentration over the range of pH values measured.

Figure 1a–c summarizes the results of a series of $^{152}\text{Eu(III)}$ sorption edge measurements (series C) and an isotherm determination (series D) carried out in the presence of Co(II) and

Table 4. Sorption of Co(II), Ni(II), and Eu(III) on Ca-SWy-1 in 0.066 M Ca(NO₃)₂ at pH 7 as a function of Co(II) concentration.

Co(II) concentration (mol L ⁻¹)	Blocking metal		Index metal	
	$\log R_d$ Co(II) (L kg ⁻¹)	$\log R_d$ Ni(II) (L kg ⁻¹)	$\log R_d$ Ni(II) (L kg ⁻¹)	$\log R_d$ Eu(III) (L kg ⁻¹)
–	$2.6 \pm 0.2^*$	$2.3 \pm 0.2^*$	$3.7 \pm 0.2^*$	
1×10^{-5}	2.0 ± 0.2	1.9 ± 0.2	3.8 ± 0.2	
3×10^{-5}	1.9 ± 0.2	2.0 ± 0.2	3.9 ± 0.2	
1×10^{-4}	1.4 ± 0.3	1.5 ± 0.3	3.8 ± 0.2	
3×10^{-4}	1.2 ± 0.3	1.3 ± 0.3	3.9 ± 0.2	
1×10^{-3}	–	–	3.8 ± 0.2	

* $\log R_d$ values measured in single-metal tracer experiments.

Table 5. Ni sorption ($\log R_d$ in L kg⁻¹) on Na-SWy-1 in 0.1 M NaClO₄ in the absence and presence of Co(II) blocking metal concentrations at different pH values.

pH	Co(II) blocking metal concentration (M)		
	none*	8.5×10^{-6}	1.0×10^{-4}
6.1 ± 0.1	2.4 ± 0.2	2.2 ± 0.2	2.0 ± 0.2
7.1 ± 0.1	3.3 ± 0.2	2.5 ± 0.2	2.2 ± 0.2
8.1 ± 0.1	3.9 ± 0.2	2.8 ± 0.2	2.5 ± 0.2

* Taken from Baeyens and Bradbury (1997).

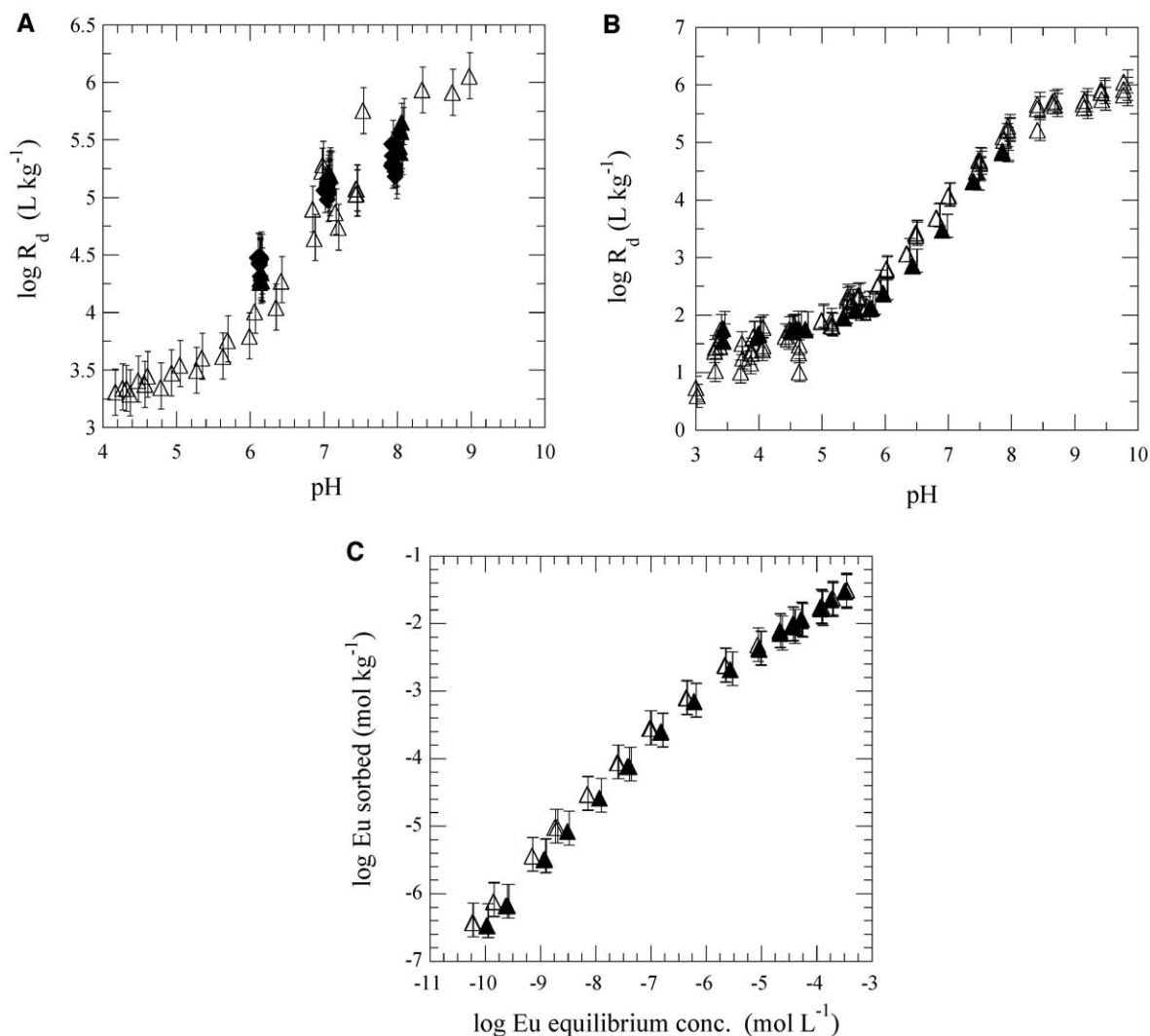


Fig. 1. Eu sorption edges on (a) Na-SWy-1 (Exp. 18, 19) and (b) Ca-SWy-1 (Exp. 20), and a Eu sorption isotherm on (c) Ca-SWy-1 (Exp. 21). Open symbols are measurements in the absence of blocking metal; filled symbols are measurements in the presence of blocking metals (see Table 2 for experimental details).

Zn(II) as blocking metals at various concentrations and under different conditions. The measurements in the presence of blocking metals (filled symbols) are compared with data measured under similar conditions in the absence of Co(II) or Zn(II) (open symbols). The data in all of these figures, irrespective of the concentrations of Co(II) or Zn(II), or the pH, or whether a Ca- or a Na-montmorillonite system is considered, or whether an Eu(III) sorption edge or isotherm is measured, show that the uptake of Eu(III) remains essentially unaffected by the presence of bivalent blocking metals, i.e., between Eu(III) and the relatively high concentrations of Co(II) and Zn(II), competitive sorption effects are absent.

4. DISCUSSION

4.1. Multiple Strong Site Capacities on Montmorillonite

The experimental data show clearly that all metals are not mutually competitive but rather that competition is selective. In

those cases where the chemical properties of the index and blocking metals are similar, competitive effects are observed. The effect of competition is that the sorption of the index metal in the presence of a blocking metal is reduced with respect to the value determined in sorption experiments where it is measured alone. Where the chemical characteristics of the index and blocking metal are sufficiently different, no competitive effects are observed and the sorption of the index metal is the same irrespective of the presence or absence of the blocking metal. The chemical properties which appear to be important from the combinations of metals available so far from this study are valence, hydrolysis behavior, aqueous speciation, and possibly the size and steric characteristics of the sorbing complexes. A general statement as to how similar or dissimilar the chemical behavior has to be for competition to occur or to not occur cannot be deduced from this work alone. It is suggested that the primary criteria for deciding whether competitive effects are likely or not are the valence and the hydrolysis

behavior. If the former are the same and the latter very similar, then competitive effects would be anticipated. Ni(II), Co(II), and Zn(II) exhibit unambiguous sorption competition effects, as do Eu(III), Nd(III), and Am(III). The thermodynamic properties of the trivalent lanthanides and the trivalent actinides are essentially the same (NEA, 2003), and sorption edge measurements of Cm(III) and Eu(III) (Rabung et al., 2005) have been shown in other studies to be the same. Hence it is anticipated that the trivalent lanthanides and actinides (including Pu(III)) will be competitive with one another. Tetravalent actinides would also be expected to be mutually competitive and competitive with Zr(IV), Hf(IV), and Sn(IV). Likewise the common divalent transition metals Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) would be expected to be mutually competitive because their hydrolysis behavior is so similar. In this context Pd(II) would not be expected to be competitive with the above transition metals because although they have a common valence its hydrolysis characteristics are significantly different. On the basis of the above preliminary criteria, competition between divalent transition metals and trivalent lanthanides, Th(IV), and U(VI), and between Th(IV) and U(VI) would not be expected, as was found experimentally. Nevertheless, a fair degree of speculation is already included in some of the assessments given above, and it is evident that a significant amount of additional experimental work will be required to quantify, and better define, the competitive sorption issue.

However, the above does not answer the question of why competitive effects at the montmorillonite surface are observed for certain index and blocking metal combinations and not for others. Because only wet chemistry data are available, explanations of the competitive sorption effects measured must be considered to be somewhat tentative at this stage. The most simple explanation of the experimental results, but possibly not the only one, is that sorption competition implies that the same sorption sites are involved in the uptake process, and that no competition implies that different sites are involved. In other words, and in broad terms, metals of the same valence appear to access the same set of strong sites, and metals in different valence states appear to access different sets of strong site types. The aqueous species, their pH stability regions, their charge, and the number of water molecules in the first hydration sphere all depend on metal valence. It is probably the combination of these factors (as mentioned above), rather than the valence per se, which will play a significant role in determining the interaction with clay mineral surfaces and what constitutes a preferred sorption site.

The results from competitive sorption experiments cannot be explained with a single set of strong sites and an interpretation based on multiple sets of strong sites would seem to be a more promising concept. Multi-site proton adsorption models based on mineral structure and bond valence have been under development for some time (Hiemstra et al., 1989, 1996; Hiemstra and Van Riemsdijk, 1996). Extensions of the updated MUSIC model (Hiemstra et al., 1996; Venema, 1998) have recently been applied to clay mineral systems, in particular to describe the titration behavior of montmorillonite (Tournassat et al., 2004).

4.2. 2SPNE SC/CE Sorption Model

A simple 2-site protolysis nonelectrostatic surface complexation and cation exchange (2SPNE SC/CE) model (see Appendix) has been used to quantitatively describe the sorption edges and isotherms in single-sorbate systems of many metals in different valence states, including all of the metals used in this study (Bradbury and Baeyens, 1997, 1999, 2002, 2005). The model is essentially a very simple one in which the pH and concentration-dependent uptake of metals onto montmorillonite is described in terms of only two amphoteric edge site types ($\equiv\text{SOH}$ sites), strong and weak sites, each with a fixed capacity and having the same protolysis constants (Table A1). At trace metal concentrations sorption is considered to occur predominantly on the strong sites. What is perhaps most surprising is that such a simple model has been successfully used to model sorption edges and isotherms of metals with valencies from II to VI over a wide range of conditions, considering the complexity of clay mineral surfaces and edges in contact with an aqueous phase. Furthermore, a very good linear correlation in log-log space (a linear free energy relationship, LFER (see, for example, Schindler et al., 1976; Stumm et al., 1980; Dzombak and Morell, 1990; Martell and Hancock, 1996), was found between the surface complexation constants on strong sites, deduced by applying the 2SPNE SC/CE model to sorption edge measurements, and the corresponding aqueous hydrolysis constants for 11 metals (Bradbury and Baeyens, 2005) (Fig. A1).

With only a single strong site, competition at trace concentrations is “hard wired” into the model. Therefore, in cases where metals with similar chemical characteristics are considered, i.e., sorption competition is occurring, the 2SPNE SC/CE model describes the experimental measurements well. This is illustrated in Table 3 column 4, where measured data are compared with the calculated values given in parenthesis. A further illustration is given in Figure 2, where the sorption of $^{63}\text{Ni(II)}$ at trace concentration is measured as a function of pH on Na-montmorillonite with Co(II) as the blocking metal (Table 2, experiments 16 and 17).

Where metals with different chemical characteristics are concerned, and competition is not taking place, the 2SPNE SC/CE model does not reproduce the measured values. This is shown in Figure 3a and 3b, where Zn(II) is used as the blocking metal in the measurements of an $^{152}\text{Eu(III)}$ sorption edge and isotherm on Ca-montmorillonite (Table 2, experiments 20 and 21, respectively).

The difficulties of modeling competitive effects with a nonelectrostatic two-site surface complexation model have been discussed. The “failure” of the 2SPNE SC/CE model is a direct consequence of its simplicity. The problem with single-site-type nonelectrostatic models is the reverse, i.e., such models would not be able to reproduce the results where competitive effects are seen, but could probably model the cases where no interaction between the metals occurred. (This simply follows because of the high single-site capacities used in one-site models and the consequent lack of site saturation effects.) It would be interesting to see whether existing electrostatic-based models (e.g., Criscenti and Sverjensky, 2002) or multi-site models (e.g., Hiemstra et al., 1996; Kulik, 2000) are capable of describing competition.

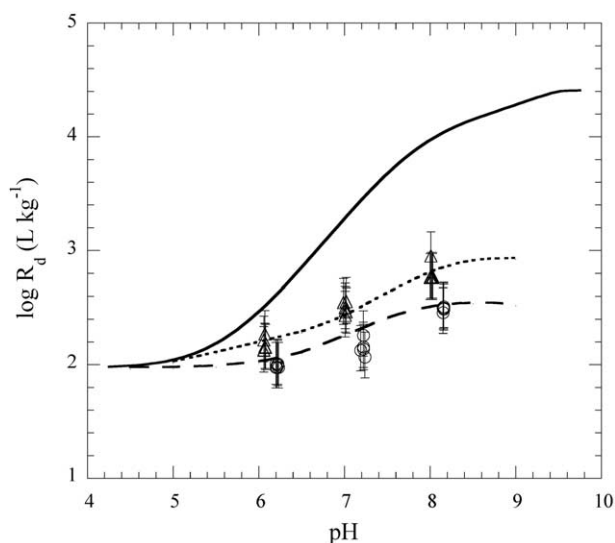


Fig. 2. Sorption values of $^{63}\text{Ni}(\text{II})$ on Na-SWy-1 measured at pH values near 6, 7, and 8 in 0.1 M NaClO_4 solution in the presence of two concentrations of $\text{Co}(\text{II})$ as blocking metal. The triangles and circles are the trace $^{63}\text{Ni}(\text{II})$ sorption values in the presence of 8.5×10^{-6} and 10^{-4} M $\text{Co}(\text{II})$ concentrations, respectively. The continuous line is the modeled sorption edge for trace $^{63}\text{Ni}(\text{II})$ in absence of $\text{Co}(\text{II})$, and the dotted and dashed lines are the modeled curves in the presence of 8.5×10^{-6} and 10^{-4} M $\text{Co}(\text{II})$, respectively, assuming competition.

4.3. 2SPNE SC/CE Model Modifications

The 2SPNE SC/CE model has been used to quantitatively reproduce 25 sorption edge data sets for eleven metals— $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Eu}(\text{III})$, $\text{Am}(\text{III})$, $\text{Sn}(\text{IV})$, $\text{Th}(\text{IV})$, $\text{Np}(\text{V})$, and $\text{U}(\text{VI})$ —with just one set of strong sites with a fixed capacity and two protolysis constants which have the same values as the weak sites (Table A1) (Bradbury and Baeyens, 2005). However, according to the proposal made

above, many of the metals in the list given should be sorbing on different sets of strong sites. The inconsistency is self-evident.

The total $\equiv\text{SOH}$ site capacity for montmorillonite of 80 mmol sites kg^{-1} was deduced from titration measurements together with average protonation/deprotonation constants. These sites were termed “weak sites” and were divided into $\equiv\text{S}^{\text{W}1}\text{OH}-$ and $\equiv\text{S}^{\text{W}2}\text{OH}-$ type sites each with a capacity of 40 mmol sites kg^{-1} . The $\equiv\text{S}^{\text{W}1}\text{OH}$ together with the strong sites were taken to be the active sites for sorption in the model and were assumed to have the same protonation/deprotonation behavior (Appendix).

A chemically plausible way needs to be found of resolving the inconsistency between the observations from the competition experiments, the proposal that there are multiple strong sites in montmorillonite, and the 2SPNE SC/CE model in which only one set of strong sites are considered. A reasonable possibility is that the multiple sets of strong sites which have been invoked to explain the competitive effects are not separate sets of sites at all but subsets of these 40 mmol $\equiv\text{S}^{\text{W}1}\text{OH}$ weak sites. Also, whether a particular subset of sites is perceived by a particular sorbing species as being part of the weak site types or a set of strong sites depends on the characteristics of the sorbing species itself. That is, there are highly favored sites for particular species within the weak sites.

An assumption in the sorption model is that the protolysis constants determined for the weak $\equiv\text{S}^{\text{W}1}\text{OH}$ sites are also valid for the $\equiv\text{S}^{\text{S}}\text{OH}$ sites. If the strong sites are viewed as subsets of the weak sites, then the protolysis constants obtained from the titration measurements are values averaged over both strong and weak site types. This is a plausible explanation as to why the above model assumption works so well.

The value of 2 mmol sites kg^{-1} montmorillonite proposed for the single strong site capacity (Table A1) was estimated from sorption isotherm measurements carried out over a wide range of concentrations for $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Eu}(\text{III})$, and $\text{U}(\text{VI})$ (see Bradbury and Baeyens, 1997, 1999, 2002, 2005). From the

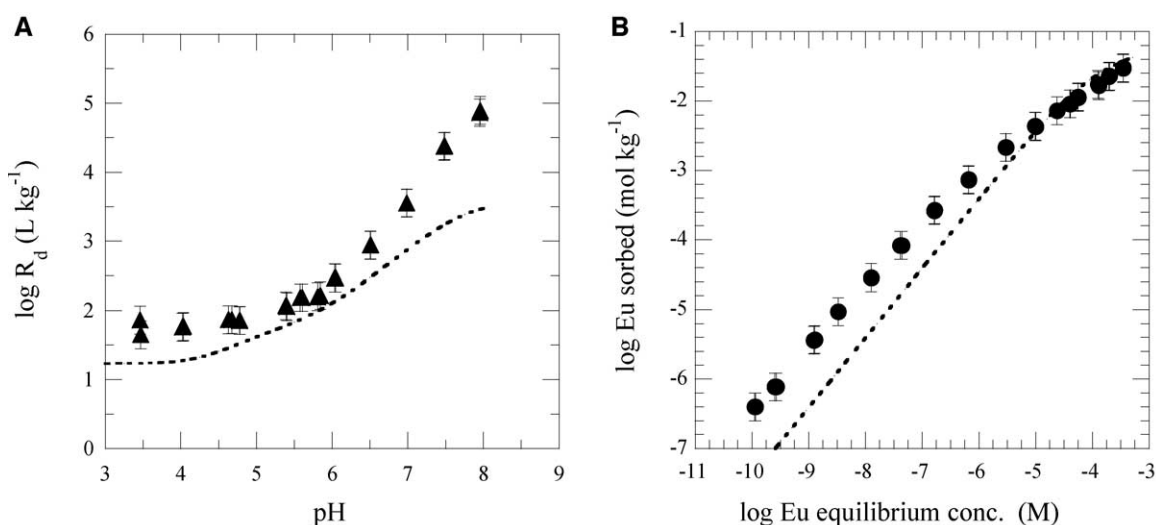


Fig. 3. (a) Sorption edge data (\blacktriangle) for $^{152}\text{Eu}(\text{III})$ in the pH range 3 to 8 in 0.066 M $\text{Ca}(\text{NO}_3)_2$ solution measured in the presence of 7.2×10^{-6} M $\text{Zn}(\text{II})$ as blocking metal. (b) Sorption isotherm data (\bullet) for $\text{Eu}(\text{III})$ at $\text{pH} = 6.7$ in 0.066 M $\text{Ca}(\text{NO}_3)_2$ solution measured in the presence of 4.3×10^{-6} M $\text{Zn}(\text{II})$ as blocking metal. The dashed lines are the sorption curves calculated in the presence of $\text{Zn}(\text{II})$ and assuming competition.

region of the sorption isotherms where the slope changes from a value of unity to less than unity, i.e., the region where the strong sites become saturated on a two-site concept for sorption, a value for the strong site capacity can be deduced. However, even though the isotherm results do put reasonably strong constraints on the range of values for the strong site capacity, this value can only be viewed as an estimate, because the measurements do not allow an exact value to be directly deduced from the experimental data because the change of slope occurs over a range of loadings/equilibrium concentrations. A realistic uncertainty on its value probably lies in the region of a factor of 2 to 3. Any variations within this range would not make any substantial differences to the modeling predictions for the experimentally measured values (see Appendix, section A2). This level of uncertainty in the strong site capacity is reasonable in view of the likely errors associated with the sorption data itself, a factor of 2 (see section 2.1). Thus, the capacities of the multiple subsets of strong sites do not need to be the same. Only an average value has been used in the modeling, and the strong site capacities which could conceivably vary between ~ 1 and ~ 4 mmol kg⁻¹ and still enable the isotherms to be modeled satisfactorily (Fig. A2a).

The LFER given in Fig. A1 (Bradbury and Baeyens, 2005) was found using the 2SPNE SC/CE model, in which only a single set of strong sites was considered. In the light of the modified strong site distribution concept given above, the use of an average $\equiv\text{S}^{\text{OH}}$ site capacity of 2 mmol kg⁻¹ and an average set of protolysis constants can be rationalized, and the overall concept becomes considerably more consistent.

5. SUMMARY AND CONCLUSIONS

The aim of this work was to carry out experiments on montmorillonite to quantify the influence of sorption competition between metals of different valence on their individual uptake characteristics. The sorption of index metals at trace concentrations was measured in the presence and absence of different blocking metals at relatively high concentrations. The concentrations of the "blocking metal" were chosen such that they were more than sufficient to saturate the strong sites on montmorillonite. Different combinations of the metals Co(II), Ni(II), Zn(II), Eu(III), Nd(III), Am(III), Th(IV), and U(VI) were used in the competition experiments on conditioned Na- and Ca-SWy-1 in 0.1 M NaClO₄ or 0.066 M Ca(NO₃)₂ background electrolytes, respectively. The main conclusion drawn from this part of the work was that all metals are not mutually competitive but rather that competition is selective. Metals with similar chemistries (valence state, hydrolysis behavior) compete with one another and metals with dissimilar chemistries do not compete.

Sorption edges and isotherms of all the metals used in this study had been previously quantitatively modeled using the 2SPNE SC/CE model, and a LFER was established between the surface complexation constants for the strong sites and the corresponding aqueous phase hydrolysis constants for 11 metals in valence states from II to VI (Fig. A1). A consequence of the assumption that the uptake of metal species at trace concentrations takes place predominantly on one set of strong sites with a relatively low capacity (~ 2 mmol kg⁻¹) is that the model would predict strong competitive effects irrespective of

valence state of the metals involved. From this point of view, the 2SPNE SC/CE model was only able to model results from experiments in which competition occurred between metals which are chemically similar (valence state, hydrolysis behavior), e.g., Ni, Co, and Zn compete, as do trivalent lanthanides and actinides. The competition behavior of metals which are chemically dissimilar, and therefore did not compete with one another, e.g., divalent transition metals vs. trivalent lanthanides, Th(IV), and U(VI) and Th(IV) vs. U(VI), was not predicted by the model.

To explain the competitive effects observed experimentally, it was proposed that multiple sets of strong sites exist as subsets of the 40 mmol kg⁻¹ of $\equiv\text{S}^{\text{W}}\text{OH}$ weak sites. Such a concept would provide a rationale for the assumption in the model that the protolysis constants for the strong and weak sites have the same value, i.e., average values for protolysis constants are obtained from titration measurements for the weak sites which include the subsets of strong sites. Further, it was illustrated that the value used for the strong site capacity in the model of 2 mmol kg⁻¹ was an estimated average, and it was shown in a modeling exercise that this value could in fact vary between ~ 1 and ~ 4 mmol kg⁻¹ and still enable the isotherms to be modeled satisfactorily. Thus, the subsets of strong sites would not have to have the same fixed capacity values to be consistent with the modeling.

In light of the modified strong site distribution concept given above, the LFER found between the surface complexation constants on strong sites and the corresponding aqueous hydrolysis constants using the 2SPNE SC/CE model with a single set of strong sites with a fixed capacity and one set of protolysis constants (values given in Table A1) can now be rationalized and the overall concept becomes considerably more consistent.

An important finding from the competition experiments is that a spectrum of strong site capacities on montmorillonite are involved in the uptake of metals of different valencies. This is in general accord with the recent multi-site proton adsorption model for montmorillonite proposed by Tournassat et al. (2004), based on the work of Hiemstra et al. (1996) and Venema et al. (1998). However, it is worth recalling that even multi-site models, having tens of possible sorption site types, are not capable at their current level of development of describing the range of sorption competition results given here. Sorption site types associated with the uptake of particular metals, together with the corresponding site characteristics and surface complexation constants, cannot be specified.

From an operational viewpoint the simple 2SPNE SC/CE model, with the current strong site capacity and protolysis constant values, can model multimetal multivalent competitive systems if it can be specified which metals are competitive and which are not. It is simply a question of defining different strong site sets in the model (each set having the same characteristics) and specifying which groups of metals have access to which sites. This can be readily achieved in the currently used MINSORB code (Bradbury and Baeyens, 1997).

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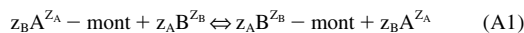
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APPENDIX

A1. SORPTION MODEL

The 2SPNE SC/CE model used to describe the uptake of aqueous metal species on montmorillonite has been described in detail previously (Bradbury and Baeyens, 1997, 1999, 2002) and only an outline is given below together with the associated parameters. The cation exchange reaction of a metal B, of valence z_B , exchanging with a metal A, of valence z_A , on montmorillonite in the A-form, can be written as



Following the Gaines and Thomas (1953) convention, the selectivity coefficient, ${}^B K_c$, for Reaction A1 can be defined as:

$${}^B K_c = \frac{(N_B)^{z_A} \cdot [A]^{z_B} \cdot (\gamma_A)^{z_B}}{(N_A)^{z_B} \cdot [B]^{z_A} \cdot (\gamma_B)^{z_A}} \quad (\text{A2})$$

where N_A and N_B = equivalent fractional occupancies, defined as the equivalents of A (or B) sorbed per kg of solid divided by the cation

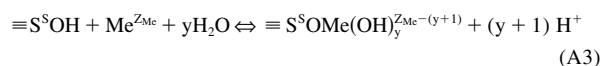
Table A1. Summary of site types, site capacities, and protolysis constants determined for Na-montmorillonite (Bradbury and Baeyens, 1997) and used as nonadjustable parameters in the model calculations of the sorption edges on Na- and Ca-montmorillonites.

Site types	Site capacities
$\equiv\text{S}^{\text{S}}\text{OH}$	$2.0 \times 10^{-3} \text{ mol kg}^{-1}$
$\equiv\text{S}^{\text{W}^1}\text{OH}$	$4.0 \times 10^{-2} \text{ mol kg}^{-1}$
$\equiv\text{S}^{\text{W}^2}\text{OH}$	$4.0 \times 10^{-2} \text{ mol kg}^{-1}$
Cation exchange	$8.7 \times 10^{-1} \text{ eq. kg}^{-1}$
Surface complexation formation reactions	$\log K_{\text{protolysis}}$
$\equiv\text{S}^{\text{S}}\text{OH} + \text{H}^+ \leftrightarrow \equiv\text{S}^{\text{S}}\text{OH}_2^+$	4.5
$\equiv\text{S}^{\text{S}}\text{OH} \leftrightarrow \equiv\text{S}^{\text{S}}\text{O}^- + \text{H}^+$	-7.9
$\equiv\text{S}^{\text{W}^1}\text{OH} + \text{H}^+ \leftrightarrow \equiv\text{S}^{\text{W}^1}\text{OH}_2^+$	4.5
$\equiv\text{S}^{\text{W}^1}\text{OH} \leftrightarrow \equiv\text{S}^{\text{W}^1}\text{O}^- + \text{H}^+$	-7.9
$\equiv\text{S}^{\text{W}^2}\text{OH} + \text{H}^+ \leftrightarrow \equiv\text{S}^{\text{W}^2}\text{OH}_2^+$	6.0
$\equiv\text{S}^{\text{W}^2}\text{OH} \leftrightarrow \equiv\text{S}^{\text{W}^2}\text{O}^- + \text{H}^+$	-10.5

exchange capacity, CEC (equiv. kg^{-1}); [A] and [B] = aqueous concentrations (M); and γ_A and γ_B = aqueous phase activity coefficients.

The selectivity coefficients used in this model calculations for the index and blocking metals on Na- and Ca-montmorillonite investigated in this work are given in Bradbury and Baeyens (2005). The CEC of Na-SWy-1 is 0.87 eq. kg^{-1} (Baeyens and Bradbury, 1997). The 2SPNE SC/CE model envisages pH-dependent sorption reactions taking place on two different sorption site types (strong $\equiv\text{S}^{\text{S}}\text{OH}$ and weak $\equiv\text{S}^{\text{W}^1}\text{OH}$ sites). The $\equiv\text{S}^{\text{S}}\text{OH}$ sites have a relatively low capacity (2 mmol kg^{-1}) and form strong surface complexes, whereas the $\equiv\text{S}^{\text{W}^1}\text{OH}$ sites have a much larger capacity (40 mmol kg^{-1}) but form weaker surface complexes. These site capacities were fixed in all of the modelling calculations, as were the protolysis constants, which were assumed to be the same for both the $\equiv\text{S}^{\text{S}}\text{OH}$ and the $\equiv\text{S}^{\text{W}^1}\text{OH}$ sites. In Table A1 values for protolysis constants are given for montmorillonite.

The general form of the surface complexation reaction of a metal Me with valence Z_{Me} on strong sites can be written as



In a nonelectrostatic model, the corresponding surface complexation constant, ${}^{\text{S}}K_y$, can be expressed as:

$${}^{\text{S}}K_y = \frac{[\equiv\text{S}^{\text{S}}\text{OMe}(\text{OH})_y^{Z_{\text{Me}}-(y+1)}]}{[\equiv\text{S}^{\text{S}}\text{OH}]} \cdot \frac{f_{\equiv\text{S}^{\text{S}}\text{OMe}(\text{OH})_y^{Z_{\text{Me}}-(y+1)}}}{f_{\equiv\text{S}^{\text{S}}\text{OH}}} \cdot \frac{\{\text{H}^+\}^{(y+1)}}{\{\text{Me}^{Z_{\text{Me}}}\}} \quad (\text{A4})$$

where { } terms are aqueous activities, [] terms are concentrations, and f terms are surface activity coefficients.

The computer code MINSORB (Bradbury and Baeyens, 1997) was used to model all the sorption data presented in this study. MINSORB is basically the geochemical speciation code MINEQL (Westall et al., 1976) containing subroutines for calculating simultaneously cation exchange and surface complexation with a nonelectrostatic model. Aqueous activity coefficients were calculated using the Davies relation with a value of 0.3 for the C_D constant (Davies, 1962).

The model has been used to quantitatively describe the uptake behavior of 11 metals on conditioned Na- and Ca-montmorillonites over a wide range of conditions (Bradbury and Baeyens, 2005). A linear free energy relationship, LFER, was established between surface complexation constants of the different sorbed species on strong sites for all of these metals and the corresponding aqueous hydrolysis constants (Fig. A1).

The site capacities and protolysis constants given in Table A1 were fixed in the modeling. Hydrolysis constants were taken from Baes and Mesmer (1976), except in the case of the actinides, where the thermodynamic data for Th(IV) were taken from Neck and Kim (2001) and those for Am(III) and U(VI) from Hummel et al. (2002). The surface complexation constants and hydrolysis constant values listed in Bradbury and Baeyens (2005) were used in the modeling studies in this work.

A2. CONSTRAINTS ON STRONG SITE CAPACITIES AND PROTOLYSIS CONSTANTS

For certain metals, namely Ni(II), Zn(II), Eu(III), and U(VI), detailed sorption isotherm measurements over a wide range of concentrations have been made (Bradbury and Baeyens, 1997, 2002, 2005). The form of the isotherms was the same in all four cases and allowed estimates to be made of the capacity of the strong sites on this two-site approach to sorption. From the region of the curve where the slope of the isotherm changes from a value of unity to less than unity, i.e., the region where the strong sites become saturated, a value for the strong site capacity can be reasonably well estimated. The measurements do not allow an exact value to be directly deduced from the experimental data, because the change of slope occurs over a range of loadings/equilibrium concentrations. Nevertheless, the isotherm results do put relatively strong constraints on the range of values that strong site capacities may have. A single strong site capacity of $2 \text{ mmol sites per kg montmorillonite}$ was used to successfully model not only the iso-

therm data for the four metals listed above but also 25 sorption edge data sets for 11 metals (see section A1).

The strong site capacity is an estimate, and a realistic uncertainty on its value probably lies in the region of a factor of 2 to 3. Any variations within this range would not make any substantial differences to the modeling predictions for the experimentally measured sorption edges and isotherms. This level of uncertainty in the strong site capacity is reasonable in view of the likely errors associated with the sorption data itself, ± 0.2 log units.

The value chosen for the strong site capacity becomes particularly important for modeling in the region of the isotherm where these sites begin to become saturated. This is illustrated using as an example a plot of the log of the distribution ratio for Ni(II) versus the log of the equilibrium Ni(II) concentration, as shown in Figure A2a. The curve has been modeled for different strong site capacities for a good fit in the plateau region, i.e., the linear sorption region.

If different sets of strong sites are involved in the sorption of metals of different valence states (see section 5), the implication from the modeling is that capacities can only vary within a factor of 2–3 around the average value of 2 mmol sites per kg.

The other fixed parameter values used in the modeling, besides the site capacities, are the protolysis constants. These were extracted from

the titration data of montmorillonite suspensions where the behavior is determined by the weak sites in the strong-weak site concept (Bradbury and Baeyens, 1997). An assumption in the sorption model is that the protolysis constants determined for the weak sites are also valid for the strong sites, and this assumption, especially in the modelling of sorption edge data, appears to work well (Bradbury and Baeyens, 2005). The shape of the sorption edge is dependent on the values of the protolysis constants. Figure A2b illustrates the effect on the form of a calculated Ni edge by varying the deprotonation constant while keeping all other parameters fixed (cation exchange has been excluded from the calculations for reasons of clarity). For example, an increase in the deprotonation constant leads to a decrease the sorption “plateau” values but does not change the position of the sorption edge.

Thus, variations in key model parameters can cause significant alterations to the form of sorption edges and isotherms in different ways. The point being made is that the data set given in Table A1 may not be unique, and it may well be possible to find other parameter value combinations which are capable of modeling all of the titration/sorption edge/sorption isotherm measurements in a consistent manner, but larger variations than factors of 2–3 would lead to difficulties in reproducing the measurements.