

Technical Report 17-11

**Estimates of the influence of
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sorption competition on the
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MX-80 bentonite and Opalinus Clay**

November 2017

M.H. Bradbury, M. Marques Fernandes,
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Paul Scherrer Institut, Villigen PSI

**National Cooperative
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Radioactive Waste**

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Preface

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institute is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of Swiss radioactive waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI Bericht and a Nagra Technical Report.

Abstract

In a geologic repository for radioactive waste a wide variety of metals from various sources, e.g. from backfill materials, from canister corrosion and from the dissolution of spent fuel and vitrified waste will be in solution in the porewaters. These stable and radioactive isotopes are simultaneously present and are an integral part of a realistic repository system.

Two effects need to be distinguished. The first is that even though individual radionuclides may be present at trace levels it is the total concentration (radioactive + stable isotopes) which determines the sorption. The second effect is that dissolved metals can compete with one another for the available sorption sites on the backfill material and the host rock. Both effects, higher total concentrations and sorption competition, lead to reduced sorption values.

It is clearly an inherently important issue to quantify their influence on the transport of released radionuclides through the multi-barrier system in a deep repository. The only practical means of assessing the influence of competitive sorption in MX-80 bentonite and Opalinus Clay, and bound its effects, is via modelling. This has been addressed in this report based on experimental results and modelling with the 2 site protolysis non-electrostatic surface complexation cation exchange (2SPNE SC/CE) sorption model. Generally, competitive sorption arises between metals which are chemically similar (valence state, hydrolysis behaviour) and which fit on the same Linear Free Energy Relationship (LFER). Three main groups of dissolved metals were considered: divalent transition metals, trivalent actinides / lanthanides and tetravalent actinides. Competitive sorption occurs between the metals within each group but not with metals from different groups.

The main conclusions drawn were:

- For divalent transition metals the main competitive metal ion is ferrous iron, arising from the saturation of siderite, and leads to a reduction in sorption of approximately two orders of magnitude compared with trace concentrations in MX-80 bentonite and Opalinus Clay.
- Competitive sorption is also taking place between trivalent actinides and lanthanides. The effect of the competition i.e. sorption reduction, depends on the sum of their local concentrations. In a worst case, calculated reductions of a factor of 10 to 100 may be anticipated in both MX-80 bentonite and Opalinus Clay compared with the values at trace concentration.
- For tetravalent actinides sorption competition is taking place, and sorption reductions of factor ~ 10 and ~ 3 may be anticipated in MX-80 bentonite and Opalinus Clay, respectively, compared with the values at trace concentration.

Zusammenfassung

In einem geologischen Tiefenlager für radioaktive Abfälle wird langfristig eine Vielzahl von Metallen (stabile und radioaktive Isotope) im Porenwasser gelöst auftreten. Diese stammen z.B. aus dem Verfüllmaterial, der Korrosion der Behälter für hochaktive Abfälle und der Auflösung von abgebrannten Brennelementen und verglasten Abfällen. Solche komplexen Porenwässer bilden einen integralen Bestandteil bei der Betrachtung eines realistischen Tiefenlagersystems.

Zwei Effekte spielen hierbei eine entscheidende Rolle. Erstens bestimmt nicht die Spurenkonzentration eines einzelnen Radionuklids die Sorption, sondern es ist hier die Gesamtkonzentration eines Elements (d.h. radioaktive + stabile Isotope) massgebend. Zweitens können gelöste Metalle untereinander um die vorhandenen Sorptionsplätze in Verfüllmaterial und Wirtgestein konkurrieren. Beide Effekte – die hohe Gesamtkonzentration eines Elements und mögliche Konkurrenzeffekte für die Sorption – können zu deutlich tieferen Sorptionswerten beitragen.

Um belastbare Aussagen über die langfristige Entwicklung eines geologischen Tiefenlagers für radioaktive Abfälle treffen zu können, ist es daher wichtig, den Einfluss der frei gesetzten Radionuklide auf den Transport durch das Multibarrierensystem eines Tiefenlagers zu quantifizieren. Der einzig praktikable Weg, Einfluss und Auswirkung der kompetitiven Sorption in MX-80 Bentonit und Opalinuston zu beurteilen, ist die Modellierung nasschemischer Daten. Diese wurde mit dem "2 site protolysis non electrostatic surface complexation cation exchange" (2SPNE SC/CE) Sorptionsmodell durchgeführt. Es zeigte sich generell, dass die kompetitive Sorption zwischen Metallen, die chemisch ähnlich sind (bezüglich Wertigkeit, Hydrolyseverhalten) und für die die gleiche Lineare-Freie-Energie-Beziehung LFER gilt, eine Rolle spielt. Dabei wurden drei Hauptgruppen von gelösten Metallen in Betracht gezogen: a) zweiwertige Übergangsmetalle, b) dreiwertige Aktiniden / Lanthaniden und c) vierwertige Aktiniden. Die Ergebnisse zeigten, dass kompetitive Sorption nur unter Metallen innerhalb derselben Gruppe, jedoch nicht unter Metallen unterschiedlicher Gruppen erfolgt.

Die wichtigsten Schlussfolgerungen dieser Studie sind:

- Bei den zweiwertigen Übergangsmetallen ist zweiwertiges Eisen das dominierende kompetitive Metall, dessen Konzentration in Lösung durch die Löslichkeit von Siderit bestimmt wird. Hohe Eisenkonzentrationen führen zu einer Verminderung der Sorptionswerte von zweiwertigen Übergangsmetallen um ungefähr zwei Grössenordnungen, verglichen mit deren jeweiligen Spurenelementkonzentrationen in MX-80 und Opalinuston.
- Kompetitive Sorption findet auch zwischen dreiwertigen Aktiniden und Lanthaniden statt. Der Effekt der Konkurrenz bzw. die Reduktion der Sorptionswerte hängen dabei von der Summe deren lokaler Konzentrationen ab. Schlimmstenfalls ist von einer berechneten Reduktion für dreiwertige Aktiniden und Lanthaniden um einen Faktor 10 bis 100, im Vergleich zu deren jeweiligen Spurenelementkonzentrationen in MX-80 und Opalinuston auszugehen.
- Für vierwertige Aktiniden spielt die kompetitive Sorption ebenfalls eine Rolle. Die erwartete Sorptionsreduktion beträgt hier ca. Faktor 10 für MX-80 Bentonit bzw. ca. 3 für Opalinuston, verglichen mit den jeweiligen Spurenelementkonzentrationen.

Résumé

Dans un dépôt en couches géologiques profondes pour déchets radioactifs, un large éventail de métaux issue de sources différents telle que la corrosion des conteneurs, la dissolution du combustible usés et déchets vitrifiés, seront présent dans les eaux interstitielles. Ces éléments stables et radioactifs présents simultanément, font partie intégrante de l'inventaire réaliste d'un dépôt. Il faut distinguer deux effets. D'une part, bien que des radionucléides individuels soient présents à l'état de trace, c'est la concentration totale en nucléides (*c.à.d.* radioactif + stable) qui détermine le degré de sorption. D'autre part, les métaux dissous peuvent concurrencer pour les sites de sorption disponible dans la bentonite et dans la roche d'accueil. Ces deux effets engendrent une diminution des valeurs de sorption.

Par conséquent, il est important de quantifier l'impact de ces deux effets sur le transport des radionucléides libérés, à travers le system de barrières. La seule façon appropriée d'estimer l'influence de la sorption compétitive dans la bentonite MX-80 et dans l'Argile à Opalinus est à travers de la modélisation. Dans le présent rapport, la sorption concurrentielles est traitée à partir de résultats expérimentaux et de modélisation avec le model "2 site protolysis non electrostatic surface complexation cation exchange" (2SPNE SC/CE). De manière générale, les métaux chimiquement proches (valence, hydrolyse) et qui suivent la même relation linéaire d'énergie libre (LFER) sont compétitifs entre eux. Trois principaux groupes de métaux ont été pris en compte : les métaux de transition divalents, les lanthanides, ainsi que pour les actinides tri- et tétravalent. Les métaux d'un même groupe sont compétitifs entre eux mais ne sont pas en concurrence avec des métaux d'autres groupes.

En résumé :

- La présence de fer ferreux provenant de l'équilibre avec la sidérite engendre une diminution de la sorption des métaux de transition divalents dans la bentonite MX-80 et l'Argile à Opalinus d'environ deux ordres de grandeurs en comparaison avec les concentrations trace.
- Les lanthanides et actinides trivalent sont compétitifs entre eux. L'effet compétitif, *c.à.d.* la diminution de la sorption dépend de la somme de leurs concentrations respectives. Dans le pire des cas on peut s'attendre à une réduction allant d'un facteur 10 à 100 dans la bentonite MX-80 et l'Argile à Opalinus en comparaison avec les concentrations trace.
- De même les actinides tétravalents sont compétitifs entre eux. Une réduction d'un facteur 10 est prédite pour la bentonite MX-80 et d'un facteur 3 pour l'Argile à Opalinus en comparaison avec les concentrations trace.

Table of Contents

Preface	I
Abstract	III
Zusammenfassung.....	V
Résumé	VII
Table of Contents	IX
List of Tables.....	X
List of Figures	XI
1 Introduction	1
2 Background	3
3 Modifications to the 2SPNE SC/CE model.....	5
4 Factors influencing the sorption of radionuclides in real systems	7
4.1 Presence of stable isotopes	7
4.2 Complexation with anionic ligands in real systems.....	7
4.3 Summary.....	10
5 Illustrative example of a repository near-field competitive sorption scenario.....	11
5.1 General.....	11
5.2 Maximum limit concentrations.....	11
5.3 Calculation procedure.....	12
5.4 Divalent metals.....	13
5.5 Trivalent metals.....	16
5.6 Tetravalent metals.....	18
5.6.1 Tc(IV), Po(IV) and Zr(IV).....	18
5.6.2 Sn(IV).....	19
5.6.3 Th(IV), Np(IV) and U(IV).....	19
6 The influence of competitive sorption on sorption values in Opalinus Clay.....	21
6.1 Divalent metals.....	21
6.2 Trivalent metals.....	22
6.3 Tetravalent metals.....	23
7 Summary of results and conclusions.....	25
8 References.....	27

Appendix A: Metal hydrolysis and surface complexation data for montmorillonite and illite	A-1
Appendix B: Auxiliary thermodynamic data	B-1
Appendix C: MX-80 mineralogy and porewater chemistry	C-1
Appendix D: Solubility limits of safety-relevant elements in the SF/HLW bentonite near-field	D-1
Appendix E: Opalinus Clay mineralogy and porewater chemistry	E-1

List of Tables

Tab. 4.1: Porewater compositions at pH = 7.25.....	9
Tab. 4.2: Eu speciation in the simple background electrolyte (Tab. 4.1, Case A) and in a complex porewater composition at pH = 7.25 (Tab. 4.1, Case B).....	9
Tab. 5.1: "Maximum limit concentrations" of metals in the porewater of a bentonite near-field of a high level waste repository (Tab. D-1 in Appendix D).....	12
Tab. 5.2: Summary of calculations for divalent elements (Group 1, Tab. 5.1).....	14
Tab. 5.3: Summary of calculations for trivalent elements (Group 2, Tab. 5.1).	16
Tab. 5.4: Summary of calculations for tetravalent elements (Group 3, Tab. 5.1).....	20
Tab. 6.1: Ni(II) sorption in Opalinus Clay at trace concentration (no competition) and in the presence of 5.2×10^{-5} M Fe(II).....	22
Tab. 6.2: Comparison of sorption values in Opalinus Clay for trivalent actinides / lanthanides calculated at trace concentrations with no competition and at maximum limit concentrations with competition.	22
Tab. 6.3: Comparison of sorption values in Opalinus Clay for tetravalent actinides calculated at trace concentrations with no competition and at maximum limit concentrations with competition.	23
Tab. 7.1: Comparison of sorption values for trivalent lanthanides and actinides considering their maximal limit concentrations and taking into account competitive sorption.	26
Tab. 7.2: Comparison of sorption values for tetravalent actinides considering their maximal limit concentrations and taking into account competitive sorption.	26
Tab. A-1: Hydrolysis and surface complexation reactions and constants for Ni(II) and Fe(II).....	A-1
Tab. A-2: Hydrolysis and surface complexation reactions and constants for Eu/Sm/Ho(III), Am/Ac/Cm(III) and Pu(III).	A-1

Tab. A-3:	Hydrolysis and surface complexation reactions and constants for Th(IV), U(IV) and Np(IV).....	A-2
Tab. B-1:	Aqueous thermodynamic data for divalent metals taken from the PSI/Nagra TDB 12/07 (Thoenen et al. 2014).....	B-1
Tab. B-2:	Aqueous thermodynamic data for trivalent metals taken from the PSI/Nagra TDB 12/07 (Thoenen et al. 2014).....	B-1
Tab. B-3:	Aqueous thermodynamic data for tetravalent metals taken from the PSI/Nagra TDB 12/07 (Thoenen et al. 2014).....	B-2
Tab. C-1:	Reference MX-80 mineralogy (Müller-Vonmoos & Kahr 1983).....	C-1
Tab. C-2:	Bentonite porewater obtained after 10'000 years of exchange between the bentonite starting system and the Opalinus Clay reference system without a low-pH shotcrete liner.	C-1
Tab. D-1:	Solubility limits (in mol/kg H ₂ O) of safety-relevant elements in the SF/HLW near-field (bentonite).	D-1
Tab. E-1:	Reference mineralogy and values for the bounding minerals for Opalinus Clay (Traber & Blaser 2013).....	E-1
Tab. E-2:	Porewater composition of Opalinus Clay (Mäder 2009).	E-1

List of Figures

Fig. 4.1:	Eu isotherms on montmorillonite in two different water compositions at pH = 7.25.	8
Fig. 5.1:	Fe(II) sorption isotherm and the sorption of trace Zn in the presence of increasing Fe(II) concentrations ($Zn_{tot} = 3 \times 10^{-8}$ M) on a synthetic iron-free montmorillonite (Soltermann et al. 2014).	13
Fig. 5.2:	Calculated Ni sorption isotherm for MX-80 in the bentonite porewater (pH 7.79); (a), (b) in the absence of competing metals and (c), (d) in the presence of Fe(II) at siderite saturation, 3.7×10^{-5} M.	15
Fig. 5.3:	Calculated Eu sorption isotherm for MX-80 in the bentonite porewater (pH 7.79) (a), (b) in the absence of competing metals and (c), (d) in the presence of competing metals whose equilibrium concentrations are as given in Tab. 5.1.....	17
Fig. 5.4:	Aqueous speciation of Tc(IV) in 0.1 M NaClO ₄ as function of pH.....	18
Fig. 5.5:	Aqueous speciation of Zr(IV) in 0.1 M NaClO ₄ as function of pH.	18
Fig. 5.6:	Aqueous speciation of Sn(IV) in 0.1 M NaClO ₄ as function of pH.	19
Fig. 5.7:	Aqueous speciation of Th(IV), U(IV) and Np(IV) in 0.1 M NaClO ₄ as a function of pH.	20
Fig. 6.1:	Calculated Ni sorption isotherm in the Opalinus Clay / porewater (pH 7.20) system.	21

1 Introduction

In order to obtain a (quasi) mechanistic understanding of radionuclide uptake on clay minerals, bentonite and argillaceous rocks, sorption experiments have been carried out on purified clay minerals under well-defined conditions in simple background electrolytes as a function of pH at trace concentrations (sorption edges) or as a function of concentration at constant pH and ionic strength (sorption isotherms) by, e.g., Baeyens & Bradbury 1997, Bradbury & Baeyens 1999, 2002, 2009a and b. As a result of these studies a sorption model, the "2 site protolysis non electrostatic surface complexation cation exchange (2SPNE SC/CE) model", was developed and has been successfully applied to quantitatively describe the uptake of numerous radionuclides of differing valences as a function of pH and concentration on the 2:1 clay minerals montmorillonite and illite under a wide range of conditions (Bradbury & Baeyens 1997, 2005a, 2009a and b). The experience gained over the past decade or more has led to the conclusion that the model, together with the associated parameters, can be used with confidence and provides a good quantitative description of sorption in systems where 2:1 clay minerals (montmorillonite, illite, illite-smectite mixed layers) are the dominant sorbing phases. For example, sorption isotherms measured on Opalinus Clay, MX-80 bentonite and Hungarian Boda Claystone in complex water chemistries have been quantitatively well reproduced using this model (Bradbury & Baeyens 2011, Marques Fernandes et al. 2015).

Sorption is described in terms of cation exchange and surface complexation. Generally, one or the other mechanism dominates the uptake, depending on the chemical conditions, but both mechanisms are always operating together and are calculated simultaneously using the sorption model embedded in a geochemical speciation code, MINSORB (Bradbury & Baeyens 1997). The interpretations and conclusions drawn in this report are based on the concepts and assumptions contained in the 2SPNE SC/CE sorption model and the calculations carried out with it and, of course, are restricted to the data available.

In a deep geological repository for high level waste, stable elements are present and arise from many different sources: they are in the porewaters, in the tunnel backfill materials and host rock formations, they come from the corrosion of the carbon steel canister, and finally they are dissolved from the spent fuel and vitrified high-level waste simultaneously with the radionuclides. These stable elements, which are an integral part of a realistic repository system, and the released radionuclides themselves, can all compete with one another for the sorption sites on the backfill material and the host rock, and thus reduce their uptake on them. The influence of competitive sorption is not intrinsically included in the sorption model, except in the cation exchange component, see below. It is clearly an inherently important issue to quantify the influence of locally high concentrations in the near-field and competitive sorption on the transport of released radionuclides through the multi-barrier system in a deep repository (e.g., see Bradbury & Baeyens 2005b and Pfingsten et al. 2011). The impact of cation competition needs to be properly investigated in order to be adequately considered in the development of the sorption databases in future safety analyses.

2 Background

In two recent publications, Baeyens & Bradbury (2017) and Bradbury & Baeyens (2017), Thermodynamic Sorption Data Bases (TSDBs) for montmorillonite and illite, respectively, have been developed. These reports contain a description of the 2SPNE SC/CE model, summaries of the model parameters, a list of the basic model assumptions, metal surface complexation constants for strong and weak sites, selectivity coefficients, linear free energy relationships for divalent, trivalent and tetravalent metals, the selected metal hydrolysis constants used in the modelling of sorption edge/isotherm data. A list of thermodynamic constants used to model with the bottom-up approach the sorption in MX-80 bentonite and Opalinus Clay under realistic geochemical conditions is also contained in these reports. The information and data given in the two TSDBs will be used in the modelling of the sorption and sorption competition in the near- and far-fields under the conditions described. A summary of the observations regarding sorption competition and the generalisations deduced from them is given below.

Bradbury and Baeyens (2005b) have investigated the competitive sorption behaviour between various combinations and concentrations of Co(II), Ni(II), Zn(II), Eu(III), Nd(III), Am(III), Th(IV) and U(VI) on montmorillonite, where one element was present at trace concentration (given in red below) and the other element at high concentration (blocking element). Soltermann et al. (2014) have investigated the competitive sorption between Fe(II) and Zn(II) on a synthetic iron-free montmorillonite. The conclusions from these studies can be summarised as follows:

Trace/Blocking element:

- Ni(II)/Co(II) competitive Zn(II)/Fe(II) competitive
- Am(III)/Eu(III) competitive
- Th(IV)/Ni(II) not competitive
- U(VI)/Ni(II) not competitive
- Th(IV)/Eu(III) not competitive
- Np(V)/Eu(III) not competitive
- U(VI)/Eu(III) not competitive

This sorption "blocking" behaviour can be further generalised as follows:

1. (II) compete with (II)
2. (III) compete with (III)
3. (IV) compete with (IV)
4. (V) compete with (V)
5. (VI) compete with (VI)

and

- a) (II) do not compete with (III), (IV), (V) and (VI)
- b) (III) do not compete with (IV), (V) and (VI)
- c) (IV) do not compete with (II), (III), (V) and (VI)
- d) (V) do not compete with (II), (III), (IV) and (VI)
- e) (VI) do not compete with (II), (III), (IV) and (V).

where the roman numerals represent the valence state of the elements.

The evidence for those valences given in bold type comes from batch sorption measurements on montmorillonite (Bradbury & Baeyens 2005b, Soltermann et al. 2014).

From the above generalisations, it seems that sorption competition arises between metals which are chemically similar (valence state, hydrolysis behaviour.) A further criterion for competitive sorption appears to be that the surface complexation constants / hydrolysis constants relationships for the metals should fit on the same linear free energy relationship (see Baeyens & Bradbury 2017 and Bradbury & Baeyens 2017).

For tetravalent metals, the aqueous concentrations accessible in laboratory experiments are so low that all combinations of tetravalent metals would be able to sorb on the available strong sites without having any influence on the sorption of each other. Thus, although relation 3 is anticipated to be valid, competitive sorption effects amongst tetravalent elements would be expected to be negligible. Relation (c) is also likely to be the realistic situation in a repository.

For hexavalent elements, there are no important radionuclides other than U(VI), and then only under oxidising conditions (relation e). Note: although Mo is also a hexavalent element, it exists exclusively as an anionic species and would not be expected to be competitive.

The main open question concerning the above competition statements is the behaviour of pentavalent radionuclides, i.e.:

- Statement 4): (V) compete with (V) and
- Statement d): (V) do not compete with (II), (III), (IV) and (VI).

There is currently neither spectroscopic nor experimental evidence available to support the statements except that Np(V) does not compete with Eu(III). Thus statements (4) and (d) must be regarded as assumptions at the present time.

In contrast to cation exchange, where all cations compete with one another for the planar sorption sites according to the value of their respective selectivity coefficients, modelling competition on edge sites with the 2SPNE SC/CE sorption model requires that it is specified which metals are competitive and which are not. Different strong site sets have to be defined in the model (each set having the same site capacity and protolysis characteristics), for each group of competing metals. This can be readily achieved in the currently used MINSORB code, see Bradbury & Baeyens (2005b).

Finally, the main dissolved metals in the majority of porewaters are alkali and alkaline earth metals such as Na, K, Ca, Mg, Sr and Ba which do not generally form strong surface complexes at pH values < 10 (Dzombak & Morel 1990, Baeyens & Bradbury 1995) and therefore do not compete with transition metals, heavy metals, trivalent metals etc. for the surface edge sorption sites.

3 Modifications to the 2SPNE SC/CE model

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 ($\sim 2 \text{ mmol kg}^{-1}$) is that the model would predict competitive effects irrespective of the valence state of the metals involved.

From this point of view, the 2SPNE SC/CE sorption model was only able to model results from experiments in which competition occurred between metals which are chemically similar (valence state, hydrolysis behaviour), e.g. Ni(II), Co(II) and Zn(II), and trivalent actinides / lanthanides. The sorption behaviour of combinations of metals which are chemically dissimilar, and do not compete with one another, e.g. divalent transition metals and trivalent actinides / lanthanides, Th(IV) and Eu(III); and U(VI) and Eu(III), could not be reproduced by the model.

In order to explain the competitive effects observed experimentally, the strong site / weak site concept was retained in the 2SPNE SC/CE sorption model but required modification. Instead of a single strong site with a fixed capacity, it was proposed that multiple sets of strong sites exist as subsets of the $\equiv \text{S}^{\text{W1}}\text{OH}$ weak sites, with average site capacities of $\sim 2 \text{ mmol kg}^{-1}$ (the site capacity of 40 mmol kg^{-1} for the weak sites was retained). 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 includes the subsets of strong sites (see Bradbury & Baeyens 2005b).

Also, in the light of the modified strong site distribution concept given above, the LFER ("Linear Free Energy Relationship") 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 (Bradbury & Baeyens 2005a) can now be rationalised and the overall concept becomes considerably more consistent.

An important finding from the competition experiments is that a spectrum of strong sites on clay minerals is involved in the uptake of metals of different valences at trace concentrations. From an operational viewpoint the simple 2SPNE SC/CE sorption model, with the current strong site capacity and protolysis constant values, can model multi-metal multi-valent competitive systems if it is 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 & Baeyens 1997).

The major implication for the sorption of any metal within a group of metals which exhibit competitive sorption is that it is not the equilibrium aqueous concentration of the individual metal which determines its sorption, but rather the sum of all the competitive effects of all of the other metals at their respective concentrations. Thus, the inventories of metals within a particular group and the solubility limits of the group members take on a more significant importance.

4 Factors influencing the sorption of radionuclides in real systems

4.1 Presence of stable isotopes

When considering real systems, a number of factors that may influence the sorption of radionuclides on clays and rocks need to be born in mind. The first is that even though the radionuclides themselves may be at trace concentrations, there may be stable isotopes present in the systems which means that the total concentration (stable + active) is much higher than "trace". This effect in itself may decrease the sorption of all nuclides which exhibit non-linear sorption. Further, for certain groups of metals which exhibit competitive sorption, e.g. divalent transition metals, trivalent actinides / lanthanides, it is the sum of all the aqueous concentrations of the members in the group which determines the overall sorption of the group members and not their individual concentrations. Thus, for example, if Ni is present at trace concentration but there are other transition metals present whose total concentration is much higher, then the Ni sorption will be determined by this higher total concentration.

4.2 Complexation with anionic ligands in real systems

Compared to sorption data measured in batch tests with simple background electrolytes, there is a further factor which tends to reduce the sorption in real systems and that is complexation with anionic ligands in the generally complex natural waters. Complexation tends to increase the fraction of non-sorbing aqueous species and thereby leads to a reduction in sorption. This is often accounted for by the "speciation factor", described in many previous publications on the development of Sorption Databases (SDBs) in safety analysis (Bradbury & Baeyens 2003a and b, Baeyens et al. 2014). However, the application of such a speciation factor as part of the modification procedure converting batch sorption values measured in simple electrolytes to those appropriate to complex rock / water systems is only valid for trace concentrations (in terms of the 2SPNE SC/CE sorption model this means that the loadings on the strong sites are well below saturation).

The calculated speciation factor is a constant, essentially independent of the equilibrium concentration of the nuclide being considered. Its effect is therefore to reduce any sorption value on an isotherm measured in the simple 1:1 electrolyte by a constant factor. At higher concentrations, speciation in the complex water chemistry not only reduces the sorption but also modifies the form of the isotherm compared with the one measured in a simple background electrolyte. A reduction in sorption through speciation implies per se that the uptake on the solid is less for a given equilibrium concentration in the complex water chemistry case i.e. at the same equilibrium concentration the nuclide loading on the solid is less. According to the 2SPNE SC/CE sorption model this in turn implies that the saturation of the strong sites takes place at higher equilibrium concentrations in complex water chemistries. This therefore leads to a change in the shape of the sorption isotherm in the complex water chemistry compared to that in the simple electrolyte. In other words, the isotherm measured in a simple 1:1 electrolyte cannot be converted to an isotherm corresponding to the complex porewater chemistry by the simple application of a speciation conversion factor. The montmorillonite isotherm in the complex porewater chemistry is not simply (linearly) reduced by the speciation conversion factor to the same degree over the whole concentration range (the only region where there is a linear reduction is for loadings much less than the strong site saturation value).

These effects are illustrated in Fig. 4.1 for Eu sorption on montmorillonite. The red solid curve is the montmorillonite isotherm measured in a simple 1:1 electrolyte (Tab. 4.1, Case A) and, at the pH considered, only cations, positively charged and neutral hydrolysis species exist in solution, all of which sorb. The blue solid line corresponds to an Eu isotherm on montmorillonite calculated for a water chemistry (Tab. 4.1, Case B) in which Eu forms aqueous complexes with carbonate, sulphate and chloride. The results of the speciation calculations are given for the two cases considered here in Tab. 4.2. Thus, at any given total concentration in the two cases, the concentration of sorbing species in the simple electrolyte is greater than in the complex porewater chemistry which implies that the sorption is higher, as can be seen in Fig. 4.1. However, there is another effect which is that the strong sites saturate at a higher total Eu concentration in the complex porewater chemistry case than in the simple electrolyte case (because of the speciation). This is illustrated by the dotted red and blue lines in Fig. 4.1. Therefore, the shape of the isotherms in the two cases is different and the effect is that the two isotherms get closer together as the Eu equilibrium concentration increases (indicated by the black arrows in Fig. 4.1). Thus, the shape of the montmorillonite isotherm is dependent not only on the equilibrium concentration of Eu, but also on its aqueous speciation, which in turn depends on the composition of the complex porewater chemistry and of course the pH.

Finally, the question then arises as to what is meant by "trace", i.e. up to until what concentration can the conversion factor approach be used. A simple answer is that as long as the sorption of a particular nuclide on montmorillonite / illite in a simple electrolyte lies in the linear sorption range, the concentration can be regarded as being "trace". Or, alternatively, from the point of view of the 2SPNE SC/CE sorption model, the equilibrium nuclide concentration can be regarded as "trace" provided that the loadings on the strong sites are well below saturation. As a broad indicator, equilibrium concentrations $< 10^{-8}$ M can be regarded as "trace".

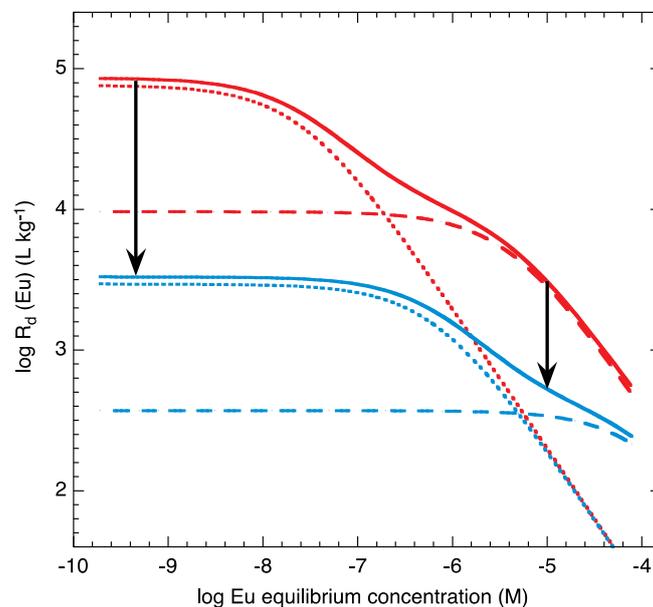


Fig. 4.1: Eu isotherms on montmorillonite in two different water compositions at pH = 7.25.

Calculations are carried out with the 2SPNE SC/CE sorption model. The contribution to the overall sorption (solid lines) by the strong (dotted lines) and the weak (dashed lines) sites are also shown.

Tab. 4.1: Porewater compositions at pH = 7.25.

Simple 1:1 background electrolyte, (Case A) and complex water chemistry (Case B).

Element	Case A: Simple background electrolyte	Case B: Complex porewater chemistry
	Concentration [M]	
Na	2.74×10^{-1}	2.74×10^{-1}
K	-	1.55×10^{-3}
Mg	-	7.64×10^{-3}
Ca	-	1.32×10^{-2}
ClO ₄	2.74×10^{-1}	-
Cl	-	1.91×10^{-1}
HCO ₃ /CO ₃	-	2.83×10^{-3}
SO ₄	-	6.16×10^{-2}

Tab. 4.2: Eu speciation in the simple background electrolyte (Tab. 4.1, Case A) and in a complex porewater composition at pH = 7.25 (Tab. 4.1, Case B).

The total Eu equilibrium concentration in both solutions is equal to 10^{-6} M.

Aqueous species	Case A: Simple background electrolyte	Case B: Complex porewater chemistry
	Species [%]	
Eu ³⁺	78.6	4.4
EuOH ²⁺	19.6	1.1
Eu(OH) ₂ ⁺	1.8	< 0.1
EuCO ₃ ⁺	-	35.5
Eu(CO ₃) ₂ ⁻	-	0.3
EuSO ₄ ⁺	-	35.5
Eu(SO ₄) ₂ ⁻	-	21.5
EuCl ²⁺	-	1.7

4.3 Summary

Briefly, in summary, because a radionuclide may be present at trace concentrations in a real system (say $< 10^{-8}$ M), it does not automatically mean that its sorption behaviour is that associated with trace concentrations. Factors such as:

- The presence of stable isotopes in the systems may mean that the total concentration (stable + active) is much higher than "trace".
- The presence of groups of metals which exhibit competitive sorption e.g. divalent transition metals, trivalent actinides / lanthanides. It is then the sum of all the aqueous concentrations of the members in the group which determines the overall sorption of the group members and not their individual concentrations.

Finally, the application of speciation factors as part of the modification procedure converting batch sorption values measured in simple electrolytes to those appropriate to complex rock / water systems is only valid for trace concentrations. At higher concentrations (especially considering the factors above), speciation in the complex water chemistry not only reduces the sorption but also alters the form of the isotherm compared with the one measured in a simple background electrolyte. Therefore, speciation conversion factors calculated at trace concentrations may not be valid at higher concentrations.

5 Illustrative example of a repository near-field competitive sorption scenario

5.1 General

In real systems, the influence of competition on radionuclide sorption depends upon the cocktail of metals present in the aqueous phase, their concentrations and their speciation i.e. the water chemistry, the sorbents present and the surface complexation constants. The fact that competitive sorption is a real issue, which may lead to reduced sorption values in all concentration ranges, has been illustrated experimentally (see Figs. 2.1 and 2.2). However, gaining a quantitative insight into the potential magnitude of the reduction in sorption values caused by competitive sorption in real systems is not easy, especially when the wide range of possible conditions is considered. It is unrealistic to expect that this problem can be solved experimentally in such varied and complex systems.

The only practical possibility to assess the influence of competitive sorption, and bound its effects, is via modelling. Having stated this, it must also be realised that a modelling approach has its limitations. These are associated with the assumptions in the sorption model itself and the uncertainties in the large volumes of data and parameters required to make the calculations. All of the values and data used in the following calculations are taken from Baeyens & Bradbury (2017) and Bradbury & Baeyens (2017) for montmorillonite / bentonite and illite / Opalinus Clay, respectively.

5.2 Maximum limit concentrations

The starting point for the calculations in this illustrative example are the recommended "maximum limit concentrations" of the most important metal nuclides in the bentonite near-field of a high-level waste repository as listed in Tab. B-1 in Appendix B (Berner 2014). From this table the metals have been divided, in the first instance, into three broad categories according to their valence together with their concentrations, Group 1: divalent transition and divalent heavy metals, Group 2: trivalent metals and Group 3: tetravalent metals, Tab. 5.1.

As stated in Chapter 2, whether metals exhibit competitive sorption depends not only on valence, but also on similarities in hydrolysis behaviour and on consistency in the LFER representation (Baeyens & Bradbury 2017 and Bradbury & Baeyens 2017). The nuclides given in bold type in each individual group are considered to sorb competitively with one another, whereas those nuclides given in italics are considered to be non-competitive. Further explanations are given in sections 5.4 and 5.6.

Tab. 5.1: "Maximum limit concentrations" of metals in the porewater of a bentonite near-field of a high level waste repository (Tab. D-1 in Appendix D).

Group 1: Divalent metals		Group 2: Trivalent metals		Group 3: Tetravalent metals	
Nuclide	Max. limit conc. [M]	Nuclide	Max. limit conc. [M]	Nuclide	Max. limit conc. [M]
Fe *	3.7×10^{-5}	Sm	2.0×10^{-7}	Zr	1.0×10^{-7}
Ni	6.0×10^{-5}	Ho	3.0×10^{-6}	Sn	9.0×10^{-8}
Pb	9.0×10^{-7}	Ac	3.0×10^{-6}	Th	4.0×10^{-9}
Be	9.0×10^{-7}	Pu	7.0×10^{-10}	U	2.0×10^{-7}
Pd	6.0×10^{-8}	Am	3.0×10^{-6}	Np	1.0×10^{-8}
		Cm	3.0×10^{-6}	Tc	4.0×10^{-9}
				Po	7.0×10^{-7}

* Fe(II) is included in the table because it is ubiquitous in the porewater and arises from the saturation of siderite (see Appendix C, Tab. C-2).

5.3 Calculation procedure

On the basis of the evidence and restrictions given above, it is assumed that competitive sorption occurs between the metals within each of these three groups but not between metals in different groups.

In the calculations illustrating the influence of competitive sorption at high concentrations, the "maximum limit concentrations" given in Tab. 5.1 are taken to be equilibrium values existing simultaneously in the bentonite porewater. This is already a very extreme approach. Diffusion away from the source of radioactive waste material into the bentonite and sorption processes would tend to decrease these concentrations in the porewater resulting in itself in an increase in sorption and a decrease in competition with increasing distance into the bentonite.

Also, in reality, it is likely that chemically similar metals at such high concentrations would form solid solution phases or co-precipitate, with the consequent decrease in concentrations.

For each of the three groups of nuclides in Tab. 5.1 the calculations were carried out using the 2SPNE SC/CE model and the data given in Appendices A, B, C and D. The modelling procedure was as follows.

First, calculations were made in the MX-80 bentonite porewater / mineral system to produce sorption values for each individual nuclide at trace concentration with no competition (Tabs. 5.2 to 5.4, row 1). These sorption values are approximately the same as those derived previously for the MX-80 SDB (Baeyens et al. 2014).

Secondly, sorption values for each individual nuclide at the equilibrium concentrations given in Tab. 5.1 were calculated with no competition (Tabs. 5.2 to 5.4, row 2).

Eu was taken as the chemical analogue for the trivalent lanthanides Sm and Ho and the same surface complexation constants were assumed. Am was taken as the chemical analogue for Ac and Cm. However, the hydrolysis and surface complexation constants for Eu(III) and Am(III) are very similar (Baeyens & Bradbury 2017) and Eu(III) is therefore a very reasonable chemical analogue for all of the above trivalent metals.

Thirdly, in any one group of nuclides in Tab. 5.1, sorption values for each nuclide were calculated simultaneously with all of the others at the corresponding (equilibrium) concentrations given in Tab. 5.1 in the MX-80 bentonite / porewater system (Tabs. 5.2 to 5.4, row 3) i.e. competition included.

5.4 Divalent metals

Soltermann et al. (2014) have studied the competitive sorption behaviour between Zn(II) and Fe(II) on a synthetic iron-free montmorillonite. In order to determine whether sorption competition was taking place or not, the sorption of a Zn(II) was measured at trace concentration in the presence of sequentially increasing concentrations of Fe(II) (the "blocking" element). If the sorption of Zn remained constant as a function of the blocking Fe(II) concentration, then sorption competition was not active. If on the other hand, the sorption of Zn at trace concentration decreased as a function of the Ni(II) concentration, then sorption competition was occurring. The results for the Zn(II)/Fe(II) experiments are shown in Fig. 5.1 and indicate that these two transition metals are competitive.

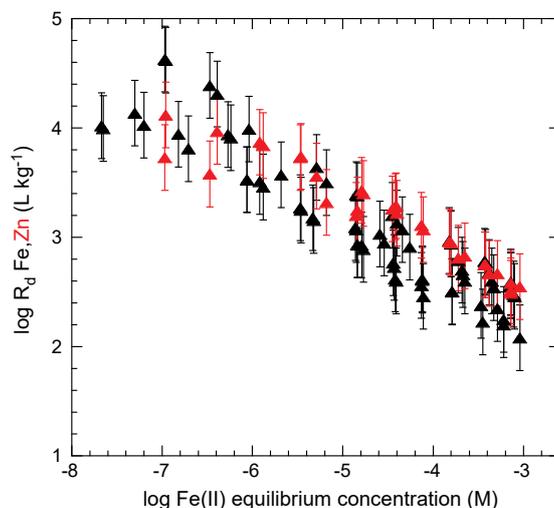


Fig. 5.1: Fe(II) sorption isotherm and the sorption of trace Zn in the presence of increasing Fe(II) concentrations ($Zn_{tot} = 3 \times 10^{-8} \text{ M}$) on a synthetic iron-free montmorillonite (Soltermann et al. 2014).

(▲) Fe(II), (▲) Zn.

There are no reliable sorption data available for Pb(II), Be(II) and Pd(II). These metals hydrolyse more strongly than divalent transition metals. In the case of Pb(II) the surface complexation constant for the first surface complex ($\equiv S^{\text{S}}\text{OPb}^+$) falls outside the LFER derived for divalent metals on montmorillonite (Figure 4.7 in Baeyens & Bradbury 2017). In the pH range 5 to 9 the major sorbing species for Be(II) are most probably BeOH^+ , and for Pd(II), $\text{Pd}(\text{OH})_2^0$ (see for example Figures 7.8 and 7.9 respectively in Baeyens & Bradbury 2017), whereas the divalent cation is the main sorbing species for the transition metals. Due to the lack of data it is somewhat difficult to

say whether or not sorption competition takes place. The sorption of Be(II) is certainly more complex than the transition metals and the main sorbing species for Pd(II) is the neutral hydroxyl species which probably sorbs very strongly and accesses different sorption sites to bivalent cations. It is assumed here that Pb(II), Be(II) and Pd(II) do not compete with divalent transition metals.

With reference to Tab. 5.1, the main competition between divalent transition metals takes place between Ni(II) and Fe(II). The latter arises in the porewaters of bentonite and Opalinus Clay through saturation with siderite (Mäder 2009). Hydrolysis and surface complexation reactions and constants for Ni(II) and Fe(II) are given in Appendix A, Tab. A-1.

The reductions in sorption at high concentrations compared with those at trace concentrations arise predominantly from nonlinear sorption behaviour, as illustrated in Fig. 5.2a for Ni. The sorption values for Ni(II) and Fe(II) at the maximum limit concentrations (Tab. 5.1) are given in Tab. 5.2, row 2.

Tab. 5.2: Summary of calculations for divalent elements (Group 1, Tab. 5.1).

Calculation conditions	log R _d [L kg ⁻¹]	
	Fe	Ni
Trace concentrations with no competition	5.7	3.5
Ni(II) at the maximum limit concentrations and Fe(II) saturation with siderite with no competition	2.8	2.0
Simultaneous calculations for Ni(II) at the maximum limit concentrations and Fe(II) saturation with siderite with competition	2.8	1.6

The influence of Fe(II) competition at a constant concentration of 3.7×10^{-5} M (siderite saturation) on the Ni(II) isotherm is shown in Fig. 5.2c and d. The change in the Ni(II) isotherm is mainly the result of a reduction in the contributions of the strong sites to Ni(II) sorption due to the competitive sorption effects of Fe(II) i.e. the strong sites are mainly occupied by Fe(II). The tendency is for the Ni(II) sorption to be dominated by the weak sites, and for the sorption to become constant as a function of concentration.

In Fig. 5.2a and b it can be clearly seen that the Ni(II) sorption isotherm (black lines) is essentially determined by sorption on the strong sites (red lines) right up to the "maximum limit concentration" of Ni(II). At increasing Ni equilibrium concentrations, the sorption on the weak sites becomes more important (blue lines). At the "maximum limit concentration" of Ni(II) of 6×10^{-5} M (see Tab. 5.1) the Ni(II) sorption is already reduced by more than one order of magnitude compared to its value at trace concentrations.

In Fig. 5.2c and d the sorption isotherm of Ni(II) up to the "maximum limit concentration" is calculated in the presence of Fe(II) at its equilibrium concentration given in Tab. 5.1. As can be seen, the sorption of Ni(II) becomes essentially linear over the whole concentration range because sorption on the strong sites has been greatly reduced through the competition by Fe(II), and the Ni(II) uptake is occurring predominantly on the weak sites. For Ni(II) at trace concentrations the influence of competition is significant, but the competitive effects decrease with increasing equilibrium Ni(II) concentrations.

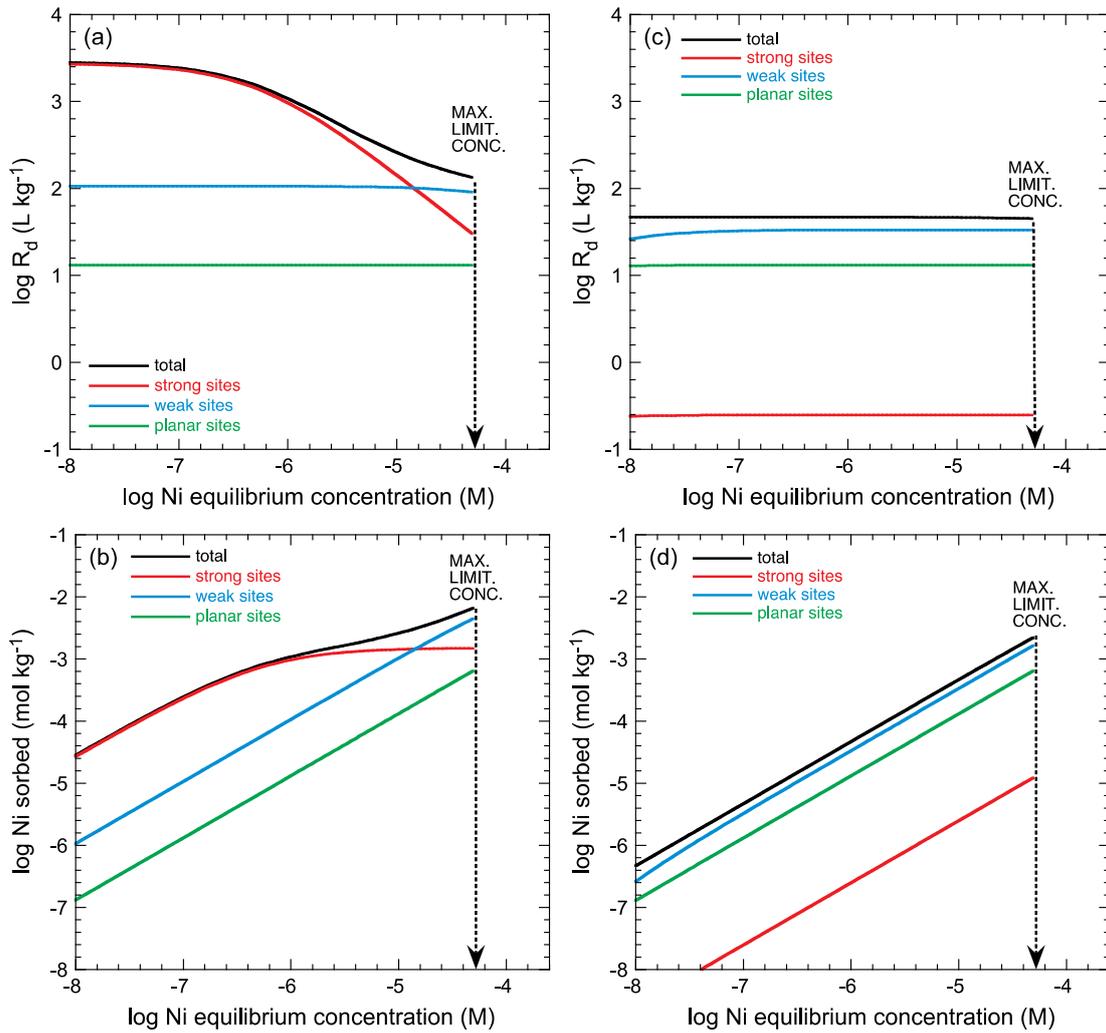


Fig. 5.2: Calculated Ni sorption isotherm for MX-80 in the bentonite porewater (pH 7.79); (a), (b) in the absence of competing metals and (c), (d) in the presence of Fe(II) at siderite saturation, 3.7×10^{-5} M.

The contributions to the overall sorption (black lines), from the strong sites (red lines), from the weak sites (blue lines), and from cation exchange (green lines) are given.

5.5 Trivalent metals

All of the trivalent metals listed in Tab. 5.1 are taken to be mutually competitive. The surface complexation constants for montmorillonite for Sm, Ho, Ac, Pu and Cm were obtained from the LFER in Figure 4.7 in Baeyens & Bradbury (2017) and are summarised in Appendix A, Tab. A-2.

Solid liquid distribution ratios for Sm(III), Ho(III), Ac(III), Am(III), Cm(III) and Pu(III) at trace and maximum limit concentrations are given in Tab. 5.3. Again, the influence of concentration on their distribution ratios can be clearly seen.

Tab. 5.3: Summary of calculations for trivalent elements (Group 2, Tab. 5.1).

Calculation conditions	log R _d [L kg ⁻¹]					
	Sm	Ho	Ac	Am	Cm	Pu
Trace concentrations with no competition	4.1	4.1	4.7	4.7	4.7	4.7
Max. limit concentrations with no competition	3.7	3.1	3.3	3.3	3.3	4.7
Simultaneous calculations for all metals at maximum limit concentrations with competition	2.8	2.8	3.0	3.0	3.0	2.8

As an illustrative example of the influence of competition, Fig. 5.3 shows the isotherm for Eu(III) calculated in the presence of the trivalent metals at the concentrations given in Tab. 5.1. (Eu(III) was chosen for this simulation since there are no weak site data for the other trivalent metals, see Appendix A, Tab. A-3. Also, note that in the calculations Eu(III) is not considered to precipitate.)

For the trivalent metals (Tab. 5.1) the reduction factors for the full competition calculation (Tab. 5.3, row 3) are less than for Ni(II), essentially because the total concentration of trivalent metals is considerably less and hence the strong sites are still making an important contribution to the overall sorption.

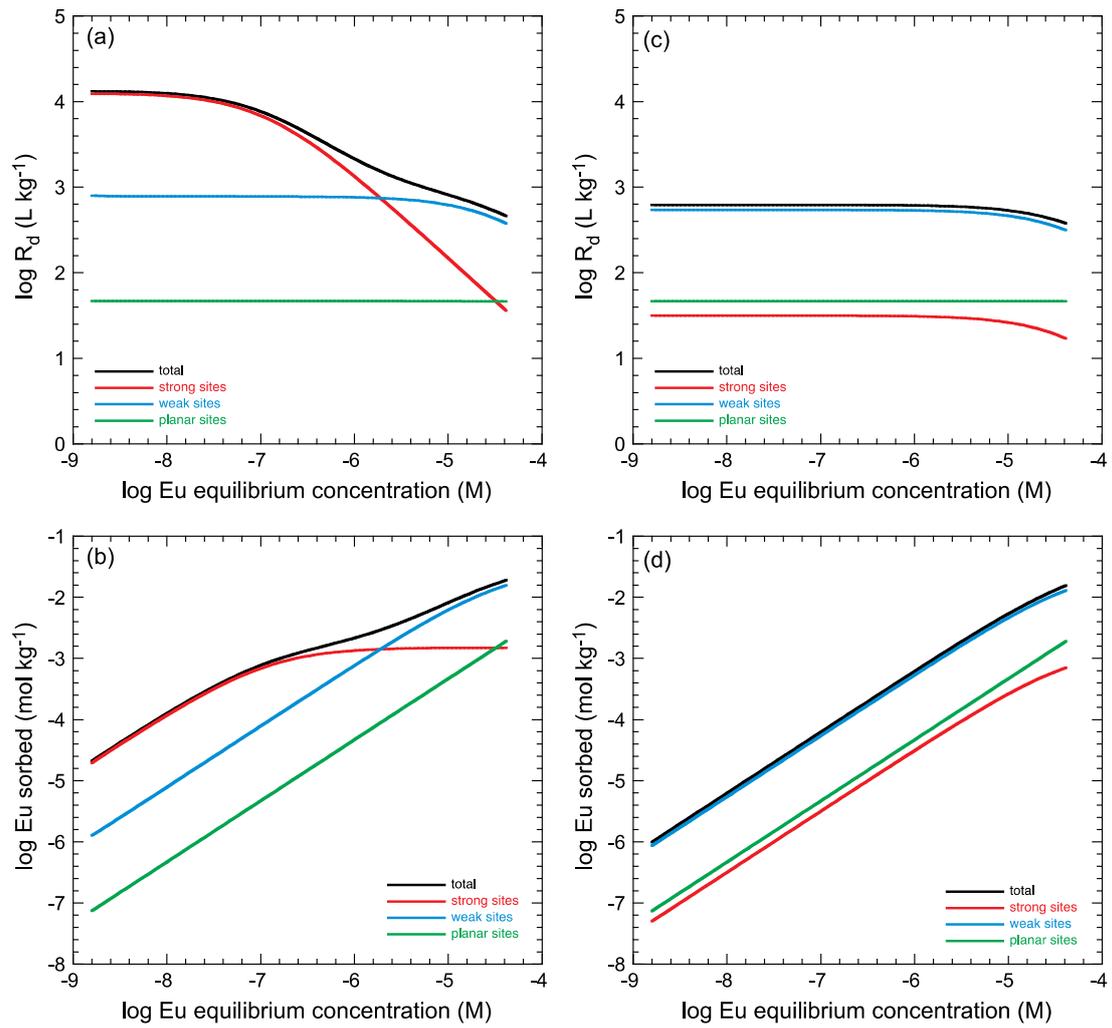


Fig. 5.3: Calculated Eu sorption isotherm for MX-80 in the bentonite porewater (pH 7.79) (a), (b) in the absence of competing metals and (c), (d) in the presence of competing metals whose equilibrium concentrations are as given in Tab. 5.1.

The contributions to the overall sorption (black lines), from the strong sites (red lines), from the weak sites (blue lines), and from cation exchange (green lines) are shown.

5.6 Tetravalent metals

5.6.1 Tc(IV), Po(IV) and Zr(IV)

There are no reliable sorption data for Tc(IV), Po(IV) and Zr(IV). In addition, the hydrolysis data for Tc(IV) and Zr(IV) are somewhat uncertain. In the case of Po(IV) they are unknown. Consequently, it is not possible to say anything about the sorption behaviour of Po(IV) and it is assumed here to be non-competitive with the tetravalent actinides

The hydrolysis behaviour of Tc(IV) is shown in Fig. 5.4. The main Tc(IV) species in the pH range 5 to 9 is an oxy-hydroxy complex and is of a different nature to the tetravalent actinides species. According to the "competition criteria" given in Chapter 2, Tc(IV) is not considered to be competitive with the tetravalent actinides.

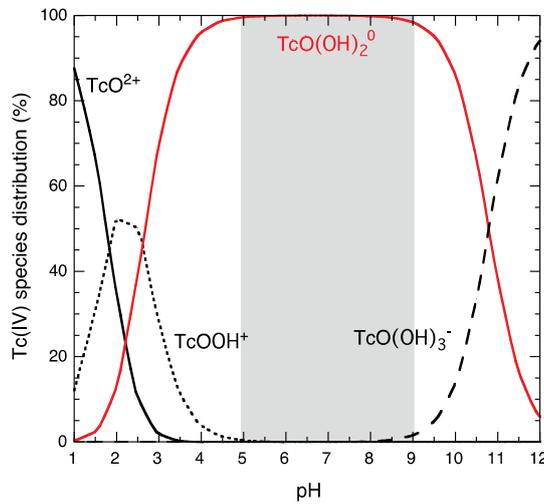


Fig. 5.4: Aqueous speciation of Tc(IV) in 0.1 M NaClO₄ as function of pH.

The hydrolysis behaviour of Zr(IV) is shown in Fig. 5.5.

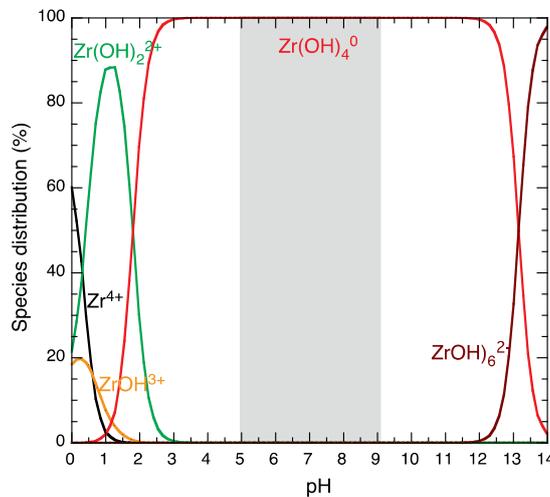


Fig. 5.5: Aqueous speciation of Zr(IV) in 0.1 M NaClO₄ as function of pH.

In the pH range 5 to 9 the neutral tetrahydroxy complex of Zr(IV) is dominant *cf.* Sn(IV) in the following section. Tetrahydroxy complexes tend to sorb strongly, however, since a pentavalent hydroxy species for Zr(IV) does not exist, it was not possible to estimate a surface complexation constant from a LFER. Again, because of a general lack of data regarding the sorption characteristics of Zr(IV) a definitive statement regarding its sorption competitiveness with the tetravalent actinides could not be made.

5.6.2 Sn(IV)

A Sn(IV) sorption edge has been measured and modelled (see for example Figure 3.8 in Baeyens & Bradbury 2017). However, there was considerable uncertainty regarding the hydrolysis data and the speciation calculations indicated that the major aqueous species in the pH range 5 to 9 were Sn(OH)_4^0 and Sn(OH)_5^- , Fig. 5.6) but according to the modelling the main sorbing aqueous species were Sn(OH)_3^+ and Sn(OH)_4^0 ; dominated by the former. This constellation was inconsistent with all previous modelling experiences.

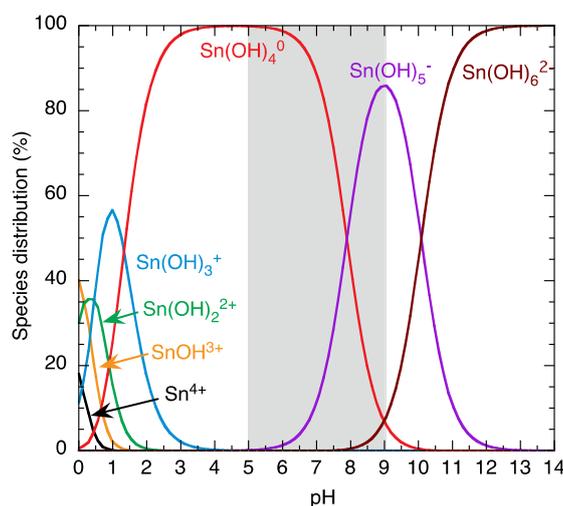


Fig. 5.6: Aqueous speciation of Sn(IV) in 0.1 M NaClO_4 as function of pH.

5.6.3 Th(IV), Np(IV) and U(IV)

The speciation of the tetravalent actinides is summarised in Fig. 5.7. It is very clear from these plots that their hydrolysis behaviour is very similar and the strong site surface complexation constants for U(IV) and Np(IV) can be derived from the LFER obtained for Th(IV) (see Figure 4.12 in Baeyens & Bradbury 2017) and are summarised in Appendix A, Tab. A-4.

For tetravalent elements there are no experimental sorption isotherms available in the open literature because of solubility constraints, and hence surface complexation constants for weak sites are not available. Any estimates based on the linear free energy relationship for weak sites (Figure 4.17 in Baeyens & Bradbury 2017) lay well outside the range of the experimental data available and for this reason were considered to be too uncertain to be used.

For the sorption competitive tetravalent actinides Th(IV), U(IV) and Np(IV) sorption calculations were based on the uptake on strong sites only (Tab. 5.4).

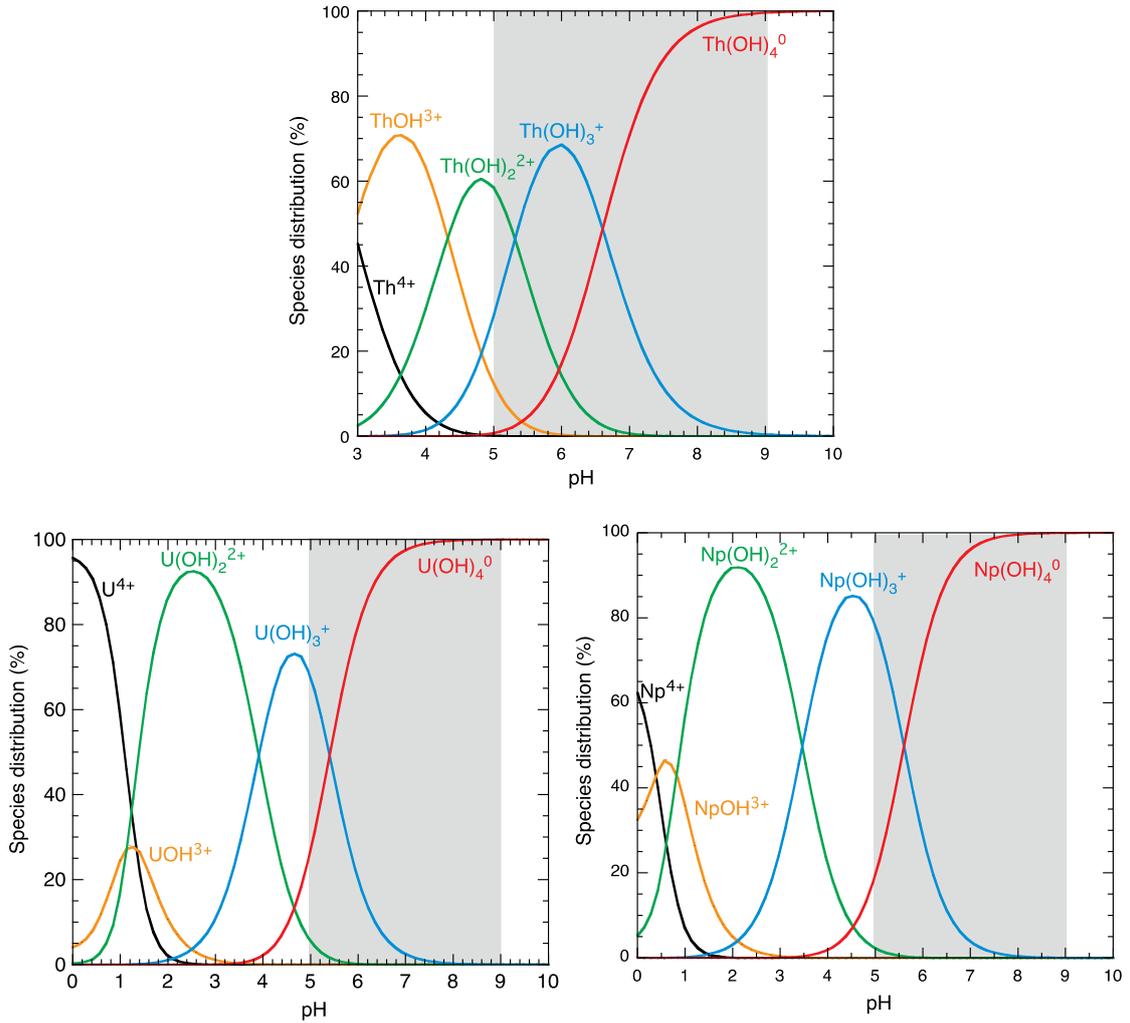


Fig. 5.7: Aqueous speciation of Th(IV), U(IV) and Np(IV) in 0.1 M NaClO₄ as a function of pH.

Tab. 5.4: Summary of calculations for tetravalent elements (Group 3, Tab. 5.1).

Calculation conditions	log R _d [L kg ⁻¹]		
	Th	U	Np
Trace concentrations with no competition	5.4	4.9	5.5
Max. limit concentrations with no competition	5.2	3.9	5.0
Simultaneous calculations for all metals at max. limit concentrations with competition	4.3	3.7	4.4

6 The influence of competitive sorption on sorption values in Opalinus Clay

The Opalinus Clay mineralogy and porewater chemistry are given in Appendix E, Tabs. E-1 and E-2 respectively.

6.1 Divalent metals

The Opalinus Clay porewater is also saturated with respect to siderite and the Fe(II) equilibrium concentration is slightly higher than in the bentonite porewater, 5.2×10^{-5} M compared with 3.7×10^{-5} M. This implies that Fe(II) will effectively block the strong sites to the uptake of Ni(II). The sorption isotherm for Ni(II) in the Opalinus Clay / porewater system is given in Fig. 6.1. Similar as for the MX-80 bentonite the Ni isotherms are presented in the absence (Fig. 6a and b) and presence of ferrous iron (Fig. 6.1c, d). The calculations were made using the data in Bradbury & Baeyens (2017, Appendices C and D) and in this report Appendices B and E.

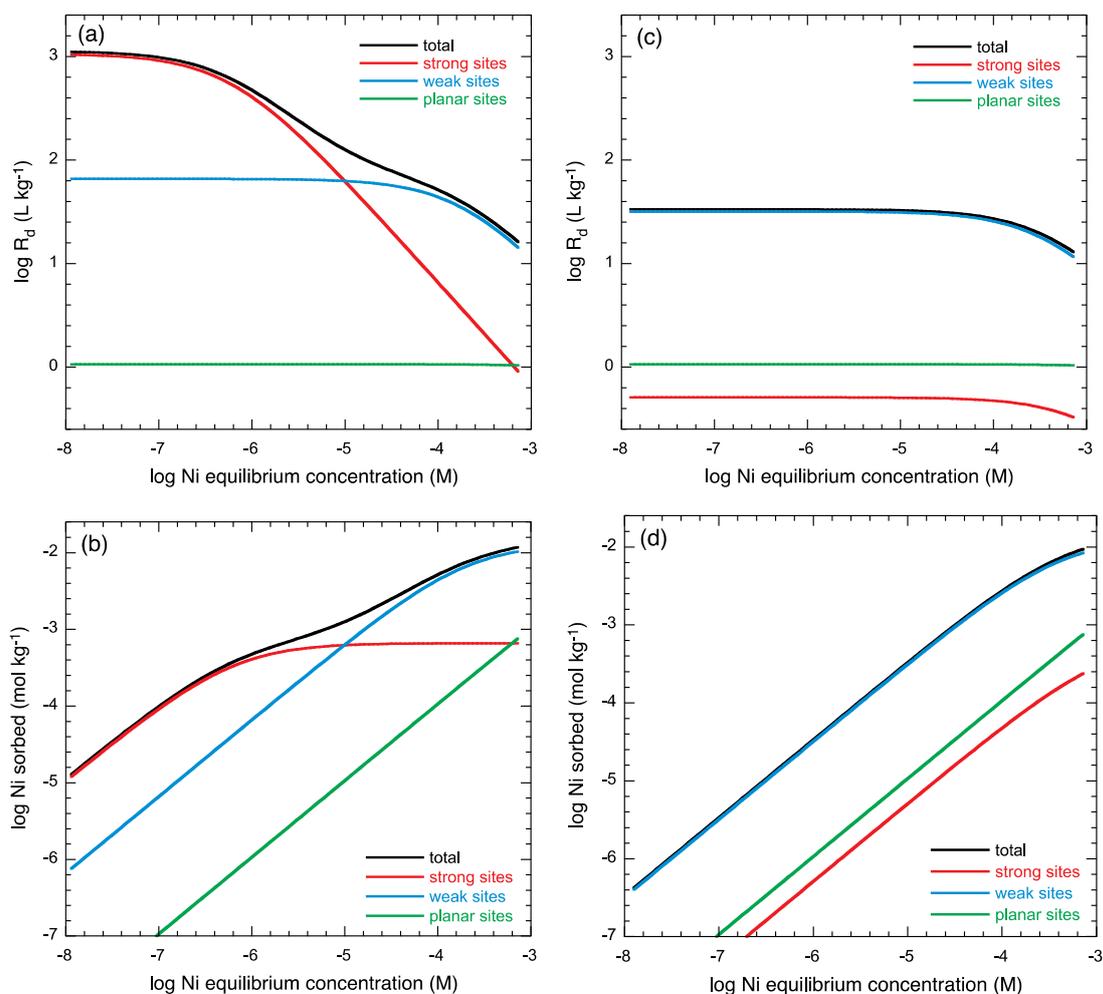


Fig. 6.1: Calculated Ni sorption isotherm in the Opalinus Clay / porewater (pH 7.20) system. The contributions to the overall sorption (black lines), from the strong sites (red line), from the weak sites (blue line), and from cation exchange (green line) are given.

As can be seen from Fig. 6.1 the sorption of Ni(II) in Opalinus Clay in the presence of 5.2×10^{-5} M Fe(II) is dominated by the uptake on weak sites and is linear as a function of Ni equilibrium concentration up to $\sim 4 \times 10^{-5}$ M which is the solubility limit of Ni in the Opalinus Clay / pore-water system. The solubility limiting phase is NiCO₃.

The influence of competitive sorption by Fe(II) on the uptake of Ni(II) is further illustrated in Tab. 6.1.

Sorption values for Ni(II) at trace concentration with no competition and in the presence of Fe(II) at siderite saturation over all Ni(II) concentrations (constant sorption) are given in Tab. 6.1. The reduction in sorption is approximately a factor of 40.

Tab. 6.1: Ni(II) sorption in Opalinus Clay at trace concentration (no competition) and in the presence of 5.2×10^{-5} M Fe(II).

Calculation conditions	log R _d [L kg ⁻¹]	
	Fe	Ni
Trace concentrations with no competition	4.3	3.0
Simultaneous calculations for Ni(II) at max. solubility limit in the presence of Fe(II) saturation with siderite	2.0	1.4

6.2 Trivalent metals

Competitive sorption effects between trivalent actinides / lanthanides in Opalinus Clay is anticipated. The effect of the competition i.e. sorption reduction, depends on the sum of their local concentrations. The concentrations in the Opalinus Clay will depend on how long the source concentration into the MX-80 is maintained and the diffusion time. The former is an inventory issue and the latter will be a function of the diffusion coefficient in bentonite and the spatial and temporal development of sorption through the 80 cm of bentonite backfill. A very conservative case may be considered in that the input concentrations into the Opalinus Clay are considered be the same as the source concentration inputs into the bentonite i.e. no inventory limitations and long diffusion times. The calculations in Opalinus Clay for this worst case scenario are given in Tab. 6.2 and indicate that the maximum possible reductions in sorption lie in the region of factors between ~ 10 to 100 compared with the values at trace concentration.

Tab. 6.2: Comparison of sorption values in Opalinus Clay for trivalent actinides / lanthanides calculated at trace concentrations with no competition and at maximum limit concentrations with competition.

Calculation conditions	log R _d [L kg ⁻¹]		
	Sm and Ho	Ac, Am and Cm	Pu
Trace concentrations with no competition	3.2	3.9	4.0
Simultaneous calculations for all metals at max. limit concentrations with competition	2.1	2.4	2.0

6.3 Tetravalent metals

At the bentonite / Opalinus Clay boundary the concentrations of the tetravalent actinides will always be less than or equal to the maximum limit concentrations (Tab. 6.1) but are very difficult to estimate. Following the arguments given in section 6.2 for trivalent metals, the competitive sorption calculations in Opalinus Clay are, for the worst-case scenario i.e. at the maximum limits of concentration, given in Tab. 6.3 (data in Bradbury & Baeyens 2017, Appendices C and D and in this report, Appendices B and E). The indications are that the maximum possible reductions in sorption are ~ 3 compared with the values at trace concentration.

Tab. 6.3: Comparison of sorption values in Opalinus Clay for tetravalent actinides calculated at trace concentrations with no competition and at maximum limit concentrations with competition.

Calculation conditions	log Ra [L kg ⁻¹]		
	Th	U	Np
Trace concentrations with no competition	3.7	3.4	4.4
Simultaneous calculations for all metals at maximum limit concentrations with competition	3.3	3.0	4.0

7 Summary of results and conclusions

In real systems there are two main factors which may lead to a decrease in radionuclide sorption value compared to those at trace concentrations which are normally considered in Sorption Data Bases (SDB) used in Performance Assessment calculations, see for example Baeyens et al. (2014). These are concentration effects and competition effects.

Thus, even though the radionuclides themselves may be at trace concentrations, there may be stable isotopes present in the systems which means that the total concentration (stable + active) is much higher than "trace". This leads to a decrease in sorption for all radionuclides which exhibit non-linear sorption.

Certain groups of metals may exhibit competitive sorption because they are taken up by the same type of sites on clay minerals e.g. divalent transition metals, trivalent actinides / lanthanides. In such a case the sum of all the aqueous concentrations of the members in the group determines the overall sorption of the group members and not their individual concentrations.

In this report a more fundamental approach using the 2SPNE SC/CE sorption model has been taken. Both concentration and competition effects have been considered simultaneously for the sorption calculations in the MX-80 bentonite and Opalinus Clay systems. Radionuclide concentrations ("maximum limit concentrations") were taken from Berner (2014).

The reductions in sorption resulting from competition and/or high concentrations are predominantly due to a reduction in the contributions of the strong sites to sorption. The results can be summarised as follows:

Competing divalent transition metals

MX-80 Bentonite: The bentonite porewater is saturated with siderite which gives rise to a fixed Fe(II) concentration of 3.7×10^{-5} M which is the main competitive sorption metal for divalent transition metals. The influence of Fe(II) competition almost eliminates the contribution of strong sites to Ni(II) sorption. Thus Ni(II) sorbs predominantly on the weak sites and the sorption becomes constant as a function of concentration. The sorption is reduced from a log R_d value of 3.5 L kg⁻¹ at trace concentrations to a constant log R_d value of 1.6 L kg⁻¹ i.e. by almost 2 orders of magnitude.

Opalinus Clay: Opalinus Clay porewater is also saturated with respect to siderite giving a fixed Fe(II) concentration of 5.2×10^{-5} M. The argumentation for the influence of Fe(II) sorption competition on the sorption of divalent transition metals is the same as for MX-80 bentonite. Ni(II) sorption is reduced from a log R_d value of 3.0 L kg⁻¹ at trace concentrations to a constant log R_d value of 1.4 L kg⁻¹, i.e. by a factor of ~ 40.

Competing trivalent metals

MX-80 Bentonite and Opalinus Clay: Because the evolution in time and space of the concentrations of lanthanides / actinides in the Opalinus Clay is difficult to calculate, and depends on, amongst other factors, waste inventories and the sorption profiles in the MX-80 bentonite, a worst-case calculation for sorption in Opalinus Clay at the maximum limit concentrations (Tab. 7.1) taking competition into account was carried out and is shown in Tab. 7.1. The values for Opalinus Clay are compared with the values calculated for MX-80.

Tab. 7.1: Comparison of sorption values for trivalent lanthanides and actinides considering their maximal limit concentrations and taking into account competitive sorption.

System	log Ra [L kg ⁻¹]		
	Sm and Ho	Ac, Am and Cm	Pu
MX-80 bentonite	2.8	3.0	2.8
Opalinus Clay	2.1	2.4	2.0

Competing tetravalent actinides metals

MX-80 Bentonite and Opalinus Clay: The competitive sorption between tetravalent actinides in the MX-80 bentonite system at the maximum limit concentrations saturates the strong sites and thereby has an influence on their individual sorption values. The same is true at the bentonite/Opalinus Clay boundary since, in the worst case, the concentrations of the tetravalent actinides will also be at the maximum limit concentrations. The sorption in MX-80 bentonite and Opalinus Clay at the maximum limit concentrations (extremely conservative) is summarised in Tab. 7.2.

Tab. 7.2: Comparison of sorption values for tetravalent actinides considering their maximal limit concentrations and taking into account competitive sorption.

System	log Ra [L kg ⁻¹]		
	Th	U	Np
MX-80 bentonite	4.3	3.7	4.4
Opalinus Clay	3.3	3.0	4.0

Finally, it should be stated once more that the results presented here are based on calculations with the 2SPNE SC/CE sorption model and are subject to the assumptions and restrictions associated with it. All of the calculations used the data contained in Baeyens & Bradbury (2017) and Bradbury & Baeyens (2017) for montmorillonite/bentonite and illite/Opalinus Clay, respectively.

The sorption databases to be developed for future safety analysis will be based on the bottom-up approach where competitive sorption will be included in the sorption model calculations.

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Appendix A: Metal hydrolysis and surface complexation data for montmorillonite and illite

Tab. A-1: Hydrolysis and surface complexation reactions and constants for Ni(II) and Fe(II).

The surface complexation constants were obtained from Appendices B, C and D in Baeyens & Bradbury (2017) and Bradbury & Baeyens (2017).

Hydrolysis reaction	Log _{OH} K _x	Surface complexation reaction	log ^S K _{x-1}	
			mont.	illite
Ni ²⁺ + H ₂ O ⇌ NiOH ⁺ + H ⁺	-9.86	≡S ^S OH + Ni ²⁺ ⇌ ≡S ^S ONi ⁺ + H ⁺	-0.6	0.7
		≡S ^{W1} OH + Ni ²⁺ ⇌ ≡S ^{W1} ONi ⁺ + H ⁺	-3.3	-1.8
Ni ²⁺ + 2H ₂ O ⇌ Ni(OH) ₂ ⁰ + 2H ⁺	-19	≡S ^S OH + Ni ²⁺ + H ₂ O ⇌ ≡S ^S ONiOH ⁰ + 2H ⁺	-10	-8.2
Ni ²⁺ + 3H ₂ O ⇌ Ni(OH) ₃ ⁻ + 3H ⁺	-30	≡S ^S OH + Ni ²⁺ + 2H ₂ O ⇌ ≡S ^S ONi(OH) ₂ ⁻ + 3H ⁺	-20	-17.3
Fe ²⁺ + H ₂ O ⇌ FeOH ⁺ + H ⁺	-9.1	≡S ^S OH + Fe ²⁺ ⇌ ≡S ^S OFe ⁺ + H ⁺	1.7	2.1 *
		≡S ^{W1} OH + Fe ²⁺ ⇌ ≡S ^{W1} OFe ⁺ + H ⁺	-2.0	-1.2 *

* From LFER, Table 6.1 in Bradbury & Baeyens (2017)

Tab. A-2: Hydrolysis and surface complexation reactions and constants for Eu/Sm/Ho(III), Am/Ac/Cm(III) and Pu(III).

The surface complexation constants were obtained from Appendices C and D in Baeyens & Bradbury (2017) and Bradbury & Baeyens (2017).

Hydrolysis reaction	Log _{OH} K _x	Surface complexation reaction	log ^S K _{x-1}	
			mont.	illite
Eu ³⁺ + H ₂ O ⇌ EuOH ²⁺ + H ⁺	-7.2	≡S ^S OH + Eu ³⁺ ⇌ ≡S ^S OEu ²⁺ + H ⁺	1.6	1.9
		≡S ^{W1} OH + Eu ³⁺ ⇌ ≡S ^{W1} OEu ²⁺ + H ⁺	-0.5	0.3
Eu ³⁺ + 2H ₂ O ⇌ Eu(OH) ₂ ⁺ + 2H ⁺	-15.1	≡S ^S OH + Eu ³⁺ + H ₂ O ⇌ ≡S ^S OEuOH ⁺ + 2H ⁺	-6.4	-4.7
		≡S ^{W1} OH + Eu ³⁺ + H ₂ O ⇌ ≡S ^{W1} OEuOH ⁺ + 2H ⁺	-	-6.2
Eu ³⁺ + 3H ₂ O ⇌ Eu(OH) ₃ ⁰ + 3H ⁺	-26.2	≡S ^S OH + Eu ³⁺ + 2H ₂ O ⇌ ≡S ^S OEu(OH) ₂ ⁰ + 3H ⁺	-14	-12.7
Am ³⁺ + H ₂ O ⇌ AmOH ²⁺ + H ⁺	-7.2	≡S ^S OH + Am ³⁺ ⇌ ≡S ^S OAm ²⁺ + H ⁺	2.3	3.1
		≡S ^{W1} OH + Am ³⁺ ⇌ ≡S ^{W1} OAm ²⁺ + H ⁺	-0.5	0.3
Am ³⁺ + 2H ₂ O ⇌ Am(OH) ₂ ⁺ + 2H ⁺	-15.1	≡S ^S OH + Am ³⁺ + H ₂ O ⇌ ≡S ^S OAmOH ⁺ + 2H ⁺	-5.9	-4.5
		≡S ^{W1} OH + Am ³⁺ + H ₂ O ⇌ ≡S ^{W1} OAmOH ⁺ + 2H ⁺	-	-6.2
Am ³⁺ + 3H ₂ O ⇌ Am(OH) ₃ ⁰ + 3H ⁺	-26.2	≡S ^S OH + Am ³⁺ + 2H ₂ O ⇌ ≡S ^S OAm(OH) ₂ ⁰ + 3H ⁺	-14	-13
Pu ³⁺ + H ₂ O ⇌ PuOH ²⁺ + H ⁺	-6.9	≡S ^S OH + Pu ³⁺ ⇌ ≡S ^S OPu ²⁺ + H ⁺	1.6 *	2.5 **
		≡S ^{W1} OH + Pu ³⁺ ⇌ ≡S ^{W1} OPu ²⁺ + H ⁺	-0.6 *	0.7 **
Pu ³⁺ + 2H ₂ O ⇌ Pu(OH) ₂ ⁺ + 2H ⁺	-14.8	≡S ^S OH + Pu ³⁺ + H ₂ O ⇌ ≡S ^S OPuOH ⁺ + 2H ⁺	-5.3 *	-3.8 **
		≡S ^{W1} OH + Pu ³⁺ + H ₂ O ⇌ ≡S ^{W1} OPuOH ⁺ + 2H ⁺	-	-6.1 **
Pu ³⁺ + 3H ₂ O ⇌ Pu(OH) ₃ ⁰ + 3H ⁺	-25.9	≡S ^S OH + Pu ³⁺ + 2H ₂ O ⇌ ≡S ^S OPu(OH) ₂ ⁰ + 3H ⁺	-14.6 *	-12.7 **

* From LFER, Table 6.1 in Baeyens & Bradbury (2017)

** From LFER, Table 6.1 in Bradbury & Baeyens (2017)

Tab. A-3: Hydrolysis and surface complexation reactions and constants for Th(IV), U(IV) and Np(IV).

The surface complexation constants for Th(IV) were obtained from Baeyens & Bradbury (2017) and Bradbury & Baeyens (2017). The surface complexation constants for U(IV) and Np(IV) were obtained from the LFER, Figure 4.12 in Baeyens & Bradbury (2017) and Figure 4.11 in Bradbury & Baeyens (2017) for montmorillonite and illite, respectively.

Hydrolysis reaction	$\log_{\text{OH}^-} K_x$	Surface complexation reaction	$\log {}^s K_{x-1}$	
			mont.	illite
$\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ThOH}^{3+} + \text{H}^+$	-2.2	$\equiv\text{S}^s\text{OH} + \text{Th}^{4+} \rightleftharpoons \equiv\text{S}^s\text{OTh}^{3+} + \text{H}^+$	7.2	7.4
$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	-6.0	$\equiv\text{S}^s\text{OH} + \text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{OThOH}^{2+} + 2\text{H}^+$	2.7	2.3
$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	-11.0	$\equiv\text{S}^s\text{OH} + \text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{OTh}(\text{OH})_2^+ + 3\text{H}^+$	-2.6	-2.4
$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4^0 + 4\text{H}^+$	-17.5	$\equiv\text{S}^s\text{OH} + \text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{OTh}(\text{OH})_3^0 + 4\text{H}^+$	-9.1	-8.8
$\text{U}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{U}(\text{OH})_2^{2+} + 2\text{H}^+$	-1.1	$\equiv\text{S}^s\text{OH} + \text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{OUOH}^{2+} + 2\text{H}^+$	7.7	7.1
$\text{U}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{U}(\text{OH})_3^+ + 3\text{H}^+$	-4.7	$\equiv\text{S}^s\text{OH} + \text{U}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{OU}(\text{OH})_2^+ + 3\text{H}^+$	4.0	3.6
$\text{U}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{U}(\text{OH})_4^0 + 4\text{H}^+$	-10	$\equiv\text{S}^s\text{OH} + \text{U}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{OU}(\text{OH})_4^0 + 4\text{H}^+$	-1.4	-1.6
$\text{Np}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_2^{2+} + 2\text{H}^+$	0.35	$\equiv\text{S}^s\text{OH} + \text{Np}^{4+} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{ONpOH}^{2+} + 2\text{H}^+$	9.2	8.5
$\text{Np}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_3^+ + 3\text{H}^+$	-2.80	$\equiv\text{S}^s\text{OH} + \text{Np}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{ONp}(\text{OH})_2^+ + 3\text{H}^+$	5.9	5.4
$\text{Np}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_4^0 + 4\text{H}^+$	-8.30	$\equiv\text{S}^s\text{OH} + \text{Np}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^s\text{ONp}(\text{OH})_4^0 + 4\text{H}^+$	0.3	0.1

Appendix B: Auxiliary thermodynamic data

Additional aqueous thermodynamic data used to calculate sorption values in the bentonite porewater and the Opalinus Clay porewater systems are summarised below.

Tab. B-1: Aqueous thermodynamic data for divalent metals taken from the PSI/Nagra TDB 12/07 (Thoenen et al. 2014).

Metal complex	Ni	Fe
MeCl	0.08	0.14
MeCl ₂	-	-
MeCl ₃	-	-
MeCl ₄	-	-
MeSO ₄	2.35	2.25
Me(SO ₄) ₂	-	-
Me(SO ₄) ₃	-	-
MeHSO ₄	-	3.068
MeCO ₃	4.2	4.38
Me(CO ₃) ₂	< 6	-
MeHCO ₃	≈ 11.3	12.33

Tab. B-2: Aqueous thermodynamic data for trivalent metals taken from the PSI/Nagra TDB 12/07 (Thoenen et al. 2014).

Metal complex	Cm/Am/Ac	Pu	Eu/Ho/Sm
MeCl	0.24	1.2	1.1
MeCl ₂	-0.74	-	1.5
MeSO ₄	3.30	3.9	3.95
Me(SO ₄) ₂	3.70	5.7	5.7
MeCO ₃	8.0	8.0	8.1
Me(CO ₃) ₂	12.9	12.9	12.1
Me(CO ₃) ₃	15.0	15.0	-
MeHCO ₃	3.1	-	-

Tab. B-3: Aqueous thermodynamic data for tetravalent metals taken from the PSI/Nagra TDB 12/07 (Thoenen et al. 2014).

Metal complex	Np	U	Th
MeCl	1.5	1.72	1.70
MeCl ₂	-	-	-
MeSO ₄	6.85	6.58	6.17
Me(SO ₄) ₂	11.05	10.51	9.69
Me(SO ₄) ₃	-	-	10.748
Me(CO ₃) ₄	38.9	35.22	-
Me(CO ₃) ₅	37.8	34.1	31.0
MeOH(CO ₃) ₄	-	-	21.6
Me(OH) ₂ (CO ₃) ₂	-	-	8.8
Me(OH) ₄ CO ₃	-	-	-15.6

Appendix C: MX-80 mineralogy and porewater chemistry

Tab. C-1: Reference MX-80 mineralogy (Müller-Vonmoos & Kahr 1983).

Also in Baeyens et al. (2014, Table 8.1). The CEC of MX-80 is 787 meq/kg (Bradbury & Baeyens 2003b).

Mineralogy	MX-80 [wt. %]
Smectite	75
Calcite	0.7
Siderite	0.7
Quartz	15.2
Pyrite	0.3
Feldspar	5 – 8
Organic carbon	0.4
Kaolinite	< 1
Mica	< 1

Tab. C-2: Bentonite porewater obtained after 10'000 years of exchange between the bentonite starting system and the Opalinus Clay reference system without a low-pH shotcrete liner.

See Table 1 in Berner (2014).

BPW after 10'000 years	
ϵ_{bulk}	0.36
pH	7.79
Eh [V]	-0.204
I [mol/kg]	0.239
log pCO ₂ [bar]	-3.20
Na [mol/kg H ₂ O]	1.919×10^{-1}
K [mol/kg H ₂ O]	1.217×10^{-3}
Mg [mol/kg H ₂ O]	5.126×10^{-3}
Ca [mol/kg H ₂ O]	8.997×10^{-3}
Sr [mol/kg H ₂ O]	5.606×10^{-5}
Ba [mol/kg H ₂ O]	1.119×10^{-7}
Fe [mol/kg H ₂ O]	3.698×10^{-5}
C ^{IV} [mol/kg H ₂ O]	8.994×10^{-4}
S ^{VI} [mol/kg H ₂ O]	3.005×10^{-2}
Cl [mol/kg H ₂ O]	1.607×10^{-1}
Al [mol/kg H ₂ O]	1.472×10^{-8}
Si [mol/kg H ₂ O]	1.820×10^{-4}

Appendix D: Solubility limits of safety-relevant elements in the SF/HLW bentonite near-field

Solubility values selected for transport/dose calculations for the provisional safety analyses within the Sectoral Plan for Deep Geological Repositories are presented in Tab. D-1 (*cf.* Berner 2014, Appendix A: Solubility limits used for dose calculations, Table A1).

Tab. D-1: Solubility limits (in mol/kg H₂O) of safety-relevant elements in the SF/HLW near-field (bentonite).

Element	Reference value
Be(II)	9×10^{-7}
C _{inorg}	9×10^{-4}
Cl	not limited
Ca(II)	9×10^{-3}
Ni(II)	6×10^{-5}
Se(-II)	5×10^{-9}
Sr(II)	1×10^{-4}
Zr(IV)	1×10^{-7}
Nb(V)	7×10^{-5}
Mo(VI)	2×10^{-5}
Tc(IV)	4×10^{-9}
Pd(II)	6×10^{-8}
Ag(I)	1×10^{-5}
Sn(IV)	9×10^{-8}
I(-I)	not limited
Cs(I)	not limited
Sm(III)	2×10^{-7}
Ho(III)	3×10^{-6}
Pb(II)	9×10^{-7}
Po(IV)	7×10^{-7}
Ra(II)	3×10^{-10}
Ac(III)	3×10^{-6}
Th(IV)	4×10^{-9}
Pa(V)	5×10^{-9}
U(IV)	2×10^{-7}
Np(IV)	1×10^{-8}
Pu(III)	7×10^{-10}
Am(III)	3×10^{-6}
Cm(III)	3×10^{-6}

Appendix E: Opalinus Clay mineralogy and porewater chemistry

Tab. E-1: Reference mineralogy and values for the bounding minerals for Opalinus Clay (Traber & Blaser 2013).

See also Baeyens et al. (2014, Table 3.1.1).

Mineral	Reference [wt.-%]
Illite	24
Illite/smectite mixed layer	9
Smectite	0
Kaolinite	18
Chlorite	9
Quartz	20
Calcite	13
Dolomite + Ankerite	0.4
K-feldspar	2
Plagioclase	0.9
Siderite	4
Pyrite	1

Tab. E-2: Porewater composition of Opalinus Clay (Mäder 2009).

See also Baeyens et al. 2014, Table 3.2.1).

Reference	
pH	7.20
pE	-2.78
I [mol/kg _{H2O}]	0.23
log pCO ₂ [bar]	-2.20
Na [mol/kg _{H2O}]	1.64×10^{-1}
K [mol/kg _{H2O}]	2.60×10^{-3}
Mg [mol/kg _{H2O}]	9.65×10^{-3}
Ca [mol/kg _{H2O}]	1.25×10^{-2}
Sr [mol/kg _{H2O}]	2.11×10^{-4}
Fe ^{II} [mol/kg _{H2O}]	5.24×10^{-5}
Cl [mol/kg _{H2O}]	1.60×10^{-1}
F [mol/kg _{H2O}]	1.53×10^{-4}
S ^{VI} [mol/kg _{H2O}]	2.47×10^{-2}
C ^{IV} [mol/kg _{H2O}]	2.51×10^{-3}
Si [mol/kg _{H2O}]	1.78×10^{-4}