**Predicting the uptake of Cs, Co, Ni, Eu, Th and U on
argillaceous rocks using sorption models for illite**

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Abstract

Reliable predictions of radiocontaminant migration are a requirement for the establishment of radioactive waste repositories. Parametrization of the necessary sorption models seems to be, however, extremely challenging given the multi-mineralic composition of the lithosphere. In this study it is shown for two argillaceous rocks - Boda and Opalinus Clay relevant for the Hungarian and Swiss repository concepts, respectively- that this task can be substantially simplified by taking into account only the most sorptive mineral fraction, namely the 2:1 clay minerals illite and illite/smectite mixed layers. Two different models were required to blind predict the sorption isotherms of Cs, Co, Ni, Eu, Th and UO₂ measured on the two clay rock samples in a synthetic porewater. Cs sorption was modelled with the generalised Cs (GCs) sorption model and the sorption of the other cations with the 2 site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) model. The 2SPNE SC/CE model for illite was extended with surface complexation reactions on weak sites for Co, Ni, Eu, UO₂ and on strong sites for Eu-carbonato complexes. Complementary to the sorption measurements and modelling, Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy was used to probe the retention mechanism of Ni on illite, Boda and Opalinus Clay at higher loadings. The reliable blind predictions of the selected metal cations, which are representative for monovalent alkaline metals, divalent transition metals, lanthanides, and trivalent, tetravalent and hexavalent actinides, confirms the applicability of this simplified bottom up approach, and, renders the underlying sorption models particularly useful to predict sorption for the wide range of cations to be considered in the safety analysis of radioactive waste repositories in clay-rich environments.

Keywords: radionuclide sorption, argillaceous rocks, 2:1 clay minerals, porewater composition, sorption modelling, blind prediction, EXAFS, Eu-carbonato surface complexes

1. Introduction

The sorption of radioactive elements on mineral surfaces along potential migration paths is an important process in retarding their ultimate transport in the aqueous phase, and as such plays a significant role in environmental safety assessment studies of deep geological radioactive repositories.

Sorption in most natural environments *like* soils, sediments, or rock formations, is inherently too complex and multi-faceted to be easily predicted. Although radiocontaminant uptake has to be quantified over a wide range of geochemical conditions (mineralogy, porewater chemistry), most of the available data are expressed in terms of empirical parameters/relations which are difficult to extrapolate beyond their restricted range of validity. Consequently, fundamental understanding of the sorption processes in the near and far fields of a radioactive waste repository and the development of sorption models able to predict reliably the long term fate of radionuclides under realistic geochemical conditions is crucial.

Two fundamentally different approaches have emerged in the past to model cation retention in multi-mineralic environments (Davis et al., 1998): the component additivity (CA) and the general composite (GC) approach. The predictive CA or so-called bottom up approach takes into account all minerals constituting the natural system and assumes that each mineral has unique surface sites with characteristic sorption properties. In this case sorption models for each single mineral composing the mineral assemblage are necessary. Sorption by the mixture of minerals is then calculated by combining in an additive way the different models, *i.e.* based on the relative reactive amounts of each mineral. CA modelling can be substantially simplified when one mineral component is assumed to control sorption (NEA, 2005; Payne et al., 2013).

In the semi-empirical GC top down approach, it is assumed that the surface composition of the mineral assemblage is inherently too complex to be quantified in terms of the contributions of individual phases. Instead generic surface functional groups are assigned to the mineral mixture, with

the stoichiometry and formation constants for each sorption equilibrium determined by fitting experimental data. The GC approach is merely a fitting rather than a predicting procedure. Both approaches have been tested more or less successfully on different mineralogical complex systems *i.e.* natural or self-assembled (Cowan et al., 1992; Turner et al., 1996; Van Benschoten et al., 1998; Waite et al., 2000; Arnold et al., 2001; Prikryl et al., 2001, Barnett et al., 2002; Davis et al. 2002; Davis et al., 2004; Payne et al., 2004; Richter et al., 2005; Goldberg et al., 2007; Hartmann et al., 2008; Serrano et al., 2009; Alessi et al., 2010; Reich et al., 2010; Chen et al. 2014).

Argillaceous rocks are considered by many waste management programmes as suitable host formations for the deep geological disposal of radioactive waste, *e.g.* Opalinus Clay in Switzerland (Nagra, 2002); Boda Claystone Formation in Hungary (Lázár and Máthé, 2012), Boom and Ypresian Clays in Belgium (Ondraf, 2001); and Callovo-Oxfordian and Toarcian clays in France (Andra, 2001, Bonin, 1998). Clay minerals such as illite and illite/smectite mixed layers are major 2:1 clay mineral components of many argillaceous rocks and may consist of 50 % or more of the total mass. Besides their physical properties *like* plasticity, swelling behaviour, or low permeability, one of the most important characteristics of clay minerals is their generally strong cation adsorption. All these properties contribute to limiting the transport of radionuclides into the geo- and biosphere.

The basic philosophy chosen in this study is a simplified CA approach, assuming that in clay-dominated environments, 2:1 type clay minerals are the preferential sinks for radionuclides. This approach has proven to be successful in predicting sorption on bentonite (mainly montmorillonite) and Mont Terri Opalinus Clay (mainly illite) by using the corresponding sorption model for montmorillonite or for illite (Bradbury and Baeyens, 2011). The aim of this work is to test the capabilities of two models developed for illite, the generalised Cs (GCs) sorption model (Bradbury and Baeyens, 2000) and the 2 site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) model (Bradbury and Baeyens, 2009a,b) together with their associated parameters to blind predict sorption isotherms of Cs(I), Co(II), Ni(II), Eu(III), Th(IV) and U(VI)

measured on two different argillaceous rocks, namely the Hungarian Boda Claystone Formation and Swiss Opalinus Clay in their corresponding complex porewaters. The metals used were chosen to provide a broad range of chemical behaviour *i.e.* monovalent alkaline metals, divalent transition metals, lanthanides, and trivalent, tetravalent and hexavalent actinides. For this purpose, the 2SPNE SC/CE model for illite had to be supplemented with surface complexation (SC) reactions and constants for the so-called weak sites determined from sorption isotherms for Co, Ni, Eu and uranyl (UO₂) measured on Na-illite at a fixed pH and in 0.1 M NaClO₄ background electrolyte.

Lanthanides and trivalent actinides form very strong aqueous carbonate complexes and a previous study has shown that Eu-carbonato complexes form at the montmorillonite surface (Marques Fernandes et al., 2008). To verify whether such ternary Eu-carbonato complexes do also form on illite, the influence of atmospheric pCO₂ on the sorption of Eu on illite was investigated, and, SC reactions and constants derived were further implemented in the 2SPNE SC/CE model.

2. Materials and Methods

2.1 Clay and rock samples: mineralogy and porewater chemistry

Illite: The source material used was Illite du Puy (IdP) (Gabis, 1958) collected from an 80 m thick Oligocene geological formation in the region of Le Puy-en-Velay (Haute-Loire), France. The preparation procedure for the purification and conversion into the homo-ionic Na form has been described in detail in Bradbury and Baeyens (2009a). The cation exchange capacity (CEC), determined using the ¹³⁴Cs isotopic method was 225 meq·kg⁻¹ (Baeyens and Bradbury, 2004).

Boda and Opalinus Clay: The Hungarian Boda Claystone Formation and the Swiss Opalinus Clay are both considered as potential host formations for high-level radioactive waste repositories.

The Upper Permian sedimentary sequence of the Boda Clay is located in West-Mecsek Mountains, South Western Hungary. The sediments of the Boda Clay are dominantly red and reddish brown in colour, reflecting the oxidizing nature of the depositional and early diagenetic environments. The Boda Clay was deposited about 250 Ma ago in a shallow-water salt lake environment surrounded by

dry to saline mudflat, under semi-arid to arid climatic conditions (Lázár and Máthé, 2012). Two distribution areas of Boda Clay are known in West-Mecsek Mountains, the peri anticlinal structure of the West-Mecsek Anticline Block and the Gorica Block. These two areas have been selected as most appropriate for deep geological disposal. The sample used in this study was taken from the borehole Ib-4 located in the Gorica block at a depth of 540 m (Breitner et al., 2015).

The Opalinus Clay sample originates from a geothermal well in Schlattingen in northeastern Switzerland and was cored at a depth of 938 m below surface (SLA-938). The siting area is located in the Tabular Jura at the northern boundary of the Molasse Basin. The sedimentary sequence at the location of the Schlattingen borehole comprises marine limestones, shales and marls covered by tertiary rocks of the Alpine Molasse. The Opalinus Clay was deposited about 180 Ma ago in a shallow marine environment.

The mineralogical compositions of both rock samples were determined by X-ray diffraction and are given in Table S1 in the Supporting Information (SI). The 2:1 type clay minerals *i.e.* illite and illite/smectite mixed layers content in the rock samples was 50 and 47 wt.% for Boda and Opalinus Clay, respectively. The CEC determined using the ^{134}Cs isotopic dilution method (Baeyens and Bradbury, 2004) was measured to be $0.113 \text{ eq}\cdot\text{kg}^{-1}$ for Boda Clay Ib-4-540 and $0.183 \text{ eq}\cdot\text{kg}^{-1}$ for Opalinus Clay SLA-938 (Table S1 in the SI). The synthetic Boda and Opalinus Clay porewater compositions in equilibrium with atmospheric pCO_2 , used in the sorption measurements, are summarized in Table S2 in the SI. As already mentioned above one major difference between both rock formations is their marine and lacustrine origin which is reflected by different ionic strength of their respective porewaters.

2.2 Sorption experiments on illite and argillaceous rock samples

Supra-pure grade chemicals and ultrapure de-ionised water were used to prepare all the solutions. The radioisotopes ^{60}Co , ^{63}Ni , ^{134}Cs , ^{152}Eu and ^{228}Th in 0.1 M HCl purchased from Eckert and Ziegler, Isotope Products Laboratories (California, USA) and ^{233}U source solution ($4\cdot 10^{-3} \text{ M}$) in 1 M

HCl were used in the sorption measurements. Details of the experiments are summarized in Table S3 in the SI.

2.2.1 Co sorption isotherm on illite

The Co sorption isotherm on illite was determined in 0.1 M NaClO₄ at a solid to liquid (S:L) ratio of 2.2 g·L⁻¹ at pH~7.1 in the presence of 2·10⁻³ M MOPS (C₇H₁₅NO₄S, Fluka) to prevent pH drift. The measurements were carried out under inert atmosphere conditions in a N₂-flooded glove box to avoid CO₂ contamination.

Standard solutions covering the Co concentration ranges required were prepared at pH~7.1 in 0.1 M NaClO₄ background electrolyte and were labelled by adding known quantities of ⁶⁰Co. These tracer solutions were allowed to equilibrate for at least one day in their polyethylene containers for wall sorption to be completed before use in the sorption experiments. All the Co solutions were thermodynamically stable. Aliquots of clay suspensions and the appropriately ⁶⁰Co labelled standard solutions were transferred into 40 ml centrifuge tubes and shaken end-over-end for 1 week. After this equilibration period, phase separation was obtained using a Beckman Coulter Avanti™ J30i High-Performance Centrifuge (1 hour at 108,000g max.) and aliquots of the supernatant solutions were taken for radio assay. The sorption measurements were carried out in triplicate. The pH of the supernatant of each sample was measured after phase separation using a Metrohm combined electrode. The electrode was calibrated against commercially Merck™ buffers for pH 4, 7 and 10. Radiochemical assays of ⁶⁰Co in the supernatant solutions were performed using a Canberra Packard Cobra Quantum γ-counter together with standard labelled solutions.

2.2.2 Eu sorption on illite in the presence of carbonate

Sorption edge measurements of ¹⁵²Eu trace concentration ([Eu_{tot}] < 2·10⁻⁹ M) as a function of pH in equilibrium with atmospheric pCO₂ were carried out to quantify the influence of carbonate on the sorption of Eu on illite. The appropriate concentrations of carbonate and bicarbonate necessary to reproduce atmospheric pCO₂ conditions were prior calculated theoretically for each pH value and

then adjusted in the experiment as a function of pH using $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solutions. Samples were prepared in 40 ml centrifuges tubes at a S:L ratio of $2 \text{ g}\cdot\text{L}^{-1}$ (Table S3 in the SI). After labelling with ^{152}Eu , the illite suspensions were shaken end-over-end for 7 days. For details on phase separation, pH measurements and sampling see section 2.2.1. Radiochemical assays of ^{152}Eu in the supernatants were performed using a Canberra Packard Cobra Quantum γ -counter together with standard ^{152}Eu labelled solutions.

2.2.3 Sorption experiments on Boda and Opalinus Clay

For the sorption experiments on Boda and Opalinus Clay, the rock samples were ground and sieved in order to obtain crushed rock material with particle sizes $\leq 63 \mu\text{m}$.

Conditioning of Boda and Opalinus Clay samples: Prior to the sorption measurements, the crushed core samples were conditioned to the synthetic Boda and Opalinus Clay porewaters given in Table S2 in the SI. The procedure was the same for both rocks. The conditioning of the samples and the sorption experiments were carried out in equilibrium with atmospheric pCO_2 . Dialysis bags were washed with de-ionised water before filling with crushed rock and synthetic porewater. The bags were sealed so that an air pocket was trapped inside which promoted a good mixing during end-over-end shaking. The dialysis bags were placed in a 2 L polyethylene flask filled with synthetic porewater and then shaken for 24 hours. After this time, the equilibrated solutions in the flasks were replaced by fresh synthetic porewater and the bottles were again shaken for 24 hours. This procedure was repeated four times. Finally, each rock suspension inside the dialysis bags was emptied into a quantity of the last equilibrated synthetic porewater to yield sorbent concentrations of ~ 20 to $40 \text{ g}\cdot\text{L}^{-1}$. The exact rock content in the final suspensions was determined by heating weighed aliquots to constant weight at 105°C and correcting for the salt content. The concentrations of the major elements Na, K, Mg, Ca, Sr, Si and S (SO_4^{2-}) in the liquid phases of the Boda and Opalinus Clay batches after the conditioning procedures were very similar to the synthetic porewaters.

Batch sorption experiments: Sorption isotherms for Cs, Co, Ni, Eu, Th and UO₂ were measured on both argillaceous rocks in their respective conditioned synthetic porewater at the corresponding pH. The experiments were carried out under atmospheric conditions since the synthetic porewater and the rock suspension were in equilibrium with atmospheric CO₂ partial pressure. Because of aqueous solubility limits under the chemical conditions of the porewater (pH ~8) the sorption measurements for Th could only be carried out at trace concentrations (Neck and Kim, 2001).

Standard solutions covering the required nuclide concentration ranges were prepared in the conditioned synthetic porewaters for each element and were labelled with the corresponding radioisotope. Aliquots of rock suspensions and the appropriately labelled standard solutions were transferred into 40 ml centrifuge tubes and shaken end-over-end for 1 week. Experimental details (*i.e.* S/L ratio, pH, concentration range) are summarized in Table S3 in the SI. Phase separation, pH measurements and sampling procedure are the same as described in section 2.2.1. Aqueous activities were measured using either a Canberra Packard TRI-CARB 2750 TR/LL liquid scintillation counter (⁶³Ni, ²³³U), or a Canberra Packard Cobra Quantum γ-counter (¹³⁴Cs, ⁶⁰Co, ¹⁵²Eu, ²²⁸Th).

2.3 Presentation of the data

The sorption results in this work are presented as sorption isotherms (sorbed radionuclide concentrations (C_{sorb}) vs. equilibrium concentrations (C_{eq})) in a plot of $\log C_{\text{sorb}}$ vs. $\log C_{\text{eq}}$. C_{sorb} and C_{eq} of the radionuclide are calculated from the measured activity of the supernatant solution and the known activity of the initial solution.

The quantity of C_{sorb} is calculated as:

$$C_{\text{sorb}} = \frac{A_{\text{in}} - A_{\text{eq}}}{A_{\text{s}}} \cdot \frac{V}{m}$$

where C_{sorbed} is the amount of metal sorbed ($\text{mol}\cdot\text{kg}^{-1}$), A_{in} is the initial activity concentration ($\text{Bq}\cdot\text{L}^{-1}$), A_{eq} is the equilibrium activity concentration ($\text{Bq}\cdot\text{L}^{-1}$), A_s is the specific activity ($\text{Bq}\cdot\text{mol}^{-1}$), V is the volume of the liquid phase (L), and m is the mass of the solid phase (kg).

The equilibrium concentration, C_{eq} ($\text{mol}\cdot\text{L}^{-1}$), is given by:
$$C_{\text{eq}} = \frac{A_{\text{eq}}}{A_s}$$

Note that for the Cs, Co, Ni, Eu and UO_2 data sets the experimental error is ± 0.3 log units. For the strongly sorbing Th, however, the experimental error is ± 0.5 log units, because the radio assay measurements of this element are close to the background activities.

2.4 EXAFS measurements.

For the Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy measurements Ni loaded illite, Boda and Opalinus Clay samples were prepared in a batch mode in 200 ml polypropylene vessels in a similar way to that described in section 2.2, but in the absence of ^{63}Ni tracer. After equilibration, the suspensions were centrifuged, the supernatant solutions discarded and the wet pastes were filled into polyethylene sample holders and sealed with Kapton tape.

Co EXAFS could not be investigated because of the strong interference of the Co and Fe fluorescence lines, the latter stemming from Fe intrinsically present in illite and the rock samples. For Th, Eu and UO_2 , the loadings at the highest equilibrium concentrations (Figs. 7 - 9) are not sufficient to perform reliable EXAFS measurements.

The Ni K-edge spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL, Menlo Park, CA) on beamline 11-2 under normal ring operating conditions (3 GeV, 500 mA). All spectra were recorded at room temperature using a Si(220) double crystal LN_2 -cooled monochromator and a Canberra 100-pixel Ge solid-state monolith. To reduce unwanted fluorescence noise (*i.e.* elastic and Compton scattering) by samples, Co filter and Soller slits were used. Energy calibration was performed simultaneously by measuring in transmission mode a Ni foil (8333 eV).

EXAFS scans were collected up to a k range of $12 \text{ \AA}^{-1}$ from each of the Ni loaded samples and averaged to improve the signal to noise ratio (typically ~ 3 -10 scans). EXAFS data were reduced using the Athena-Artemis-IFEFFIT package (Newville 2001; Ravel and Newville 2005). The resulting EXAFS $\chi(k)$ spectrum was weighted by k raised to the power of 3 to compensate for the dampening of the EXAFS amplitude with increasing k . Radial structure functions were obtained from $k^3\chi(k)$ functions (typical range $2 - 10 \text{ \AA}^{-1}$) using a Kaiser-Bessel window (with $dk = 1 \text{ \AA}^{-1}$).

3. Predictive Modelling

As already mentioned in the introduction, to blind predict sorption of the selected radionuclides on both argillaceous rocks, a simplified component additivity or bottom up approach was chosen.

This approach is based on the hypothesis that the uptake of radionuclides in argillaceous rocks is predominantly controlled by sorption on the major clay mineral components. Quantitative predictions are then possible based on the knowledge and understanding of the mechanistic sorption processes on these clay minerals, and the models developed to describe them. The 2:1 clay minerals illite and illite/smectite mixed layers are major components of Boda and Oplinus Clay rocks and their respective contents are given in Table S1 in the SI. A further assumption is that illite/smectite mixed layer minerals have essentially the same sorption characteristics as illite. This assumption cannot be confirmed unambiguously because sorption data for this clay mineral are very sparse in the open literature.

For the quantitative description of radionuclide uptake on illite two different sorption models have been developed in the past, the GCs model (Bradbury and Baeyens, 2000) and the 2SPNE SC/CE model (Bradbury and Baeyens, 2009a,b). These two models were used for the predictive modelling exercise and a detailed description of both sorption models for illite is given in the SI.

In calculating sorption values with the 2SPNE SC/CE model, radionuclide aqueous speciation plays a very important role. The correctness and completeness of the thermodynamic database used in the

calculations are critical. A summary of the thermodynamic data used for the speciation calculations is given in Table S8 (hydrolysis) and Table S9 (major inorganic ligands) in the SI together with the source references. Because of their very close thermodynamic properties, Eu(III) and Am(III) are often used as chemical analogues (Choppin, 1995). For this reason and to be consistent with the SC constants for Eu on illite from Bradbury and Baeyens (2009a), Am(III) hydrolysis and Am(III) - chloro, -sulphato and -carbonato complexation constants were used in the calculations. Aqueous activity coefficients were calculated using the Davies relation with a value of 0.3 for the C_D constant (Davies, 1962).

The computer code MINSORB (Bradbury and Baeyens, 1997) was used for all the calculations. MINSORB is basically the geochemical speciation code MINEQL (Westall et al. 1976) containing sub-routines for calculating simultaneously cation exchange and surface complexation.

The modelling procedure applied here can be summarized as follows:

- For Cs, the sorption values were calculated with the GCs model (Table S4 in the SI) scaled to the 2:1 clay content of the considered rock sample in its porewater composition.
- The sorption of Co, Ni, Eu, Th and UO_2 was calculated with the 2SPNE SC/CE model for illite (Table S4, S5, S6 and S7 in the SI) scaled to the 2:1 clay content of the given rock sample in 0.1 M $NaClO_4$ at the pH of its porewater (Table S2 in the SI). In a second step, the sorption of the different elements was calculated in the respective porewaters compositions *i.e.* taking into account the aqueous speciation (Table S2 in the SI) using the thermodynamic data given in Tables S8 and S9 in the SI.

In this study, the predicted sorption isotherms for Cs, Co, Ni, Eu, Th and UO_2 on both argillaceous rocks are compared with experimentally measured data.

4 Results and discussion

4.1 Sorption on illite

4.1.1 Sorption isotherms for Co, Ni, Eu and UO₂ on illite

Fig. 1 shows the sorption isotherms for Co, Ni, Eu and UO₂ on Na-IdP in 0.1 M NaClO₄ together with the model curves. Ni and Eu sorption isotherms at pH ~7.1 were taken from Poinssot et al. (1999) and Bradbury and Baeyens (2005), respectively. The UO₂ isotherm at pH~5.8 was taken from Bradbury and Baeyens (2005). Experimental details are summarized in Table S3 in the SI. Bradbury and Baeyens (2009a,b) showed only sorption edges for these elements and only SC constant for the strong sites ($\log {}^sK$) were required to fit this data. SC constants for the weak sites ($\log {}^wK$) were derived by fitting iteratively the sorption isotherms and edges for Co, Ni, Eu and UO₂ and the best fit parameters are summarised in Table S5 and S7 in the SI. Note that the SC constant for the Co strong site complex ($\equiv S^sOCo^+$) obtained in this study is higher than the one obtained from the sorption edge given in Bradbury and Baeyens (2009a). This difference is due to the fact that the edge measured in the latter study had a higher Co carrier concentration compared to the trace measurements in Fig. 1a.

Fig. 1. Sorption isotherm measurements for Co (pH = 7.1), Ni (pH = 7.2), Eu (pH = 7.1 and UO₂ (pH = 5.8) on illite in 0.1 M NaClO₄. Symbols: measured data; solid lines: best-fit using the 2SPNE SC/CE model. Broken lines: contributions of strong sites, weak sites and planar sites to the overall sorption. ■) Ni EXAFS samples.

4.1.2 Sorption of Eu on illite in the presence of carbonate

The uptake of Eu(III) at trace concentration as a function of pH on Na-IdP in 0.1 M NaClO₄ in the absence of carbonate (taken from Bradbury and Baeyens, 2009a) and in the presence of carbonate are shown in Fig. 2. The influence of carbonate on the Eu sorption by illite is very similar to montmorillonite (Marques Fernandes et al., 2008). No influence is observed up to pH ~ 8, the log R_d values are close to those measured in the carbonate-free system ($\log R_d = 5.6 \pm 0.3 \text{ L}\cdot\text{kg}^{-1}$). At pH

values greater than 8, however, a pronounced decrease in the Eu sorption is observed with increasing pH and carbonate concentration. The $\log R_d$ value decreases to $\sim 3.5 \pm 0.3$ ($\text{L}\cdot\text{kg}^{-1}$) at pH ~ 9.8 .

Fig. 2. (a) Eu sorption edges on Na-IdP in 0.1 M NaClO_4 ($\blacktriangle$) in the absence of carbonate (from Bradbury and Baeyens, 2009a) and ($\blacktriangle$) in equilibrium with air (this study). Black solid line: modelled curve in the absence of carbonate. Black broken line: prediction in the presence of carbonate assuming that aqueous Eu-carbonato complexes do not sorb; (b) Red solid line: best-fit taking into account Eu-carbonato surface complexes. Dashed and broken curves: contribution of the Eu surface complexes to the overall sorption.

The same stepwise modelling approach used in Marques Fernandes et al. (2008) was applied and the results of the model calculations are shown in Fig. 2. The SC reactions and associated stability constants for the carbonate free system obtained by Bradbury and Baeyens (2009a,b) used to calculate the black solid line in Fig. 2a are given in Table S7 in the SI. The black broken line in Fig. 2a represents the modelling for Eu in the presence of carbonate when considering Eu carbonate complexes as non-sorbing species. It is evident that this modelling approach underestimates Eu sorption, and hence, other surface sorption reactions must be involved.

The red solid line in Fig. 2b shows the modelling when considering in addition the formation of the following Eu-carbonato surface complexes:

Including these surface reactions into the model, reproduced the experimental data well. The Eu-carbonato SC reactions on strong sites with their corresponding stability constants are given in Table S7 in the SI. The contribution to the overall sorption of the major individual Eu surface species as a function of pH for constant $p\text{CO}_2$ of $10^{-3.5}$ bar are shown in Fig. 2b.

4.2 Sorption results and blind prediction of Cs, Co, Ni, Eu, Th and UO₂ on Boda and Opalinus Clay

4.2.1 Caesium sorption on Boda and Opalinus Clay

The experimental results of the Cs sorption isotherms on Boda and Opalinus Clay are presented in Fig. 3. In the data analysis of the isotherms the intrinsic inventories of elements of the argillaceous rocks undergoing cation exchange, *e.g.* Cs and Rb, were also taken into account. The intrinsic inventory yields the total individual element content of the rock which includes quantities present within the lattice of the clay minerals as well as those which are more readily available and could potentially take part in the sorption experiments. The intrinsic inventories of Cs and Rb as determined by ICP-MS are given in Table S10 in the SI. The modelling results obtained using the GCs model and the corresponding parameters (Table S4 in the SI), are shown in Fig. 3 (black lines). Potassium is the major cation competing with Cs for sorption on FES and type II sites for both argillaceous rocks.

Fig. 3. Sorption isotherms of Cs on Boda and Opalinus Clay. Symbols: experimental results. Black lines: prediction. Coloured solid lines: contribution of FES (red), type II (blue) and planar sites (green) to the overall sorption.

The sorption of Cs on Boda Clay is dominated by the type II and the planar sites. As can be seen, the measured data and the predicted values for Boda Clay (Fig. 3a) are in good agreement for Cs equilibrium concentrations above 10^{-4} M. At lower Cs equilibrium concentrations the predicted values are at the maximum 0.5 log units higher than the experimental data. Lowering the ${}^{\text{Cs}}_{\text{Na}}K_c$ value for the type II sites would yield a very good fit (see also Van Loon et al., 2009), however, this was not the aim of the modelling exercise. Another potential factor for the overprediction could be competition with Rb (which is present in Boda Clay at $\sim 2.5 \text{ mmol}\cdot\text{kg}^{-1}$, Table S10 in the SI). However, taking Rb competition into account in the modelling using the selectivity coefficients given in Bradbury and Baeyens (2000) did not have any noticeable effect on the predictions.

In the case of Cs on Opalinus Clay (Fig. 3b), the agreement between experimental data and the blind prediction is very good. The calculated values lie within the experimental error bars of ± 0.3 log units. As mentioned in section 3.3, the modelling was done with the illite and illite/smectite mixed layers content and not only with the illite weight fraction as proposed in the original GCs model (Bradbury and Baeyens, 2000).

4.2.2 Cobalt and nickel sorption on Boda and Opalinus Clay

The results of the sorption measurements (symbols) of Co and Ni on both argillaceous rock samples and the blind predictions, using the 2SPNE SC/CE model for illite (black solid lines), are shown in Figs. 4 and 5, respectively. The red broken lines in these figures represent the sorption scaled over the respective content of 2:1 type clays in 0.1 M NaClO₄ at the pH values of the respective porewaters. The difference between the red broken lines and the black solid lines illustrates the effect of the porewater chemistry, *i.e.* aqueous speciation at the given pH and ionic strength.

On Boda Clay the predicted sorption values for Co (Fig. 4a) and Ni (Fig. 5a) are higher compared to Na-IdP at Co/Ni equilibrium concentrations $\geq 3 \cdot 10^{-7}$ M. This effect is due to the low ionic strength (*I*) of the Boda porewater, $I \sim 3.3 \cdot 10^{-2}$ M (Table S2 in the SI). Under these conditions of low *I* and high metal concentration, sorption by cation exchange becomes dominant for divalent cations.

The sorption of Co and Ni on both rock samples exhibits the same trend. At equilibrium concentrations below $\sim 10^{-7}$ - 10^{-6} M, the agreement between experimental data and the predictive modelling is within or close to the error bars of ± 0.3 log units. However, at higher equilibrium concentrations, the model calculations clearly underpredict the sorption of Ni and Co up to one log unit. The uptake of Ni on Opalinus Clay is systematically underpredicted by 0.3 - 1 log units over the whole Ni equilibrium concentration range. The evident underprediction of sorption at higher concentrations was further investigated by EXAFS, and will be presented in the next section.

Fig. 4. Co sorption isotherms on Boda and Opalinus Clay. Symbols: experimental results. Red broken lines: sorption scaled to the 2:1 clay content in 0.1 M NaClO₄ at pH 8.1 and 7.7, for Boda and Opalinus Clay respectively. Black solid lines: prediction.

Fig. 5. Ni sorption isotherms on Boda and Opalinus Clay. Symbols: experimental results. Red broken lines: sorption scaled to the 2:1 clay content in 0.1 M NaClO₄ at pH 8.1 and 7.5, for Boda and Opalinus Clay respectively. Black solid lines: prediction. ■) Ni EXAFS samples.

4.2.2.1 Ni EXAFS data

Two Boda Clay samples Ni-Ib_1 and Ni-Ib_2 with 5 and 60 mmol·kg⁻¹ Ni, respectively, and two Opalinus Clay samples Ni-OPA_1 and Ni-OPA_2 with 13 and 27 mmol·kg⁻¹ Ni, respectively, were prepared in their corresponding porewaters. Additionally one illite sample, Ni-IdP with 21 mmol·kg⁻¹ Ni, was prepared as a reference for a Ni inner-sphere surface complex. The Ni loadings of these EXAFS samples agree well with the independently determined sorption isotherms as indicated by the orange symbols in Figs. 1b, 5a and 5b.

Fig. 6 show the Ni-K edge EXAFS spectra of the Ni-loaded Boda and Opalinus Clay samples, along with four reference spectra: a Ni surface complex on illite, Ni-layered double hydroxides (LDH), Ni-phyllsilicate and α -Ni(OH)₂. The spectrum of Ni-Ib_1 with only 5 mmol·kg⁻¹ Ni is extremely noisy due to the intense Fe fluorescence interference of the rock matrix and no analysis was attempted.

1 The k^3 weighted χ spectra of Ni-Ib_2, Ni-OPA_1 and Ni-OPA_2 (Fig. 6a) are nearly identical and
 2 are characterized by a multifrequency wave shape with distinct features at ~ 5.2 and $7.3 \text{ \AA}^{-1}$. These
 3 features are characteristic for specific Ni-solids (Scheinost and Sparks, 2000) and can be used as a
 4 fingerprint to discriminate sorption from precipitation. In contrast, the spectrum of Ni on illite (Ni-
 5 IdP) does not exhibit any of these features, suggesting a less ordered environment and/or the
 6 presence of light backscatter *i.e.* Al, Si, typical for medium to high divalent metal sorption on clay
 7 minerals (Dähn et al. 2002, 2011). Furthermore, the radial structure functions of Ni-Ib and Ni-OPA
 8 exhibit a backscattering contribution at $2.7 \text{ \AA}$ ($R + R$) originating from Ni-Ni interaction, similar to
 9 the spectra of the Ni-solids. As expected, this contribution is not present in the spectra of Ni-IdP
 10 sample (Fig. 6b).

11
 12 Fig. 6. a) Raw k^3 -weighted $\chi(k)$ spectra of Ni sorbed on Boda and Opalinus clay and of Ni-reference
 13 samples: Ni-IdP (this study), Ni-LDH (from Scheinost and Sparks, 2000), Ni-phylllosilicate (from
 14 Ford et al., 1999) and α -Ni(OH)₂ and b) the corresponding radial structure functions. Shaded areas

1 indicate the appearance of distinct features arising from Ni-Ni single and multiple scattering
2 interactions characteristic for specific Ni-precipitates (except for Ni-IdP).

3 An accurate identification of the Ni-precipitate on the rock samples is not possible because of the
4 noise of the data. Nevertheless, the spectroscopic similarities with the Ni-solids and the difference
5 with Ni-IdP clearly indicate that under the given experimental conditions the uptake of Ni by Boda
6 and Opalinus Clay is no longer controlled by a sorption process, but by a surface induced
7 precipitation of Ni solids. (Note that even the highest initial Ni solutions were below the solubility
8 product of Ni-hydroxides and Ni-carbonates.) Similar spectroscopic observations were recently made
9 by Chen et al. (2014), in their study on the uptake of Ni on Callovo-Oxfordian clayrock. These
10 surface precipitates explain the mismatch between the experimental sorption data and the predicted
11 curves for both rock samples, and is probably also valid for the underestimation of Co sorption at
12 higher equilibrium concentration. The formation of such surface precipitates has been extensively
13 investigated (Scheidegger et al., 1997; Ford et al., 1999; Scheinost et al., 2000; Dähn et al., 2001;
14 Voegelin et al., 2002; Schlegel and Manceau, 2006; Tan et al., 2014). However, the activation
15 mechanism for the formation of such surface induced precipitate on Boda and Opalinus Clay is
16 currently not understood.

17 **4.2.3 Europium sorption on Boda and Opalinus Clay**

18 The results of the Eu sorption measurements on Boda and Opalinus Clay and the corresponding blind
19 predictions are shown in Fig. 7. The sorption scaled to the 2:1 type clay content in 0.1 M NaClO₄ at
20 the pH of the corresponding porewater is illustrated by the red broken curves.

21 The reduction of the sorption is due to the formation of aqueous Eu-carbonato complexes which are
22 dominant in the porewaters. If the formation of Eu-carbonato surface complexes is not considered,
23 the calculations underpredict the measurements by ~ 0.5 to 0.8 log units for both rock samples as
24 illustrated by the blue solid curves in Fig. 7. The black solid lines are the results of the blind
25 predictions when taking into account the formation of Eu-carbonato surface complexes. Including

these SC reactions and constants derived in section 4.1.2 significantly improves the modelling results and the predicted curve lies within the error bars for Boda Clay and perfectly matches the experimental data for Opalinus Clay.

Fig. 7. Eu sorption isotherms on Boda and Opalinus Clay. Symbols: experimental results. Red broken lines: sorption scaled to the 2:1 clay content in 0.1 M NaClO₄ at pH 8.1 and 7.8 for Boda and Opalinus Clay respectively. Blue solid lines: prediction in the respective porewaters considering aqueous Eu-carbonato complexes as non-sorbing. Black solid lines: prediction in the respective porewaters including the SC reactions for Eu-carbonato surface complexes.

4.2.4 Thorium sorption on Boda and Opalinus Clay

The predicted sorption isotherms of Th on Boda and Opalinus Clay presented in Fig. 8 are in a good agreement with the experimental data and lie within the experimental error bars of ± 0.5 log units. The aqueous speciation of Th in the both porewaters is dominated by the neutral Th-tetrahydroxo complex. In contrast to Eu and UO₂ the formation and consequently the influence of the aqueous speciation (*i.e.* (hydroxo)-carbonate complexes for Th) is negligible as illustrated by the difference between the red broken and black solid lines in Fig. 8.

Fig. 8. Th sorption isotherms on Boda and Opalinus Clay. Symbols: experimental results. Red broken lines: sorption scaled to the 2:1 clay content in 0.1 M NaClO₄ at pH 7.9 and 7.7 for Boda and Opalinus Clay respectively. Black solid lines: prediction.

4.2.5 Uranyl sorption on Boda and Opalinus Clay

The predictive modelling results for UO₂ sorption isotherms on both samples are presented in Fig. 9. The modelling of the UO₂ sorption isotherm on Opalinus Clay reproduces well the experimental data, whereas on Boda Clay the sorption is systematically slightly underpredicted. A maximum deviation of ± 0.6 log units is observed in the low UO₂ equilibrium concentration range where the influence of the aqueous speciation is most pronounced (red broken lines). Despite this slight deviation, the modelling result is very good since the aqueous speciation for uranyl in these porewaters is playing an extremely important role. At trace concentration the pronounced decrease in sorption is mainly due to the formation of uranyl carbonate and uranyl calcium carbonate complexes. This is illustrated in Fig. 8 where reduction factors up to 3 orders of magnitude are calculated (difference between red broken lines and black solid lines). Clearly, both samples show that such aqueous complexes are important and can severely influence the mobility of uranyl in argillaceous rocks.

Fig. 9. UO_2 sorption isotherms on Boda and Opalinus Clay. Symbols: experimental results. Red broken lines: sorption scaled to 2:1 clay content in 0.1 M NaClO_4 at pH 8.1 and 7.7 for Boda and Opalinus Clay respectively. Black solid lines: prediction.

5. Summary and conclusions

In the context of deep geological disposal of radioactive waste, it is very important to make reliable predictions on the fate of (radio-)contaminants in realistic geochemical environments. In this study a simplified bottom-up approach, assuming that only the 2:1 clay minerals *i.e.* illite and illite/smectite mixed layers are the main sorbents, was applied to quantitatively describe the uptake of metals in clay-rich rocks.

First, the 2SPNE SC/CE sorption model was extended by including SC reactions on the strong sites for Eu-carbonato complexes obtained from pH dependent sorption measurements of Eu on IdP in equilibrium with atmospheric pCO_2 . For Co, Ni, Eu and UO_2 SC reactions on the weak sites were obtained from the simultaneous fitting of sorption edge and isotherm data for the respective element. Cs, Co, Ni, Eu, Th and UO_2 isotherms were measured on the Hungarian Boda Clay and Swiss Opalinus Clay in synthetic porewaters under atmospheric conditions. Blind predictions were made by applying the GCs and 2SPNE SC/CE sorption models developed for illite, scaled to the 2:1 clays content, and, taking into account the aqueous speciation of the radionuclides in the porewaters.

1 For Cs, the modelling reproduced very well the isotherm on Opalinus Clay. On Boda Clay, the
2 isotherm at Cs equilibrium concentrations below $\sim 10^{-5}$ M was less well reproduced. Further, it was
3 observed that the FES sites were not required in the modelling which might be explained by the fact
4 that part of these low capacity sites are already blocked (*e.g.* by K) or that they even do not exist in
5 the illite present in the Boda Clay.

6 The predictions for the divalent metals Co and Ni on both argillaceous samples follow the same trend.
7 At equilibrium concentrations below 10^{-7} to 10^{-6} M the agreement between experiment and the blind
8 predictive modelling is good, even so a slight underprediction for Ni on Opalinus Clay is observed.
9 At metal equilibrium concentrations above $\sim 10^{-6}$ M the calculations clearly underpredict the sorption
10 for both elements on both rock samples. The reason for the discrepancy between modelling and
11 experiment at higher equilibrium concentrations is likely the formation of surface precipitates as
12 could be demonstrated by Ni EXAFS measurements. The modelling approach does not consider the
13 formation of precipitates implying that in environments where the uptake of metals is governed by
14 such processes the model is no longer applicable. The surface precipitate formed could not be
15 unambiguously identified because of the rather noisy quality of the spectra. Further investigations are
16 needed to identify the solid phase and the mechanism for such a surface induced precipitation.

17 Eu sorption isotherms on both rocks could be very well predicted by assuming the formation of Eu-
18 carbonato surface complexes. Not taking into account these ternary complexes clearly
19 underpredicted the sorption by ~ 0.5 to 0.8 log units over the entire Eu concentration range
20 investigated.

21 For Th and UO_2 the blind predictions reproduce the experimental data well. The modelled curves for
22 both elements on Boda and Opalinus Clay lie within or close to the experimental error bars.

23 In contrary to the expectations, mineral components present in the Boda Clay, such as the zeolite
24 analcime with its high cation exchange capacity ($\sim 4.5 \text{ eq}\cdot\text{kg}^{-1}$ (GSA Resources, 2000)) and hematite,
25 apparently have negligible influence on the uptake of the studied elements on Boda Clay.

Despite their different mineralogies and porewater chemistries, the simplified bottom-up approach blind predicts the uptake of the different metal ions on both argillaceous rocks quite well, concluding that this approach and the underlying sorption models can be used to predict the uptake of Cs, Co, Ni, Eu, Th and uranyl in natural argillaceous rocks providing that sorption is the only retention mechanism.

It is foreseen in future work to test this approach on other rocks covering larger ranges of clay contents and porewater chemistries.

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