

# Technical Report 09-07

**Comparison of the reference Opalinus  
Clay and MX-80 bentonite sorption  
data bases used in the Entsorgung-  
nachweis with sorption data bases  
predicted from sorption measure-  
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for the Disposal of  
Radioactive Waste**

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## Abstract

In Stage 2 of the Sectoral Plan for 'Deep Geological Disposal' preliminary safety analyses will be carried out for potential sites identified within regions previously selected as being suitable for constructing HLW and L/ILW radioactive waste repositories. The rock formations in question are Opalinus Clay (HLW, L/ILW) and 'Brauner Dogger', Effingen Member and Helvetic Marl (L/ILW). Sorption data bases for all of these host rocks are required to perform the planned preliminary safety analyses.

In a previous report (Bradbury et al. 2010), a methodology was described for developing sorption data bases for argillaceous rocks, so called Generic Rock Sorption Data Bases. In Bradbury et al. (2010) it was argued that the main factor influencing sorption on argillaceous rocks is the phyllosilicate mineral content, particular the 2:1 clay mineral content (illite/smectite/illite-smectite mixed layers). The second important influence is the water chemistry which determines the radionuclide species in the aqueous phase. Primarily sorption measurements on illite were used and these data were converted to the defined conditions in the argillaceous rock by using a series of so called conversion factors to take into account differences in mineralogy, in pH and in radionuclide speciation. Finally, a Lab→Field conversion factor ( $CF_{\text{Lab} \rightarrow \text{Field}}$ ) was applied to adapt sorption data measured in dispersed systems (batch experiments) to intact rock under in-situ conditions. The intention in Stage 2 of the Sectoral Plan is to use this methodology to develop sorption data bases (SDB) for the host rocks under consideration (Opalinus Clay, 'Brauner Dogger', Effingen Member and Helvetic Marl).

Since this methodology for generating SDBs is relatively new, a direct means of creating confidence in its application and verifying its applicability was required. Hence, it was decided to compare and contrast the sorption values obtained in the manner described above with those in an already existing SDB for Opalinus Clay used in the Entsorgungsnachweis (Nagra 2002).

In order to test the procedure further, a second such study was undertaken with MX-80 bentonite. A SDB for MX-80 bentonite was derived from measurements made on montmorillonite using the same methodology and compared with the values used in the Entsorgungsnachweis (Nagra 2002).

The main conclusion from detailed comparisons made for both Opalinus Clay and MX-80 bentonite is that very strong evidence has been provided to demonstrate that the same basic approach as used here can be applied with confidence to other argillaceous rock systems for which direct sorption measurement data may be sparse or missing.

## Zusammenfassung

In Etappe 2 des Sachplans geologische Tiefenlager werden provisorische Sicherheitsanalysen für die potenziellen Standorte innerhalb der bereits identifizierten Standortregionen für Lager für hochaktive (HAA) sowie für schwach- und mittelaktive (SMA) Abfälle durchgeführt. Die betreffenden Wirtgesteine sind Opalinuston, 'Brauner Dogger', Effinger Schichten und Mergel des Helvetikums. Zur Durchführung der geplanten Sicherheitsanalysen werden Sorptionsdatenbanken für diese Wirtgesteine benötigt.

Ein früherer Bericht (Bradbury et al., 2010) beschreibt eine Methode zur Entwicklung von Sorptionsdatenbanken für Tongestein, sogenannte Generische Sorptionsdatenbanken. In Bradbury et al. (2010) wurde diskutiert, dass der wichtigste Einflussfaktor für die Sorption auf Tongestein der Gehalt an Schichtsilikaten ist, insbesondere der Gehalt an 2:1-Tonmineralen (Illit, Smektit und Illit/Smektit-Wechselagerungen). Der zweite wichtige Einflussfaktor ist die Chemie des Porenwassers, da sie die Radionuklidspeziation in der wässrigen Phase bestimmt. Die Sorptionsdatenbank basiert in erster Linie auf Sorptionsmessungen auf Illit, welche dann auf die definierten Bedingungen der Tongesteine übertragen wurden. Dabei kam eine Reihe von Konvertierungsfaktoren zur Anwendung, um Unterschiede in der Mineralogie, im pH-Wert und der Radionuklidspeziation zu berücksichtigen. Schliesslich wurde ein Konvertierungsfaktor Labor→Feld angewandt, um die in Suspension gemessenen Sorptionsdaten auf intaktes Gestein unter In-situ-Bedingungen zu übertragen. Es ist vorgesehen, die hier beschriebene Methode in Etappe 2 des Sachplans geologische Tiefenlager zur Erarbeitung der Sorptionsdatenbanken (SDB) für die in Frage kommenden Wirtgesteine zu nutzen.

Weil diese Methode zum Aufbau von Sorptionsdatenbanken relativ neu ist, ist es notwendig, die Anwendbarkeit zu überprüfen und so Vertrauen in die Methode zu schaffen. Daher wurde entschieden, die nach der beschriebenen Methode berechneten Sorptionswerte mit einer bereits existierenden Sorptionsdatenbank für Opalinuston aus dem Entsorgungsnachweis (Nagra, 2002) zu vergleichen. Für einen weiteren Test des Verfahrens wurde eine zweite Studie mit MX-80 Bentonit durchgeführt. Nach der gleichen Methode wurde aus Messdaten auf Montmorillonit eine Sorptionsdatenbank für MX-80 Bentonit erstellt und mit den Werten aus dem Entsorgungsnachweis (Nagra, 2002) verglichen.

Aus dem detaillierten Vergleich wurde sowohl für Opalinuston als auch für MX-80 eine wichtige Schlussfolgerung gezogen: Es konnte demonstriert werden, dass der hier benutzte Ansatz auf andere Tongesteine, für die wenige oder gar keine Sorptionsmessungen vorliegen, sicher anwendbar ist.

## Résumé

Au cours de l'étape 2 du plan sectoriel «Dépôts en couches géologiques profondes», des analyses préliminaires de sûreté seront réalisées pour chacun des sites d'implantation potentiels proposés pour le stockage en couches géologiques des déchets de haute activité (DHA), ainsi que des déchets de faible et de moyenne activité (DFMA). Les roches d'accueil potentielles sont les argiles à Opalinus, le 'Brauner Dogger' («Dogger brun»), les Couches d'Effingen et les formations marneuses de l'Helvétique. Afin d'effectuer les analyses de sûreté prévues, des bases de données de sorption sont nécessaires pour chacune des roches d'accueil potentielles.

Dans un précédent rapport, Bradbury et al. (2010) ont décrit une méthode pour l'élaboration de bases de données de sorption génériques pour les formations argileuses. Dans ce rapport, la teneur en phyllosilicates type 2:1 (illite, smectite, interstratifiés illite/smectite) est présentée comme le principal facteur influant sur le degré de sorption. Le deuxième facteur influant sur la sorption est la composition chimique des eaux interstitielles, qui contrôle la spéciation des radionucléides dans la phase aqueuse. La base de données de sorption repose principalement sur des valeurs de sorption obtenues pour l'illite. Par le biais de facteurs de conversion, on a ajusté ces valeurs aux conditions génériques définies pour les différentes roches argileuses, en prenant en compte les différences de minéralogie, de valeurs pH et de spéciation. Un facteur de conversion Laboratoire→Roche a été utilisé pour les données de sorption obtenues à partir d'expériences en suspension, de façon à les convertir aux conditions in situ de la roche argileuse intacte. Il est prévu d'appliquer cette méthode dans l'étape 2 du plan sectoriel afin d'élaborer des bases de données de sorption pour les différentes roches argileuses (argiles à Opalinus, 'Brauner Dogger', Couches d'Effingen et formations marneuses de l'Helvétique).

L'utilisation de cette méthode pour élaborer des bases de données de sorption étant relativement récente, il était nécessaire d'accroître le degré de confiance en cette approche et d'en vérifier l'applicabilité. On a par conséquent décidé de comparer les valeurs de sorption obtenues par cette méthode aux valeurs d'une base de données utilisée pour les argiles à Opalinus dans le cadre de l'étude de faisabilité «Entsorgungsnachweis» (Nagra, 2002).

Lors d'un deuxième test, l'applicabilité de cette méthode a été vérifiée pour la bentonite MX-80. Le même procédé a été utilisé pour convertir les valeurs de sorption expérimentales obtenues pour la montmorillonite en valeurs de sorption pour la MX-80. La base de données de sorption pour la MX-80 ainsi élaborée a été comparée à celle utilisée pour le projet «Entsorgungsnachweis» (Nagra, 2002).

En conclusion, les comparaisons détaillées effectuées tant pour les argiles à Opalinus que pour la MX-80 ont permis de démontrer de manière convaincante que la méthode utilisée ici pouvait être appliquée à d'autres formations argileuses pour lesquelles il existe peu ou pas de données expérimentales de sorption.



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## 1 Introduction

The methodology for providing sorption data bases (SDBs) used in performance assessment (PA) studies for deep geological repository options and for backfill and sealing materials has been documented in detail elsewhere (Bradbury & Baeyens 1997, Bradbury & Baeyens 2003a,b). The SDBs in the Entsorgungsnachweis for Opalinus Clay and MX-80 bentonite (Bradbury & Baeyens 2003a,b) contain data derived from different sources: measurements on Opalinus Clay and MX-80 bentonite, on the clay minerals illite and montmorillonite, and on other systems. The methodology for producing SDBs is continuously under development in the Laboratory for Waste Management (LES) at PSI (Bradbury et al. 2010). The aim is to select robust sorption values in a clear, transparent, and traceable manner. The ultimate goal is to set up a thermodynamic SDB (TD-SDB) based on a mechanistic understanding of the sorption processes, and use the associated sorption models and parameters to calculate distribution ratios ( $R_d$  values) under any given conditions (mineralogy, water chemistry). Although this endeavour is being pursued energetically (Bradbury & Baeyens 2005a, 2009b), the realisation of a TD-SDB is still some way off. However, a significant part of the measured data and knowledge gained in this activity is applied in many different ways in the SDB work for PA, as will be amply illustrated in the following.

Regarding argillaceous rock systems, one of the basic premises in developing SDBs is that the 2:1 clay mineral fraction is predominantly responsible for the uptake of radionuclides (Bradbury et al. 2010). The 2:1 clay mineral contents of Opalinus Clay is ~32 wt. % (reference mineralogy in Nagra 2002) and consists essentially of illite and illite/smectite mixed layers. It is assumed that illite/smectite mixed layers have sorption characteristics which are very similar to illite. Although this cannot be defended unambiguously, because hardly any sorption data exist for the mixed layer clay minerals, this approach is supported by some recent work in which sorption isotherms of Ni(II), Co(II), Eu(III), Th(IV) and U(VI) measured on Opalinus Clay (OPA) in a realistic ground water composition were successfully modelled using the illite sorption model (Bradbury & Baeyens 2009a,b) and scaled over the illite + illite/smectite mixed layer content of OPA, the so called "bottom up" approach (Bradbury & Baeyens, unpublished data). Thus, illite sorption values are used to develop an SDB for OPA and the illite + illite/smectite mixed layer content is taken to be the sorbing phases with the same sorption properties as illite.

In this report, the sorption values obtained from the procedures described are compared with those in the SDB for Opalinus Clay (Bradbury & Baeyens 2003a) used in the Entsorgungsnachweis (OPA-EN SDB) described in Nagra (2002). The aim is to test whether the methodology based on a generic approach (2:1 clay minerals) can reproduce the OPA-EN SDB, which was specifically derived for Opalinus Clay. Further, sorption data for specific elements (Ni(II), Sr(II), Sn(IV), Cs(I), Eu(III) and Th(IV)) derived with this generic methodology were checked against measured data obtained independently. A second study was undertaken with MX-80 bentonite. An SDB for MX-80 bentonite, which contains ~75 wt. % montmorillonite, was derived from measurements made on Na-montmorillonite using the same methodology as for the case of Opalinus Clay. The thus obtained  $R_d$  values are compared and contrasted with those in the MX-80-EN SDB (Bradbury & Baeyens 2003b) also used in the Entsorgungsnachweis (Nagra 2002).

A successful reproduction of previously developed sorption data bases with the method used in this study would strengthen confidence in the continuous development of the approach and the ability to derive realistic sorption data for the variety of argillaceous host rocks identified in Nagra (2008).



## 2 Methodology and conversion factors

### 2.1 Methodology

The basic procedure is very similar to that which has been described previously in detail elsewhere (Bradbury & Baeyens 2003a,b, Bradbury et al. 2010). For completeness and ease of understanding an outline of the methodology is given below.

One of the main conclusions drawn from previous work on generic SDBs (Bradbury et al. 2010) was that for most radionuclides the main sorbing minerals in argillaceous rocks are 2:1 type clay minerals, illite + smectite + illite/smectite mixed layers. Also, experimental and modelling investigations on montmorillonite and illite have shown clearly that the surface complexation behaviour of these two important clay minerals are similar: similar edge site capacities; similar Linear Free Energy Relationships between metal surface complexation constants and the corresponding hydrolysis constants (Bradbury & Baeyens 2005a, 2009a,b). As discussed in Bradbury et al. (2010) the approach taken here will be to use illite source sorption data wherever possible and scale this data over the wt. % of the 2:1 type clay minerals (illite + smectite + illite/smectite mixed layers) in the argillaceous rock in question. Illite/smectite mixed layers cannot be treated separately because insufficient data and no sorption model exist. For the reasons given in the Introduction it is assumed that illite/smectite mixed layers have sorption characteristics essentially the same as illite.

A simple set of reference conditions for the illite source data were chosen; pH = 7 and 0.1 M NaClO<sub>4</sub>.

Illite source sorption data measured at trace concentrations are selected wherever possible. The most important parameters for sorption, besides the mineralogy, are the pH and the porewater composition, from which an aqueous speciation factor can be calculated. The selected illite sorption data are converted to sorption values for the OPA using conversion factors defined in the following sections. For OPA, the mineralogy and water chemistry for the “reference case” (Tables 4.1 and 4.2 respectively) have been taken and hence the pH and the illite + illite/smectite mixed layers fraction in the OPA are given, and the speciation factor can be calculated using the water composition. (The MX-80 case is described separately in Chapter 5.)

### 2.2 Conversion factors

#### 2.2.1 Mineralogy conversion factor: CF<sub>MIN</sub>

The conversion factor which takes into account the differences in mineralogy is given by an equation of the form:

$$CF_{MIN} = (MIN_{OPA} / MIN_{ILLITE}) \quad (2.1)$$

where,

CF<sub>MIN</sub> = mineralogy conversion factor

MIN<sub>OPA</sub> = illite + illite/smectite mixed layer weight fraction in OPA

MIN<sub>ILLITE</sub> = 1 (100% illite)

### 2.2.2 Speciation conversion factor, $CF_{SPEC}$

The complexation of radionuclides with inorganic and organic ligands has an influence on sorption and therefore corrections need to be made to reflect the variations in aqueous speciation in the different water chemistries considered. A plausible procedure is given below.

In oxide and clay mineral systems it is widely observed that the formation of positively charged or neutral hydrolysed species does not adversely influence sorption behaviour. Indeed, very high metal sorption is often measured in regions where neutral hydroxy species dominate. (See for example Schultess & Huang 1990; Gorgeon 1994; Turner et al. 1998.) Whether or not other neutral and positively charged complexes can also be taken up by sorbents is less clear, but remains a possibility. In order to make a correction to sorption values taking into account the differences in radionuclide speciation in different water chemistries, species which sorb and those which do not sorb have to be distinguished. The proposal put forward for metals is to define free cations, and positively charged and neutral hydrolysed species as being sorbing. All other species are treated as being non-sorbing. (This assumption errs on the conservative side, see for example Bradbury et al. 2010.)

The conversion factor used for modifying sorption values according to the speciation in different water chemistries is simply:

$$CF_{SPEC} = F_{OPA} / F_{ILLITE} \quad (2.2)$$

where

$CF_{SPEC}$  is the speciation conversion factor.

$F_{OPA}$  is the fraction of sorbing radionuclide species calculated to be present in the aqueous phase in the OPA reference porewater.

$F_{ILLITE}$  the fraction of sorbing radionuclide species calculated to be present in the aqueous phase in the illite system.

Attempts to correct for speciation differences in this manner are, of course, sensitively dependent on the quality and consistency of the stability constants in the thermodynamic data bases. The Nagra/PSI thermodynamic data base (TDB) (Hummel et al. 2002) has been used throughout this report\*. This version of the TDB was used here because it was also used in the derivation of the OPA-EN SDB (Bradbury & Baeyens 2003a). Since the aim of this report is to compare SDBs, the same TDB was used in both cases. Speciation calculations for redox sensitive radionuclides were carried out in a redox coupled mode.

It was noted in some previous work, Bradbury & Baeyens (2003a,b), that the above scheme was not appropriate for Th(IV); also used as the analogue for other tetravalent actinides. Speciation calculations using the stability constants in Hummel et al. (2002) indicated that negatively charged hydroxy-carbonato complexes become very important in the pH ranges of interest in calcite saturated solutions, such as in the OPA system. However, sorption measurements of Th(IV) on OPA in such solutions showed that the reductions in sorption calculated on the basis of the above hypothesis were more than an order of magnitude greater than found experimentally (Lauber et al. 2000). In view of this discrepancy, a simplifying assumption was made i.e. the speciation factor was taken as the fraction of species existing in the tetravalent state in

---

\* The exceptions to this are Bi(III), Co(II), Pa(V), Pb(II) and Sb(III). The thermodynamic data used to calculate the speciation of these elements are given in NTB 09-03, Appendix A7.

the redox coupled speciation calculations. This assumption was more or less in accord with the experimental findings of Lauber et al. (2000). However, it needs to be noted that this was an „operational decision“ and the authors consider that there are major problems with speciation calculations for tetravalent actinides using the stability constants in Hummel et al. (2002). (See also the more detailed discussion in Bradbury et al. 2010.)

### 2.2.3 pH conversion factors, $CF_{pH}$

When metal sorption at trace concentrations is investigated in clay mineral systems, in simple background electrolytes, at moderate concentrations, as a function of pH, many metals sorb by surface complexation which gives rise to a strong increase in sorption in the pH range from approximately  $\sim 5$  to  $\sim 7 - 8$ . (The exception to this is the alkaline and alkaline-earth metals which sorb predominantly by cation exchange.) Above pH  $\sim 7 - 8$  either a plateau is observed (constant sorption) or a decrease in sorption occurs due to the formation of (mainly) non-sorbing negatively charged hydrolysed species.

In the case of very strongly hydrolysing metals, the sorption is high and constant over almost the whole pH range investigated (Bradbury & Baeyens 2005a, 2009a,b).

For metal uptake by surface complexation, corrections for the differences in pH when converting sorption values from one system to another can be significant. Thus it is important to define this conversion factor carefully.

The strategy followed in this work is to use sorption edges of metals and anions on illite and derive a pH conversion factor from the experimental data. This procedure is illustrated for 2 cases, a metal ( $Ni^{2+}$ ) and an oxyanion ( $SeO_3^{2-}$ ).

As can be seen in Fig. 2.1, the log of the Ni distribution ratio increases essentially linearly as a function of pH in the range  $\sim 4$  to  $\sim 8$ . Below and above these pH values the sorption remains approximately constant.

The slope (m) of the dotted line drawn through the experimental data is given by:

$$m = \frac{\log R_{d2} - \log R_{d1}}{pH_2 - pH_1} \quad (2.3)$$

Thus the pH conversion factor,  $CF_{pH}$ , needed to convert a sorption value,  $R_{d1}$ , measured at  $pH_1$ , to the sorption value corresponding to a different pH,  $pH_2$ , can be defined by re-arranging Eq. 3 i.e.

$$CF_{pH} = \frac{R_{d2}}{R_{d1}} = 10^{m(pH_2 - pH_1)} \quad (2.4)$$

Eq. 4 is valid for any  $pH/R_d$  combination which lie within the linear region of the sorption edge.

Or, for the specific case being considered here,

$$R_{d, OPA} = R_{d, ILLITE} \cdot CF_{pH} = R_{d, ILLITE} \cdot 10^{m(pH_{OPA} - pH_{ILLITE})} \quad (2.5)$$

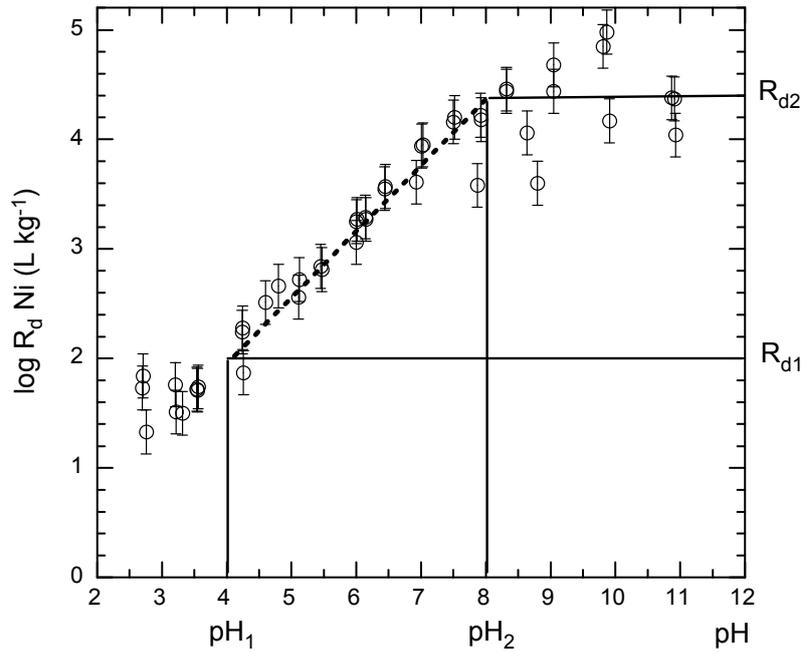


Fig. 2.1: Ni sorption edge measured on Na-illite at trace concentration in a 0.1 M NaClO<sub>4</sub> background electrolyte (Bradbury & Baeyens 2009a).

For the measured sorption edge of each element on illite, the slope  $m$ , and the pH range over which this slope is constant, can be evaluated. Eq. 4 can then be used to calculate the corresponding  $CF_{pH}$  values.

In Fig. 2.2 an example of an oxyanion, Se(IV) sorption edge on Na-illite is shown (Bruggeman 2006). The same expression as given in Eq. 4 can be used to evaluate the pH conversion factor.

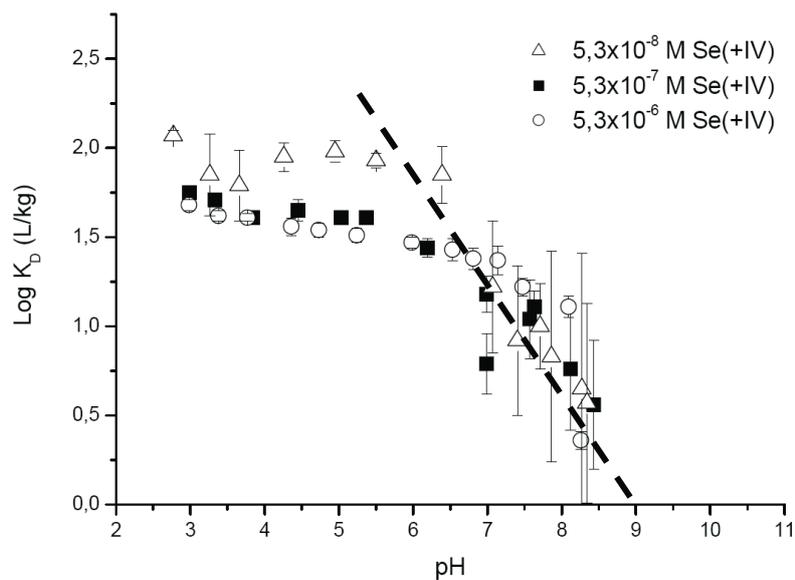


Fig. 2.2: A selenite sorption edge on Na-illite in 0.1 M NaClO<sub>4</sub> (from Bruggeman 2006). The slope of the broken line is -0.6.

A summary of the radionuclides for which a slope and pH range were derived from experimental sorption edge data is given below.

Tab. 2.1: Slope values, “m”, in Eq. 3, used to calculate pH conversion factors,  $CF_{pH}$ , in Eq. 4.

Radionuclide	slope	pH range	Source
Co(II)	0.8	6 - 9	Bradbury & Baeyens (2009a)
Ni(II)	0.6	4 - 8	Bradbury & Baeyens (2009a)
Pb(II)	0.65	5 - 7	Ulrich & Degueudre (1992)
Eu(III)	0.8	4 - 8	Bradbury & Baeyens (2009a)
Am(III)	0.9	4 - 7	Bradbury & Baeyens (2009b)
Bi(III)	0.6	5 - 7	Ulrich & Degueudre (1992)
Se(IV)	-0.6	6 - 9	Bruggeman (2006)
Mo(VI)	-0.3	4 - 8	Theng (1971)

Note that for the elements listed below, which exhibit sorption plateaus, no  $CF_{pH}$  conversion factors are required in the range of pH values given.

- Th(IV): sorption plateau from pH 5 to 10 (Bradbury & Baeyens 2009b)
- Sn(IV): sorption plateau from pH 3 to 10 (Bradbury & Baeyens 2009a)
- Tc(IV): assumed sorption plateau from pH 3 to 10 (Bradbury et al. 2010)
- Pa(V): sorption plateau from pH 4 to 10 (Bradbury & Baeyens 2009b)

Also, no pH corrections are needed for Cs(I), Ca(II), Sr(II) and Ra(II) since the sorption mechanism for these elements is cation exchange and the sorption values are calculated for each individual metal in the illite/OPA reference water chemistry system, see section 3.2.

#### 2.2.4 Formulation

The above procedures can be summarised as follows. Consider that a selected illite source sorption value for a radionuclide (RN) measured under well defined conditions needs to be transposed into the corresponding value for OPA at the reference conditions. The illite source data are:

$R_{d, \text{ILLITE}}$ ,  $MIN_{\text{ILLITE}}$ ,  $pH_{\text{ILLITE}}$ ,  $F_{\text{ILLITE}}$  and variation of the distribution coefficient with pH from the sorption edge data is given by:  $10^{m(pH_1 - pH_2)}$ . (Note that where the source data were measured in a “pure illite” system,  $MIN_{\text{ILLITE}}$  equals unity.)

The distribution ratio,  $R_{d, \text{OPA}}$ , is required for the OPA at the reference conditions. The OPA reference mineralogical and water composition conditions yield  $MIN_{\text{OPA}}$ ,  $pH_{\text{OPA}}$ ,  $F_{\text{OPA}}$  values.

Then,

$$R_{d,OPA} = R_{d,ILLITE} \cdot CF_{MIN} \cdot CF_{SPEC} \cdot CF_{pH} \quad (2.6)$$

where:

$$CF_{MIN} = (MIN_{OPA} / MIN_{ILLITE})$$

$$CF_{SPEC} = (F_{OPA} / F_{ILLITE})$$

$$CF_{pH} = 10^{m(pH_{OPA} - pH_{ILLITE})}$$

### 2.3 Chemical analogues

In many cases the source data were "in house" and literature sorption edge measurements. However, there were also many cases where sorption data were either too poor to be used or did not exist at all. In such cases chemical analogues were used. Table 2.2 lists all the elements and their chemical analogues used in this work which were selected according to the scheme given in Bradbury et al. (2010).

Tab. 2.2: Overview of chemical analogues.

<b>Radionuclide</b>	<b>Chemical analogue</b>
Ni(II)	Cd(II)
Pb(II)	Be(II), Pd(II)
Eu(III)	Ce(III), Pm(III), Sm(III), Ho(III)
Am(III)	Ac(III), Pu(III), Cm(III)
Th(IV)	U(IV), Np(IV), Pu(IV)
Sn(IV)	Zr(IV), Hf(IV)
Bi(III)	Sb(III)
Se(IV)	Po(IV)

In cases where chemical analogy is invoked, the sorption value for the analogue element in the OPA reference conditions is taken i.e.  $R_{d \text{ ANALOG OPA}}$ . The only further correction factor which needs to be applied to obtain the  $R_{d \text{ RN OPA}}$  value for the radionuclide in question is one which takes into account any differences in aqueous speciation between the two i.e.

$$CF_{\text{SPEC RN OPA}} = F_{\text{SPEC RN OPA}} / F_{\text{SPEC ANALOG OPA}} \quad (2.7)$$

where

$F_{\text{SPEC RN OPA}}$  is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the OPA reference porewater.

$F_{\text{SPEC ANALOG OPA}}$  is the fraction of the chemical analogue concentration calculated to be present in the aqueous phase as sorbing species in the OPA reference porewater.

$$R_{d \text{ RN OPA}} = R_{d \text{ ANALOG OPA}} \cdot CF_{\text{SPEC RN OPA}} \quad (2.8)$$

## 2.4 Competitive sorption effects

The majority of sorption data originates from batch type experiments in which it is usual to measure the sorption behaviour of a single metal at a time. In complex systems, such as a deep underground radioactive waste repository, many radionuclides and inactive metal contaminants will be simultaneously present at different concentrations in the aqueous phase. Under such circumstances, competitive sorption effects may be an important issue.

In a recent study (Bradbury & Baeyens 2005c), competitive effects on the uptake of metals on montmorillonite (as a model 2:1 clay mineral) were investigated at trace concentrations in the presence of different metals at high concentrations. One of the main findings from this experimental work was that all metals are not mutually competitive, but rather competition is selective. Metals with similar chemistries (valence state, hydrolysis behaviour) compete with one another but metals with dissimilar chemistries do not compete e.g. divalent transition metals with trivalent lanthanides, or Th(IV) with U(VI).



### 3 Source sorption data

#### 3.1 Illite source data sets

The illite source sorption data sets for the elements contained in the OPA-EN SDB (Bradbury & Baeyens 2003a, Tab. 10 in NTB 02-19) are given in Table 3.1, column 2, together with the corresponding references, column 5. The pH and the speciation factors for the source illite data are also given in Table 3.1, columns 3 and 4 respectively. For the majority of elements, the source sorption values were selected at pH 7 in a simple NaClO<sub>4</sub> background electrolyte for which the speciation factors were unity.

In all cases, except three, sorption values were taken from illite measurements. The source data for Pb(II) and Sb(III) (using Bi(III) as the chemical analogue) arise from measurements on montmorillonite (Ulrich & Degueldre 1992), and for Nb(V), from measurements on sedimentary rocks (Legoux et al. 1992). (For convenience these source data have the same nomenclature as the illite data in Table 3.1, i.e.  $R_{d,ILLITE}$ ,  $pH_{ILLITE}$ ,  $F_{ILLITE}$  but are indicated by an asterisk: \*.

Tab. 3.1: Selected illite source sorption values ( $R_{d,ILLITE}$ ) together with the source pH ( $pH_{ILLITE}$ ), speciation factor ( $F_{ILLITE}$ ) and the source data references.

Radionuclide	$R_{d,ILLITE}$ (m <sup>3</sup> kg <sup>-1</sup> )	$pH_{ILLITE}$	$F_{ILLITE}$	Source data reference
Co(II)	1.6	7.0	1.0	Illite: Bradbury & Baeyens (2009a)
Ni(II)	4.0	7.0	1.0	Illite: Bradbury & Baeyens (2009a)
Se(IV)	0.018	7.0	1.0	Illite: Bruggeman (2006)
*Nb(V)	1			Sedimentary rocks: Legoux et al. (1992)
Mo(VI)	0.016	8.2	1.0	Illite: Motta & Miranda (1989)
Tc(IV)	2.5	7.0	1.0	Expert judgement (see below)
Sn(IV)	250	7.0	0.89	Illite: Bradbury & Baeyens (2009a)
*Bi(III)	32	7.0	1.0	Montmorillonite: Ulrich & Degueldre (1992)
Eu(III)	100	7.0	1.0	Illite: Bradbury & Baeyens (2009a)
	400	7.0	1.0	Illite: Bradbury & Baeyens (2005b)
*Pb(II)	32	7.0	0.93	Montmorillonite: Ulrich & Degueldre (1992)
Th(IV)	250	7.0	1.0	Illite: Bradbury & Baeyens (2009b)
Pa(V)	50	7.0	1.0	Illite: Bradbury & Baeyens (2009b)
Am(III)	300	7.0	1.0	Illite: Bradbury & Baeyens (2009b)

For the elements H(HTO), C<sub>org.</sub>, Cl(-I), Se(-II) and Ag(I) sorption values of zero were selected by Bradbury & Baeyens (2003a), and in the intervening time no new information has arisen warranting a change to this view. However, for Ru(IV) and I(-I) sorption values were selected in

the OPA-EN SDB. More recent information given in Bradbury et al. (2010) led to the conclusion that these elements should also be assigned zero sorption. The elements with  $R_d$  values equal to zero are not included in Table 3.1.

The alkaline (Cs) and alkaline-earth (Ca, Sr, Ra) elements sorb via a cation exchange mechanism and the sorption values are directly calculated from a cation exchange sorption model (see section 3.2). The sorption value for inorganic carbon is calculated from isotopic exchange with the calcite in the OPA system, and hence this value remains unchanged. These elements are also not included in Table 3.1.

### Comments to Table 3.1

#### Pb(II) and Bi(III)

Ulrich & Degueldre (1992) measured the sorption of Pb(II) and Bi(III) at trace concentrations on montmorillonite as a function of ionic strength and pH. The lowest values measured at pH = 7 were chosen, see Fig. 3.1. The surface complexation characteristics of montmorillonite and illite are similar, see Bradbury & Baeyens (2005a, 2009b), with the uptake on illite being generally stronger. For the above reasons the sorption values for Pb and Bi included in Table 3.1 are considered to be conservative. Note that in previous work, Bradbury & Baeyens (2003a), the source Pb sorption values were selected from measurements on a somewhat ill-defined sediment (Koss et al. 1992). Upon a re-evaluation of the data situation, it was decided that it was better to take the measurements on montmorillonite because of the availability of recent information on the similarity of the sorption behaviour of illite and montmorillonite.

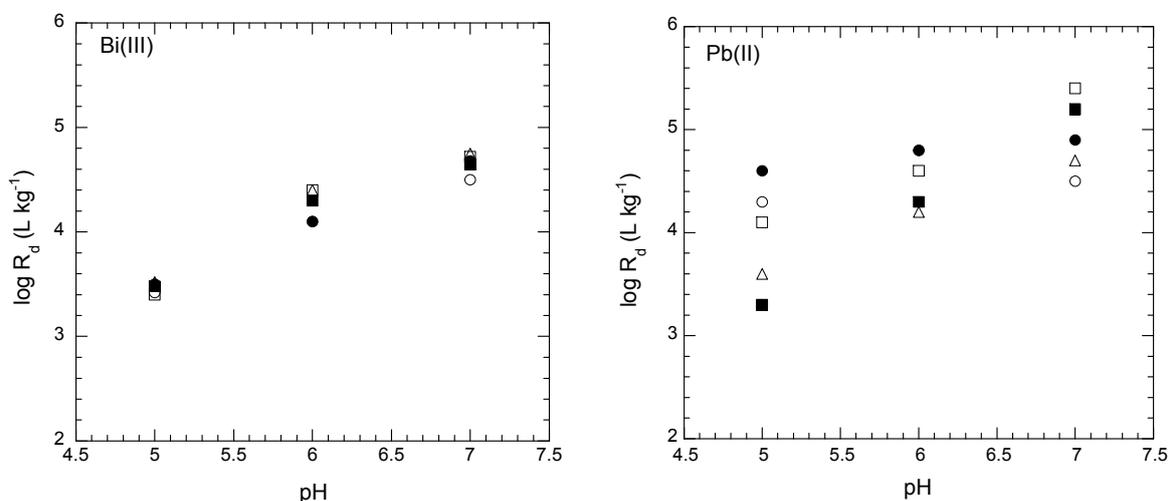


Fig. 3.1: (a) Bi(III) and (b) Pb(II) sorption data from Ulrich & Degueldre (1992) re-plotted as a sorption edge. NaClO<sub>4</sub> background electrolyte at 0.01 M (○); 0.02 M (●); 0.05 M (□); 0.1 M (■) and 0.2 M (△).

#### Eu(III): chemical analogue for Ce(III), Pm(III), Sm(III), Ho(III)

Sorption edges results for Eu on Na-illite have been reported in Bradbury & Baeyens (2005b) and Bradbury & Baeyens (2009a). Two sets of Eu sorption values for Na-illite were selected at pH = 7; 160 to 400 m<sup>3</sup> kg<sup>-1</sup> (Bradbury & Baeyens 2005b) and 100 m<sup>3</sup> kg<sup>-1</sup> (Bradbury & Baeyens 2009a) i.e. values differing by a factor of ~4.

**Ru(III/IV)**

No sorption data at all could be found for Ru(III/IV). The thermodynamic data available are sparse and uncertain and no chemical analogue for which reliable sorption data are available readily suggests itself. Because of this extreme lack of information, Ru(III/IV) has been taken as non sorbing.

**Tc(IV)**

There are no reliable sorption data for Tc(IV). The solubility is very low, and speciation calculations indicate that the neutral  $\text{TcO}(\text{OH})_2^0$  species is dominant in simple 1:1 electrolyte solutions from pH ~ 3 to ~ 10.

In the cases of Th(IV) and Sn(IV) the dominant aqueous species in the pH range ~4 to ~10 is the neutral tetrahydroxy complex and the sorption of these two elements on clay minerals (illite, montmorillonite) is very high and constant in this pH range (Bradbury & Baeyens 2005a, 2009a,b). If it is accepted that the key sorption indicators are the presence of hydroxy ions in an overall neutral species, a similar sorption behaviour between a neutral tetrahydroxy complex and a neutral  $\text{TcO}(\text{OH})_2^0$  species might be expected. Given the lack of reliable quantitative experimental data, a nominal sorption value for Tc(IV) on illite of 2 orders of magnitude below that of Sn(IV) and Th(IV) is given i.e.  $2.5 \text{ m}^3 \text{ kg}^{-1}$ . (The speciation factor corresponding to the reference water for Tc(IV) is unity.)

**Nb(V)**

In the case of Nb(V), the only data available are those from Legoux et al. (1992). The "one off" sorption results measured at different pH values by Legoux et al. (1992) for four sediments with different clay mineral contents are given in Table 3.2. The illite/glaucanite and smectite values are given. The presence of the other minerals (kaolinite, < 2 wt. % and palygorskite, 1.4 wt. % in sediment A) has been neglected.

Tab 3.2: Sorption data for Nb(V) in a synthetic groundwater on various sediments. (Nb equilibrium concentration <  $10^{-10}$  M). Taken from Legoux et al. (1992).

<b>Solid phase</b>	<b>Clay content (wt. %)</b>	<b>pH<sub>source</sub></b>	<b>R<sub>d</sub> measured (m<sup>3</sup> kg<sup>-1</sup>)</b>
Sediment A	7.2	7.6	2.6
Sediment B	12.6	5.9	1.5
Sediment C	15.3	6.6	1.7
Sediment D	8.0	8	2.1

The Legoux et al. (1992) data for the sorption of Nb(V) at different pH values (5.9 to 8) on sediments with different 2:1 clay mineral contents (7.2 to 15.3 wt. %) seem to be independent of both of these parameters i.e. a sorption value of around  $2 \text{ m}^3 \text{ kg}^{-1}$  is measured in all cases, and this is somewhat difficult to understand.

The sorption mechanism for Nb(V) is not known, and there is no sorption model to guide the selection of sorption values under different conditions. If the main sorbing species is taken to be  $\text{Nb}(\text{OH})_5^0$ , then at pH ~ 6 the negatively charged  $\text{Nb}(\text{OH})_6^-$  species already begins to form, and

this is taken to be non-sorbing. Further, nothing is known about the complexation of Nb(V) with carbonate. Again, in the range of water chemistries investigated by Legoux et al. (1992), these factors do not seem to have played an important role.

Thus, there are considerable difficulties in applying this data for Nb(V) to other systems. However, Legoux et al.'s experiments do at least indicate that Nb(V) sorbs, and some credit should be taken for this; but Nb(V) needs to be treated as a special case.

The following is recommended on the basis of conservatism. A sorption value of  $1 \text{ m}^3 \text{ kg}^{-1}$  is taken for any systems which lie in the range of the main parameters in Legoux et al.'s experiments i.e. for average clay mineral contents of approximately 10 wt. % and pH values in the range 6 to 8.

For any systems with a  $\text{pH} > 8$ , the sorption of Nb(V) is set to zero for speciation reasons. If the 2:1 clay mineral content in an argillaceous rock is  $>10 \text{ wt. \%}$ , then, on a conservative approach, no additional credit is taken for this. However, for 2:1 clay mineral contents  $> 0$  and  $< 10 \text{ wt. \%}$ , sorption will occur, and in such cases the sorption value of  $1 \text{ m}^3 \text{ kg}^{-1}$  should be reduced proportionally i.e. by a reduction factor of  $X/10$ , where "X" is the 2:1 clay mineral wt% content.

### 3.2 Cation Exchange

For those metals sorbing primarily by cation exchange, sorption values for illite were calculated directly in the OPA reference water chemistry, Table 4.2, using the selectivity coefficients for illite given in Table 3.3. The calculated sorption values for illite were then converted to  $R_d$  values for OPA using the mineral conversion factor.

Tab. 3.3: Cation exchange reactions and corresponding selectivity coefficients ( $K_c$ ) on the planar sites, type-II sites and frayed edge sites of illite (Taken from Bradbury & Baeyens 2000, 2005b). (Illite CEC =  $0.2 \text{ Eq kg}^{-1}$ ).

Cation exchange reactions:	$\log K_c$	Site capacities
Planar sites (PS)		$1.6 \times 10^{-2} \text{ Eq kg}^{-1}$
$\text{Na-PS} + \text{K}^+ \rightleftharpoons \text{K-PS} + \text{Na}^+$	1.1	
$\text{Na-PS} + \text{Cs}^+ \rightleftharpoons \text{Cs-PS} + \text{Na}^+$	1.6	
$2\text{Na-PS} + \text{Me}^{2+} \rightleftharpoons \text{Me-PS} + 2\text{Na}^+$	1.05	
Type II sites (II-S)		$4.0 \times 10^{-3} \text{ Eq kg}^{-1}$
$\text{Na-II-S} + \text{K}^+ \rightleftharpoons \text{K-II-S} + \text{Na}^+$	2.1	
$\text{Na-II-S} + \text{Cs}^+ \rightleftharpoons \text{Cs-II-S} + \text{Na}^+$	3.6	
Frayed edge sites (FES)		$5.0 \times 10^{-4} \text{ Eq kg}^{-1}$
$\text{Na-FES} + \text{K}^+ \rightleftharpoons \text{K-FES} + \text{Na}^+$	2.4	
$\text{Na-FES} + \text{Cs}^+ \rightleftharpoons \text{Cs-FES} + \text{Na}^+$	7.0	

$\text{Me}^{2+} = \text{Ca}^{2+} \text{ or } \text{Sr}^{2+} \text{ or } \text{Ra}^{2+}$

## 4 Application to the Opalinus Clay reference system

### 4.1 OPA reference water chemistry and mineralogy

In this chapter a SDB is derived for the OPA system (OPA-Illite SDB) based on the source data set for illite given in Chapter 3. The reference mineralogy and porewater composition used in the Entsorgungsnachweis (Nagra 2002) for OPA have been taken for this exercise and these data sets are given in Tables 4.1 and 4.2 respectively.

Tab. 4.1: Reference mineralogy for Opalinus Clay from Benken and reference OPA groundwater composition (Nagra 2002).

Mineral	Benken OPA (wt. %)		
Calcite	16	pH	7.24
Dolomite/Ankerite	1	log p-CO <sub>2</sub>	-2.20 bar
Siderite	4	Eh	-0.167 V
Quartz	20	I.S.	0.23 M
K-Feldspar	2	Temperature	25 °C
Albite	1	Dissolved constituents	Conc. (M)
Pyrite	1.1	Na	1.69 x 10 <sup>-1</sup>
Illite	18	K	5.65 x 10 <sup>-3</sup>
Illite/Smectite ML	14	Mg	7.48 x 10 <sup>-3</sup>
Kaolinite	17	Ca	1.05 x 10 <sup>-2</sup>
Chlorite	5	Sr	3.04 x 10 <sup>-4</sup>
Organic Carbon	0.6	Alkalinity as HCO <sub>3</sub>	2.50 x 10 <sup>-3</sup>
		C <sub>inorg.</sub>	2.70 x 10 <sup>-3</sup>
		S(VI) as SO <sub>4</sub>	2.40 x 10 <sup>-2</sup>
		S(-II) as H <sub>2</sub> S	1.41 x 10 <sup>-11</sup>
		F	1.67 x 10 <sup>-4</sup>
		Cl	1.60 x 10 <sup>-1</sup>
		Br	2.40 x 10 <sup>-4</sup>
		Fe (total)	4.33 x 10 <sup>-5</sup>
		Mn (total)	2.42 x 10 <sup>-5</sup>
		Al (total)	1.78 x 10 <sup>-8</sup>
		U (total)	6.96 x 10 <sup>-9</sup>
		Si (total) as SiO <sub>2</sub> aq.	1.78 x 10 <sup>-4</sup>

The potential contributions of kaolinite (a 1:1 clay mineral) and chlorite (a 2:1:1 mineral), present in Opalinus Clay at levels of ~17 wt. % and ~5 wt. % respectively (Table 4.1), to the overall sorption have not been included. The reason is that little or no sorption data exist for them and thus including their contribution was not possible. If kaolinite and chlorite were

assumed to behave as 2:1 clay minerals, then this would lead to an overall increase in the calculated sorption values by a factor of  $\sim 1.7$  in this case. On the other hand, not including them implies that the predicted sorption values are conservative.

#### 4.2 Illustrative application example

As an illustration of the application of the procedure, the case of Ni(II) is considered. The  $R_{d\text{ILLITE}}$  value was chosen from sorption edge measurements carried out on illite in 0.1 M  $\text{NaClO}_4$  at  $\text{pH} = 7$  (Bradbury & Baeyens 2009a). The speciation factor,  $F_{\text{ILLITE}}$ , was calculated according to the procedure given in Chapter 2. Since the sorption measurements were carried out on “pure illite”, the illite weight fraction ( $\text{MIN}_{\text{ILLITE}}$ ) is equal to unity. The source sorption data, and associated parameters, are summarised in Table 4.3.

Tab. 4.3: Illite parameters for Ni(II) taken from Table 3.1.

Element	$R_{d\text{ILLITE}}$ ( $\text{m}^3 \text{kg}^{-1}$ )	$\text{MIN}_{\text{ILLITE}}$	$F_{\text{ILLITE}}$	$\text{pH}_{\text{ILLITE}}$
Ni(II)	4.0	1.0	1.0	7.0

Note, since it is known that the reference pH for OPA is 7.24, and a sorption edge for Ni on illite was available, the sorption value for Ni could have been selected at a pH of 7.24. However, the purpose in this example is to illustrate the general procedure since it is not always the case that edge data are available.

For the OPA reference system, Tables 4.1 and 4.2, the 2:1 type clay mineral fraction (illite + illite/smectite ML) and the pH are known, and the speciation factor for Ni can be calculated, Table 4.4.

Tab. 4.4: OPA parameters for Ni(II) obtained from Tables 4.1 and 4.2.

$\text{MIN}_{\text{OPA}}$	$F_{\text{OPA}}$	$\text{pH}_{\text{OPA}}$
0.32	0.67	7.24

From the values given in Tables 4.3 and 4.4, the mineral, speciation and pH conversion factors can be determined (see section 2.2) and the Ni(II) sorption value for OPA calculated according to Eq. 6, Table 4.5.

Tab. 4.5: Conversion factors and  $R_{d\text{OPA}}$  for Ni(II).

$R_{d\text{ILLITE}}$ ( $\text{m}^3 \text{kg}^{-1}$ )	$\text{CF}_{\text{MIN}}$	$\text{CF}_{\text{SPEC}}$	$\text{CF}_{\text{pH}}$	$R_{d\text{OPA}}$ ( $\text{m}^3 \text{kg}^{-1}$ )
4.0	0.32	0.67	1.39	1.2

Applying this procedure to all of the elements in Table 3.1, the chemical analogues listed in Table 2.2, and including the sorption values due to cation exchange calculated from the data in Table 3.3, the OPA sorption values derived from illite sorption data are given in Table 4.6, column 2, the OPA-Illite SDB. The values contained in the OPA-EN SDB used in the Entsorgungsnachweis (Bradbury & Baeyens 2003a) are given in column 3 for comparison. The ratios of the two values are presented in column 4.

Tab. 4.6: Sorption values for OPA calculated from illite data (OPA-Illite SDB) and the OPA sorption values used in the Entsorgungsnachweis, OPA-EN SDB, Table 10 in NTB 02-19.

Element	$R_d$ values OPA-Illite SDB ( $m^3 kg^{-1}$ )	$R_d$ values OPA-EN SDB ( $m^3 kg^{-1}$ )	$\frac{R_{d\text{ OPA-Illite SDB}}}{R_{d\text{ OPA-EN SDB}}}$
H(HTO)	0	0	-
C <sub>inorg.</sub>	1.6E-3	1.6E-3	<b>1.0</b>
C <sub>org.</sub>	0	0	-
Cl(-I)	0	0	-
Ca(II)	9.0E-4	1.1E-3	<b>0.8</b>
Co(II)	0.57	0.49	<b>1.2</b>
Ni(II)	1.2	0.93	<b>1.3</b>
Se(-II)	0	0	-
Sr(II)	9.0E-4	1.1E-3	<b>0.8</b>
Zr(IV)/Hf(IV)	7.2	10.9	<b>0.7</b>
*Nb(V)	1	4	-
Mo(VI)	9.9E-3	1.7E-2	<b>0.6</b>
*Tc(IV)	2.5	55.4	-
*Ru(III/IV)	0	5	-
Pd(II)	15.0	5	<b>3.0</b>
Ag(I)	0	0	-
Cd(II)	0.23	0.18	<b>1.3</b>
Sn(IV)	73	110	<b>0.7</b>
Sb(III)	10.2	5.6	<b>1.8</b>
I(-I)	0	3.5E-05	-
Cs(I)	1.0	0.55	<b>1.8</b>
Eu(III)/Ce(III)/ Pm(III)/Sm(III)/ Ho(III)	1.8 – 7.2	59.8	<b>0.03 – 0.12</b>
Pb(II)	2.1	2.7	<b>0.8</b>
Po(IV)	4.1E-3	0.18	<b>0.02</b>
Ra(II)	6.1E-4	7.6E-4	<b>0.8</b>
Th(IV)	80	55.4	<b>1.4</b>
Pa(V)	16	5.0	<b>3.2</b>
U(IV)	29.6	20.5	<b>1.4</b>
Np(IV)	80	55.4	<b>1.4</b>
Pu(III)	5.3	18.5	<b>0.3</b>
Am(III) Ac(III)/Cm(III)	4.3	17	<b>0.3</b>

\* For these metals, a totally different approach was used here to that for OPA-EN SDB (Bradbury and Baeyens 2003a). No ratio  $R_{d\text{ OPA-Illite SDB}}/R_{d\text{ OPA-EN SDB}}$  is calculated.

### 4.3 Discussion

Considering Table 4.6, column 4, it may be readily appreciated that ~ 70 % of the radionuclide sorption values predicted for OPA on the basis of illite data as described in this work, are within a factor of 2 ( $0.5 < R_{d \text{ OPA-Illite SDB}}/R_{d \text{ OPA-EN SDB}} < 2$ ) of the values contained in the OPA-EN SDB generated for the Entsorgungsnachweis (Bradbury & Baeyens 2003a), and can essentially be considered to be the same. (Elements with zero sorption and  $C_{\text{inorg.}}$ , for which the same method was used to calculate the sorption in both cases, are excluded from the comparison. Also, the chemical analogues for which the speciation factors are the same, are listed together in Table 4.6).

As a general comment, it may be stated that the mineralogical conversion factor ( $CF_{\text{MIN}}$ ) used in the approach described here is, in the majority of cases, the weight fraction of the 2:1 type clay minerals in the OPA i.e. 0.32. In the case of the OPA-EN SDB (Bradbury & Baeyens 2003a) the  $CF_{\text{MIN}}$  was calculated based on the respective CEC values of OPA (106 meq kg<sup>-1</sup>) and illite (200 meq kg<sup>-1</sup>), which yielded a value of 0.53. Thus in the OPA-Illite SDB the approach is more conservative and would, on the basis of this parameter alone, tend to predict values which are a factor of ~1.7 lower.

For Nb(V), Tc(IV) and Ru(III/IV) the sorption knowledge base is especially poor. No comparison with the values in OPA SDB was made because a totally different approach was used here.

For the elements Pd(II), Po(IV), Pa(V) and Eu(III)/Am(III) and analogues the ratios  $R_{d \text{ OPA-Illite SDB}}/R_{d \text{ OPA-EN SDB}}$  are different by more than a factor of 2. The reasons for the differences are discussed below for each element.

#### **Pd(II)**

In the OPA-EN SDB, an “expert judgement” approach was used for Pd(II), whereas in this work the element Pb(II) was chosen as a chemical analogue for Pd(II).

#### **Po(IV)**

Se(IV) was taken as the chemical analogue to derive sorption values for Po(IV). The sorption data for Se(IV) on illite were taken from the work of Bruggeman (2006), see Fig. 2.2. These data have a very high reliability factor. The Se(IV) values given in the OPA-EN SDB come from measurements on samples of OPA from Mont Terri (Lauber et al. 2000), and are nearly a factor of 80 higher. The reason for this very large discrepancy is not known. However, there were some inconsistencies in the measurements of Lauber et al. (2000) i.e. the sorption of Se(IV) decreased with decreasing pH whereas, in fact, as an oxyanion, it should have increased. On balance, the Se(IV) sorption value used to derive the Po(IV) sorption in the OPA-Illite SDB approach is considered to be more reliable than in OPA-EN SDB.

#### **Pa(V)**

The sorption value for Pa(V) given in the OPA-EN SDB was based on an “expert judgement”. The Pa(V) sorption value given in the OPA-Illite SDB approach is based on new measurements of Pa(V) on illite and for this reason is the preferred value.

### **Trivalent lanthanides and actinides (Eu(III), Am(III) and chemical analogues)**

The root cause of the differences between the sorption values derived for Eu(III) and Am(III) in the OPA-Illite SDB and in the OPA-EN SDB are essentially the same, and have to do with the strong formation of carbonate complexes in the OPA reference porewater.

Where the source data are from illite (sorption measured in the absence of carbonate) the speciation conversion factors ( $CF_{SPEC}$ ) used to obtain the corresponding sorption values in the OPA system are very small (circa 0.05) and therefore this has a large reduction effect on the sorption value. This is the case for the OPA-Illite SDB.

The sorption sources for Eu(III) and Am(III) used to derive  $R_d$  values in the OPA-EN SDB, were taken from carbonate containing systems (assumed calcite or “atmosphere” saturated systems). Because conversions were calculated from one carbonate saturated system to another carbonate saturated system (the reference OPA system) the speciation factors in both cases were small but their quotient, the speciation conversion factor, was quite large (greater than 0.5) and thus had only a minor effect on the calculated sorption value.

Despite the low calculated speciation factors for Eu(III) and Am(III) in the source systems used for the OPA-EN SDB (OPA, Lauber et al. (2000), and illite under “atmospheric conditions”, Gorgeon (1994), respectively) the sorption values in both cases were high. This could imply that either the carbonate complexation constants in Hummel et al. (2000) are too high (if carbonates do not sorb) or that carbonate complexes can sorb.

In any event, the  $R_d$  values given in the OPA-Illite SDB are clearly more conservative than those in the OPA-EN SDB.

## **4.4 Comparison with sorption measurements on Opalinus Clay**

The sorption data base in the Entsorgungsnachweis (Bradbury & Baeyens 2003a) contains data derived from different sources: measurements on Opalinus Clay, on the clay mineral illite or on other systems. A comparison of the values measured on Opalinus Clay for the metals Ni(II), Sr(II), Sn(IV), Cs(I), Eu(III), Th(IV), with those derived in this report is of special interest when evaluating the performance of the method. However, it should be noted that the sorption measurements on Opalinus Clay were carried out in a synthetic NaCl-type pore water ( $I = 0.3$ , pH 6.3 and 7.8) and these values were then converted to the Opalinus Clay reference pore water (Nagra 2002) using similar correction factors to those given in section 2.2. With the exception of Eu(III), all the  $R_d$  values derived from measurements on Opalinus Clay were reproduced within a factor of two by the methodology described (cf. Table 4.6). The reason for the difference in the Eu(III) value has already been discussed in section 4.3. This comparison shows that the differences between the measured and derived sorption values for Opalinus Clay are similar to the uncertainties associated with the experimental measurements.



## 5 MX-80 bentonite SDB derived on the basis of sorption data measurements on Na-montmorillonite

### 5.1 Introduction

The aim in this chapter is to derive a SDB for MX-80 bentonite, MX-80-Mont SDB, based on sorption data measured on Na-montmorillonite, (MX-80 bentonite contains ~75 wt. % montmorillonite.) The  $R_d$  values will then be compared on an element by element basis with those contained in the sorption data base used in the Entsorgungsnachweis (Nagra 2002), MX80-EN SDB, (Bradbury & Baeyens 2003b).

### 5.2 Methodology and conversion factors

The procedures used are the same as those described in Chapter 2 for Opalinus Clay; illite is replaced by montmorillonite (Mont).

#### 5.2.1 Conversion factors

##### 5.2.1.1 Mineral conversion factor: $CF_{MIN}$

$$CF_{MIN} = (MIN_{MX80} / MIN_{MONT}) \quad (5.1)$$

where,

$CF_{MIN}$  = mineralogy conversion factor

$MIN_{MX80}$  = montmorillonite weight fraction in MX-80 bentonite (= 0.75)

$MIN_{MONT}$  = 1 (100% montmorillonite)

Mineral conversion factor = 0.75.

##### 5.2.1.2 Speciation conversion factor, $CF_{SPEC}$

The same speciation factors used previously in the MX80-EN SDB (Bradbury & Baeyens 2003b), and documented in Curti (2001), are applied to calculate speciation conversion factors.

The conversion factor used for modifying sorption values according to the speciation in different water chemistries is simply:

$$CF_{SPEC} = F_{MX80} / F_{MONT} \quad (5.2)$$

where,

$CF_{SPEC}$  is the speciation conversion factor.

$F_{MX80}$  is the fraction of sorbing radionuclide species calculated to be present in the aqueous phase in the MX-80 bentonite reference porewater.

$F_{MONT}$  the fraction of sorbing radionuclide species calculated to be present in the aqueous phase in the montmorillonite system.

Sorbing species are considered, as before, to be free cations, and positive and neutral hydrolysed species only.

### 5.2.1.3 pH conversion factors, $CF_{pH}$

For metals which sorb by surface complexation, corrections for any differences in pH when converting sorption values from one system to another can be significant. (Alkaline and alkaline-earth metals which sorb predominantly by cation exchange do not have an associated pH conversion factor.)

For the measured sorption edge of each element on montmorillonite, the slope  $m$ , and the pH range where this slope is constant, can be evaluated. Eq. 9 can then be used to calculate the corresponding  $CF_{pH}$  value.

$$CF_{pH} = \frac{R_{d2}}{R_{d1}} = 10^{m(pH_2 - pH_1)} \quad (5.3)$$

(See Fig. 2.1 for the definitions of  $R_{d1}$ ,  $pH_1$ ;  $R_{d2}$ ,  $pH_2$  and  $m$ )

A summary of the radionuclides for which a slope and pH range were derived from experimental sorption edge data on montmorillonite is given in Table 5.1.

Tab. 5.1: Slope values, “ $m$ ”, for sorption edges on montmorillonite used to calculate pH conversion factors,  $CF_{pH}$ , Eq. 9.

Radionuclide	slope	pH range	Source
Co(II)	0.68	6 - 8	Tiller & Hodgson (1960) “smectite”
Ni(II)	0.6	6 - 9	Baeyens & Bradbury (1997)
Cd(II)	0.65	6.6 – 7.5	Zachara et al. (1993) “smectite”
Pb(II)	0.65	5 - 7	Ulrich & Degueldre (1992)
Eu(III)	0.8	5.5 – 8.5	Bradbury & Baeyens (2005)
Am(III)/Eu(III)	0.84	5 – 7.5	Bradbury & Baeyens (2006)
Bi(III)	0.6	5 - 7	Ulrich & Degueldre (1992)
Se(IV)	-0.4	5 – 8	Bradbury & Baeyens (unpublished data)
Mo(VI)	-0.3	4 - 8	Theng (1971) “clays”

As in the case for illite, section 2.2.3, no  $CF_{pH}$  conversion factors are required, in the range of the pH values given, for those elements which exhibit sorption plateaus on montmorillonite.

- Th(IV): sorption plateau from pH 5 to 11 (Bradbury & Baeyens 2005).
- Sn(IV): sorption plateau from pH 3 to 9 (Bradbury & Baeyens 2005).
- Tc(IV): assumed sorption plateau from pH 3 to 10 (Bradbury et al. 2010).
- Pa(V): sorption plateau from pH 4 to 11 (Bradbury & Baeyens 2006).

### 5.2.2 Chemical analogues

The elements and their chemical analogues used in this work are listed in Table 2.2. Note that for Cd(II), sorption data on montmorillonite were available and no chemical analogue was needed here. In cases where chemical analogy is invoked, the conversion approach is exactly the same as described in section 2.3.

$$R_{d\text{ RN MX80}} = R_{d\text{ ANALOG MX80}} \cdot CF_{\text{SPEC RN MX80}}$$

### 5.2.3 Formulation

The above procedures can be summarised as follows. For a montmorillonite source data set of  $R_{d\text{ MONT}}$ ,  $MIN_{\text{MONT}}$ ,  $pH_{\text{MONT}}$ ,  $F_{\text{MONT}}$ , and where the distribution ratio,  $R_{d\text{, MX80}}$ , is required for the MX-80 reference conditions with  $MIN_{\text{MX80}}$ ,  $pH_{\text{MX80}}$ ,  $F_{\text{MX80}}$  values, then

$$R_{d\text{, MX80}} = R_{d\text{ MONT}} \cdot CF_{\text{MIN}} \cdot CF_{\text{SPEC}} \cdot CF_{\text{pH}} \quad (5.4)$$

where:

$$CF_{\text{MIN}} = (MIN_{\text{MX80}} / MIN_{\text{MONT}})$$

$$CF_{\text{SPEC}} = (F_{\text{MX80}} / F_{\text{MONT}})$$

$$CF_{\text{pH}} = 10^{m(pH_{\text{MX-80}} - pH_{\text{MONT}})}$$

## 5.3 Source sorption data

### 5.3.1 Montmorillonite

The montmorillonite  $R_d$  values selected from the source sorption data sets for the elements contained in the MX80-EN SDB (Bradbury & Baeyens 2003b, Table 8 in NTB 02-18), and used in the development of the MX-80-Mont SDB, are given in Table 5.2. The speciation factors and pH values for the source montmorillonite data are also given in Table 5.2. For the majority of elements, the source sorption values were selected at pH 7 in a simple  $\text{NaClO}_4$  background electrolyte for which the speciation factors were unity.

For the elements  $C_{\text{organic}}$ , Cl(-I), Se(-II) and Ag(I) sorption values of zero were selected by Bradbury and Baeyens (2003b). Upon reviewing these choices, no reasons were found to change them.

For Ru(III/IV) a sorption value was selected by expert judgement in the MX80-EN SDB. More recent information given in Bradbury et al. (2010) led to the conclusion that this element should also be assigned zero sorption.

A very small  $R_d$  value for iodide was given in the MX80-EN SDB. It has been replaced by zero sorption in the MX-80-Mont SDB because new measurements made under anoxic conditions showed clearly that there was no measurable sorption of iodide on MX-80 (Bradbury & Baeyens, unpublished data).

The elements with  $R_d$  values equal to zero are not included in Table 5.2.

The sorption value for inorganic carbon is calculated from isotopic exchange with the calcite in the MX-80 system, and hence this value remains unchanged.

The alkaline (Cs) and alkaline-earth (Ca, Sr, Ra) elements sorb via a cation exchange mechanism and are calculated from a cation exchange sorption model (see section 5.3.2) for montmorillonite in the reference bentonite porewater. The conversions to sorption values for MX-80 are then carried out over the mineralogical conversion factor.

In all cases, except Nb(V), sorption values are taken from montmorillonite measurements or based on chemical analogues where the sorption measurements were made on montmorillonite.

Tab. 5.2: Selected montmorillonite source sorption values ( $R_{d,MONT}$ ) together with the source pH ( $pH_{MONT}$ ), speciation factor ( $F_{MONT}$ ) and the source data references.

Radionuclide	$R_{d,MONT}$ ( $m^3 kg^{-1}$ )	$pH_{MONT}$	$F_{MONT}$	Source data reference
Co(II)	1.6	7.0	1.0	Tiller & Hodgson (1960)
Ni(II)	1.6	7.0	1.0	Baeyens & Bradbury (1997)
Se(IV)	0.14	7.0	1.0	Baeyens & Bradbury (unpubl. data)
Nb(V)	1			Legoux et al. (1992)
Mo(VI)	0.165	4.0	1.0	Motta & Miranda (1989)
Tc(IV)	5			Expert judgement
Cd(II)	0.56	7.0	1.0	Zachara et al. (1993)
Sn(IV)	1000	7.0	0.89	Bradbury & Baeyens (2005)
Bi(III)	50	7.0	1.0	Ulrich & Degueldre (1992)
Eu(III)	80 316	7.0	1.0	Bradbury & Baeyens (2005a) Bradbury & Baeyens (2006)
Pb(II)	50	7.0	0.93	Ulrich & Degueldre (1992)
Th(IV)	500	7.0	1.0	Bradbury & Baeyens (2005a)
Pa(V)	100	7.0	1.0	Bradbury & Baeyens (2006)
Am(III)	316	7.0	1.0	Bradbury & Baeyens (2006)

### Comments to Table 5.2

#### Nb(V)

No sorption data for Nb(V) on montmorillonite are available in the open literature. Only data on sedimentary rocks were found (Legoux et al. 1992). A similar procedure to the one presented in section 3.1 was also followed for montmorillonite, i.e. an  $R_d$  value of  $1 m^3 kg^{-1}$  was selected.

#### Tc(IV)

For the same reasons as discussed in section 3.1, tetravalent thorium is not taken directly as a chemical analogue for Tc(IV) any longer. Given the lack of reliable quantitative experimental data, a nominal sorption value for Tc(IV) on montmorillonite of 2 orders of magnitude below that of Th(IV) is given i.e.  $5 m^3 kg$ . The speciation factor corresponding to the reference water is applied.

## Mo(VI)

Molybdenum only exists in the +6 valence state, and above pH 4 the dominant aqueous species is the anionic molybdate ( $\text{MoO}_4^{2-}$ ) (Baes & Mesmer 1976). Mo(VI) was treated as being non-sorbing in the MX80-EN SDB.

However, although sorption data for  $\text{MoO}_4^{2-}$  on geological substrates are scarce, Motta & Miranda (1989) did in fact show that  $\text{MoO}_4^{2-}$  is taken up by clay minerals (kaolinite, montmorillonite and illite). An  $R_d$  value of  $0.17 \text{ m}^3 \text{ kg}^{-1}$  at pH = 4 for  $\text{MoO}_4^{2-}$  could be extracted from their measurements on montmorillonite (25 °C, equilibrium concentration of  $10^{-4} \text{ M}$ ) but the pH dependency could not be deduced nor could reliable data be extracted at lower Mo concentrations because the results were presented on a linear scale.

The (approximate) pH dependency of  $\text{MoO}_4^{2-}$  uptake could be deduced from results presented by Theng (1971) on  $\text{MoO}_4^{2-}$  retention by soil clays. The sorption decreased in the pH range 4 to 8 by a factor of approximately 2 for each unit increase in pH, and this was taken as the basis for the pH conversion factor.

### 5.3.2 Cation Exchange

For those metals sorbing primarily by cation exchange, sorption values were calculated for montmorillonite in the reference MX-80 porewater chemistry. A CEC value of  $870 \text{ meq. kg}^{-1}$  was selected for montmorillonite. This value was taken from a larger number of CEC measurements on SWy-1 montmorillonite (Baeyens & Bradbury 1997). The selectivity coefficients for K-Na, Mg-Na and Ca-Na, Table 5.3, were taken from the porewater chemistry studies on MX-80 bentonite, Bradbury and Baeyens (2002). This is considered to be valid since montmorillonite is the only clay mineral in MX-80 and constitutes ~75 wt. %. The calculated  $R_d$  values are then scaled over the mineral conversion factor.

Tab. 5.3: Cation exchange reaction and corresponding selectivity coefficients ( $K_c$ ) for montmorillonite (taken from Bradbury and Baeyens 2002). CEC for montmorillonite =  $870 \text{ meq. kg}^{-1}$ .

Exchange reaction	$K_c$
$\text{Na-mont} + \text{K}^+ \Leftrightarrow \text{K-mont} + \text{Na}^+$	4
$\text{Na-mont} + \text{Cs}^+ \Leftrightarrow \text{Cs-mont} + \text{Na}^+$	15 <sup>#</sup>
$2 \text{ Na-mont} + \text{Mg}^{2+} \Leftrightarrow \text{Mg-mont} + 2 \text{ Na}^+$	2.2
$2 \text{ Na-mont} + \text{Ca}^{2+} \Leftrightarrow \text{Ca-mont} + 2 \text{ Na}^+$	2.6 <sup>*</sup>

<sup>#</sup> Bradbury & Baeyens (Unpublished data)

<sup>\*</sup>  $\text{Ca}^{2+} = \text{Sr}^{2+} = \text{Ra}^{2+}$

## 5.4 Application to the MX-80 bentonite reference system

### 5.4.1 MX-80 bentonite reference water chemistry and mineralogy

The reference mineralogy and porewater composition used in the Entsorgungsnachweis (Nagra 2002) for MX-80 bentonite have been taken, and these data sets are given in Tables 5.4 and 5.5 respectively.

Tab. 5.4: Reference MX-80 mineralogy (Müller-Vonmoos & Kahr 1983).

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. 5.5: Reference porewater at pH = 7.25 for compacted MX-80 bentonite having an initial dry density of 1770 kg m<sup>-3</sup>. (Taken from Curti & Wersin 2002.)

pH	7.25
log p-CO <sub>2</sub>	-2.2 bar
Eh	-0.193 V
I.S.	0.34 M
Temperature	25 °C
Dissolved constituents	Conc. (M)
Na	2.74 x 10 <sup>-1</sup>
K	1.55 x 10 <sup>-3</sup>
Mg	7.64 x 10 <sup>-3</sup>
Ca	1.32 x 10 <sup>-2</sup>
Sr	1.90 x 10 <sup>-5</sup>
C <sub>inorg.</sub>	2.83 x 10 <sup>-3</sup>
SO <sub>4</sub>	6.16 x 10 <sup>-2</sup>
F	1.67 x 10 <sup>-4</sup>
Cl	1.91 x 10 <sup>-1</sup>
Br	2.40 x 10 <sup>-4</sup>
Fe (total)	4.33 x 10 <sup>-5</sup>
Mn (total)	2.43 x 10 <sup>-5</sup>
Al (total)	1.92 x 10 <sup>-8</sup>
Si (total) as SiO <sub>2</sub> aq.	1.80 x 10 <sup>-4</sup>

### 5.4.2 Application

Applying the procedure described in sections 5.2 and 5.3 to all of the elements in Table 5.2, the chemical analogues listed in Table 2.2, and including the sorption values due to cation exchange calculated from the data in Table 5.3, the MX-80 bentonite  $R_d$  values derived from montmorillonite sorption data are given in Table 5.6, column 2. The values contained in the MX80-EN SDB (Bradbury and Baeyens 2003b) are given in column 3 for comparison. The ratios of the two values are presented in column 4.

Tab. 5.6: Sorption values for MX-80 bentonite calculated from montmorillonite data, and the MX-80 bentonite sorption values given in MX80-EN SDB (Bradbury & Baeyens 2003b).

Element	$R_d$ values MX-80-Mont SDB ( $m^3 kg^{-1}$ )	$R_d$ values MX-80-EN SDB ( $m^3 kg^{-1}$ )	$\frac{R_{d \text{ MX-80-Mont SDB}}}{R_{d \text{ MX-80-EN SDB}}}$
$C_{inorg.}$	6.7E-5	6.7E-5	<b>1</b>
$C_{org.}$	0	0	-
Cl(-I)	0	0	-
Ca(II)	2.7E-03	3.3E-03	<b>0.8</b>
Co(II)	9.8E-01	6.4E-01	<b>1.5</b>
Ni(II)	8.1E-01	2.3E-01	<b>3.5</b>
Se(-II)	0	0	-
Sr(II)	2.8E-03	3.3E-03	<b>0.8</b>
Zr(IV)/Hf(IV)	67	81	<b>0.8</b>
*Nb(V)	1	30	-
Mo(VI)	1.3E-02	0	-
*Tc(IV)	5	63	-
*Ru(III/IV)	0	5	-
Pd(II)	55	5	<b>11</b>
Ag(I)	0	0	-
Cd(II)	6.1E-02	1.0E-01	<b>0.6</b>
Sn(IV)	843	810	<b>1</b>
Sb(III)	37.5	41.6	<b>0.9</b>
I(-I)	0	5.0E-04	-
Cs(I)	3.2E-02	1.2E-01	<b>0.3</b>
Eu(III)/Ce(III)/Pm(III)	2.9	4.7	<b>0.6</b>
Sm(III)/Ho(III)	11.3		<b>2.4</b>
Pb(II)	5.7	7.9	<b>0.7</b>
Po(IV)	8.3E-02	6.8E-02	<b>1.1</b>
Ra(II)	1.6E-03	2.1E-03	<b>0.8</b>
Th(IV)	375	63	<b>6</b>
Pa(V)	75	5	<b>15</b>
U(IV)	293	49.1	<b>6</b>
Np(IV)	375	63	<b>6</b>
Am(III)/Ac(III)/ Cm(III)/Pu(III)	9.5	26.8	<b>0.4</b>

\* For these metals, a totally different approach was used here to that for MX-80-EN SDB (Bradbury & Baeyens 2003b). No ratio  $R_{d \text{ MX-80-Mont SDB}}/R_{d \text{ MX-80-EN SDB}}$  is calculated.

## 5.5 Discussion

About 50 % of the radionuclide sorption values were within a factor of 2 of one another, Table 5.6, column 4, and can be regarded as being essentially the same. Elements with zero sorption ( $C_{org.}$ , Cl(-I), Se(-II), Ru(III/IV), Ag(I) and I(-I)) and  $C_{inorg.}$ , for which the same method was used to calculate the sorption in both cases, are excluded from the comparison.

For Nb(V), Tc(IV) and Ru(III/IV) the sorption knowledge base is especially poor. No comparison with the values in MX-80 SDB was made because a totally different approach was used here.

For the elements Ni(II), Cs(I), Pd(II), Eu(III), Th(IV), Pa(V) and Am(III) the ratios  $R_d$  MX80-Mont SDB/ $R_d$  MX80-EN SDB are different by more than a factor of 2. The reasons for the differences are discussed below for each element.

### Ni(II)

The Ni sorption measurements used in the MX80-EN SDB were measured on MX-80 in the synthetic porewater given below in Table 5.7. It should be noted that this water contains an equilibrium porewater concentration of Mn of  $\sim 1.3 \cdot 10^{-6}$  M. It is now well established that metals with similar chemical characteristics and which are in the same valence state tend to compete for the same sorption sites (Bradbury and Baeyens 2005c). Competitive sorption effects can be particularly significant when the radionuclide in question is present at trace concentrations. Thus, the Mn in the MX-80 synthetic porewater will compete with Ni and reduce its sorption. (Calculations with the 2SPNE SC/CE sorption model estimate a reduction of Ni sorption by approximately a factor of 2.) This effect is not included in the sorption values derived from montmorillonite, and hence the tendency is that the Ni sorption value in MX80-Mont SDB is slightly over estimated by using this approach.

### Cs(I)

In the MX80-Mont SDB, Cs sorption was calculated using a  $Cs^+-Na^+$  selectivity coefficient of 15 for montmorillonite (Bradbury & Baeyens, unpublished data). The value in the MX80-EN SDB was derived from a Cs sorption isotherm on MX-80 in a synthetic porewater, Table 5.7. Analysis showed that the MX-80 bentonite contained illite at the low wt. % level. This small quantity of illite, which has a very high affinity for Cs at trace concentrations ( $< 10^{-8}$  M), leads to a higher sorption value than would be calculated by considering montmorillonite alone. For this reason the Cs sorption value in the MX80-EN SDB is higher than in the MX80-MONT SDB. If the quantity of illite present is known, Cs sorption coefficients at trace concentrations can be calculated.

Tab. 5.7: Synthetic bentonite porewater (SBPW) composition used in the sorption isotherm determination for Cs(I) and Ni(II) on MX-80. (Bradbury and Baeyens 2009c).

Temperature	25 °C
log p-CO <sub>2</sub>	- 3.5 bar
pH	7.6
*I.S.	0.7
Dissolved constituents	Conc. (M)
Na	5.68 x 10 <sup>-1</sup>
K	2.80 x 10 <sup>-3</sup>
Mg	2.30 x 10 <sup>-2</sup>
Ca	3.01 x 10 <sup>-2</sup>
Sr	2.67 x 10 <sup>-4</sup>
Al	4.16 x 10 <sup>-8</sup>
Fe	-
Mn	1.3 x 10 <sup>-6</sup>
F	7.42 x 10 <sup>-5</sup>
Cl	6.19 x 10 <sup>-1</sup>
SO <sub>4</sub>	2.92 x 10 <sup>-2</sup>
C <sub>inorg.</sub>	4.23 x 10 <sup>-4</sup>
Si	1.81 x 10 <sup>-4</sup>

\* Note that the Cs and Ni sorption measurements were made at a time when the MX-80 bentonite porewater was not well established. Hence the ionic strength is higher than in the later determined reference MX-80 bentonite porewater, Table 5.5.

### Pd(II)

In the MX80-EN SDB, an “expert judgement” approach was used for Pd(II), whereas in the MX80-Mont SDB case, Pb(II) was chosen as a chemical analogue. Experimental data are available for Pb(II), and this latter procedure was preferred. This resulted in a higher selected sorption value for Pd(II) than in the MX80-EN SDB. (Note that under the anticipated Eh/pH conditions in the repository, Pd(II) is expected to be reduced to Pd metal, with a correspondingly very low solubility. Hence the value given here is intended to cover the “what if” situation where Pd does not precipitate as expected.)

**Eu(III): chemical analogue for Ce(III), Pm(III), Sm(III), Ho(III)**

Sorption edges of Eu have been measured on montmorillonite on two separate occasions and the results have been reported in Bradbury and Baeyens (2005, 2006). (On the latter occasion a sorption edge of Am(III) was measured at the same time, and the Eu and Am sorption edges were very similar.) Comparison of the two Eu data sets revealed that sorption edges were shifted with respect to one another. (The reason for this is unclear.) Thus two Eu sorption values for montmorillonite were selected at pH = 7 reflecting this “shift”;  $80 \text{ m}^3 \text{ kg}^{-1}$  (Bradbury & Baeyens 2005a) and  $316 \text{ m}^3 \text{ kg}^{-1}$  (Bradbury & Baeyens 2006) i.e. values differing by a factor of  $\sim 4$ . The end result is that the value chosen in the MX80-EN SDB from a sorption isotherm measured on MX-80 ( $4.7 \text{ m}^3 \text{ kg}^{-1}$ ) lies between the derived values in the MX80-Mont approach i.e. 2.9 and  $11.3 \text{ m}^3 \text{ kg}^{-1}$ .

**Th(IV): chemical analogue for U(IV), Np(IV)**

Sorption values for tetravalent actinides rely on using Th(IV) as an analogue. Further, the thermodynamic data for tetravalent actinides (Hummel et al. 2002) is unsure, which leads to uncertainties in applying speciation conversion factors. Also, it is not known whether tetravalent hydroxy carbonate complexes sorb or not. Under these circumstances, measurements on the simulated chemical system would provide the best guide for sorption values i.e. the sorption values for tetravalent actinides given in the MX80-EN SDB are to be preferred over the derived values in the MX80-Mont SDB. The value for U(IV) is lower than those for Th(IV) and Np(IV) because part of U is still in an hexavalent oxidation state which is taken into account in the speciation factor. This is done to be consistent with the MX80-EN SDB.

**Pa(V)**

The sorption value for Pa(V) given in the MX80-EN SDB was based on an “expert judgement”. The Pa(V) sorption value given in the MX80-Mont SDB approach is based on new measurements of Pa(V) on montmorillonite (Bradbury and Baeyens 2006) and for this reason is the preferred value.

**Am(III): chemical analogue for Cm(III), Ac(III), Pu(III)**

In the MX80-EN SDB, the Am source data was selected from sorption edge measurements carried out under “atmospheric conditions” by Gorgeon (1994). Equilibrium with air was assumed in using this data to derive a sorption value for MX-80, although this equilibrium was probably not reached at pH  $\sim 7$  during the experimental time i.e. the speciation factor calculated was probably far too small. (The speciation factor was, in fact, similar to that in the MX-80 reference porewater yielding an overall speciation conversion factor of 0.67.) This initial assumption was likely to have led to an underestimation of the influence of carbonate complexation on the sorption of Am on MX-80 i.e. an overestimation of the sorption. The Am sorption value deduced in the MX80-Mont SDB approach from the data given in Bradbury and Baeyens (2006) avoided this underestimation of the influence of Am complexation with carbonate on sorption and consequently led to a lower (more realistic) sorption value.

## 6 Summary and Conclusions

Two approaches based on similar principles have been used to derive SDBs for Opalinus Clay and MX-80 bentonite. In the one case sorption measurements on illite provided the source data for the construction of a SDB for OPA, and in the other, the source data for an MX-80 bentonite SDB were sorption measurements on montmorillonite. The procedures used to modify the source sorption data on the two clay minerals so that they applied to the Opalinus Clay and MX-80 bentonite systems are fully described in Chapter 2 and section 5.2 respectively.

One of the major aims of this report was to compare the SDBs resulting from this approach with SDBs for Opalinus Clay (Bradbury & Baeyens 2003a) and MX-80 bentonite (Bradbury & Baeyens 2003b) which had previously been used in the Entsorgungsnachweis (Nagra 2002). That is, to compare and contrast the sorption values derived from the “clay mineral building blocks” with those in existing SDBs which had been previously derived from a mixture of data sources and procedures. The main questions to be answered were:

- how close (or not) were the sorption values,
- if there were differences, why were there differences,
- which of the approaches could be considered to produce the more robust/defensible values.

Based on the results from these two test cases, the aim was to be able to make a well founded judgement on the suitability and appropriateness of the “clay mineral building block” methodology, particularly as a procedure for developing SDBs for host rock systems where sorption data were sparse.

### *Opalinus Clay system*

A comparison of the sorption values derived by the OPA-Illite SDB approach, and those given in the OPA-EN SDB, clearly showed that the independent OPA-Illite SDB approach yielded essentially comparable values in the majority of cases (~ 70 %). In those instances where the compared values were not within a factor of 2 of one another, the values derived for the OPA-Illite SDB were considered, in general, to be more reliable than the corresponding values previously given in OPA-EN SDB (See section 4.3 for a case by case discussion.) The results of this comparative exercise illustrate clearly that the application of the OPA-Illite SDB methodology, coupled with up-to-date knowledge, produced a SDB which was superior and better defensible than the SDB for OPA produced in the past by a different, less systematic approach. This is so despite the fact that experimental data measured on OPA were used in the latter case.

### *MX-80 Bentonite*

The broad results of the SDB comparison exercise with MX-80 bentonite were very similar to those for Opalinus Clay. For ~ 50 % of the radionuclides, the sorption values were within a factor of 2 of one another i.e. essentially the same. For those cases where there were greater differences, new and more detailed knowledge and understanding allowed more realistic, robust and better defensible sorption values to be chosen. For example, the selected  $R_d$  values for the elements Pd(II), Am(III) and Pa(V) in the MX80-Mont SDB are outside the factor 2 range, but are considered to be of a higher quality and better justified than those in the MX80-EN SDB. In the case of Ni(II), the value given in the MX80-EN SDB was probably better because the result from the experiment on MX-80 included the influence of sorption competition from Mn(II), whereas the MX80-Mont SDB Ni sorption value did not. However, it should be noted that Fe(II) from siderite in bentonite is also an important competitive metal with respect to Ni

sorption, and this was not present in the Ni sorption experiments on MX-80 because they were performed in air (Fe(III)), and is therefore not accounted for in the MX80-EN SDB. In other words “process knowledge” is important here and such effects can be calculated or estimated in the “clay mineral building block” approach and will be included in the future SDBs developed for the different host rock formations under consideration. (A similar situation exists for Cs and the inclusion of a low weight fraction of illite in the calculations.)

The main conclusion from this work is that very strong evidence has been provided to demonstrate that the same basic approach as described here can be applied with confidence to other argillaceous rock systems for which direct sorption measurement data may be sparse or missing.

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