

Technical Report 12-04

Sorption Data Bases for Argillaceous Rocks and Bentonite for the Provisional Safety Analyses for SGT-E2

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In the original version of this report the values for Tc(IV), Sn(IV) and Eu(III) in Tab. A1 in Appendix A (p. A-1) were interchanged. This error has been corrected.

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Abstract

In Stage 1 of the Sectoral Plan for Deep Geological Repositories, four rock types have been identified as being suitable host rocks for a radioactive waste repository, namely, Opalinus Clay for a high-level (HLW) and a low- and intermediate-level (L/ILW) repository, and 'Brauner Dogger', Effingen Member and Helvetic Marls for a L/ILW repository. Sorption data bases (SDBs) for all of these host rocks are required for the provisional safety analyses, including all of the bounding porewater and mineralogical composition combinations. In addition, SDBs are needed for the rock formations lying below Opalinus Clay (lower confining units) and for the bentonite backfill in the HLW repository.

In some previous work Bradbury et al. (2010) have described a methodology for developing sorption data bases for argillaceous rocks and compacted bentonite. The main factors influencing the sorption in such systems are the phyllosilicate mineral content, particular the 2:1 clay mineral content (illite/smectite/illite-smectite mixed layers) and the water chemistry which determines the radionuclide species in the aqueous phase. The source sorption data were taken predominantly from measurements on illite (or montmorillonite in the case of bentonite) and converted to the defined conditions in each system considered 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 was applied to adapt sorption data measured in dispersed systems (batch experiments) to intact rock under in-situ conditions. This methodology to develop sorption data bases has been applied to the selected host rocks, lower confining units and compacted bentonite taking into account the mineralogical and porewater composition ranges defined.

Confidence in the validity and correctness of this methodology has been built up through additional studies: (i) sorption values obtained in the manner described above have been compared with those in already existing SDBs for Opalinus Clay and bentonite used in Project Opalinus Clay (Entsorgungsnachweis; see Bradbury & Baeyens 2010), (ii) blind sorption model predictions of isotherms on MX-80 bentonite and Opalinus Clay in realistic groundwater compositions have been compared with measured isotherms (Bradbury & Baeyens 2011), and finally, (iii) blind predictions made using the above methodology have been compared with recent sorption measurements on argillaceous rocks (Baeyens et al. 2014). In all cases the results obtained in the different comparative approaches have been consistent with the predictions made using the methodology described.

In a few cases the mineralogy of the rock type was too poor in clay minerals to apply this approach. SDBs were nevertheless developed but based on a methodology in which calcite was the main sorbing phase. The procedure is fully described in the present report.

Further, a methodology for the derivation of SDBs for a host rock altered by hyperalkaline solutions from a cement based repository is described and the resulting SDBs for Effingen Member and Helvetic Marls are given.

Zusammenfassung

In Etappe 1 des Sachplans geologische Tiefenlager wurden vier Wirtgesteine, die für ein Lager für radioaktive Abfälle geeignet sind, identifiziert. Diese Gesteine sind: Opalinuston für ein Lager für hochaktive (HAA) und schwach- und mittelaktive Abfälle (SMA) sowie 'Brauner Dogger', Effinger Schichten und Helvetische Mergel für ein Lager für SMA. Für die provisorischen Sicherheitsanalysen werden Sorptionsdatenbanken (SDB) für all diese Wirtgesteine benötigt. Dies schliesst auch die möglichen Varianten der Porenwässer und der mineralogischen Zusammensetzung der Gesteine ein. Ausserdem sind SDB für die unteren Rahmengesteine des Opalinustons und für das Versatzmaterial Bentonit im HAA-Lager erforderlich.

In einer früheren Arbeit beschrieben Bradbury et al. (2010) ein Verfahren zur Entwicklung von Sorptionsdatenbanken für Tongesteine und kompaktierten Bentonit. Die hauptsächlichen Einflussfaktoren für die Sorption in diesen Systemen sind der Gehalt an Schichtsilikaten, insbesondere an 2:1-Tonmineralen (Illit, Smektit und Illit-Smektit-Wechselagerungen), sowie die Porenwasserchemie welche die Speziation der Radionuklide in der wässrigen Phase bestimmt. Die Sorptionsquelldaten entstammen vorwiegend Messungen auf Illit (oder Montmorillonit für die Bentonit SDB). Sie wurden auf die definierten Bedingungen eines jeden Systems umgerechnet indem eine Reihe sogenannter Konvertierungsfaktoren benutzt wurde. Diese berücksichtigen Unterschiede in der Mineralogie, dem pH-Wert und der Radionuklidspeziation. Schliesslich wurde ein Konvertierungsfaktor Labor → Feld verwendet, um die Sorptionsmessungen von dispergierten Systemen (Batch-Experimenten) auf intaktes Gestein unter In-situ-Bedingungen zu übertragen. Dieses Verfahren zur Entwicklung von Sorptionsdatenbanken wurde auf die ausgewählten Wirt- und Rahmengesteine sowie auf kompaktierten Bentonit unter Berücksichtigung der mineralogischen und der Porenwasserzusammensetzung angewendet.

Das Vertrauen in die Gültigkeit und Richtigkeit dieses Verfahrens wurde durch zusätzliche Studien gestärkt: (i) Sorptionswerte basierend auf der oben genannten Methode wurden mit denen in einer bereits existierenden SDB für Opalinuston und Bentonit aus dem Entsorgungsnachweis verglichen (Bradbury & Baeyens 2010), (ii) blinde Vorhersagen von Sorptionsisothermen auf MX-80 Bentonit und auf Opalinuston in realistischen Grundwasserzusammensetzungen wurden mit gemessenen Isothermen verglichen (Bradbury & Baeyens 2011) und (iii) blinde Vorhersagen anhand des oben beschriebenen Verfahrens wurden mit neuen Sorptionsmessungen (Baeyens et al. 2014) verglichen. In allen Fällen waren die Ergebnisse der einzelnen zum Vergleich genutzten Ansätze konsistent mit den Vorhersagen des hier beschriebenen Verfahrens.

In einigen wenigen Fällen enthielten die Gesteine zu wenig Tonminerale, um diesen Ansatz zu verwenden. Es wurde trotzdem eine SDB erstellt, indem ein Verfahren, bei dem Calcit die hauptsächlich sorbierende Phase darstellt, zur Anwendung kam. Die Prozedur ist im vorliegenden Bericht vollständig beschrieben.

Weiterhin wird eine Methode zur Ableitung von SDB für Wirtgesteine, die durch hochalkalische Lösungen aus einem zementbasierten Lager beeinflusst wurden, beschrieben. Entsprechende SDB für die Effinger Schichten und die Helvetischen Mergel werden gegeben.

Résumé

Au cours de l'étape 1 du plan sectoriel « Dépôts en couche géologiques profondes », quatre roches d'accueil potentielles ont été identifiées. Il s'agit d'une part des argiles à Opalinus (pour les dépôts destinés aux déchets de haute activité (DHA) et aux déchets de faible et de moyenne activité (DFMA) et d'autre part du 'Dogger brun' ('Brauner Dogger'), des Couches d'Effingen et des formations marneuses de l'Helvétique (dépôt DFMA seulement). Afin d'effectuer les analyses de sûreté provisoire, des bases de données de sorption sont nécessaires pour chacune de ces roches d'accueil, en tenant compte des différentes combinaisons possibles des différentes compositions minéralogiques et chimiques des eaux interstitielles. De plus, des bases de données de sorption sont requises pour les couches situées en dessous de la couche des argiles à Opalinus ainsi que pour la bentonite compactée prévue pour la barrière ouvragée dans le dépôt profond pour les DHA.

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 et la bentonite compactée. La teneur en phyllosilicates type 2:1 (illite, smectite, interstratifiés illite/smectite) ainsi que la composition chimique des eaux interstitielles, qui contrôle la spéciation des radionucléides dans la phase aqueuse, sont considérées comme les facteurs clés influant sur le degré de sorption. La base de données de sorption repose principalement sur des valeurs de sorption obtenues pour l'illite (ou montmorillonite dans le cas de la bentonite), qui ont été converties par le biais de facteurs de conversion aux conditions génériques définies pour les différentes roches argileuses. Ces facteurs ont été utilisés pour prendre en compte des différences de minéralogie, de valeurs pH et de la spéciation. Finalement, un facteur de conversion Laboratoire → Roche a été utilisé pour convertir les données de sorptions obtenues à partir d'expériences en suspension, aux conditions in situ de la roche argileuse intacte. Cette approche a été utilisée afin d'élaborer des bases de données de sorption pour les différentes roches argileuses ainsi que pour la bentonite compactée en prenant en compte les différentes compositions minéralogiques et chimiques des eaux interstitielles.

La confiance dans la validité et robustesse de cette approche est accrue par des études supplémentaires: (i) les valeurs de sorption obtenues par cette approche ont été comparées aux valeurs des bases de données pour les argiles à Opalinus et la bentonite utilisé dans le Entsorgungsnachweis (Bradbury & Baeyens 2010), (ii) des isothermes sur la bentonite et les argiles à Opalinus ont été calculées avec cette approche en considérant des compositions d'eaux interstitielles réalistes et ont été comparées aux valeurs de sorption obtenues expérimentalement (Bradbury & Baeyens 2011), et finalement (iii) les résultats de calculs obtenues par cette approche ont été comparées à des valeurs de sorption mesurées (Baeyens et al. 2014). Dans tous les cas les résultats obtenus dans les différents exercices de comparaison sont en accord avec les valeurs obtenues en utilisant l'approche décrite.

Dans certains cas la teneur en phyllosilicates était trop faible pour appliquer cette approche. Cependant des bases de données de sorption ont été élaborées en considérant seulement la rétention par la calcite. La procédure est décrite dans ce rapport.

Par ailleurs, ce rapport décrit une méthode permettant de dériver des bases de données de sorption pour une roche d'accueil altérée par des solutions hyperalcalines provenant d'un dépôt à forte composante cimentaire. Il fournit ensuite les bases de données correspondantes pour les Couches d'Effingen et les formations marneuses de l'Helvétique.

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1 Introduction

As part of Stage 1 of the Sectoral Plan for Deep Geological Repositories, Nagra has proposed six regions which are suitable for hosting a repository for low- and intermediate-level waste (L/ILW) and three regions for high-level waste (HLW; Nagra 2008). In the current Stage 2 of the Sectoral Plan, Nagra will propose at least two siting regions each for the L/ILW repository and for the HLW repository for further consideration. Provisional safety analyses for all siting regions are part of the procedure and support the evaluation and selection process. The host rocks to be considered can all be classified as argillaceous rocks (clay rock and marl) in which released radionuclides will migrate mainly by diffusion. The provisional safety analyses need geochemical models and parameters to describe the migration of radionuclides in the geosphere and the bentonite buffer in a quantitative way. An adequate sorption data base is one of the key parameter sets to quantify the radionuclide retardation in the host rocks. In this report the necessary sorption data bases (SDBs) are derived for the various combinations of rock/porewater systems at trace radionuclide concentrations. In addition the SDBs for the lower confining units and MX-80 bentonite are also given in this report.

The methodology for deriving sorption data bases for argillaceous rocks was first applied to Palfris marl host rocks (Bradbury & Baeyens 1997a) for the safety analyses of an L/ILW repository (Nagra 1994). This methodology was further developed for the SDBs required for Opalinus Clay (Bradbury & Baeyens 2003a) and bentonite (Bradbury & Baeyens 2003b) which were used in the Project Opalinus Clay (Entsorgungsnachweis; see Nagra 2002). For Stage 2 of the Sectoral Plan, the procedure was further developed and generalised for the SDBs for argillaceous rocks (Bradbury et al. 2010). 2:1 clay minerals (illite, smectite, illite-smectite mixed layers) were taken as the dominant sorbents. Therefore, sorption edge measurements on pure illite and montmorillonite were chosen as the source data. Chapter 2 describes the methodology to derive the SDBs applicable to the argillaceous host rocks, the MX-80 bentonite and the lower confining units for the provisional safety analyses in the Sectoral Plan Stage 2.

The transfer of the sorption values from the source data to the rocks needs information on the mineralogical composition of the rocks (quantitative clay mineral analysis) and on the porewater composition. The mineralogical data have been defined by the University of Bern from mineralogical investigations on samples from drilling cores (Traber & Blaser 2013, Traber 2013). The porewaters of the host rock formations were defined based on geochemical modelling taking all the available data into account (Mäder 2009a and b, 2010). Besides a reference composition, variants are given covering possible ranges of salinity and $p\text{CO}_2$. These data are summarised in Chapter 3.

From the knowledge of the clay mineralogy and the chemical speciation of the radionuclide in the porewater, two conversion factors have been calculated. The mineralogy conversion factor CF_{MIN} represents the mass fraction of 2:1 clay minerals of the whole rock where the source sorption data are measured on (illite, montmorillonite). The speciation conversion factor CF_{SPEC} accounts for the influence of aqueous cation complexation on sorption; only free cations and neutral and positively charged hydrolysed species are considered to be sorbing. These factors are applied to the source R_d value at the given pH of the porewater. A summary of the illite source data is given in Chapter 4.

Sorption data bases have been derived for all four host rocks (Chapter 5) and for three lower confining units (Chapter 6). Due to the range of possible mineralogies and porewaters, the sorption data base for each host rock consists of several sets of R_d values. Thus, the sensitivity of the sorption behaviour of each radionuclide to the input data and the overall uncertainty in the sorption data can be estimated.

In three cases no 2:1 type clay minerals were present. Since calcite is dominant in these rock units (70 to 100 %), a specific SDB based on calcite was developed and is discussed in Chapter 7.

Sorption data bases for MX-80 bentonite are treated separately in Chapter 8. The methodology used to generate SDBs for MX-80 bentonite is similar to that for the host rocks; the only difference is that montmorillonite is the dominant 2:1 type clay mineral.

The uncertainties associated with the selected sorption values are treated in Chapter 9. An overall summary is given in Chapter 10.

SDBs for the following rock types are given in this report:

1. Opalinus Clay
2. 'Brauner Dogger'
 - 'Brauner Dogger' Clay-rich sequences
 - 'Brauner Dogger' Sandy limestone sequences
3. Effingen Member
 - Effingen Member Calcareous marl sequences
 - Effingen Member Limestone sequences
 - Effingen Member Limestone sequences (calcite)
4. Helvetic Marls
 - Helvetic Marls
 - Helvetic Marls Limestone sequences
 - Helvetic Marls (vein infill, calcite)
5. Lower confining units
 - Toniger Lias
 - Toniger Keuper
 - Arietenkalk
 - Arietenkalk (calcite)
6. MX-80 Bentonite

2 Methodology, conversion factors and uncertainties

2.1 Methodology

The basic procedure is very similar to that which has been described previously in detail elsewhere (Bradbury & Baeyens 2003a and b, Bradbury et al. 2010). The difference here in procedures to those given in Bradbury et al. (2010) is that the pH conversion factor is unity (section 2.2.3) because the source R_d values are selected at the same pH value as the corresponding porewater. Furthermore, the updated PSI/Nagra 07/12 thermodynamic data base was used (Thoenen et al. 2014) and Th(IV) has been chosen as a chemical analogue for Po(IV) (section 4.7.2). 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 is similar: similar edge site capacities; similar Linear Free Energy Relationships between metal surface complexation constants and the corresponding hydrolysis constants (Bradbury & Baeyens 2005a, 2009a and 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 Bradbury et al. (2010) it is assumed that illite/smectite mixed layers have sorption characteristics essentially the same as illite.

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 argillaceous rocks using conversion factors defined in the following sections.

2.2 Conversion factors

2.2.1 Mineralogy conversion factor: CF_{MIN}

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

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

Where:

CF_{MIN} = mineralogy conversion factor

$MIN_{ARG\ ROCK}$ = illite + illite/smectite mixed layer weight fraction in argillaceous rock.

MIN_{ILLITE} = 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 procedure developed to take these factors into account 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 e.g. 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 (see Appendix A). All other species are treated as being non-sorbing (this assumption errs on the conservative side; see e.g. Bradbury et al. 2010). One exception is made for U(VI) where sorption modelling on montmorillonite (Bradbury & Baeyens 2005, Marques Fernandes et al. 2012) and on illite (Bradbury & Baeyens 2009b) clearly indicate that the negatively charged $UO_2(OH)_3^-$ species also is sorbing by surface complexation.

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

$$CF_{SPEC} = SF_{ARG\ ROCK} / SF_{ILLITE} \quad (2.2)$$

Where:

CF_{SPEC} is the speciation conversion factor.

$SF_{ARG\ ROCK}$ is the fraction of sorbing radionuclide species in a specific redox state calculated to be present in the aqueous phase in the argillaceous rock porewaters.

SF_{ILLITE} is the fraction of sorbing radionuclide species in a specific redox state 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 newly updated PSI/Nagra thermodynamic data base (12/07) (Thoenen et al. 2014) has been used throughout this report.

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 5 to 7 – 8. (The exception to this is the alkaline and alkaline-earth metals which sorb predominantly by cation exchange.) Above pH ~ 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 and b).

The strategy followed in this work is to use sorption edges of metals and anions on illite and select the R_d values at the appropriate pH of the porewater in question. This leads to a simplified approach since no conversion factor for pH is required. For the work presented in this report only in the case for Mo(VI) a pH conversion factor was used, and this is treated in the corresponding section.

2.2.4 Lab to field conversion factor, $CF_{\text{Lab} \rightarrow \text{Field}}$

In the general development of previous SDBs a Lab \rightarrow Field transfer factor was used to take into account the reduction of sorption values measured on crushed rock to be applied to the in situ intact/compacted systems. Transfer factors for argillaceous rocks, compacted bentonite and calcite have been derived on the basis of surface area measurements made on intact and crushed rock samples (Bradbury & Baeyens 1998a). The main conclusion from this work was that for argillaceous rock systems and compacted bentonite the Lab \rightarrow Field transfer factor is unity. For the case of calcite, a Lab \rightarrow Field transfer factor of 0.05 has been taken. These conversion factors have been applied throughout this work.

2.2.5 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 the argillaceous rock at a specified condition. The illite source data are:

$R_{d, \text{ILLITE}}$, MIN_{ILLITE} and SF_{ILLITE} (note that the source data were measured in a "pure illite" system, hence MIN_{ILLITE} equals unity).

The distribution ratio, $R_{d, \text{ARG ROCK}}$, is required for the host rock at the selected conditions. The argillaceous rock mineralogical and water composition conditions yield $MIN_{\text{ARG ROCK}}$, $pH_{\text{ARG ROCK}}$, $SF_{\text{ARG ROCK}}$ values.

Then,

$$R_{d, \text{ARG ROCK}} = R_{d, \text{ILLITE}} \cdot CF_{\text{MIN}} \cdot CF_{\text{pH}} \cdot CF_{\text{SPEC}} \cdot CF_{\text{Lab} \rightarrow \text{Field}} \quad (2.3)$$

where:

$$CF_{\text{MIN}} = (MIN_{\text{ARG ROCK}} / MIN_{\text{ILLITE}})$$

$$CF_{\text{SPEC}} = (SF_{\text{ARG ROCK}} / SF_{\text{ILLITE}})$$

$$CF_{\text{pH}} = 1 \text{ (except in the case of Mo(VI))}$$

$$CF_{\text{Lab} \rightarrow \text{Field}} = 1 \text{ (except in the case of calcite)}$$

It should be noted that this methodology is only valid for trace radionuclide concentrations.

In the general case, for speciation calculations carried out in a fully coupled redox mode, radionuclides may exist in different redox states simultaneously in solution at equilibrium. Under these circumstances, the species in each redox state will contribute to the overall sorption according to an equation of the form

$$R_{d,ARG\ ROCK}(Rn) = [(R_{d,ILLITE\ Rn(X)} \cdot CF_{SPEC\ Rn(X)} + (R_{d,ILLITE\ Rn(Y)} \cdot CF_{SPEC\ Rn(Y)} + (R_{d,ILLITE\ Rn(Z)} \cdot CF_{SPEC\ Rn(Z)} + \dots)] \cdot CF_{MIN} \cdot CF_{Lab \rightarrow Field} \quad (2.4)$$

Where $Rn(X)$, $Rn(Y)$ and $Rn(Z)$ represent the different oxidation states of the radionuclide.

The R_d value for a radionuclide in a specific oxidation state (e.g. $Rn(X)$) is given by the following equation

$$R_{d,ARG\ ROCK\ Rn(X)} = R_{d,ILLITE\ Rn(X)} \cdot CF_{SPEC\ Rn(X)} \cdot CF_{MIN} \cdot CF_{Lab \rightarrow Field} \quad (2.5)$$

Eqs. 2.4 and 2.5 are valid for a fixed pH.

3 Host rock mineralogies and porewater chemistries

This chapter summarises the mineralogical compositions of the different host rocks and the porewater chemistries for which the SDBs have been compiled. The aim of this overview is to have all information in place so that the derivation of the different SDBs becomes more transparent and traceable.

The mineralogical compositions of each of the argillaceous host rocks are generally the same in terms of the minerals present, but do exhibit some variability in the individual mineral weight fractions. Since the 2:1 clay minerals determine the sorption in the approach used here, the upper and lower bound sorption values given are determined by the upper and lower bound 2:1 clay mineral wt. fractions for each host rock.

In the few cases where 2:1 clay minerals are not present, and the sorption is determined by calcite, the calcite weight fraction in the reference mineralogy is used to provide sorption values (see Chapter 7).

In the special case of inorganic carbon where the sorption is determined by calcite (section 4.7.5), lower and upper bound values for the calcite weight fraction are used to provide the lower and upper bound sorption values, respectively.

3.1 Mineralogical compositions of the host rocks

3.1.1 Opalinus Clay

The mineralogical composition for the Opalinus Clay has been defined by Traber & Blaser (2013) and is specific for the Sectoral Plan Stage 2. A reference mineralogy together with two bounding (upper and lower bound) mineralogies is given in Tab. 3.1.

Tab. 3.1: Reference mineralogy and values for the bounding mineral content for Opalinus Clay (Traber & Blaser 2013).

Mineral	Reference [wt.-%]	Lower bound [wt.-%]	Upper bound [wt.-%]
Illite	24	15	35
Illite/smectite mixed layer	9	4	25
Smectite	0	0	0
Kaolinite	18	10	30
Chlorite	9	2	15
Quartz	20	10	30
Calcite	13	5	35
Dolomite + Ankerite	0.4	0	2
K-feldspar	2	0	5
Plagioclase	0.9	0	2
Siderite	4	0	15
Pyrite	1	0.3	3

3.1.2 'Brauner Dogger'

The mineralogical compositions for the 'Brauner Dogger' Clay-rich sequences and the 'Brauner Dogger' Sandy limestone sequences have been defined by Traber & Blaser (2013) and are specific for the Sectoral Plan Stage 2. A reference mineralogy together with upper and lower bounding values for the mineralogies of 'Brauner Dogger' Clay-rich sequences and 'Brauner Dogger' Sandy limestone sequences is given in Tabs. 3.2 and 3.3, respectively.

Tab. 3.2: Reference mineralogy and values for the bounding mineral content for 'Brauner Dogger' Clay-rich sequences (Traber & Blaser 2013).

Mineral	Reference [wt.-%]	Lower bound [wt.-%]	Upper bound [wt.-%]
Illite	15	4	30
Illite/smectite mixed layer	12	1	20
Smectite	0	0	0
Kaolinite	14	4	25
Chlorite	5	1	10
Quartz	19	5	35
Calcite	30	5	60
Dolomite + Ankerite	2	0	10
K-feldspar	3	0	5
Plagioclase	1	0	2
Siderite	0.7	0	6
Pyrite	1	0.2	3

Tab. 3.3: Reference mineralogy and values for the bounding mineral content for 'Brauner Dogger' Sandy limestone sequences (Traber & Blaser 2013).

Mineral	Reference [wt.-%]	Lower bound [wt.-%]	Upper bound [wt.-%]
Illite	3	1.25	5
Illite/smectite mixed layer	4	1.25	10
Smectite	0	0	0
Kaolinite	3	0	5
Chlorite	1	0	10
Quartz	39	20	50
Calcite	39	20	70
Dolomite + Ankerite	0	0	2
K-feldspar	6	0	10
Plagioclase	3	0	5
Siderite	0	0	0
Pyrite	0.6	0	2

In Traber & Blaser (2013) a lower bound of the total clay mineral content of 5 wt.-% was defined for 'Brauner Dogger' Sandy limestone sequences. The individual clay minerals (illite, smectite, kaolinite etc.) each have a lower bound of zero, i.e., in a certain rock layer one or several of these minerals can reach a value of zero, but not all at the same time. As the 2:1 clay minerals account for ca. one half of the total clay mineral content, a value of 2.5 wt.-% was used for the sum of illite and illite/smectite mixed layer and this value was distributed equally among both minerals (1.25 wt.-%, *cf.* Tab. 3.3).

3.1.3 Effingen Member

The mineralogical compositions for the Effingen Member Calcareous marl sequences and the Effingen Member limestone sequences have been defined by Traber & Blaser (2013) and are specific for the Sectoral Plan Stage 2. A reference mineralogy together with upper and lower bounding values for the mineralogies of these host rocks is given in Tabs. 3.4 and 3.5.

Tab. 3.4: Reference mineralogy and values for the bounding mineral content for Effingen Member Calcareous marl sequences (Traber & Blaser 2013).

Mineral	Reference [wt.-%]	Lower bound [wt.-%]	Upper bound [wt.-%]
Illite	11	5	27
Illite/smectite mixed layer	9	5	13
Smectite	0.1	0	1
Kaolinite	6	0	14
Chlorite	1	0	3
Quartz	10	6	14
Calcite	57	40	70
Dolomite + Ankerite	4	0	9
K-feldspar	1	0	1
Plagioclase	0	0	0
Siderite	0	0	0
Pyrite	1	0.4	2

Tab. 3.5 indicates that for the lower limit data no clay minerals are present and hence the CF_{MIN} is equal to zero. For this case a SDB for calcite is used and the reference calcite content is considered, i.e. 76 wt.-%. The SDBs derived for calcite are discussed in Chapter 7.

Tab. 3.5: Reference mineralogy and values for the bounding mineral content for Effingen Member Limestone sequences (Traber & Blaser 2013).

Mineral	Reference [wt.-%]	Lower bound [wt.-%]	Upper bound [wt.-%]
Illite	4.1	0	11
Illite/smectite mixed layer	4.7	0	10
Smectite	0.4	0	2
Kaolinite	2.7	0	6
Chlorite	0.1	0	1
Quartz	6	1	9
Calcite	76	62	99
Dolomite + Ankerite	3	0	11
K-feldspar	0.1	0	1
Plagioclase	0	0	0
Siderite	0	0	0
Pyrite	1	0	1

3.1.4 Helvetic Marls

The mineralogical compositions for the Helvetic Marls (not or very little disturbed host rock) and the Helvetic Marls Limestone sequences have been defined by Traber & Blaser (2013) and are specific for the Sectoral Plan Stage 2. A reference mineralogy together with upper and lower bounding values for the mineralogies of these host rocks is given in Tabs. 3.6 and 3.7.

Reference mineralogies for cataclastic shear-zones (water conducting feature) for Fault Gouge and Limestone sequences ("Auflockerungszone der Mergelabfolge") are the same as the reference values of the host rock (Tab. 3.6).

The mineralogy of the Limestone sequences ("Auflockerungszone der Kalkbänke") is the same as the reference mineralogy of the calcareous marl sequences (Tab. 3.7).

The reference mineralogy for infill of water conducting systems is 100 % calcite. For this feature a SDB for calcite has been derived (see Chapter 7).

Tab. 3.6: Reference mineralogy and values for the bounding mineral content for Helvetic Marls (Traber & Blaser 2013).

Not disturbed or very little disturbed host rock.

Mineral	Reference [wt.-%]	Lower bound [wt.-%]	Upper bound [wt.-%]
Illite	12	3	27
Illite/smectite mixed layer	10	1	19
Smectite	0	0	0
Kaolinite	0.3	0	1
Chlorite	8	2	18
Quartz	18	7	35
Calcite	42	10	80
Dolomite + Ankerite	6	0	15
K-feldspar	0.1	0	0.3
Plagioclase	1	0	4
Siderite	0	0	0
Pyrite	1	0.4	2

Tab. 3.7: Reference mineralogy for Helvetic Marls Limestone sequences (Traber & Blaser 2013).

Mineral	Reference [wt.-%]
Illite	2.6
Illite/smectite mixed layer	1.3
Smectite	0
Kaolinite	0.2
Chlorite	0.9
Quartz	6
Calcite	84
Dolomite + Ankerite	3
K-feldspar	0
Plagioclase	1
Siderite	0
Pyrite	0.5

3.2 Porewater chemistries of the host rocks

A summary of all the porewater chemistries used in the derivation of SDBs are given in this section. There are two key parameters related to the porewaters. First, the pH of the porewater is required to select the source illite (montmorillonite) sorption value from the sorption edge measurements. Secondly, the speciation factors are calculated in the various porewaters and are required to modify the source sorption data for the specific host rock porewater system. The speciation calculations are presented in the Appendix. The porewater chemistries of MX-80 bentonite are given in Chapter 8.

3.2.1 Opalinus Clay, 'Brauner Dogger' Clay-rich sequences and 'Brauner Dogger' Sandy limestone sequences

The porewater compositions for the Opalinus Clay, 'Brauner Dogger' clay-rich sequences and 'Brauner Dogger' sandy limestone sequences are considered the same (Mäder 2009a). Tab. 3.8 presents the reference case and the variations which were considered to bound the uncertainties in the porewater chemistry.

Tab. 3.8: Porewater compositions of Opalinus Clay, 'Brauner Dogger' Clay-rich sequences and 'Brauner Dogger' Sandy limestone sequences (Mäder 2009a).

		Reference	High pCO ₂	Low pCO ₂	High salinity
pH		7.20	7.00	7.50	7.01
pε		-2.78	-2.55	-3.13	-2.56
Ionic strength	[mol/kg _{H2O}]	0.23	0.23	0.23	0.76
log pCO ₂	[bar]	-2.20	-1.80	-2.80	-2.50
Na	[mol/kg _{H2O}]	1.64E-01	1.65E-01	1.64E-01	5.28E-01
K	[mol/kg _{H2O}]	2.60E-03	2.62E-03	2.60E-03	1.77E-03
Mg	[mol/kg _{H2O}]	9.65E-03	9.77E-03	9.55E-03	3.76E-02
Ca	[mol/kg _{H2O}]	1.25E-02	1.27E-02	1.24E-02	4.97E-02
Sr	[mol/kg _{H2O}]	2.11E-04	2.12E-04	2.09E-04	4.22E-04
Fe ^{II}	[mol/kg _{H2O}]	5.24E-05	5.43E-05	5.09E-05	2.46E-04
Cl	[mol/kg _{H2O}]	1.60E-01	1.60E-01	1.60E-01	6.62E-01
F	[mol/kg _{H2O}]	1.53E-04	1.52E-04	1.53E-04	1.11E-04
S ^{VI}	[mol/kg _{H2O}]	2.47E-02	2.47E-02	2.47E-02	2.11E-02
C ^{IV}	[mol/kg _{H2O}]	2.51E-03	4.15E-03	1.21E-03	1.06E-03
Si	[mol/kg _{H2O}]	1.78E-04	1.78E-04	1.79E-04	1.72E-04

Note that these compositions differ slightly from those reported by Mäder (2009a), which were calculated without fluorite saturation.

3.2.2 Effingen Member

Tab. 3.9 presents the reference case and the variations which were considered to bound the uncertainties in the porewater chemistry for the Effingen Member.

Tab. 3.9: Porewater compositions for Effingen Member Calcareous marl sequences and Effingen Member Limestone sequences (Mäder 2009b).

		Reference *	Lowest Cl	High SO ₄	High pCO ₂ (low pH)
pH		7.31	7.09	7.25	6.80
pε		-2.94	-2.74	-2.83	-2.36
Ionic strength	[mol/kg _{H2O}]	0.68	0.29	0.54	0.68
log pCO ₂	[bar]	-3.19	-2.35	-2.76	-2.18
Na	[mol/kg _{H2O}]	3.74E-01	1.56E-01	3.75E-01	3.74E-01
K	[mol/kg _{H2O}]	1.99E-03	8.28E-04	1.99E-03	1.99E-03
Mg	[mol/kg _{H2O}]	4.52E-02	1.88E-02	2.64E-02	4.54E-02
Ca	[mol/kg _{H2O}]	6.04E-02	2.52E-02	3.46E-02	6.06E-02
Sr	[mol/kg _{H2O}]	8.11E-04	1.05E-03	2.98E-04	8.14E-04
Fe ^{II}	[mol/kg _{H2O}]	2.90E-04	1.09E-04	1.55E-04	2.94E-04
Cl	[mol/kg _{H2O}]	5.66E-01	2.34E-01	4.45E-01	5.66E-01
F	[mol/kg _{H2O}]	1.08E-04	1.19E-04	1.19E-04	1.08E-04
S ^{VI}	[mol/kg _{H2O}]	1.15E-02	5.51E-03	2.69E-02	1.15E-02
C ^{IV}	[mol/kg _{H2O}]	4.29E-04	1.51E-03	8.92E-04	1.50E-03
Si	[mol/kg _{H2O}]	1.74E-04	1.77E-04	1.75E-04	1.74E-04

Note that these compositions differ slightly from those reported by Mäder (2009b), which were calculated without fluorite saturation.

* In Mäder (2009b) this porewater is referred to "low-salinity" reference porewater (see Table 7.8 in Mäder 2009b).

3.2.3 Helvetic Marls

Tab. 3.10 presents the reference case and the variations which were considered to bound the uncertainties in the porewater chemistry for the Helvetic Marls.

Tab. 3.10: Porewater compositions for Helvetic Marls and Helvetic Marls Limestone sequences (Mäder 2010).

		Na-Cl "Base-case"	Na-Cl High pCO ₂	Na-Cl Low pCO ₂	Na-Cl Low pε	High Na-Cl
pH		7.47	7.01	7.95	7.46	7.16
pε		-3.42	-2.90	-3.97	-4.84	-3.00
Ionic strength	[mol/kg _{H2O}]	0.21	0.22	0.21	0.21	0.52
log pCO ₂	[bar]	-2.10	-1.21	-3.05	-2.07	-2.14
Na	[mol/kg _{H2O}]	1.98E-01	2.06E-01	1.95E-01	1.98E-01	4.61E-01
K	[mol/kg _{H2O}]	2.34E-03	2.42E-03	2.31E-03	2.34E-03	5.16E-03
Mg	[mol/kg _{H2O}]	1.33E-03	1.47E-03	1.28E-03	1.33E-03	6.86E-03
Ca	[mol/kg _{H2O}]	2.28E-03	2.52E-03	2.19E-03	2.27E-03	1.12E-02
Sr	[mol/kg _{H2O}]	1.62E-04	1.80E-04	1.55E-04	1.62E-04	7.81E-04
Fe ^{II}	[mol/kg _{H2O}]	1.10E-05	1.40E-05	0.98E-05	5.49E-16	5.47E-05
Cl	[mol/kg _{H2O}]	2.02E-01	2.02E-01	2.02E-01	2.02E-01	5.00E-01
F	[mol/kg _{H2O}]	2.82E-04	2.75E-04	2.85E-04	2.82E-04	1.57E-04
S ^{-II}	[mol/kg _{H2O}]	5.16E-11	5.89E-11	5.31E-11	2.00E-04	2.25E-11
S ^{VI}	[mol/kg _{H2O}]	2.00E-04	2.00E-04	2.00E-04	2.50E-09	4.00E-04
C ^{-IV}	[mol/kg _{H2O}]	3.50E-15	7.93E-15	1.40E-15	1.11E-03	4.14E-16
C ^{IV}	[mol/kg _{H2O}]	5.41E-03	1.59E-02	1.80E-03	5.56E-03	2.79E-03
Si	[mol/kg _{H2O}]	1.78E-04	1.77E-04	1.80E-04	1.78E-04	1.74E-04

Note that these compositions differ slightly from those reported by Mäder (2010), which were calculated without fluorite saturation.

4 Radionuclides and source sorption data

4.1 Elements considered

For the provisional safety analyses for the ILW type waste (potential host rock Helvetic Marls) and for SF, HLW and L/ILW the safety relevant radionuclides have been defined (Nagra 2008) and are listed in Tab. 4.1. The oxidation state for each element is also indicated in this table. Because of the prevailing in situ reducing conditions only the lower valence states for the redox sensitive elements are considered in this report.

Tab. 4.1: Elements considered in the present report.

Nuclide	SF, HLW, ILW	L/ILW
Be(II)	√	√
C _{inorg}	√	√
C _{org}	√	√
K(I)	√	√
Cl(-I)	√	√
Ca(II)	√	-
Co(II)	√	√
Ni(II)	√	√
Se(-II)	√	√
Sr(II)	√	√
Zr(IV)	√	-
Nb(V)	√	√
Mo(VI)	√	√
Tc(IV)	√	-
Pd(II)	√	-
Ag(I)	√	√
Sn(IV)	√	√
I(-I)	√	√
Cs(I)	√	√
Sm(III)	√	-
Eu(III)	√	-
Ho(III)	√	-
Pb(II)	√	√
Po(IV)	√	√
Ra(II)	√	√
Ac(III)	√	√
Th(IV)	√	√
Pa(V)	√	√
U(IV)	√	√
Np(IV)	√	√
Pu(III)	√	√
Am(III)	√	√
Cm(III)	√	√

4.2 Illite source data

Illite source sorption edge data sets are available for the elements Co(II), Ni(II), Eu(III), Am(III), Sn(IV), Th(IV), Pa(V) and Mo(VI) are discussed below.

The source sorption values were generally selected from experiments with illite in a simple NaClO_4 background electrolyte. The experiments have been carried out in a controlled N_2 atmosphere glove box in the absence of CO_2 . For the above mentioned elements, the values were selected at the pH of the porewater under consideration so that a pH correction factor was not necessary. The speciation factors for the radionuclides calculated in each of the porewaters are given in Appendix A. It should be noted that in the conditioned illite systems Si is always present and the concentration of Si at neutral pH was analysed in various clay batches and an average value of $4 (\pm 2.5) \times 10^{-5}$ M is considered in the speciation calculations. For the trivalent lanthanides/actinides the complexation with Si is important and since these complexes are considered to be non-sorbing they had to be considered in the simple NaClO_4 systems.

Co(II)

The Co edge data is taken from the sorption studies by Bradbury & Baeyens (2009a) and is reproduced in Fig. 4.1.

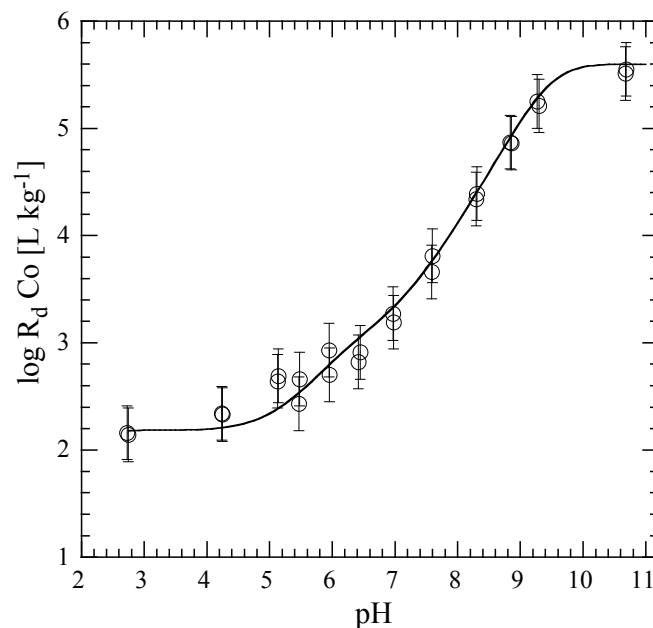


Fig. 4.1: Co(II) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO_4 (Bradbury & Baeyens 2009a).

Ni(II)

The Ni edge data is taken from the sorption studies by Bradbury & Baeyens (2009a) and is reproduced in Fig. 4.2. The scatter of the data in the pH range 7 to 9.5 is quite large. The reason for this is unknown, but reflects the uncertainty of the source sorption data. From this plot an uncertainty on the $R_{d, \text{ILLITE}}$ of ± 0.5 log units can be considered.

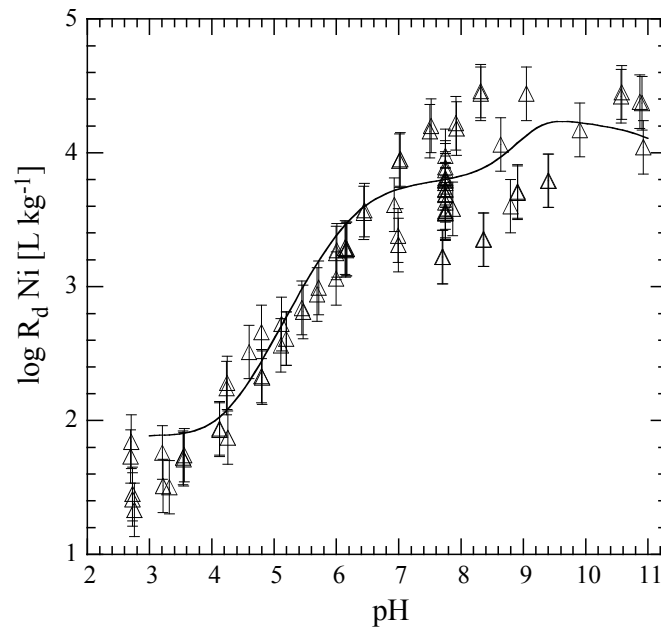


Fig. 4.2: Ni(II) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO₄ (Bradbury & Baeyens 2009a).

Eu(III)

Sorption edges results for Eu on Na-illite have been reported in Poinssot et al. (1999), Bradbury & Baeyens (2005a) and Bradbury & Baeyens (2009a). Two different data sets (sorption edges) of Eu for Na-illite are available (Poinssot et al. 1999, Bradbury & Baeyens 2009a). There exists a discrepancy between the two different data sets in the pH range between 5 and 8 which probably originates from impurities in the illite (an unknown Ca-phase) for the data set from Poinssot et al. (1999). The more recent data has been selected for the Eu(III) source data and is given in Fig. 4.3 together with the modelling.

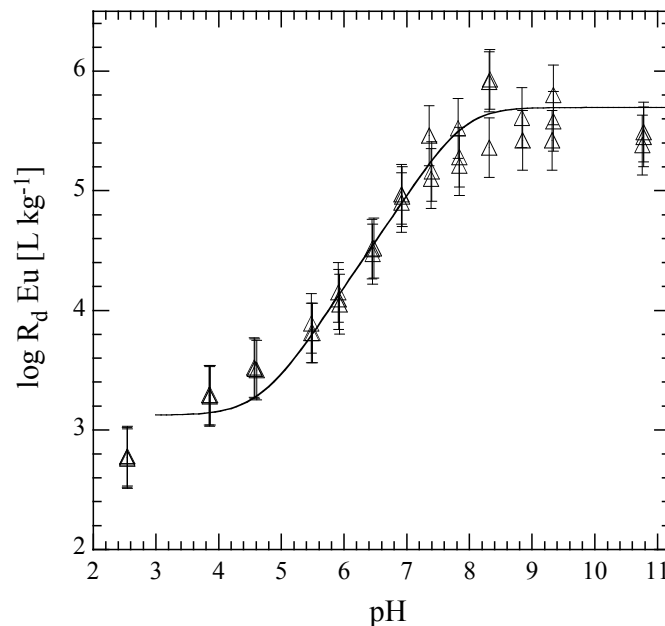


Fig. 4.3: Eu(III) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO₄ (Bradbury & Baeyens 2009a).

Am(III)

Sorption data of Am(III) on illite are available e.g. Gorgeon (1994), Bradbury & Baeyens (2009b). The data published by the latter authors are not consistent with the former. The higher Am sorption values may be due to an artefact which may arise from impurities in the illite (see above). However, if the Eu(III) data (Fig. 4.3) are compared with the data from Gorgeon at 0.1 M NaClO₄ their correspondence is good (see Fig. 4.4). Based on these results it was concluded that the Eu(III) source R_d values on illite can be taken for Am(III).

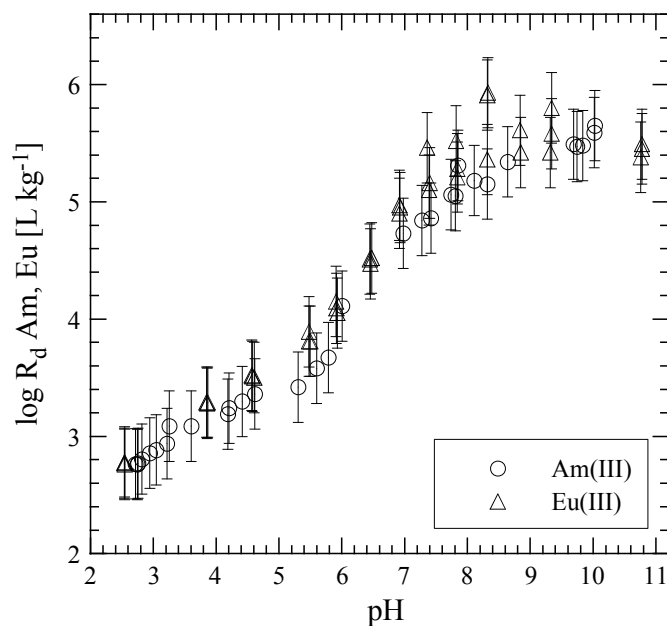


Fig. 4.4: Am(III) (Gorgeon 1994) and Eu(III) (Bradbury & Baeyens 2009b) sorption measurements on 0.1 M Na-Illite de Puy.

Sn(IV), Th(IV), Pa(V) and U(VI)

Sorption edges for Sn(IV), Th(IV), Pa(V) and U(VI) are taken from Bradbury & Baeyens (2009a and b) and are shown in Figs. 4.5, 4.6, 4.7 and 4.8, respectively. Due to the strong hydrolysis behaviour of these elements sorption is high and exhibit a plateau in the pH range between 6 and 9 (or higher).

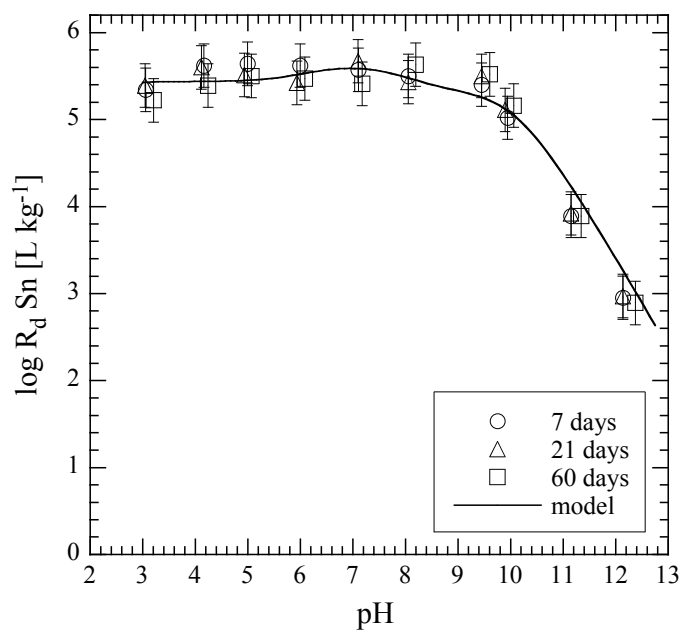


Fig. 4.5: Sn(IV) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO₄ (Bradbury & Baeyens 2009a).

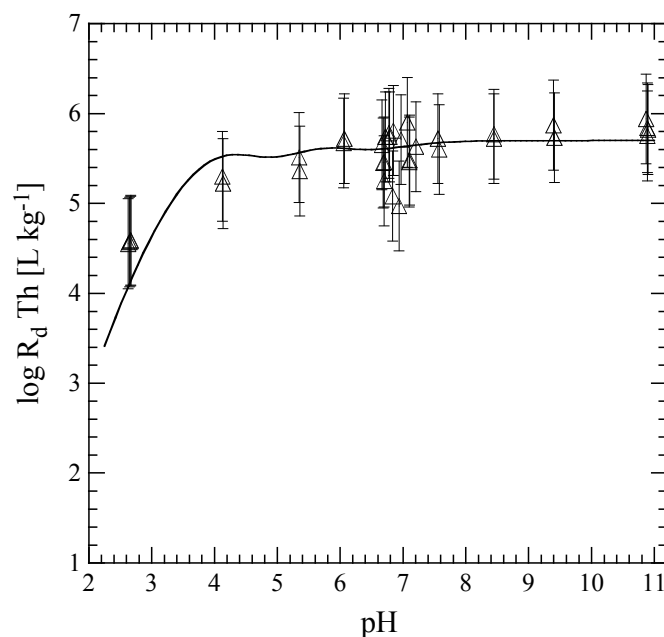


Fig. 4.6: Th(IV) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO₄ (Bradbury & Baeyens 2009b).

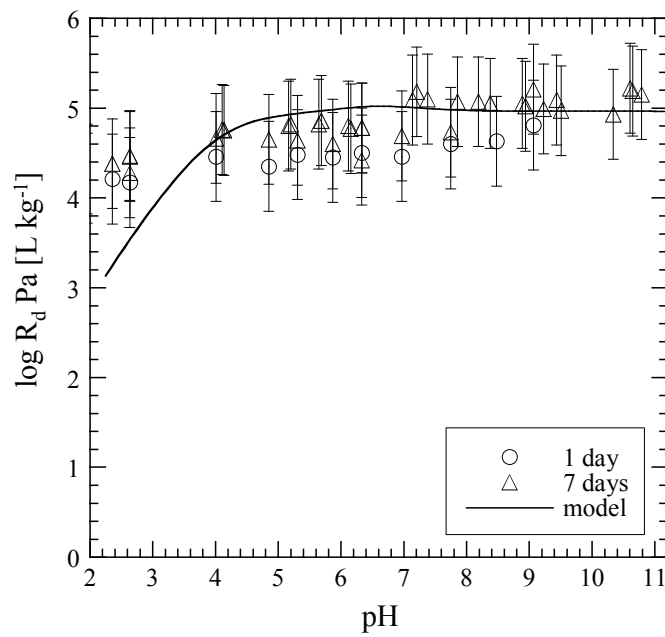


Fig. 4.7: Pa(V) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO_4 (Bradbury & Baeyens 2009b).

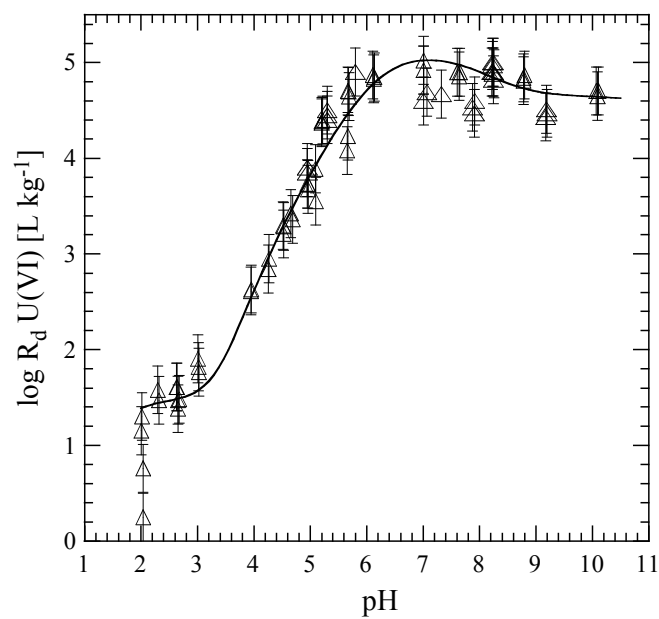


Fig. 4.8: U(VI) sorption edge measurements (symbols) and modelling (continuous line) on conditioned Na-illite in 0.1 M NaClO_4 (Bradbury & Baeyens 2009b).

Mo(VI)

Molybdenum only exists in the +VI oxidation state, and above pH 4 the dominant aqueous species is the anionic molybdate (MoO_4^{2-}) (Baes & Mesmer 1976).

No sorption edges of MoO_4^{2-} on illite exist in the open literature. However, although sorption data for MoO_4^{2-} on geological substrates are scarce, Motta & Miranda (1989) showed that MoO_4^{2-} is taken up by illite. An R_d value of $6.6 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ at pH = 8.9 for MoO_4^{2-} could be extracted from the linear part of the isotherm measurements on illite (25 °C, equilibrium concentration of $7.6 \times 10^{-5} \text{ M}$, Figure 4a in Motta & Miranda 1989). The pH dependency could not be deduced from their measurements since only one additional isotherm was available at pH = 8.2, but these measurements were carried out at 40 °C.

The (approximate) pH dependency of MoO_4^{2-} uptake could be deduced from results presented by Theng (1971) on 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.

4.3 Cation exchange: K, Ca, Sr, Ra and Cs

For those metals sorbing primarily by cation exchange, sorption values for illite were calculated directly in the porewater water chemistries (Tabs. 3.8 to 3.10), using the selectivity coefficients for illite given in Tab. 4.2. The calculated sorption values for illite were then converted to R_d values for the argillaceous rocks using the mineral conversion factor.

Tab. 4.2: 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 = 200 meq kg^{-1} .

Cation exchange reactions:	log K_c	Site capacities [meq kg^{-1}]
Planar sites (PS)		160
$\text{Na-PS} + \text{K}^+ \rightleftharpoons \text{K-PS} + \text{Na}^+$	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)		40
$\text{Na-II-S} + \text{K}^+ \rightleftharpoons \text{K-II-S} + \text{Na}^+$	2.1	
$\text{Na-II-S} + \text{Cs}^+ \rightleftharpoons \text{Cs-II-S} + \text{Na}^+$	3.6	
Frayed edge sites (FES)		0.5
$\text{Na-FES} + \text{K}^+ \rightleftharpoons \text{K-FES} + \text{Na}^+$	2.4	
$\text{Na-FES} + \text{Cs}^+ \rightleftharpoons \text{Cs-FES} + \text{Na}^+$	7.0	

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

4.4 Non-sorbing elements

For the elements C_{org.}, Cl(-I), Se(-II) and Ag(I) zero sorption values were selected by Bradbury & Baeyens (2003a) and Bradbury et al. (2010). In the intervening time no new information has arisen warranting a change to this view.

It is generally well known that dissolved organic ligands interact with mineral surfaces (see e.g. Theng 1974, Rausell-Colom & Serratosa 1987). In particular cases, such as the complexes formed between polyamines and transition metals, it has been shown that they sorb extremely strongly on clay minerals (Pleysier & Cremers 1975, Maes et al. 1978 and Peigneur et al. 1979). However, since no specific information on the types and inventories of "¹⁴C containing organics" in the repository is available, it has been assumed that they are non-sorbing.

For I(-I) sorption values were selected in the Opalinus Clay and MX-80 SDBs used in the Ent-sorgungsnachweis (Nagra 2002). More recent information given in Bradbury et al. (2010) led to the conclusion that this element should also be assigned zero sorption.

4.5 Chemical analogues

Wherever possible the source data were taken from "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. Tab. 4.3 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).

Be(II): No sorption data for Be(II) on clay minerals exist. The hydrolysis behaviour of Be is more similar to transition metals than to the elements in Group II (alkaline earths). For this reason Ni(II) is taken as the chemical analogue.

Pd(II): No sorption data for Pd(II) on clay minerals exist. The hydrolysis behaviour of Pd is very strong. Pb(II) is considered as the chemical analogue.

Ho(III), Sm(III): No relevant sorption data for these lanthanides could be found. Because of the chemical similarity to lanthanides, Eu(III) is taken as an analogue for these elements.

Ac(III), Pu(III) and Cm(III): Am(III) is taken as the chemical analogue for the trivalent actinides Ac, Pu and Cm.

The tetravalent actinides and Zr and Sn exhibit a very similar strong hydrolysis behaviour and their sorption characteristics are comparable (see e.g. Figs. 4.5 and 4.6 for illite, and Figs. 8.6 and 8.7 for montmorillonite). For this reason the following chemical analogues were chosen.

U(IV), Np(IV), Pu(IV): Th(IV) is taken as chemical analogue.

Zr(IV): Sn(IV) is taken as chemical analogue.

Tab. 4.3: The elements given in column 1 are used as chemical analogues for the elements listed in column 2.

Chemical analogue	Elements
Ni(II)	Be(II)
Pb(II)	Pd(II)
Eu(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)

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

$$CF_{\text{SPEC RN ARG ROCK}} = SF_{\text{RN ARG ROCK}} / SF_{\text{ANALOG ARG ROCK}} \quad (4.1)$$

where

$SF_{\text{RN ARG ROCK}}$ is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the argillaceous rock reference porewater.

$SF_{\text{ANALOG ARG ROCK}}$ is the fraction of the chemical analogue concentration calculated to be present in the aqueous phase as sorbing species in the argillaceous rock reference porewater.

$$R_{d \text{ RN ARG ROCK}} = R_{d \text{ ANALOG ARG ROCK}} \times CF_{\text{SPEC RN ARG ROCK}} \quad (4.2)$$

4.6 Fully coupled redox speciation calculations

The speciation calculations for the redox sensitive radionuclides Se, Tc, Pa, U, Np, Pu and Am were carried out in a fully coupled redox mode for all of the host rock and bentonite porewaters and their variations (Thoenen 2014a).

In the cases of Tc, Pa, Np, and Am the calculated major redox states were Tc(IV), Pa(V), Np(IV), and Am(III) whose aqueous species dominate their sorption behaviour and therefore only these redox states were considered in the SDBs. Se(-II) was taken to be non-sorbing. (See speciation calculations given in Thoenen (2014a).) In the cases of uranium and plutonium, mixed redox states existed in the solutions at equilibrium, and it was not clear a priori which redox species determined the overall sorption. Consequently, the overall sorption of uranium and plutonium were calculated according to Eqs. 2.4 and 2.5. The sorption values for each redox state for these radionuclides are given separately in the SDBs.

4.7 Special cases

4.7.1 Pb(II)

Ulrich & Degueldre (1992) measured the sorption of Pb at trace concentrations on montmorillonite as a function of ionic strength and pH. Fig. 4.9 shows the results for different ionic strengths and the solid line (not modelled) represent the average data in the pH range 5 to 7. An uncertainty of ± 0.5 log units is shown by the dashed lines. The values for Pb are selected from the solid line (see Fig. 4.9). The surface complexation characteristics of montmorillonite and illite are similar (see Bradbury & Baeyens 2005a and 2009b). For the above reasons the sorption values for Pb included in Tab. 5.1 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.

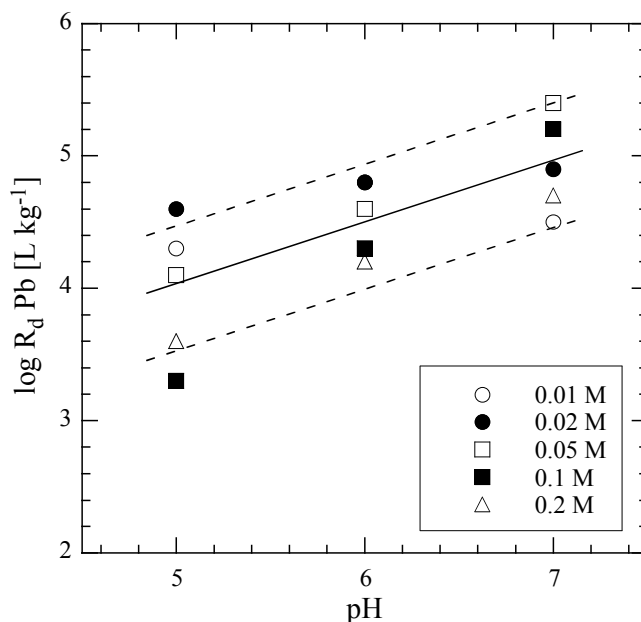


Fig. 4.9: Pb(II) sorption data on Na-montmorillonite at different NaClO_4 concentrations and pH (Ulrich & Degueldre 1992).

4.7.2 Po(IV)

In the past the oxy-anionic Se(IV) has been taken as chemical analogue for Po(IV) (Bradbury & Baeyens 2003a and 2003b) but this was based on a Pourbaix diagram with questionable thermodynamic data (Pourbaix 1966). There are strong indications that the hydrolysis behaviour of Po(IV) is strong and studies by Hataye et al. (1981a and b) indicate that the neutral $\text{Po}(\text{OH})_4$ species is dominant at $\text{pH} > 3$.

Ulrich & Degueldre (1992) measured the sorption of Po(IV) at trace concentrations on montmorillonite as a function of ionic strength (between 0.01 M to 0.2 M) and at pH 6 and 7. Under these conditions the sorption remained essentially constant with an average $\log R_d$ value of all the measurements of $3.2 \pm 1.0 \text{ L kg}^{-1}$ (see Table 2 in Ulrich & Degueldre 1992). The surface complexation characteristics for montmorillonite and illite are very similar and for this reason

this value is selected for illite (see also section 4.7.1). An uncertainty factor for the selected R_d value is taken to be 10. No speciation factors are calculated for Po(IV) because there are no data in the PSI/Nagra thermodynamic data base.

4.7.3 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 Tab. 4.4. 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. 4.4: Sorption data for Nb(V) in a synthetic groundwater on various sediments.
Nb equilibrium concentration < 10^{-10} M; taken from Legoux et al. (1992).

Solid phase	Clay content [wt.-%]	pH _{source}	R_d measured [m ³ kg ⁻¹]
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 m³ 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 Nb(OH)₅⁰, then at pH ~ 6 the negatively charged Nb(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 m³ 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 of 6 to 8.

For any systems with a 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 wt.-%, then, on a conservative approach, no additional credit is taken for this. However, for 2:1 clay mineral contents > 0 and < 10 wt.-%, sorption will occur, and in such cases the sorption value of 1 m³ 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. No speciation conversion factor is considered for this radionuclide.

4.7.4 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 and 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 Th(IV) is given. Tc(IV) can complex with carbonate and for this reason a speciation conversion factor is considered for this radionuclide.

4.7.5 Inorganic carbon

The main sorption mechanism for inorganic carbon ($\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$) is isotope exchange on calcite surfaces. Cowan et al. (1990) carried out isotopic exchange measurements of $\text{H}^{14}\text{CO}_3^-$ on calcite (particle size $\sim 10 \mu\text{m}$) at pH = 7.5 over time scales of up to 48 hours. $\text{H}^{14}\text{CO}_3^-$ exchanged with the hydrated calcite surface layer at a linear rate of $\sim 2 \times 10^{-8} \text{ mol H}^{14}\text{CO}_3^- / \text{g}/\text{hour}$ and there were no indications of saturation within the experimental time scale.

Davis et al. (1987) determined isotopic exchange rates for Ca on calcite over time periods of up to ~ 150 hours at different pH values in an artificial groundwater. At pH values of 6.5, 7.6 and 8.3 the rates of Ca isotopic exchange were 8.8×10^{-8} , 3.2×10^{-8} and 1.6×10^{-8} moles Ca/g/hour, respectively. Again, these rates did not decrease with time. The data of Cowan et al. (1990) for $\text{H}^{14}\text{CO}_3^-$ are compatible with these measurements.

Given that the most likely removal mechanism for $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$ from solution is isotopic exchange with the surface layers of CaCO_3 , the most critical (and difficult) question to answer is then how much of the intact calcite present is available to take part in this exchange.

An estimate can be made on the basis of the work of Stipp et al. (1994, 1996) who showed that Ca in the first approximately 30 monolayers, i.e. to a depth of $\sim 10^{-8} \text{ m}$, is readily accessible on time scales of the order of a few months. If we take this value of 10^{-8} m and the accessible surface area in intact calcite ($\sim 0.1 \text{ m}^2 \text{ g}^{-1}$, cf. Table 1 in Bradbury & Baeyens 1998a), then the volume of calcite available for exchange is $\sim 10^{-6} \text{ m}^3 \text{ kg}^{-1}$. For a calcite density of 2700 kg m^{-3} , this converts to $\sim 2.7 \times 10^{-3} \text{ kg kg}^{-1}$, or $\sim 0.3 \%$ of the total calcite. This estimate is certainly conservative, since more calcite is likely to become available over longer times. Note also that the above value is an in situ estimate since the surface area for intact calcite was used.

If 0.3 wt.-% of the bulk calcite is taken to be available for exchange with $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$, then the total moles of exchangeable carbonate in the solid phase is $2.7 \times 10^{-2} \text{ mol kg}^{-1}$. Thus, the $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$ sorption values for the different groundwaters can be readily obtained using their respective aqueous concentrations and the calcite contents in the argillaceous rocks (see section 3.1). Tabs. 4.5, 4.6, 4.7 and 4.8 summarise the R_d values obtained for the Opalinus Clay, 'Brauner Dogger', Effingen Member and Helvetic Marls in the different groundwaters respectively.

Some of the host rocks contain also dolomite and the same exchange mechanism can be assumed for $\text{H}^{14}\text{CO}_3^-/\text{}^{14}\text{CO}_3^{2-}$. As no parameters are available, sorption on dolomite is not considered. This assumption is conservative.

4.8 Summary

All the elements listed in Tab. 4.1 have been addressed in sections 4.2 to 4.7 and are contained in the SDBs derived in the following chapters.

Tab. 4.5: Opalinus Clay: Calcite contents, aqueous carbonate concentrations and calculated inorganic ^{14}C sorption values.

	Opalinus Clay porewater types			
	Reference	High pCO ₂	Low pCO ₂	High salinity
Isotopic exchangeable carbonate	$2.7 \times 10^{-2} \text{ mol kg}^{-1}$			
$\text{H}^{14}\text{CO}_3^-/\text{}^{14}\text{CO}_3^{2-} [\text{mol L}^{-1}]$	2.51×10^{-3}	4.15×10^{-3}	1.21×10^{-3}	1.06×10^{-3}
R_d for 100 % calcite [$\text{m}^3 \text{ kg}^{-1}$]	1.1×10^{-2}	6.5×10^{-3}	2.2×10^{-2}	2.6×10^{-2}
	R_d values [$\text{m}^3 \text{ kg}^{-1}$]:			
13 wt.-%	1.4×10^{-3}	8.5×10^{-4}	2.9×10^{-3}	3.4×10^{-3}
5 wt.-%	5.5×10^{-4}	3.3×10^{-4}	1.1×10^{-3}	1.3×10^{-3}
35 wt.-%	3.9×10^{-3}	2.3×10^{-3}	7.7×10^{-3}	9.1×10^{-3}

Tab. 4.6: 'Brauner Dogger': Calcite contents, aqueous carbonate concentrations and calculated inorganic ^{14}C sorption values.

	'Brauner Dogger' porewater types			
	Reference	High pCO ₂	Low pCO ₂	High salinity
Isotopic exchangeable carbonate	$2.7 \times 10^{-2} \text{ mol kg}^{-1}$			
$\text{H}^{14}\text{CO}_3^-/\text{}^{14}\text{CO}_3^{2-} [\text{mol L}^{-1}]$	2.51×10^{-3}	4.15×10^{-3}	1.21×10^{-3}	1.06×10^{-3}
R_d for 100 % calcite [$\text{m}^3 \text{ kg}^{-1}$]	1.1×10^{-2}	6.5×10^{-3}	2.2×10^{-2}	2.6×10^{-2}
	R_d values [$\text{m}^3 \text{ kg}^{-1}$]:			
'Brauner Dogger' Clay-rich seq.				
30 wt.-%	3.3×10^{-3}	2.0×10^{-3}	6.6×10^{-3}	7.8×10^{-3}
5 wt.-%	5.5×10^{-4}	3.3×10^{-4}	1.1×10^{-3}	1.3×10^{-3}
60 wt.-%	6.6×10^{-3}	4.0×10^{-3}	1.3×10^{-2}	1.6×10^{-2}
'Brauner Dogger' Sandy limest. seq.				
39 wt.-%	4.3×10^{-3}	2.5×10^{-3}	8.6×10^{-3}	1.0×10^{-2}
20 wt.-%	2.2×10^{-3}	1.3×10^{-3}	4.4×10^{-3}	5.2×10^{-3}
70 wt.-%	7.7×10^{-3}	4.6×10^{-3}	1.5×10^{-2}	1.8×10^{-2}

Tab. 4.7: Effingen Member: Calcite contents, aqueous carbonate concentrations and calculated inorganic ^{14}C sorption values.

	Effingen Member porewater types			
	Reference	High SO_4	High pCO_2	Lowest Cl
Isotopic exchangeable carbonate	$2.7 \times 10^{-2} \text{ mol kg}^{-1}$			
$\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$ [mol L^{-1}]	4.3×10^{-4}	8.9×10^{-4}	1.5×10^{-3}	1.5×10^{-3}
R_d for 100 % calcite [$\text{m}^3 \text{ kg}^{-1}$]	6.3×10^{-2}	3.0×10^{-2}	1.8×10^{-2}	1.8×10^{-2}
	R_d values [$\text{m}^3 \text{ kg}^{-1}$]			
Effingen Member Calc. marl seq.				
57 wt.-%	3.6×10^{-2}	1.7×10^{-2}	1.0×10^{-2}	1.0×10^{-2}
40 wt.-%	2.5×10^{-2}	1.2×10^{-2}	7.2×10^{-3}	7.2×10^{-3}
70 wt.-%	4.4×10^{-2}	2.14×10^{-2}	1.3×10^{-2}	1.3×10^{-2}
Effingen Member Limestone seq.				
76 wt.-%	4.8×10^{-2}	2.3×10^{-2}	1.4×10^{-2}	1.4×10^{-2}
62 wt.-%	3.9×10^{-2}	1.9×10^{-2}	1.1×10^{-2}	1.1×10^{-2}
99 wt.-%	6.2×10^{-2}	3.0×10^{-2}	1.8×10^{-2}	1.8×10^{-2}

Tab. 4.8: Helvetic Marls: Calcite contents, aqueous carbonate concentrations and calculated inorganic ^{14}C sorption values.

	Helvetic Marls porewater types				
	Reference	Low pCO_2	High pCO_2	High salinity	Low pe
Isotopic exchangeable IC	$2.7 \times 10^{-2} \text{ mol kg}^{-1}$				
$\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$ [mol L^{-1}]	5.4×10^{-3}	1.8×10^{-3}	1.6×10^{-2}	2.8×10^{-3}	5.6×10^{-3}
R_d for 100 % calcite [$\text{m}^3 \text{ kg}^{-1}$]	5.0×10^{-3}	1.5×10^{-2}	1.7×10^{-3}	9.6×10^{-3}	4.8×10^{-3}
	R_d values [$\text{m}^3 \text{ kg}^{-1}$]				
Helvetic Marls 42 wt.-%					
10 wt.-%	2.1×10^{-3}	6.3×10^{-3}	7.1×10^{-4}	4.0×10^{-3}	2.0×10^{-3}
80 wt.-%	5.0×10^{-4}	1.5×10^{-3}	1.7×10^{-4}	9.6×10^{-4}	4.8×10^{-4}
	4.0×10^{-3}	1.2×10^{-2}	1.4×10^{-3}	7.7×10^{-3}	3.8×10^{-3}
Helvetic Marls Limestone seq.					
84 wt.-%	4.3×10^{-3}	1.3×10^{-2}	1.5×10^{-3}	8.3×10^{-3}	4.1×10^{-3}

5 Sorption data bases for the host rocks

In this chapter the sorption data bases for the four selected host rock types (Opalinus Clay, 'Brauner Dogger', Effingen Member and Helvetic Marls) are derived. The SDBs are presented in form of summary tables corresponding to the variations in mineralogies and porewater chemistries.

5.1 Opalinus Clay

The selected illite source data ($R_{d, \text{ILLITE}}$) at the corresponding pH of the porewaters are given in Tab. 5.1. The sorption values for combinations of the four water chemistries (Tab. 3.8) and the reference mineralogy (Tab. 3.1) for the safety relevant radionuclide vector (Tab. 4.1) are derived according to the methodology described in Chapter 2 and are given in Tab. 5.2.

Tab. 5.1: Selected illite source sorption values ($R_{d, \text{ILLITE}}$) for 3 different pH values valid for Opalinus Clay, 'Brauner Dogger' and 'Brauner Dogger' Limestone sequences.

Radio-nuclide	$R_{d, \text{ILLITE}} [\text{m}^3 \text{kg}^{-1}]$			Comment
	High pCO ₂ High salinity pH = 7.0	Reference pH = 7.2	Low pCO ₂ pH = 7.5	
Co(II)	2.2	3.1	4.9	Bradbury & Baeyens (2009a): model
Ni(II)	5.4	5.6	6.0	Bradbury & Baeyens (2009a): model
Nb(V)	1.0	1.0	1.0	Sedimentary rocks: Legoux et al. (1992)
Mo(VI)	0.013	0.0115	0.009	Value of 0.0066 m ³ kg ⁻¹ selected at pH 8.9 (Motta & Miranda 1989) and CF _{pH} applied (see section 4.2)
Tc(IV)	4.0	4.0	4.0	Expert judgement (Th(IV) analogue reduced)
Sn(IV)	316	316	316	Bradbury & Baeyens (2009a): model
Eu(III)	90	125	200	Bradbury & Baeyens (2009a): model
Pb(II)	100	100	100	Ulrich & Degueldre (1992)
Po(IV)	1.6	1.6	1.6	Ulrich & Degueldre (1992)
Th(IV)	400	400	400	Bradbury & Baeyens (2009b): model
Pa(V)	100	100	100	Bradbury & Baeyens (2009b): model
U(VI)	100	100	100	Bradbury & Baeyens (2009b): model
Am(III)	90	125	200	Eu data are selected (Am too high in Bradbury & Baeyens 2009b)

Note: The selected values are derived from the modelling curves from the corresponding sorption edges (Chapter 4) as log R_d values [L kg⁻¹] and converted in the SI units [m³ kg⁻¹].

Tab. 5.2: Summary of SDBs for Opalinus Clay (R_d in $\text{m}^3 \text{kg}^{-1}$).

Opalinus Clay	Reference	High pCO_2	Low pCO_2	High salinity
pH	7.20	7.00	7.51	7.01
2:1 clay content [wt.-%]	33	33	33	33
Be(II)	1.33E+00	1.10E+00	1.45E+00	1.44E+00
$C_{\text{inorg.}}$	1.43E-03	8.45E-04	2.86E-03	3.38E-03
$C_{\text{org.}}$	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	5.05E-03	5.03E-03	5.08E-03	2.94E-03
Ca(II)	6.30E-04	6.22E-04	6.37E-04	1.32E-04
Co(II)	6.72E-01	4.69E-01	1.08E+00	3.56E-01
Ni(II)	1.34E+00	1.29E+00	1.43E+00	1.27E+00
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	6.36E-04	6.28E-04	6.44E-04	1.32E-04
Zr(IV)	1.25E+02	1.18E+02	1.47E+02	1.18E+02
Nb(V)	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Mo(VI)	3.78E-03	4.35E-03	3.07E-03	4.35E-03
Tc(IV)	1.19E+00	1.05E+00	1.28E+00	1.25E+00
Pd(II)	3.23E+01	3.13E+01	3.28E+01	2.73E+00
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	1.03E+02	1.04E+02	1.03E+02	1.04E+02
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	2.04E+00	2.03E+00	2.05E+00	1.36E+00
Sm(III)	1.50E+01	8.37E+00	3.41E+01	1.83E+01
Eu(III)	5.91E+00	3.61E+00	1.16E+01	5.72E+00
Ho(III)	1.05E+01	5.79E+00	2.48E+01	1.55E+01
Pb(II)	7.03E+00	6.24E+00	8.45E+00	1.54E+00
Po(IV)	5.28E-01	5.28E-01	5.28E-01	5.28E-01
Ra(II)	4.42E-04	4.38E-04	4.46E-04	9.74E-05
Ac(III)	7.25E+00	4.56E+00	1.35E+01	7.74E+00
Th(IV)	3.58E+01	1.70E+01	7.85E+01	1.05E+02
Pa(V)	3.30E+01	3.30E+01	3.30E+01	3.30E+01
U(IV)	1.98E-01	7.13E-02	9.24E-01	1.45E+00
U(VI)	3.72E-04	1.94E-04	1.14E-03	3.75E-03
Np(IV)	1.32E+02	1.32E+02	1.32E+02	1.32E+02
Pu(III)	7.24E+00	4.35E+00	1.46E+03	7.03E+00
Pu(IV)	3.43E-02	1.20E-02	1.53E-01	2.22E-02
Am(III)	7.25E+00	4.56E+00	1.35E+01	7.74E+00
Cm(III)	7.25E+00	4.56E+00	1.35E+01	7.74E+00
	source data for illite			
	chemical analogue (see Table 4.3)			
	set to zero			
	special cases (see section 4.7)			
	cation exchange			

Note that the R_d values for $C_{\text{inorg.}}$ do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.1).

5.2 'Brauner Dogger'

The porewater compositions for 'Brauner Dogger' are identical to the Opalinus Clay and consequently the source illite data are also the same (Tab. 5.1). The only difference is the mineralogy. The content of the 2:1 type clay minerals in the 'Brauner Dogger' is 27 wt.-% for the reference case (Traber & Blaser 2013). The SDBs for this host rock type are summarised in Tab. 5.3.

For the 'Brauner Dogger' host rock a second rock type is considered which is denoted as 'Brauner Dogger' Sandy limestone sequences. For this formation the 2:1 type clay mineral content for the reference case is different from the Clay-rich sequences and separate SDBs are derived. These are summarised in Tab. 5.4.

Tab. 5.3: Summary of SDBs for 'Brauner Dogger' Clay-rich sequences (R_d in $\text{m}^3 \text{kg}^{-1}$).

'Brauner Dogger'	Reference	High pCO_2	Low pCO_2	High salinity
Clay-rich sequences				
pH	7.20	7.00	7.51	7.01
2:1 clay content [wt.-%]	27	27	27	27
Be(II)	1.08E+00	8.97E-01	1.19E+00	1.18E+00
$C_{\text{inorg.}}$	3.30E-03	1.95E-03	6.60E-03	7.80E-03
$C_{\text{org.}}$	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	4.13E-03	4.12E-03	4.16E-03	2.40E-03
Ca(II)	5.16E-04	5.09E-04	5.21E-04	1.08E-04
Co(II)	5.50E-01	3.84E-01	8.84E-01	2.92E-01
Ni(II)	1.09E+00	1.06E+00	1.17E+00	1.04E+00
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	5.20E-04	5.13E-04	5.27E-04	1.08E-04
Zr(IV)	1.03E+02	9.62E+01	1.20E+02	9.62E+01
Nb(V)	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Mo(VI)	3.10E-03	3.56E-03	2.51E-03	3.56E-03
Tc(IV)	9.77E-01	8.62E-01	1.05E+00	1.02E+00
Pd(II)	2.64E+01	2.56E+01	2.68E+01	2.23E+00
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	8.45E+01	8.48E+01	8.41E+01	8.49E+01
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	1.67E+00	1.66E+00	1.68E+00	1.11E+00
Sm(III)	1.22E+01	6.84E+00	2.79E+01	1.49E+01
Eu(III)	4.84E+00	2.95E+00	9.53E+00	4.68E+00
Ho(III)	8.62E+00	4.74E+00	2.03E+01	1.27E+01
Pb(II)	5.75E+00	5.10E+00	6.91E+00	1.26E+00
Po(IV)	4.32E-01	4.32E-01	4.32E-01	4.32E-01
Ra(II)	3.62E-04	3.58E-04	3.65E-04	7.97E-05
Ac(III)	5.93E+00	3.73E+00	1.11E+01	6.33E+00
Th(IV)	2.93E+01	1.39E+01	6.43E+01	8.59E+01
Pa(V)	2.70E+01	2.70E+01	2.70E+01	2.70E+01
U(IV)	1.62E-01	5.83E-02	7.56E-01	1.19E+00
U(VI)	3.04E-04	1.59E-04	9.30E-04	3.07E-03
Np(IV)	1.08E+02	1.08E+02	1.08E+02	1.08E+02
Pu(III)	5.92E+00	3.56E+00	1.11E+01	5.75E+00
Pu(IV)	2.81E-02	9.83E-03	1.25E-01	1.81E-02
Am(III)	5.93E+00	3.73E+00	1.11E+01	6.33E+00
Cm(III)	5.93E+00	3.73E+00	1.11E+01	6.33E+00
	source data for illite			
	chemical analogue (see Table 4.3)			
	set to zero			
	special cases (see section 4.7)			
	cation exchange			

Note that the R_d values for $C_{\text{inorg.}}$ do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.2).

Tab. 5.4: Summary of SDBs for 'Brauner Dogger' Sandy limestone sequences (R_d in $m^3 kg^{-1}$).

'Brauner Dogger'	Reference	High pCO ₂	Low pCO ₂	High salinity
Sandy limestone sequences				
pH	7.20	7.00	7.51	7.01
2:1 clay content [wt.-%]	7	7	7	7
Be(II)	2.81E-01	2.32E-01	3.08E-01	3.05E-01
C _{inorg.}	4.29E-03	2.54E-03	8.58E-03	1.01E-02
C _{org.}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	1.07E-03	1.07E-03	1.08E-03	6.23E-04
Ca(II)	1.34E-04	1.32E-04	1.35E-04	2.80E-05
Co(II)	1.43E-01	9.95E-02	2.29E-01	7.56E-02
Ni(II)	2.83E-01	2.74E-01	3.04E-01	2.70E-01
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	1.35E-04	1.33E-04	1.37E-04	2.80E-05
Zr(IV)	2.66E+01	2.49E+01	3.12E+01	2.49E+01
Nb(V)	7.00E-01	7.00E-01	7.00E-01	7.00E-01
Mo(VI)	8.03E-04	9.22E-04	6.50E-04	9.22E-04
Tc(IV)	2.53E-01	2.23E-01	2.72E-01	2.65E-01
Pd(II)	6.85E+00	6.64E+00	6.96E+00	5.78E-01
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	2.19E+01	2.20E+01	2.18E+01	2.20E+01
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	4.33E-01	4.31E-01	4.35E-01	2.88E-01
Sm(III)	3.17E+00	1.77E+00	7.22E+00	3.87E+00
Eu(III)	1.25E+00	7.65E-01	2.47E+00	1.21E+00
Ho(III)	2.23E+00	1.23E+00	5.25E+00	3.29E+00
Pb(II)	1.49E+00	1.32E+00	1.79E+00	3.27E-01
Po(IV)	1.12E-01	1.12E-01	1.12E-01	1.12E-01
Ra(II)	9.38E-05	9.29E-05	9.45E-05	2.07E-05
Ac(III)	1.54E+00	9.68E-01	2.87E+00	1.64E+00
Th(IV)	7.59E+00	3.61E+00	1.67E+01	2.23E+01
Pa(V)	6.99E+00	7.00E+00	6.99E+00	7.00E+00
U(IV)	4.20E-02	1.51E-02	1.96E-01	3.08E-01
U(VI)	7.89E-05	4.12E-05	2.41E-04	7.95E-04
Np(IV)	2.80E+01	2.80E+01	2.80E+01	2.80E+01
Pu(III)	1.54E+00	9.22E-01	2.88E+00	1.49E+00
Pu(IV)	7.28E-03	2.55E-03	3.25E-02	4.70E-03
Am(III)	1.54E+00	9.68E-01	2.87E+00	1.64E+00
Cm(III)	1.54E+00	9.68E-01	2.87E+00	1.64E+00
	source data for illite			
	chemical analogue (see Table 4.3)			
	set to zero			
	special cases (see section 4.7)			
	cation exchange			

Note that the R_d values for C_{inorg.} do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.3).

5.3 Effingen Member

For the Effingen Member calcareous marl sequences and Effingen Member limestone sequences systems a reference porewater and 3 variations in water compositions have been defined (Mäder 2009a). The pH values of these porewaters are 7.31 (reference porewater), 7.09 (lowest Cl type porewater), 7.25 (high SO₄ porewater) and 6.8 (high pCO₂/low pH porewater). The methodology described in Chapter 2 is again applied. A summary of the selected source data at the four pH values is given in Tab. 5.5. For the Effingen Member, two different lithographies are considered.

As in the case for Opalinus Clay and 'Brauner Dogger', SDBs have been derived for each variation. The SDBs presented in Tabs. 5.6 and 5.7 are for Effingen Member Calcareous marl sequences and Effingen Member Limestone sequences, respectively. For the lower bounding mineralogical data of Effingen Member Limestone sequences (Tab. 3.5) where the 2:1 clay content is zero, the SDB is based on calcite as sorbing phase (see Chapter 7).

Tab. 5.5: Selected illite source sorption values ($R_{d, \text{ILLITE}}$) for 4 different pH values for the Effingen Member SDBs.

Radio-nuclide	$R_{d, \text{ILLITE}} [\text{m}^3 \text{kg}^{-1}]$				Comment
	pH = 7.31	pH = 7.25	pH = 7.09	pH = 6.8	
Co(II)	3.3	3.2	2.5	1.6	Bradbury & Baeyens (2009a): model
Ni(II)	5.8	5.8	5.4	4.8	Bradbury & Baeyens (2009a): model
Nb(V)	1.0	1.0	1.0	1.0	Sedimentary rocks: Legoux et al. (1992)
Mo(VI)	0.0106	0.011	0.012	0.015	Value of 0.0066 m ³ kg ⁻¹ selected at pH 8.9 (Motta & Miranda 1989) and CF _{pH} applied (see section 4.2)
Tc(IV)	4.0	4.0	4.0	4.0	Expert judgement (Th analogue reduced)
Sn(IV)	316	316	316	316	Bradbury & Baeyens (2009a): model
Eu(III)	160	140	100	60	Bradbury & Baeyens (2009a): model
Pb(II)	100	100	100	100	Ulrich & Degueldre (1992)
Po(IV)	1.6	1.6	1.6	1.6	Ulrich & Degueldre (1992)
Th(IV)	400	400	400	400	Bradbury & Baeyens (2009b): model
Pa(V)	100	100	100	100	Bradbury & Baeyens (2009b): model
U(VI)	100	100	100	100	Bradbury & Baeyens (2009b): model
Am(III)	160	140	100	60	Eu data are selected (Am too high in Bradbury & Baeyens 2009b)

Tab. 5.6: Summary of SDBs for Effingen Member Calcareous marl sequences (R_d in $m^3 kg^{-1}$).

Effingen Member	Reference	High pCO ₂	Lowest Cl	High SO ₄
Calcareous marl sequences				
pH	7.31	6.80	7.09	7.25
2:1 clay content [wt.-%]	20.1	20.1	20.1	20.1
Be(II)	1.06E+00	7.27E-01	8.46E-01	9.89E-01
C _{inorg.}	3.59E-02	1.03E-02	1.03E-02	1.71E-02
C _{org.}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	2.09E-03	2.09E-03	4.73E-03	2.19E-03
Ca(II)	8.76E-05	8.72E-05	2.51E-04	1.25E-04
Co(II)	3.73E-01	1.79E-01	3.76E-01	3.75E-01
Ni(II)	9.10E-01	7.53E-01	9.55E-01	8.53E-01
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	8.79E-05	8.76E-05	2.52E-04	1.26E-04
Zr(IV)	8.01E+01	6.86E+01	7.35E+01	7.79E+01
Nb(V)	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Mo(VI)	2.14E-03	3.04E-03	2.49E-03	2.23E-03
Tc(IV)	7.94E-01	7.22E-01	7.49E-01	7.79E-01
Pd(II)	7.92E+00	1.23E+00	1.76E+01	1.13E+01
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	6.32E+01	6.33E+01	6.30E+01	6.29E+01
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	9.56E-01	9.56E-01	2.62E+00	1.02E+00
Sm(III)	3.25E+01	7.66E+00	1.34E+01	2.07E+01
Eu(III)	8.12E+00	2.67E+00	4.60E+00	6.23E+00
Ho(III)	2.84E+01	6.43E+00	1.02E+01	1.74E+01
Pb(II)	1.48E+00	1.25E+00	4.28E+00	2.13E+00
Po(IV)	3.22E-01	3.22E-01	3.22E-01	3.22E-01
Ra(II)	7.08E-05	7.08E-05	2.23E-04	9.17E-05
Ac(III)	9.26E+00	3.54E+00	5.15E+00	7.55E+00
Th(IV)	7.69E+01	5.48E+01	4.47E+01	6.34E+01
Pa(V)	2.00E+01	2.02E+01	2.01E+01	2.02E+01
U(IV)	5.55E+00	4.82E-01	4.82E-01	1.05E+00
U(VI)	7.59E-03	1.65E-03	7.65E-04	1.95E-03
Np(IV)	8.04E+01	8.04E+01	8.04E+01	8.04E+01
Pu(III)	1.01E+01	3.13E+00	5.48E+00	7.59E+00
Pu(IV)	5.39E-02	5.07E-03	1.53E-02	3.70E-02
Am(III)	9.26E+00	3.54E+00	5.15E+00	7.55E+00
Cm(III)	9.26E+00	3.54E+00	5.15E+00	7.55E+00
	source data for illite			
	chemical analogue (see Table 4.3)			
	set to zero			
	special cases (see section 4.7)			
	cation exchange			

Note that the R_d values for C_{inorg.} do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.4).

Tab. 5.7: Summary of SDBs for Effingen Member Limestone sequences (R_d in $m^3 kg^{-1}$).

Effingen Member	Reference	High pCO ₂	Lowest Cl	High SO ₄
Limestone sequences				
pH	7.31	6.80	7.09	7.25
2:1 clay content [wt.-%]	9.2	9.2	9.2	9.2
Be(II)	4.84E-01	3.33E-01	3.87E-01	4.52E-01
C _{inorg.}	4.78E-02	1.37E-02	1.37E-02	2.28E-02
C _{org.}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	9.57E-04	9.57E-04	2.16E-03	1.00E-03
Ca(II)	4.01E-05	3.99E-05	1.15E-04	5.73E-05
Co(II)	1.71E-01	8.20E-02	1.72E-01	1.72E-01
Ni(II)	4.17E-01	3.44E-01	4.37E-01	3.91E-01
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	4.02E-05	4.01E-05	1.15E-04	5.76E-05
Zr(IV)	3.67E+01	3.14E+01	3.36E+01	3.57E+01
Nb(V)	9.20E-01	9.20E-01	9.20E-01	9.20E-01
Mo(VI)	9.85E-04	1.39E-03	1.14E-03	1.02E-03
Tc(IV)	3.63E-01	3.30E-01	3.43E-01	3.57E-01
Pd(II)	3.62E+00	5.62E-01	8.04E+00	5.16E+00
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	2.89E+01	2.90E+01	2.89E+01	2.88E+01
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	4.37E-01	4.37E-01	1.20E+00	4.66E-01
Sm(III)	1.49E+01	3.51E+00	6.14E+00	9.47E+00
Eu(III)	3.72E+00	1.22E+00	2.11E+00	2.85E+00
Ho(III)	1.30E+01	2.94E+00	4.65E+00	7.97E+00
Pb(II)	6.79E-01	5.74E-01	1.96E+00	9.75E-01
Po(IV)	1.47E-01	1.47E-01	1.47E-01	1.47E-01
Ra(II)	3.24E-05	3.24E-05	1.02E-04	4.20E-05
Ac(III)	4.24E+00	1.62E+00	2.36E+00	3.46E+00
Th(IV)	3.52E+01	2.51E+01	2.05E+01	2.90E+01
Pa(V)	9.14E+00	9.24E+00	9.20E+00	9.25E+00
U(IV)	2.54E+00	2.21E-01	2.21E-01	4.78E-01
U(VI)	3.47E-03	7.56E-04	3.50E-04	8.94E-04
Np(IV)	3.68E+01	3.68E+01	3.68E+01	3.68E+01
Pu(III)	4.64E+00	1.43E+00	2.51E+00	3.47E+00
Pu(IV)	2.47E-02	2.32E-03	6.99E-03	1.69E-02
Am(III)	4.24E+00	1.62E+00	2.36E+00	3.46E+00
Cm(III)	4.24E+00	1.62E+00	2.36E+00	3.46E+00
	source data for illite			
	chemical analogue (see Table 4.3)			
	set to zero			
	special cases (see section 4.7)			
	cation exchange			

Note that the R_d values for C_{inorg.} do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.5).

5.4 Helvetic Marls

For the Helvetic Marls two formations are considered. The first one is a non-disturbed or very little disturbed host rock (Tab. 3.6).

The second formation is a calcareous rich zone which is characterised by a very low clay mineral content (Tab. 3.7). Additional features are described by Traber & Blaser (2013) but all are characterised by identical 2:1 type clay mineral contents and the sorption characteristics for this range of rock types are the same and are treated as being the same.

In addition a further formation is consisting of nearly pure calcite with no clay minerals present. For this formation a SDB for calcite is used (Chapter 7).

For the Helvetic Marls formation one reference porewater (Na-Cl 'Base-case') and four additional porewater variations have been defined (Mäder 2010). Tab. 5.8 summarises the source sorption values taken from the sorption edge data on illite presented in Chapter 4.

Tab. 5.8: Selected illite source sorption values ($R_{d, \text{ILLITE}}$) at 4 different pH values for Helvetic Marls.

Radio-nuclide	$R_{d, \text{ILLITE}} [\text{m}^3 \text{kg}^{-1}]$				Comment
	Reference & low $p\epsilon$ pH = 7.47	High $p\text{CO}_2$ pH = 7.01	Low $p\text{CO}_2$ pH = 7.95	High NaCl pH = 7.16	
Co(II)	4.9	2.2	12.6	2.7	Bradbury & Baeyens (2009a): model curve
Ni(II)	5.8	5.4	6.6	5.5	Bradbury & Baeyens (2009a): model
Nb(V)	1	1	1	1	Sedimentary rocks: Legoux et al. (1992)
Mo(VI)	0.0095	0.013	0.0069	0.012	Value of $0.0066 \text{ m}^3 \text{kg}^{-1}$ selected at pH 8.9 (Motta & Miranda 1989) and CF_{pH} applied (see section 4.2)
Sn(IV)	316	316	316	316	Bradbury & Baeyens (2009a): model
Pb(II)	100	100	100	100	Ulrich & Degueldre (1992)
Po(IV)	1.6	1.6	1.6	1.6	Ulrich & Degueldre (1992)
Th(IV)	400	400	400	400	Bradbury & Baeyens (2009b): model
Pa(V)	100	100	100	100	Bradbury & Baeyens (2009b): model
U(VI)	100	100	80	100	Bradbury & Baeyens (2009b): model
Am(III)	200	90	360	125	Eu data are selected (Am too high in Bradbury & Baeyens 2009b)

The same procedures are followed as for the other host rocks to derive the SDBs for Helvetic Marls. Tabs. 5.9 and 5.10 summarise the SDBs for marl.

Tab. 5.9: Summary of SDBs Helvetic Marls (R_d in $\text{m}^3 \text{kg}^{-1}$).

Helvetic Marls	Reference	Low p ϵ	High pCO ₂	Low pCO ₂	High NaCl
pH	7.47	7.46	7.01	7.95	7.16
2:1 clay content [wt.-%]	22	22	22	22	22
Be(II)	7.89E-01	7.81E-01	4.32E-01	1.23E+00	8.55E-01
C _{inorg.}	2.10E-03	2.02E-03	7.14E-04	6.30E-03	4.03E-03
C _{org.}	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	3.85E-03	3.78E-03	3.70E-03	3.89E-03	1.69E-03
Co(II)	7.82E-01	4.04E-02	3.09E-01	2.13E+00	3.63E-01
Ni(II)	1.16E+00	2.30E-03	1.08E+00	1.32E+00	1.02E+00
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	1.03E-03	9.28E-04	9.20E-04	1.07E-03	1.96E-04
Nb(V)	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Mo(VI)	2.09E-03	2.11E-03	2.88E-03	1.50E-03	2.59E-03
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	7.04E+01	6.89E+01	6.87E+01	6.76E+01	7.04E+01
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	1.35E+00	1.37E+00	1.30E+00	1.37E+00	5.39E-01
Pb(II)	2.97E+00	2.95E+00	2.01E+00	4.80E+00	1.84E+00
Po(IV)	3.52E-01	3.52E-01	3.52E-01	3.52E-01	3.52E-01
Ra(II)	1.00E-03	8.93E-04	9.24E-04	1.03E-03	1.76E-04
Ac(III)	3.94E+00	3.65E+00	9.33E-01	1.08E+01	5.66E+00
Th(IV)	5.72E+00	5.45E+00	8.27E-01	3.33E+01	2.24E+01
Pa(V)	2.20E+01	2.20E+01	2.20E+01	2.11E+01	2.20E+01
U(IV)	1.23E-01	3.61E+00	1.32E-02	1.32E+00	3.87E-01
U(VI)	3.57E-05	1.34E-06	7.49E-06	1.75E-04	2.26E-04
Np(IV)	8.69E+01	8.67E+01	5.09E+01	8.80E+01	8.80E+01
Pu(III)	4.63E+00	4.77E+00	1.07E+00	1.17E+01	6.20E+00
Pu(IV)	1.94E-02	7.13E-04	1.50E-03	1.98E-01	1.14E-02
Am(III)	3.94E+00	3.65E+00	9.33E-01	1.08E+01	5.66E+00
Cm(III)	3.94E+00	3.65E+00	9.33E-01	1.08E+01	5.66E+00
	source data for illite				
	chemical analogue (see Table 4.3)				
	set to zero				
	special cases (see section 4.7)				
	cation exchange				

Note that the R_d values for C_{inorg.} do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.6).

Tab. 5.10: Summary of SDBs for Helvetic Marls Limestone sequences (R_d in $m^3 kg^{-1}$).

Helvetic Marls	Reference	Low p_e	High pCO_2	Low pCO_2	High NaCl
Limestone sequences					
pH	7.47	7.46	7.01	7.95	7.16
2:1 clay content [wt.-%]	3.9	3.9	3.9	3.9	3.9
Be(II)	1.40E-01	1.38E-01	7.67E-02	2.19E-01	1.52E-01
$C_{inorg.}$	4.20E-03	4.03E-03	1.43E-03	1.26E-02	8.06E-03
$C_{org.}$	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	6.83E-04	6.71E-04	6.55E-04	6.90E-04	2.99E-04
Co(II)	1.39E-01	7.17E-03	5.48E-02	3.77E-01	6.43E-02
Ni(II)	2.05E-01	4.07E-04	1.91E-01	2.33E-01	1.81E-01
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	1.83E-04	1.65E-04	1.63E-04	1.90E-04	3.47E-05
Nb(V)	3.90E-01	3.90E-01	3.90E-01	3.90E-01	3.90E-01
Mo(VI)	3.71E-04	3.74E-04	5.10E-04	2.66E-04	4.60E-04
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	1.25E+01	1.22E+01	1.22E+01	1.20E+01	1.25E+01
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	2.40E-01	2.43E-01	2.31E-01	2.43E-01	9.56E-02
Pb(II)	5.27E-01	5.23E-01	3.56E-01	8.50E-01	3.26E-01
Po(IV)	6.24E-02	6.24E-02	6.24E-02	6.24E-02	6.24E-02
Ra(II)	1.78E-04	1.58E-04	1.64E-04	1.82E-04	3.12E-05
Ac(III)	6.98E-01	6.47E-01	1.65E-01	1.92E+00	1.00E+00
Th(IV)	1.01E+00	9.66E-01	1.47E-01	5.90E+00	3.96E+00
Pa(V)	3.90E+00	3.90E+00	3.90E+00	3.75E+00	3.90E+00
U(IV)	2.18E-02	6.40E-01	2.34E-03	2.34E-01	6.86E-02
U(VI)	6.33E-06	2.38E-07	1.33E-06	3.10E-05	4.00E-05
Np(IV)	1.54E+01	1.54E+01	9.02E+00	1.56E+01	1.56E+01
Pu(III)	8.21E-01	8.46E-01	1.91E-01	2.08E+00	1.10E+00
Pu(IV)	3.43E-03	1.26E-04	2.65E-04	3.51E-02	2.03E-03
Am(III)	6.98E-01	6.47E-01	1.65E-01	1.92E+00	1.00E+00
Cm(III)	6.98E-01	6.47E-01	1.65E-01	1.92E+00	1.00E+00
	source data for illite				
	chemical analogue (see Table 4.3)				
	set to zero				
	special cases (see section 4.7)				
	cation exchange				

Note that the R_d values for $C_{inorg.}$ do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 3.7).

6 Sorption data bases for the Lower confining units

For the Opalinus Clay host rock the Lower confining units are also included in the provisional safety analyses. Traber (2013) has documented the host rock parameters for the underlying rock formations including the clay mineralogical content. Three geological units have been defined for which 2:1 type clay minerals are present. These are denoted "Toniger Lias", "Arietenkalk" and "Toniger Keuper". The results of the clay mineral and calcite contents in wt.-% of the total rock are given in Tab. 6.1.

Tab. 6.1: Reference clay mineralogy and calcite content for the lower confining units defined in Traber (2013).

Mineral	Toniger Lias [wt.-%]		Arietenkalk [wt.-%]		Toniger Keuper [wt.-%]	
	Reference	Lower bound	Reference	Lower bound	Reference	Lower bound
Illite	19	10	5	0	28	14
Illite/smectite mixed layer	6	3	2	0	10	5
Smectite	0	0	0	0	0	0
Kaolinite	10	5	2	0	5	2.5
Chlorite	5	2	1	0	7	3.5
Calcite	30	10	80	10	9	0

The reference Opalinus Clay groundwater composition (Tab. 3.8) is taken for the derivation of sorption values for these Lower confining units. No variations in porewater compositions were considered. The SDBs for the reference mineralogy are summarised in Tab. 6.2. For the lower bounding value of Arietenkalk where the 2:1 clay content is zero, the SDB is based on calcite as sorbing phase (see Chapter 7).

Tab. 6.2: SDBs for Lower confining units (R_d in $\text{m}^3 \text{kg}^{-1}$).

Lower confining units	SDBs in reference OPA PW (pH = 7.2)		
Hydrogeological unit	Toniger Lias	Arietenkalk	Toniger Keuper
2:1 clay content [wt.-%]	25	7	38
Be(II)	1.00E+00	2.81E-01	1.53E+00
C _{inorg.}	3.30E-03	8.80E-03	9.90E-04
C _{org.}	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00
K(I)	3.83E-03	1.07E-03	5.81E-03
Ca(II)	4.78E-04	1.34E-04	7.26E-04
Co(II)	5.09E-01	1.43E-01	7.74E-01
Ni(II)	1.01E+00	2.83E-01	1.54E+00
Se(-II)	0.00E+00	0.00E+00	0.00E+00
Sr(II)	4.82E-04	1.35E-04	7.32E-04
Zr(IV)	9.50E+01	2.66E+01	1.44E+02
Nb(V)	1.00E+00	7.00E-01	1.00E+00
Mo(VI)	2.87E-03	8.03E-04	4.36E-03
Tc(IV)	9.05E-01	2.53E-01	1.38E+00
Pd(II)	2.45E+01	6.85E+00	3.72E+01
Ag(I)	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	7.82E+01	2.19E+01	1.19E+02
I(-I)	0.00E+00	0.00E+00	0.00E+00
Cs(I)	1.55E+00	4.33E-01	2.35E+00
Sm(III)	1.13E+01	3.17E+00	1.72E+01
Eu(III)	4.48E+00	1.25E+00	6.81E+00
Ho(III)	7.98E+00	2.23E+00	1.21E+01
Pb(II)	5.33E+00	1.49E+00	8.09E+00
Po(IV)	4.00E-01	1.12E-01	6.08E-01
Ra(II)	3.35E-04	9.38E-05	5.09E-04
Ac(III)	5.49E+00	1.54E+00	8.35E+00
Th(IV)	2.71E+01	7.59E+00	4.12E+01
Pa(V)	2.50E+01	6.99E+00	3.80E+01
U(IV)	1.50E-01	4.20E-02	2.28E-01
U(VI)	2.82E-04	7.89E-05	4.28E-04
Np(IV)	1.00E+02	2.80E+01	1.52E+02
Pu(III)	5.48E+00	1.54E+00	8.33E+00
Pu(IV)	2.60E-02	7.28E-03	3.95E-02
Am(III)	5.49E+00	1.54E+00	8.35E+00
Cm(III)	5.49E+00	1.54E+00	8.35E+00
	source data for illite		
	chemical analogue (see Table 4.3)		
	set to zero		
	special cases (see section 4.7)		
	cation exchange		

Note that the R_d values for C_{inorg.} do not correlate with the 2:1 clay mineral content but with the calcite content (see Tab. 6.1).

7 Sorption data base for calcite

In three cases the host rocks do not contain any meaningful quantities of phyllosilicates and only uptake on calcite is considered to be relevant. This is the case for the lower limit mineralogies of 'Brauner Dogger' Sandy limestone sequences and Effingen Member Calcareous marl sequences, for the pure calcareous vein infills of Helvetic Marls and also Arietenkalk.

A sorption data base for calcite has been developed recently by Bradbury et al. (2010, Chapter 8) and the same approach is applied here. The starting point for deriving the calcite SDB is a compilation of sorption data measured on calcite given in Bradbury & Baeyens (1997a, Chapter 10) and further extended in Bradbury et al. (2010, Chapter 8). A summary of the available experimental data is given in Tab. 7.1. Where experimental data were available, the sorption values were directly chosen for the SDB.

Tab. 7.1: Experimentally determined sorption values on calcite (see Bradbury et al. 2010, Chapter 9) and ionic radii (in Ångstrom units) (Shannon 1976).

Element	Ionic Radii [Å]	$\log R_{d \text{ calcite}}$ [m ³ kg ⁻¹]	Source
Mn(II)	0.83	-0.8	Zachara et al. (1991)
Co(II)	0.745	-1.4	Zachara et al. (1991)
Ni(II)	0.69	-2.0	Zachara et al. (1991)
Zn(II)	0.74	0.0 -0.1	Zachara et al. (1991) Zachara et al. (1988)
Cd(II)	0.95	0.6 1.0	Zachara et al. (1991) Papadopoulos & Rowell (1988)
Sr(II)	1.18 (> 1)	-3.0	Zachara et al. (1991)
Pb(II)	1.19 (> 1)	-0.4	Rouff et al. (2005)
Eu(III)	0.95	0.86	Zavarin et al. (2005)
Th(IV)	0.94	1.15	Maiti et al. (1989)
Np(V)	0.75	-1.4 -0.66 -0.1	Herberling et al. (2008) Zavarin et al. (2005) Allard (1982)
Pu(IV)	0.86	0.04	Zavarin et al. (2005)
Pu(V)	0.76	-1.7	Zavarin et al. (2005)
Am(III)	0.975	1.3	Allard & Beall (1979)

Note: Effective ionic radii are for hexagonal coordination number.

In Bradbury et al. (2010) the sorption data given in Tab. 7.1 were correlated with the effective ionic radii (IR) in Å of the respective metals (Shannon 1976) and an acceptable linear correlation was found between these two quantities, a so-called linear free energy relationship, LFER, Fig. 7.1. (The ionic radii were chosen for the VI coordination number and for Co(II) and Mn(II) for high-spin states.) Exceptions were made for Zn(II) and the Np(V) data from Zavarin et al. (2005) and Allard (1982), see also Bradbury et al. (2010). As discussed in Bradbury et al. (2010) for a number of elements the LFER given in Fig. 7.1 is used to estimate sorption values

in the calcite SDB. Where sorption values have been estimated in this way, they are indicated as such in Tab. 7.2. Elements with an IR greater than 1.00 (equal to that of Ca) have not been considered in the carbonate-LFER since it is well known that these elements sorb/incorporate very weakly on calcite (e.g. Curti 1997). Also, the carbonate-LFER is not used for elements with an IR below the lowest value (IR = 0.69) given in Fig. 7.1. The conservative assumption was made that such elements have zero sorption. This was the case for Be(II), Cl(-I), K(I), Se(-II), Nb(V), Mo(VI), Tc(IV), Ag(I), Cs(I) and Ac(III).

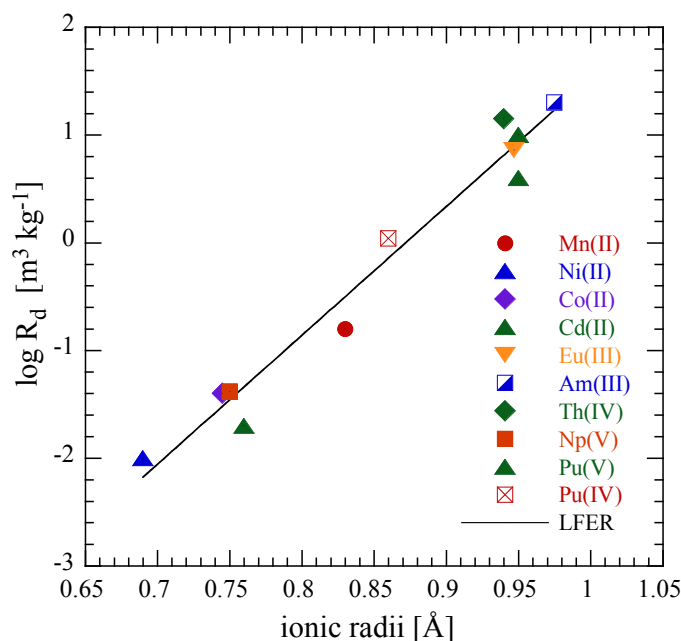


Fig. 7.1: Linear Free Energy Relation between $\log R_d$ [$\text{m}^3 \text{kg}^{-1}$] and the ionic radii (IR) in Å.

The least squares relation between $\log R_d$ and IR is given by $\log R_d = (-10.4 \pm 0.6) + (12.0 \pm 0.7) \cdot \text{IR}$ ($R^2 = 0.97$).

In a few cases where no experimental data were available and where the LFER could not be applied (IR outside the range considered) chemical analogy was invoked. This was the case for Ca and Ra where Sr has been taken as chemical analogue.

For ^{14}C as $\text{H}^{14}\text{CO}_3^-$ or $^{14}\text{CO}_3^{2-}$, the most likely removal mechanism from solution is isotopic exchange in the surface layers of calcite. The method for calculating an R_d value for inorganic carbon is described in section 4.7.5 and can be applied to any specific porewater chemistry.

The $R_{d \text{ calc}}$ values given in Tab. 7.1 are considered to be valid in the pH range ~ 7 to 9 (see Bradbury & Baeyens 1997a, Chapter 10). Since the variation of pH in the porewater is not very large no effect of pH was considered. Also, because of the uncertainties associated with the sorption mechanisms on calcite, no corrections for water chemistries were attempted (see also Bradbury et al. 2010). In the special case of the redox sensitive element uranium, only the fraction of U(IV) was considered, as U(VI) is not likely to sorb on calcite because of its lower ionic radius of 0.73 Å (Shannon 1976).

In contrary to the SDB for argillaceous rock systems where no Lab \rightarrow Field conversion factor was considered, this factor is taken to be 0.05 for calcareous systems (see Bradbury & Baeyens 1997a and Tab. 7.2).

Tab. 7.2: Calcite SDB ($\text{m}^3 \text{kg}^{-1}$) (Bradbury et al. 2010).

Ionic radii of the elements used in the LFER are given in brackets in column 5. The sorption values given below apply to the field.

Element	R_d -source	Lab → Field	R_d -calcite	Source Data
Be(II)	0	0.05	0	Set = 0 (IR = 0.45 Å)
$C_{\text{inorg.}}$	-	-	-	Calculated for a specific porewater
$C_{\text{org.}}$	0	0.05	0	Bradbury & Baeyens (1997a)
Cl(-I)	0	0.05	0	Set to zero (IR = 1.81 Å)
K(I)	0	0.05	0	Set to zero (IR = 1.38 Å)
Ca(II)	1.0E-03	0.05	5.0E-05	Sr analogue
Co(II)	4.0E-02	0.05	2.0E-03	Zachara et al. (1991)
Ni(II)	1.0E-02	0.05	5.0E-04	Zachara et al. (1991)
Se(-II)	0	0.05	0	Set to zero (IR = 1.98 Å)
Sr(II)	1.0E-03	0.05	5.0E-05	Bradbury & Baeyens (1997a)
Zr(IV)	1.7E-02	0.05	8.5E-04	Carbonate-LFER (IR = 0.72 Å)
Nb(V)	0	0.05	0	Set to zero (IR = 0.64 Å)
Mo(VI)	0	0.05	0	Set to zero (IR = 0.59 Å)
Tc(IV)	0	0.05	0	Set to zero (IR = 0.645 Å)
Pd(II)	8.3E-01	0.05	4.2E-02	Carbonate-LFER (IR = 0.86 Å)
Ag(I)	0	0.05	0	Bradbury & Baeyens (1997a)
Sn(IV)	7.6E-03	0.05	3.8E-04	Carbonate-LFER (IR = 0.69 Å)
I(-I)	0	0.05	0	Bradbury & Baeyens (1997a)
Cs(I)	0	0.05	0	Set to zero (IR = 1.67 Å)
Sm(III)	12.6	0.05	6.29E-01	Carbonate-LFER (IR = 0.958 Å)
Eu(III)	7.2	0.05	3.6E-01	Zavarin et al. (2005)
Ho(III)	2.6	0.05	1.3E-01	Carbonate-LFER (IR = 0.901 Å)
Pb(II)	0.4	0.05	2.0E-02	Rouff et al. (2005)
Po(IV)	8.0E-04	0.05	4.0E-05	Carbonate-LFER (IR = 0.94 Å)
Ra(II)	1.00E-03	0.05	5.0E-05	Sr analogue
Ac(III)	0	0.05	0	Set to zero (IR = 1.12 Å)
Th(IV)	14	0.05	4.5E-02	Maiti et al. (1989)
Pa(V)	9.1E-02	0.05	4.6E-03	Carbonate-LFER (IR = 0.78 Å)
U(IV)	1.9	0.05	9.5E-02	Carbonate-LFER (IR = 0.89 Å)
Np(IV)	1.1	0.05	5.5E-02	Carbonate-LFER (IR = 0.87 Å)
Pu(III)	40	0.05	2.0E+00	Carbonate-LFER (IR = 1.00 Å)
Am(III)	20	0.05	1.0E+00	Allard & Beall (1979)
Cm(III)	17	0.05	8.7E-01	Carbonate-LFER (IR = 0.97 Å)

Tab. 7.3 summarises the SDBs for the host rocks and the Lower confining units (Arietenkalk) where no 2:1 type clay minerals are present. The values from Tab. 7.2 (4th column) are further reduced by the calcite content of the corresponding host rock.

Tab. 7.3: Summary of the SDBs for host rocks where no 2:1 type clay minerals are present (R_d in $\text{m}^3 \text{kg}^{-1}$).

Rock formation	Effingen Member	Helvetic Marls	Lower confining units
Hydrogeological unit	Limestone sequences	Vein infill	Arietenkalk
Calcite content [wt.-%]	76	100	80
Be(II)	0.00E+00	0.00E+00	0.00E+00
C _{inorg.}	4.80E-02	5.00E-03	8.80E-03
C _{org.}	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00
K(I)	0.00E+00	0.00E+00	0.00E+00
Ca(II)	3.80E-05	-	4.00E-05
Co(II)	1.52E-03	2.00E-03	1.60E-03
Ni(II)	3.80E-04	5.00E-04	4.00E-04
Se(-II)	0.00E+00	0.00E+00	0.00E+00
Sr(II)	3.80E-05	5.00E-05	4.00E-05
Zr(IV)	6.47E-04	-	6.80E-04
Nb(V)	0.00E+00	0.00E+00	0.00E+00
Mo(VI)	0.00E+00	0.00E+00	0.00E+00
Tc(IV)	0.00E+00	-	0.00E+00
Pd(II)	3.19E-02	-	3.36E-02
Ag(I)	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	2.89E-04	3.80E-04	3.04E-04
I(-I)	0.00E+00	0.00E+00	0.00E+00
Cs(I)	0.00E+00	0.00E+00	0.00E+00
Sm(III)	4.79E-01	-	5.03E-01
Eu(III)	2.73E-01	-	2.88E-01
Ho(III)	9.88E-02	-	1.04E-01
Pb(II)	1.52E-02	2.00E-02	1.60E-02
Po(IV)	3.04E-05	4.00E-05	3.20E-05
Ra(II)	3.80E-05	5.00E-05	4.00E-05
Ac(III)	0.00E+00	0.00E+00	0.00E+00
Th(IV)	3.43E-02	4.50E-02	3.60E-02
Pa(V)	3.49E-03	4.60E-03	3.68E-03
U(IV)	1.11E-02	3.07E-02	1.19E-03
Np(IV)	4.19E-02	5.50E-02	4.40E-02
Pu(III)	1.52E+00	2.00E+00	1.60E+00
Am(III)	7.60E-01	1.00E+00	8.00E-01
Cm(III)	6.60E-01	8.70E-01	6.96E-01
	experimental data		
	Sr(II) as chemical analogue		
	set to zero		
	LFER estimate		
	calculated for reference porewater conditions		

8 Sorption data bases for MX-80 Bentonite

8.1 Introduction

In this chapter the SDBs for MX-80 bentonite which will be used in the Sectoral Plan (SGT-E2) are derived. The SDBs are based on sorption data measured on Na-montmorillonite; MX-80 bentonite contains ~ 75 wt.-% montmorillonite. SDBs are generated for one single MX-80 bentonite mineralogy and 6 different porewater chemistries. In some cases the SDBs are very similar due to the very similar porewater compositions, e.g. in the case where only the bulk density has been varied (36 % and 48 %). Nevertheless, a specific SDB was generated.

The methodology used to generate the various sorption data bases is that described in Chapter 2.

8.2 MX-80 mineralogy and porewater chemistries

8.2.1 Mineralogy

The reference mineralogy for MX-80 bentonite used in the Entsorgungsnachweis (Nagra 2002) has been taken and this data is given in Tab. 8.1.

Tab. 8.1: 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

Montmorillonite clay is dominant and the $CF_{\text{MIN}} = 0.75$ for the MX-80 bentonite SDBs.

8.2.2 Porewater chemistries

The porewater compositions have been defined in Bradbury et al. (2014). The porewater denoted as "BPW-22IsA" in Tab. 8.2 represents the reference case. The porewater in Bradbury et al. (2014) refers to that obtained after 10'000 years of exchange between their bentonite starting system and their Opalinus Clay reference system without low-pH shotcrete liner.

Tab. 8.2: Porewater compositions for MX-80 bentonite defined in Bradbury et al. (2014).
The unit for ionic strength and concentration is mol/kg_{H₂O}.

	Reference	High porosity	High salinity	High pCO ₂	Low pCO ₂
ID-Code *	CON-BPW-22lsA	CON-BPW-22lsA-p48	CON-BPW-25hsA	CON-BPW-18lsABPW-18lsA	NEW-BPW-opt2
ε _{bulk}	0.36	0.48	0.36	0.36	0.36
pH	7.27	7.28	7.08	7.07	7.79
pε	-2.84	-2.85	-2.68	-2.58	-3.44
I [mol/kg _{H₂O}]	0.365	0.348	0.785	0.369	0.239
log pCO ₂ [bar]	-2.2	-2.2	-2.5	-1.8	-3.2
Na	3.01E-01	2.85E-01	6.24E-01	3.05E-01	1.92E-01
K	1.56E-03	1.49E-03	3.15E-03	1.58E-03	1.22E-03
Mg	9.07E-03	8.41E-03	2.63E-02	9.32E-03	5.15E-03
Ca	1.30E-02	1.26E-02	3.67E-02	1.29E-02	9.11E-03
Sr	2.10E-06	1.90E-06	1.24E-05	2.18E-06	5.63E-05
Ba	-	-	-	-	1.13E-07
Fe	2.12E-05	2.04E-05	3.92E-05	4.96E-05	3.71E-05
C ^{IV}	2.96E-03	3.01E-03	1.17E-03	4.91E-03	8.98E-04
S ^{VI}	7.08E-02	7.24E-02	2.63E-02	7.21E-02	3.01E-02
Cl	2.02E-01	1.79E-01	6.99E-01	2.02E-01	1.61E-01
Al	1.08E-08	1.10E-08	7.04E-09	7.30E-09	1.47E-08
Si	1.77E-04	1.77E-04	1.72E-04	1.76E-04	1.82E-04

* ID Code as defined in Bradbury et al. (2014)

8.3 Source sorption data on montmorillonite

An overview of the source sorption edges for the elements Co(II), Ni(II), Pb(II), Eu(III), Am(III), Sn(IV), Th(IV), Pa(V) and U(VI) for which R_d values are selected is shown in Fig. 8.1 to 8.9, respectively. Except for Pb(II) (Ulrich & Degueldre 1992) all the sorption edge data have been modelled with the 2SPNE SC/CE sorption model (Bradbury & Baeyens 1997b, 2005a, 2006). Following the same procedures as for illite, the modelled curves are used to select the source $R_{d,MONT}$ values. The $R_{d,MONT}$ values for Pb(II) are taken from the continuous line in Fig. 8.3.

For Po(IV) the sorption data on Na-montmorillonite measured by Ulrich & Degueldre (1992) are selected (see section 4.7.2).

Molybdenum only exists in the +6 valence state, and above pH 4 the dominant aqueous species is the anionic molybdate (MoO_4^{2-}) (Baes & Mesmer 1976). Motta & Miranda (1989) measured the uptake of MoO_4^{2-} on montmorillonite. An R_d value of $0.17 \text{ m}^3 \text{ kg}^{-1}$ at pH = 4 for MoO_4^{2-} could be extracted from their measurements on montmorillonite (25 °C, equilibrium con-

centration of 10^{-4} M) but the pH dependency could not be deduced. The pH dependency was deduced as described in section 4.2.

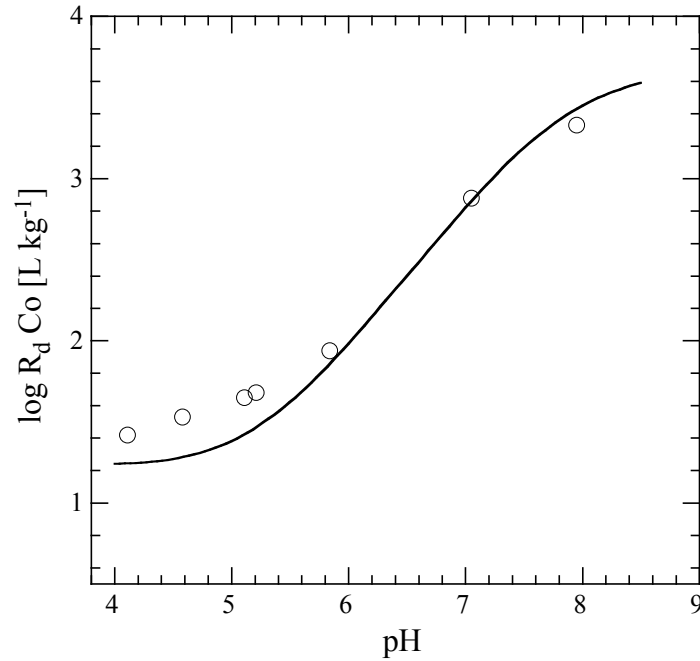


Fig. 8.1: Co(II) sorption edge measurements (symbols) and modelling (continuous line) on Ca-montmorillonite in 0.05 M CaCl_2 (Tiller & Hodgson 1960).

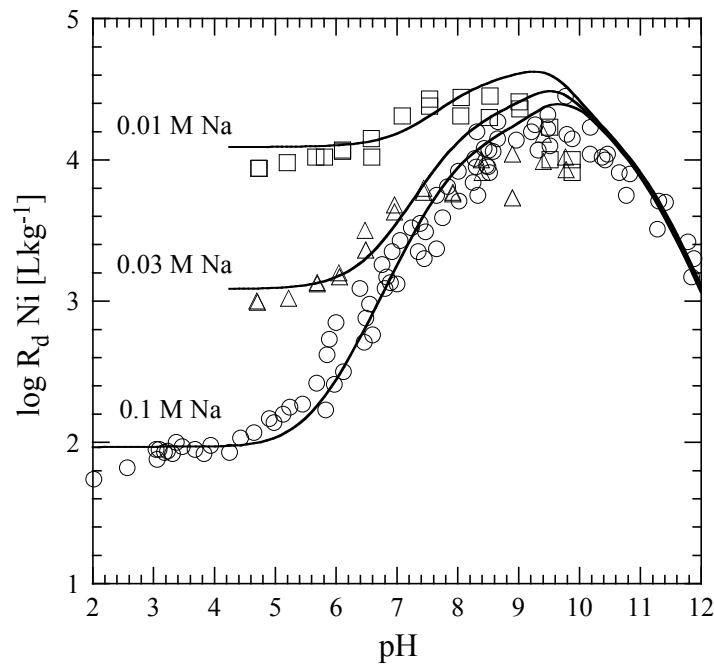


Fig. 8.2: Ni(II) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 (Bradbury & Baeyens 1997a).

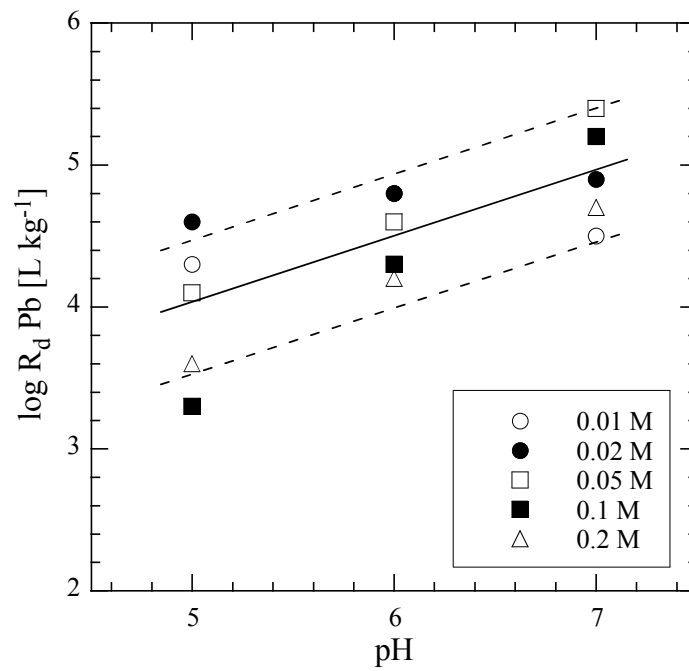


Fig. 8.3: Pb(II) sorption measurements on Na-SWy-1 (Ulrich & Degueldre 1992).

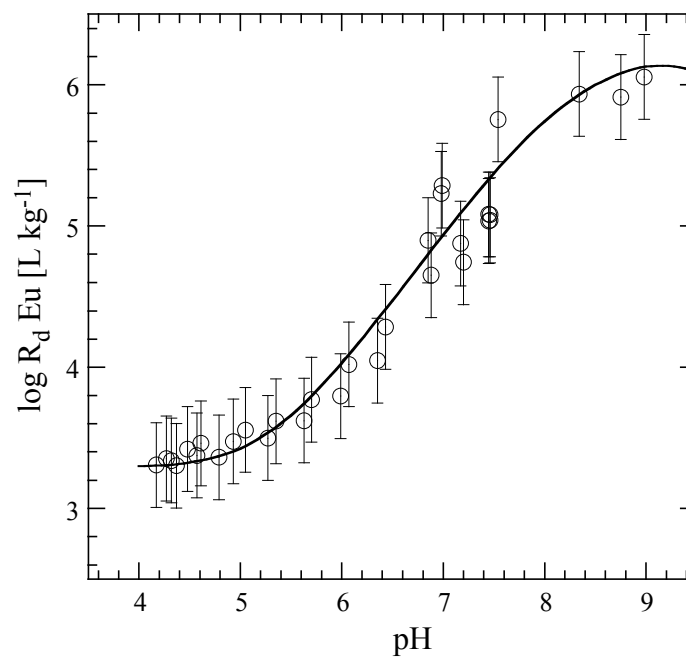


Fig. 8.4: Eu(III) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 in 0.1 M NaClO₄ (Bradbury & Baeyens 2005a).

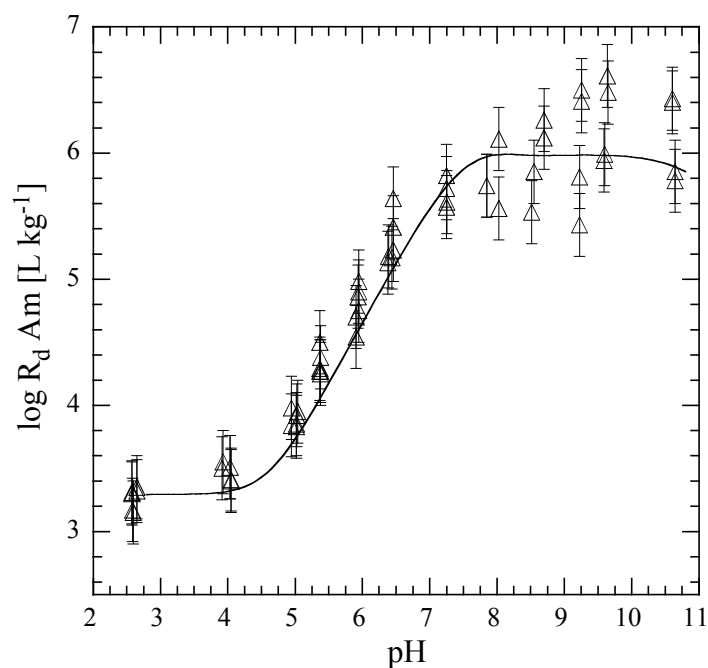


Fig. 8.5: Am(III) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 in 0.1 M NaClO₄ (Bradbury & Baeyens 2006).

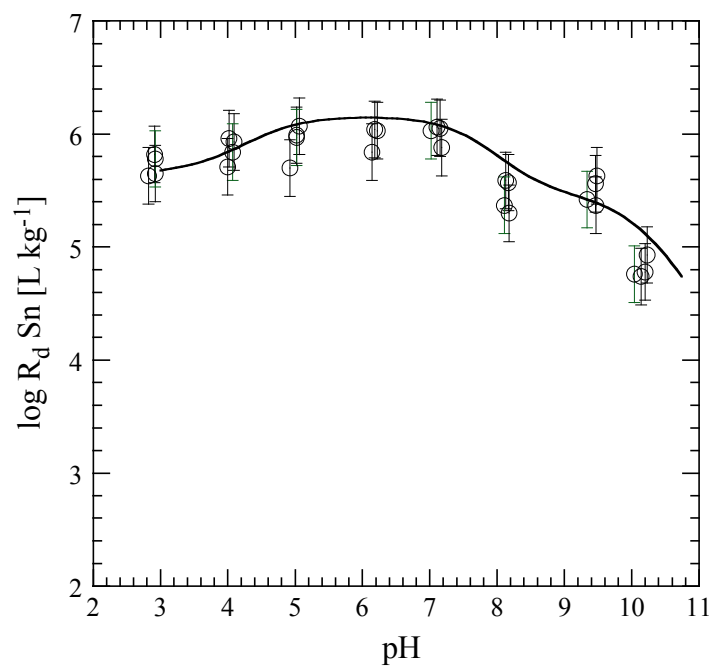


Fig. 8.6: Sn(IV) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 in 0.1 M NaClO₄ (Bradbury & Baeyens 2005a).

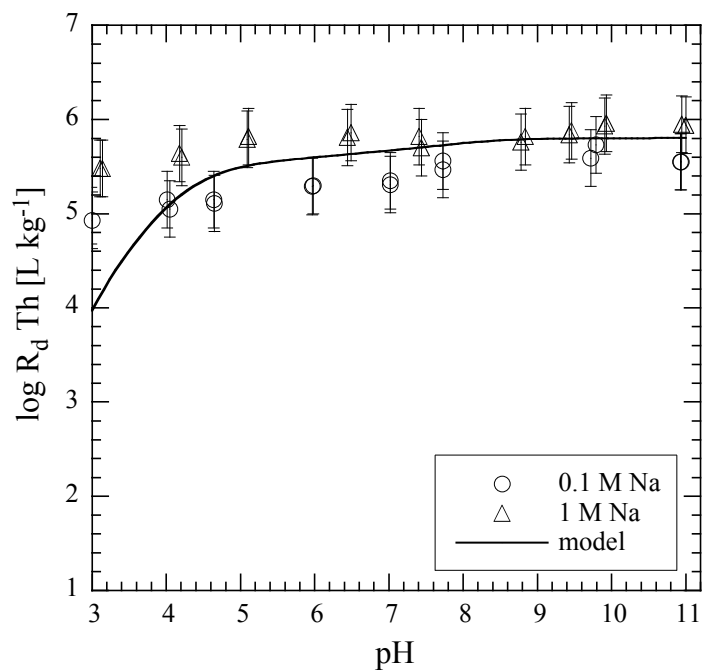


Fig. 8.7: Th(IV) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 (Bradbury & Baeyens 2005a).

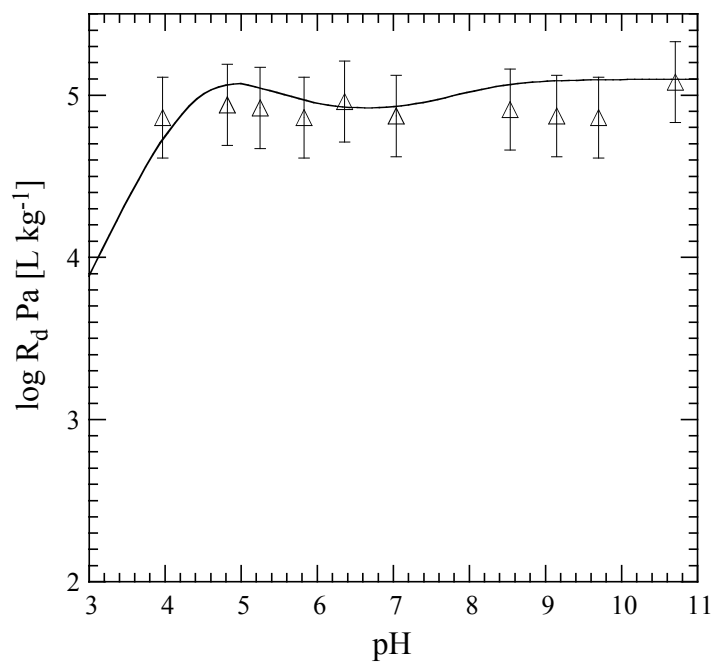


Fig. 8.8: Pa(V) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 in 0.1 M NaClO₄ (Bradbury & Baeyens 2006).

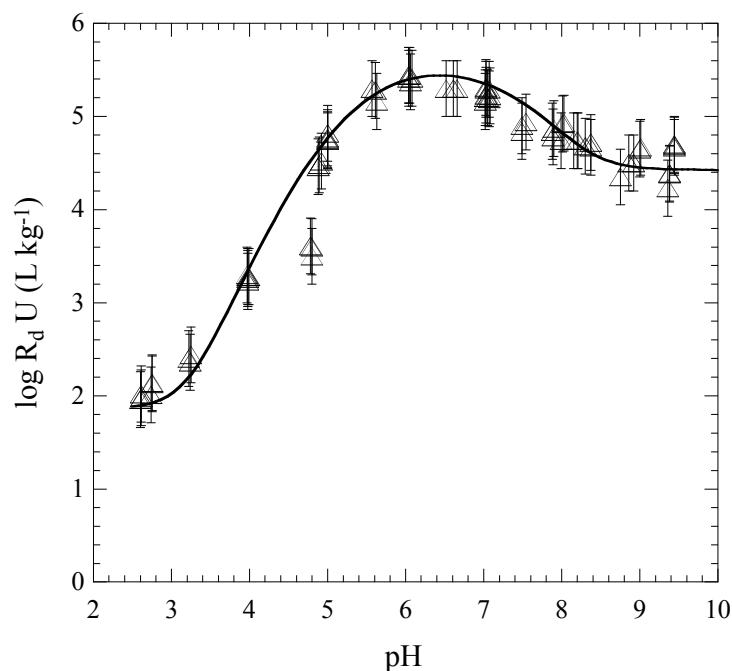


Fig. 8.9: U(VI) sorption edge measurements (symbols) and modelling (continuous line) on Na-SWy-1 in 0.1 M NaClO₄ (Marques Fernandes et al. 2012).

8.4 Non-sorbing elements, chemical analogues, cation exchange and special cases

8.4.1 Non-sorbing elements

The same considerations as in the case of illite (see section 4.4) are taken here. For the elements Cl(-I), Se(-II) and Ag(I) sorption values of zero were selected and upon reviewing these choices, no reasons were found to change them.

8.4.2 Chemical analogues

The same chemical analogues are taken as for illite (see Tab. 4.3).

8.4.3 Cation exchange

The alkaline (K, Cs) and alkaline-earth (Ca, Sr, Ra) elements sorb via a cation exchange mechanism and are calculated from a cation exchange sorption model for montmorillonite in the different MX-80 porewater chemistries. A CEC value of 870 meq kg⁻¹ was selected for montmorillonite. This value was taken from a larger number of CEC measurements on SWy-1 montmorillonite (Baeyens & Bradbury 1997b). The selectivity coefficients for K-Na, Mg-Na and Ca-Na (Tab. 8.3) were taken from the porewater chemistry studies on MX-80 bentonite, Bradbury & Baeyens (2002). Cs sorption was calculated using a Cs⁺-Na⁺ selectivity coefficient of 15 for montmorillonite (Bradbury & Baeyens, unpublished data). This is considered to be valid since montmorillonite is the only clay mineral in MX-80 and constitutes ~ 75 wt.-%. The conversions to sorption values for MX-80 are then carried out over the mineralogical conversion factor.

Tab. 8.3: Cation exchange reaction and corresponding selectivity coefficients (K_c) for montmorillonite (taken from Bradbury & Baeyens 2002).

CEC for montmorillonite = 870 meq kg⁻¹.

Cation exchange reaction	log K_c
Na-mont + K ⁺ ⇌ K-mont + Na ⁺	0.60
Na-mont + Cs ⁺ ⇌ Cs-mont + Na ⁺	1.18
2 Na-mont + Mg ²⁺ ⇌ Mg-mont + 2 Na ⁺	0.34
2 Na-mont + Ca ²⁺ ⇌ Ca-mont + 2 Na ⁺	0.41*

*Ca²⁺ = Sr²⁺ = Ra²⁺

8.4.4 Special cases

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 4.7 was also followed for montmorillonite, i.e. an R_d value of 1 m³ kg⁻¹ was selected.

Tc(IV)

For the same reasons as discussed in section 4.7, 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 the value for Th(IV) was selected.

Inorganic carbon

The sorption value for inorganic carbon is calculated from isotopic exchange with the calcite in the MX-80 system. The same approach is adopted here as described in section 4.7.5 for the host rocks. If 0.3 % of the bulk calcite in MX-80 bentonite) is taken to be available for exchange with H¹⁴CO₃⁻/¹⁴CO₃²⁻, then the total moles of exchangeable CO₃²⁻ in the solid phase is ~ 1.9 × 10⁻⁴ mol per kg of MX-80 for a calcite content of 0.7 wt.-% (Tab. 8.1). Thus, the H¹⁴CO₃⁻/¹⁴CO₃²⁻ sorption values in the MX-80 porewater chemistries can be readily obtained using the aqueous concentrations given in Tab. 8.2. The results are summarised in Tab. 8.4.

Tab. 8.4: MX-80 bentonite: Calcite content, aqueous carbonate concentrations and calculated inorganic ^{14}C sorption values.

	MX-80 bentonite porewater types				
	Reference	High porosity	High salinity	High pCO ₂	Low pCO ₂
Isotopic exchangeable carbonate	$2.7 \times 10^{-2} \text{ mol kg}^{-1}$				
$\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-} [\text{M}]$	2.96×10^{-3}	3.01×10^{-2}	1.17×10^{-3}	4.91×10^{-3}	8.93×10^{-4}
R_d for 100 % calcite [$\text{m}^3 \text{ kg}^{-1}$]	9.1×10^{-3}	9.0×10^{-3}	2.3×10^{-2}	5.5×10^{-3}	3.0×10^{-2}
	R_d values [$\text{m}^3 \text{ kg}^{-1}$]				
0.7 wt.-% calcite	6.4×10^{-5}	6.3×10^{-5}	1.6×10^{-4}	3.9×10^{-5}	2.1×10^{-4}

8.5 MX-80 bentonite

The montmorillonite R_d values selected from the source sorption data sets for the elements contained in the SDB are given in Tab. 8.5. They are selected from the curves on the edges presented in section 8.3 at 3 different pH values.

Applying the procedure described in Chapter 2 and section 8.4 to all of the elements in Tab. 4.1, the chemical analogues listed in Tab. 4.3, and including the sorption values due to cation exchange calculated from the data in Tab. 8.3, the MX-80 bentonite R_d values derived from montmorillonite sorption data are given in Tab. 8.6.

Tab. 8.5: Summary of selected montmorillonite source sorption values ($R_{d, \text{MONT}}$) for different pH values for MX-80 bentonite derived from the sorption edges given in Figs. 8.1 to 8.9.

Element	pH values			Comment
	7.07 – 7.08	7.27 – 7.28	7.79	
	$R_{d, \text{MONT}} [\text{m}^3 \text{kg}^{-1}]$			
Co(II)	0.8	1.1	2.2	Bradbury & Baeyens (2005a): model
Ni(II)	2.0	3.2	6.3	Bradbury & Baeyens (2005a): model
Nb(V)	1	1	1	Sedimentary rocks: Legoux et al. (1992)
Mo(VI)	0.020	0.017	0.012	Value of $0.17 \text{ m}^3 \text{kg}^{-1}$ selected at pH 4 (Motta & Miranda 1989) and CF_{pH} applied (see section 8.3)
Tc(IV)	5	5	5	Expert judgement (Th analogue, scaled down)
Sn(IV)	1100	1100	700	Bradbury & Baeyens (2005a): model
Eu(III)	100	160	400	Bradbury & Baeyens (2005a): model
Pb(II)	80	80	80	Ulrich & Degueldre (1992)
Po(IV)	1.6	1.6	1.6	Ulrich & Degueldre (1992)
Th(IV)	500	500	500	Bradbury & Baeyens (2005a): model
Pa(V)	100	100	100	Bradbury & Baeyens (2006): model
U(VI)	200	160	100	Marques Fernandes et al. (2012): model
Am(III)	400	630	1000	Bradbury & Baeyens (2006): model

Tab. 8.6: Summary of the SDBs for MX-80 bentonite (R_d in $\text{m}^3 \text{kg}^{-1}$).

MX-80 bentonite	Reference	High porosity	High salinity	High pCO_2	Low pCO_2
Porosity [%]	36	48	36	36	36
pH	7.27	7.28	7.08	7.07	7.79
2:1 clay content [wt.-%]	75	75	75	75	75
Be(II)	2.29E+00	2.29E+00	1.46E+00	1.40E+00	4.66E+00
$C_{\text{inorg.}}$	6.40E-05	6.30E-05	1.40E-04	3.90E-05	2.10E-04
$C_{\text{org.}}$	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cl(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
K(I)	7.13E-03	7.43E-03	3.53E-03	7.05E-03	1.01E-02
Ca(II)	2.33E-03	2.55E-03	7.50E-04	2.25E-03	5.59E-03
Co(II)	4.15E-01	4.13E-01	2.78E-01	2.95E-01	1.05E+00
Ni(II)	1.28E+00	1.26E+00	1.01E+00	7.97E-01	3.21E+00
Se(-II)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr(II)	2.33E-03	2.55E-03	7.50E-04	2.25E-03	5.63E-03
Zr(IV)	1.02E+03	1.03E+03	9.48E+02	9.48E+02	9.38E+02
Nb(V)	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Mo(VI)	1.33E-02	1.32E-02	1.52E-02	1.53E-02	9.30E-03
Tc(IV)	3.38E+00	3.38E+00	3.54E+00	2.97E+00	3.70E+00
Pd(II)	5.78E+01	5.87E+01	5.52E+00	5.51E+01	5.99E+01
Ag(I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn(IV)	8.13E+02	8.20E+02	8.21E+02	8.17E+02	5.12E+02
I(-I)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs(I)	2.93E-02	3.08E-02	1.35E-02	2.93E-02	4.03E-02
Sm(III)	3.16E+01	3.14E+01	4.22E+01	1.58E+01	1.50E+02
Eu(III)	1.31E+01	1.31E+01	1.29E+01	6.47E+00	5.25E+01
Ho(III)	2.51E+01	2.51E+01	3.52E+01	1.19E+01	1.08E+02
Pb(II)	9.54E+00	9.84E+00	2.52E+00	8.40E+00	1.69E+01
Po(IV)	1.20E+00	1.20E+00	1.20E+00	1.20E+00	1.20E+00
Ra(II)	1.28E-03	1.43E-03	5.48E-04	1.28E-03	3.68E-03
Ac(III)	7.56E+01	7.68E+01	7.26E+01	4.03E+01	1.45E+02
Th(IV)	7.69E+01	7.43E+01	2.78E+02	3.45E+01	2.69E+02
Pa(V)	7.53E+01	7.46E+01	7.48E+01	7.48E+01	7.49E+01
U(IV)	3.71E-01	3.60E-01	3.90E+00	1.14E-01	5.06E+00
U(VI)	9.06E-05	8.57E-04	1.21E-02	5.57E-04	5.45E-03
Np(IV)	3.75E+02	3.75E+02	3.75E+02	3.72E+02	3.75E+02
Pu(III)	6.24E+01	6.30E+01	6.68E+01	3.09E+01	1.50E+02
Pu(IV)	9.38E-02	9.38E-02	7.50E-02	3.30E-02	1.35E+00
Am(III)	7.56E+01	7.68E+01	7.26E+01	4.03E+01	1.45E+02
Cm(III)	7.56E+01	7.68E+01	7.26E+01	4.03E+01	1.45E+02
	source data for montmorillonite				
	chemical analogue (see Table 4.3)				
	set to zero				
	special cases (see section 8.4.4)				
	cation exchange				

9 Uncertainties of the R_d values in the SDBs

In this chapter the procedure for calculating the uncertainty on the SDB values is described. The individual uncertainty factors (UF) for each parameter in the SDB derivation process is discussed below.

9.1 Uncertainty of the source data (UF- $R_{d, \text{ILLITE/MONT}}$)

The uncertainties associated with the source data on illite and montmorillonite can be relatively easily assessed. Normally, within any single set of sorption measurements R_d values can be measured better than $\pm 10\%$. However, this is considered to be too optimistic if a general value for an overall error is sought. A formal estimate of the maximum absolute error calculated by considering the maximum error in each operation in a batch sorption experiment yielded an uncertainty in $\log R_d$ of ± 0.15 log units. Nevertheless, if sorption studies are carried out on different occasions, on different clay batches, by different technicians, the uncertainty in the $\log R_d$ values can increase to ± 0.5 log units. This is illustrated in the sorption edges plots given in sections 4.2 and 8.3 for illite and montmorillonite, respectively. This latter estimate is considered to be realistic and therefore an uncertainty factor of 3 is assigned to source data measurements, $R_{d, \text{ILLITE}}$ and $R_{d, \text{MONT}}$.

In the cases of Nb(V) and Po(IV) uncertainty factors of 5 (see section 4.7.3) and 10 (see section 4.7.2), respectively are taken.

For the elements C_{org} , Cl(-I), Se(-II), Ag(I) and I(-I) the R_d is set to zero and no uncertainty factors are considered.

9.2 Model calculations (UF-model)

Cation exchange: In the cases of K^+ , Cs^+ , Ca^{2+} , Sr^{2+} and Ra^{2+} the sorption values were derived from cation exchange calculations. In the original publications (e.g. Bradbury & Baeyens 1998b and 2000) it was clearly demonstrated that the model predictions could reproduce the experimental data within a factor 2 to 3. Consequently an uncertainty factor of 3 was applied to the R_d values for the above elements.

Inorganic C: In the approach for isotopic exchange of $H^{14}CO_3^-/^{14}CO_3^{2-}$ with calcite 30 monolayers are assumed to be involved. If, in contrast, the exchange only comprised 10 monolayers, the R_d values would decrease by a factor of 3. This value is taken as the uncertainty factor for C_{inorg} . (see section 4.7.5).

9.3 Mineralogy (UF-MIN_{ARG ROCK/MX-80})

From the spread in the mineralogies (reference, lower and upper bound values) of the various argillaceous rocks given in Tabs. 3.1 to 3.6, uncertainty factors for the mineralogical contents of the 2:1 type clay minerals were derived. To this end, the ratio of the reference value and the lower bounding value of the 2:1 clay mineral content was calculated for all host rocks. This value was rounded and used as UF-MIN_{ARG ROCK}. A summary of these values is given in Tab. 9.1.

For the calculation of the R_d values for C_{inorg} for the host rocks the calcite contents are used. For calcite the same uncertainty factors are applied as for the 2:1 type clay mineral contents.

In the case of MX-80 bentonite there are no lower and upper bounding values given and the $UF-MIN_{MX-80}$ is considered to be unity.

Tab. 9.1: Summary of the uncertainty factors for the mineralogy.

Host rock	2:1 clay mineral content			$UF-MIN_{ARG\ ROCK}$
	Reference value [wt.%]	Lower bound [wt.%]	Reference / Lower bound	
Opalinus Clay	33	19	1.7	2
'Brauner Dogger' Clay-rich sequences	27	5	5.4	5
'Brauner Dogger' Sandy limestone sequences	7	2.5	2.8	5
Effingen Member Calcareous marl sequences	20.1	10	2.0	2
Effingen Member Limestone sequences*	9.2	0	n.a.	calcite SDB
Helvetic Marls	22	4	5.5	6
Helvetic Marls Limestone sequences	3.9	-	-	6**
Toniger Lias	25	13	1.9	2
Arietenkalk*	7	0	n.a.	calcite SDB
Toniger Keuper	38	19	2.0	2

* For these rock types the lower limit values of the 2:1 type clay minerals is zero and the calcite SDB is used.

** A lower limit is not considered in Traber & Blaser (2013). The $UF-MIN_{ARG\ ROCK}$ from Helvetic Marls is applied instead.

n.a. = not applicable

9.4 Speciation (UF-SF)

A Monte Carlo procedure was used to calculate the uncertainties for the speciation factors by considering the uncertainties in the thermodynamic stability constants used to calculate radionuclide speciation in the reference porewaters of the host rocks (Thoenen 2014b). Uncertainty factors for $SF_{ARG\ ROCK}$ were calculated for the following elements Ni, Zr, Tc, Pd, Sn, Eu, Pb, Th, U, Np, Pu and Am and are summarised in Tab. 9.2. These uncertainty factors were also taken to be the same in the porewater variations of each host rock considered, e.g. high/low pCO_2 , high salinity, high sulphate etc.

For the elements Ni, Zr, Tc, Sn, Eu, Pb, Np, Pu and Am the uncertainty factors are small and consistent in the different porewaters. For Pd a high UF is calculated in the Effingen Member porewater. This is due to the high Cl concentration and the uncertainty associated with these stability constants. For Th and U very high uncertainty factors are calculated (except in the case of Th in the Effingen Member porewater). The reason is the large uncertainties associated with the stability constants of the carbonate complexes. If these complexes are dominant in the speciation calculations, the calculated uncertainty factors become large.

No uncertainty factors using the Monte Carlo procedure were calculated for MX-80 bentonite. Since the reference porewaters of Opalinus Clay and MX-80 are very similar the speciation uncertainty factors were taken to be the same for both systems.

No Monte Carlo calculations were performed for Pa. Since no chemical analogue is available for Pa(V), a conservative assumption was made by taking the most unfavorable UF in the different porewaters for the actinides. For example, in the Helvetic Marls porewater an uncertainty factor of 16.0 was chosen for Pa(V) i.e. the same value as for U(IV/VI).

Tab. 9.2: Summary of the uncertainty factors for $SF_{ARG\ ROCK}$ calculated in the reference porewaters of Opalinus Clay, Effingen Member and Helvetic Marls (Thoenen 2014b).

Radionuclide	Uncertainty factors for the speciation in the reference porewaters for the argillaceous rocks ($UF \cdot SF_{ARG\ ROCK}$)		
	Opalinus Clay	Effingen Member	Helvetic Marls
Ni(II)	1.1	1.5	1.2
Zr(IV)	1.8	1.7	-
Tc(IV)	1.1	1.0	-
Pd(II)	1.3	9.5	-
Sn(IV)	1.2	1.2	1.3
Eu(III)	1.8	2.1	-
Pb(II)	1.9	1.2	2.7
Th(IV)	11.3	1.6	13.8
U(IV/VI)	5.9	5.8	16.0
Np(IV)	1.0	1.0	1.5
Pu(III/IV)	2.1	2.6	1.7
Am(III)	2.4	2.6	2.5

- Elements not considered in L/ILW (Tab. 4.1)

Since the sorption measurements for illite and montmorillonite were all carried out in a simple $NaClO_4$ background electrolyte, the speciation factors are essentially unity except for Am(III), Eu(III), Pu(III) and Sn(IV) which form aqueous silicate complexes (Appendix A). No Monte Carlo calculations were performed for the latter radionuclides in $NaClO_4$ and the uncertainty factors for the $SF_{ILLITE/MONT}$ were taken conservatively to be the same as those for the corresponding $SF_{ARG\ ROCK/MX-80}$ in the reference porewaters.

Po(IV) and Nb(V) are special cases (see sections 4.7.2 and 4.7.3). The sorption values for the host rocks were estimated from low quality measured data and high uncertainty factors were assigned to the selected values. SF's for these elements were not calculated since no reliable thermodynamic data are available.

In all of the host rock porewaters Mo(VI) is present only as the molybdate anion and no uncertainty is assigned to the MoO_4^{2-} SF of unity.

For the elements Be(II), Sm(III), Ho(III), Ac(III) and Cm(III) sorption values were deduced by chemical analogy (Tab. 4.3). The uncertainty factors for the SF values for these elements were not calculated and it was assumed that the uncertainty was the same as the corresponding chemical analogue. For Co(II) no sufficient information on the uncertainties of the thermodynamic data is available and the uncertainty factor UF-SF for Ni(II) was used.

9.5 pH conversion factor (UF-pH)

In the majority of cases conversion factors for pH were not applied because the R_d , ILLITE/MONT values were selected at the same pH value as in the host rock porewater. However, Mo(VI) is the exception (see section 4.2) and an uncertainty factor of 2.6 was assigned to the CF_{pH} in this case (see Bradbury & Baeyens 2003a and b).

9.6 Temperature (UF-T)

Effect of temperature on sorption of Cs (cation exchange) by clay minerals and shales has been investigated by Komarneni (1979). The overall effect on all sorbents investigated is that the sorption of Cs decreases at increasing temperature. "In house" measurements of Cs on montmorillonite and illite do confirm these trends. For trace Cs sorption R_d values are reduced by a factor of ~ 4 if the temperature is increased from 25 °C to 90 °C.

"In house" measurements with Ni(II), Eu(III) and Th(IV) (surface complexation) on montmorillonite and illite do not show such a temperature dependency, merely the contrary effect is seen. This observation is confirmed by extensive sorption studies of Ni and lanthanides on montmorillonite by Tertre et al. (2005).

A temperature depending sorption study of Eu(III) on Opalinus Clay in a synthetic porewater was carried out by Schott et al. (2012). These results clearly show that Eu(III) sorption on Opalinus Clay is favoured if the temperature increases from 25 °C to 50 °C.

From the above given arguments it can be concluded that increasing temperature (with the exception of Cs and probably other cations undergoing cation exchange) will not lead to a decrease in sorption and hence the SDBs developed at room temperature can be considered as conservative if the host rock temperatures are higher than 25 °C. For K^+ , Cs^+ , Ca^{2+} , Sr^{2+} and Ra^{2+} an R_d reduction by a factor of four is assumed to cover the uncertainty due to temperatures up to 90 °C. Note that, according to Becker (2012), argillaceous host rock and confining rock temperatures may reach 80 °C, which is within the temperature range covered by the sorption measurements.

9.7 Lab → Field transfer factor (UF-Lab → Field)

For argillaceous rock the Lab → Field transfer factor is unity (see Bradbury & Baeyens 2003a and b) and no uncertainty factor is considered.

9.8 Calculation of the overall uncertainty factor for radionuclides

The general formulation to calculate R_d values in an argillaceous rock is given by:

$$R_{d, \text{ARG ROCK}} = R_{d, \text{ILLITE}} \cdot CF_{\text{MIN}} \cdot CF_{\text{SPEC}} \cdot CF_{\text{pH}} \cdot CF_{\text{Lab} \rightarrow \text{Field}} \quad (9.1)$$

In which $CF_{\text{MIN}} = (\text{MIN}_{\text{ARG ROCK}} / \text{MIN}_{\text{ILLITE}})$ and $CF_{\text{SPEC}} = \text{SF}_{\text{ARG ROCK}} / \text{SF}_{\text{ILLITE}}$

The uncertainty factors are unity for $\text{MIN}_{\text{ILLITE}}$ (100 % illite/mont), CF_{pH} and $CF_{\text{Lab} \rightarrow \text{Field}}$ (see above).

Eq. 9.1 can be rewritten as:

$$R_{d, \text{ARG ROCK}} = R_{d, \text{ILLITE}} \cdot \text{MIN}_{\text{ARG ROCK}} \cdot \text{SF}_{\text{ARG ROCK}} / \text{SF}_{\text{ILLITE}} \quad (9.2)$$

The uncertainties on the individual $R_{d, \text{ILLITE/MONT}}$, $\text{MIN}_{\text{ARG ROCK}}$ and $\text{SF}_{\text{ARG ROCK}}$ and $\text{SF}_{\text{ILLITE}}$ values are expressed as factors. For example, $R_{d, \text{ILLITE}}$ is given within an uncertainty of a factor of 3 i.e. $\log R_{d, \text{ILLITE}} \pm 0.5 \log$ units.

For example in the case of Opalinus Clay the overall error on the $R_{d, \text{OPA}}$ can be expressed as:

$$\log(\text{UF-overall}) = \sqrt{(\log(\text{UF}-R_{d, \text{IL}}))^2 + (\log(\text{UF}-\text{MIN}_{\text{OPA}}))^2 + (\log(\text{UF}-\text{SF}_{\text{OPA}}))^2 + (\log(\text{UF}-\text{SF}_{\text{IL}}))^2} \quad (9.3)$$

and the overall uncertainty factor is equal to:

$$\text{UF-overall} = 10^{\log(\text{UF-overall})} \quad (9.4)$$

Note that for radionuclides whose sorption is calculated by cation exchange a temperature uncertainty factor is included in Eq. 9.3.

In the case of Mo(VI) an uncertainty factor for CF_{pH} is included in Eq. 9.3.

9.9 Calculation of the overall uncertainty factor in case of chemical analogy

For elements where a chemical analogue is invoked, the following relations were used to derive the $R_{d, \text{RN ARG ROCK}}$ where, in the following, RN and ANALOG refer to the element and the chemical analogue, respectively (see section 4.5):

$$R_{d, \text{RN ARG ROCK}} = R_{d, \text{ANALOG ARG ROCK}} \cdot \text{SF}_{\text{RN ARG ROCK}} / \text{SF}_{\text{ANALOG ARG ROCK}} \quad (9.5)$$

and

$$R_{d, \text{ANOLOG ARG ROCK}} = R_{d, \text{ANALOG ILLITE}} \cdot CF_{\text{MIN}} \cdot \text{SF}_{\text{ANALOG ARG ROCK}} / \text{SF}_{\text{ANALOG ILLITE}} \quad (9.6)$$

Substituting for $R_{d, \text{ANOLOG ARG ROCK}}$ in Eq. 9.5 from Eq. 9.6 yields:

$$R_{d, \text{RN ARG ROCK}} = R_{d, \text{ANALOG ILLITE}} \cdot CF_{\text{MIN}} \cdot \text{SF}_{\text{RN ARG ROCK}} / \text{SF}_{\text{ANALOG ILLITE}} \quad (9.7)$$

The individual and overall uncertainty factors (UF) for the selected sorption values are given for each radionuclide in Tabs. 9.3 to 9.7.

Tab. 9.3: Summary of the overall uncertainty factors for Opalinus Clay, Toniger Lias and Toniger Keuper associated with the derived R_d in situ values, and the uncertainty factors associated with the individual conversion steps.

Element	Uncertainty factors (UF)						
	R_d ILLITE	model	MIN _{ARG ROCK}	SF _{ILLITE}	SF _{ARG ROCK}	Temp.	OVERALL
Be(II) ¹	3	-	2	1	1.1	1	3.7
C _{inorg.}	-	3	2	-	1	1	3.7
C _{org.} ²	-	-	-	-	-	-	-
Cl(-I) ²	-	-	-	-	-	-	-
K(I)	-	3	2	-	-	4	6.7
Ca(II)	-	3	2	-	-	4	6.7
Co(II)	3	-	2	1	1.1	1	3.7
Ni(II)	3	-	2	1	1.1	1	3.7
Se(-II) ²	-	-	-	-	-	-	-
Sr(II)	-	3	2	-	-	4	6.7
Zr(IV) ¹	3	-	2	1	1.8	1	4.2
Nb(V)	5	-	2	-	-	1	5.8
Mo(VI) ³	3	-	2	-	-	1	5.0
Tc(IV)	3	-	2	1	1.1	1	3.7
Pd(II) ¹	3	-	2	1	1.3	1	3.8
Ag(I) ²	-	-	-	-	-	-	-
Sn(IV)	3	-	2	1.2	1.2	1	3.8
I(-I) ²	-	-	-	-	-	-	-
Cs(I)	-	3	2	-	-	4	6.7
Sm(III) ¹	3	-	2	1.8	1.8	1	4.7
Eu(III)	3	-	2	1.8	1.8	1	4.7
Ho(III) ¹	3	-	2	1.8	1.8	1	4.7
Pb(II)	3	-	2	1	1.9	1	4.3
Po(IV)	10	-	2	-	-	1	11.1
Ra(II)	-	-	2	-	-	4	6.7
Ac(III) ¹	3	-	2	2.4	2.4	1	6.0
Th(IV)	3	-	2	1	11.3	1	15.7
Pa(V)	3	-	2	1	16.0	1	21.4
U(IV) ¹	3	-	2	1	5.9	1	9.0
Np(IV)	3	-	2	1	1.0	1	3.7
Pu(III) ¹	3	-	2	2.1	2.1	1	5.3
Am(III)	3	-	2	2.4	2.4	1	6.0
Cm(III) ¹	3	-	2	2.4	2.4	1	6.0

¹ Elements using chemical analogy: UF_{ILLITE} given in the 2nd column is the UF for the chemical analogue.

² If R_d is set to zero, no UF is considered.

³ An uncertainty factor of 2.6 from the pH conversion has been included in the overall uncertainty.

Tab. 9.4: Summary of the overall uncertainty factors for 'Brauner Dogger' Clay-rich and Sandy limestone sequences associated with the derived R_d in situ values, and the uncertainty factors associated with the individual conversion steps.

Element	Uncertainty factors (UF)						
	R_d lit.	model	MIN _{ARG ROCK}	SF _{ILLITE}	SF _{ARG ROCK}	Temp.	OVERALL
Be(II) ¹	3	-	5	1	1.1	1	7.0
C _{inorg.}	-	3	5	-	1	1	7.0
C _{org.} ²	-	-	-	-	-	-	-
Cl(-I) ²	-	-	-	-	-	-	-
K(I)	-	3	5	-	-	4	10.9
Ca(II)	-	3	5	-	-	4	10.9
Co(II)	3	-	5	1	1.1	1	7.0
Ni(II)	3	-	5	1	1.1	1	7.0
Se(-II) ²	-	-	-	-	-	-	-
Sr(II)	-	3	5	-	-	4	10.9
Zr(IV) ¹	3	-	5	1	1.8	1	7.7
Nb(V)	5	-	5	-	-	1	9.7
Mo(VI) ³	3	-	5	-	-	1	8.8
Tc(IV)	3	-	5	1	1.1	1	7.0
Pd(II) ¹	3	-	5	1	1.3	1	7.1
Ag(I) ²	-	-	-	-	-	-	-
Sn(IV)	3	-	5	1.2	1.2	1	7.1
I(-I) ²	-	-	-	-	-	-	-
Cs(I)	-	3	5	-	-	4	10.9
Sm(III) ¹	3	-	5	1.8	1.8	1	8.3
Eu(III)	3	-	5	1.8	1.8	1	8.3
Ho(III) ¹	3	-	5	1.8	1.8	1	8.3
Pb(II)	3	-	5	1	1.9	1	7.8
Po(IV)	10	-	5	-	-	1	16.6
Ra(II)	-	-	5	-	-	4	10.9
Ac(III) ¹	3	-	5	2.4	2.4	1	10.1
Th(IV)	3	-	5	1	11.3	1	22.4
Pa(V)	3	-	5	1	16.0	1	29.6
U(IV) ¹	3	-	5	1	5.9	1	14.0
Np(IV)	3	-	5	1	1.0	1	7.0
Pu(III) ¹	3	-	5	2.1	2.1	1	9.1
Am(III)	3	-	5	2.4	2.4	1	10.1
Cm(III) ¹	3	-	5	2.4	2.4	1	10.1

¹ Elements using chemical analogy: UF_{ILLITE} given in the 2nd column is the UF for the chemical analogue.

² If R_d is set to zero, no UF is considered.

³ An uncertainty factor of 2.6 from the pH conversion has been included in the overall uncertainty.

Tab. 9.5: Summary of the overall uncertainty factors for Effingen Member Calcareous marl sequences associated with the derived R_d in situ values, and the uncertainty factors associated with the individual conversion steps.

Element	Uncertainty factors (UF)						
	R_d lit.	model	MIN _{ARG ROCK}	SF _{ILLITE}	SF _{ARG ROCK}	Temp.	OVERALL
Be(II) ¹	3	-	2	1	1.5	1	3.9
C _{inorg.}	-	3	2	-	1	1	3.7
C _{org.} ²	-	-	-	-	-	-	-
Cl(-I) ²	-	-	-	-	-	-	-
K(I)	-	3	2	-	-	4	6.7
Ca(II)	-	3	2	-	-	4	6.7
Co(II)	3	-	2	1	1.5	1	3.9
Ni(II)	3	-	2	1	1.5	1	3.9
Se(-II) ²	-	-	-	-	-	-	-
Sr(II)	-	3	2	-	-	4	6.7
Zr(IV) ¹	3	-	2	1	1.7	1	4.1
Nb(V)	5	-	2	-	-	1	5.8
Mo(VI) ³	3	-	2	-	-	1	5.0
Tc(IV)	3	-	2	1	1.0	1	3.7
Pd(II) ¹	3	-	2	1	9.5	1	13.5
Ag(I) ²	-	-	-	-	-	-	-
Sn(IV)	3	-	2	1.2	1.2	1	3.8
I(-I) ²	-	-	-	-	-	-	-
Cs(I)	-	3	2	-	-	4	6.7
Sm(III) ¹	3	-	2	2.1	2.1	1	5.3
Eu(III)	3	-	2	2.1	2.1	1	5.3
Ho(III) ¹	3	-	2	2.1	2.1	1	5.3
Pb(II)	3	-	2	1	1.2	1	3.7
Po(IV)	10	-	2	-	-	1	11.1
Ra(II)	-	-	2	-	-	4	6.7
Ac(III) ¹	3	-	2	2.4	2.4	1	6.0
Th(IV)	3	-	2	1	1.6	1	4.0
Pa(V)	3	-	2	1	16.0	1	21.4
U(IV) ¹	3	-	2	1	5.8	1	8.9
Np(IV)	3	-	2	1	1.0	1	3.7
Pu(III) ¹	3	-	2	2.6	2.6	1	6.5
Am(III)	3	-	2	2.6	2.6	1	6.5
Cm(III) ¹	3	-	2	2.6	2.6	1	6.5

¹ Elements using chemical analogy: UF_{ILLITE} given in the 2nd column is the UF for the chemical analogue.

² If R_d is set to zero, no UF is considered.

³ An uncertainty factor of 2.6 from the pH conversion has been included in the overall uncertainty.

Tab. 9.6: Summary of the overall uncertainty factors for Helvetic Marls associated with the derived R_d in situ values, and the uncertainty factors associated with the individual conversion steps.

Element	Uncertainty factors (UF)						
	R_d lit.	model	MIN _{ARG ROCK}	SF _{ILLITE}	SF _{ARG ROCK}	Temp.	OVERALL
Be(II) ¹	3	-	6	1	1.2	1	8.2
C _{inorg.}	-	3	6	-	1	1	8.2
C _{org.} ²	-	-	-	-	-	-	-
Cl(-I) ²	-	-	-	-	-	-	-
K(I)	-	3	6	-	-	4	12.4
Co(II)	3	-	6	1	1.2	1	8.2
Ni(II)	3	-	6	1	1.2	1	8.2
Se(-II) ²	-	-	-	-	-	-	-
Sr(II)	-	3	6	-	-	4	12.4
Nb(V)	5	-	6	-	-	1	11.1
Mo(VI) ³	3	-	6	-	-	1	10.1
Ag(I) ²	-	-	-	-	-	-	-
Sn(IV)	3	-	6	1.3	1.3	1	8.5
I(-I) ²	-	-	-	-	-	-	-
Cs(I)	-	3	6	-	-	4	12.4
Pb(II)	3	-	6	1	2.7	1	10.2
Po(IV)	10	-	6	-	-	1	18.5
Ra(II)	-	-	6	-	-	4	12.4
Ac(III) ¹	3	-	6	2.4	2.5	1	11.8
Th(IV)	3	-	6	1	13.8	1	28.9
Pa(V)	3	-	6	1	16.0	1	32.4
U(IV) ¹	3	-	6	1	16	1	32.4
Np(IV)	3	-	6	1	1.5	1	8.5
Pu(III) ¹	3	-	6	1.7	1.7	1	9.3
Am(III)	3	-	6	2.5	2.5	1	11.8
Cm(III) ¹	3	-	6	2.5	2.5	1	11.8

¹ Elements using chemical analogy: UF_{ILLITE} given in the 2nd column is the UF for the chemical analogue.

² If R_d is set to zero, no UF is considered.

³ An uncertainty factor of 2.6 from the pH conversion has been included in the overall uncertainty.

Tab. 9.7: Summary of the overall uncertainty factors for MX-80 bentonite associated with the derived R_d in situ values, and the uncertainty factors associated with the individual conversion steps.

Element	Uncertainty factors (UF)						
	R_d lit.	model	MIN _{MX-80}	SF _{MONT}	SF _{MX-80}	Temp.	OVERALL
Be(II) ¹	3	-	1	1	1.1	1	3.0
C _{inorg.}	-	3	1	-	1	1	3.0
C _{org.} ²	-	-	-	-	-	-	-
Cl(-I) ²	-	-	-	-	-	-	-
K(I)	-	3	1	-	-	4	5.9
Ca(II)	-	3	1	-	-	4	5.9
Co(II)	3	-	1	1	1.1	1	3.0
Ni(II)	3	-	1	1	1.1	1	3.0
Se(-II) ²	-	-	-	-	-	-	-
Sr(II)	-	3	1	-	-	4	5.9
Zr(IV) ¹	3	-	1	1	1.8	1	3.5
Nb(V)	5	-	1	-	-	1	5.0
Mo(VI) ³	3	-	1	-	-	1	4.3
Tc(IV)	3	-	1	1	1.1	1	3.0
Pd(II) ¹	3	-	1	1	1.3	1	3.1
Ag(I) ²	-	-	-	-	-	-	-
Sn(IV)	3	-	1	1.2	1.2	1	3.1
I(-I) ²	-	-	-	-	-	-	-
Cs(I)	-	3	1	-	-	4	5.9
Sm(III) ¹	3	-	1	1.8	1.8	1	4.0
Eu(III)	3	-	1	1.8	1.8	1	4.0
Ho(III) ¹	3	-	1	1.8	1.8	1	4.0
Pb(II)	3	-	1	1	1.9	1	3.6
Po(IV)	10	-	1	-	-	1	10.0
Ra(II)	-	-	1	-	-	4	5.9
Ac(III) ¹	3	-	1	2.4	2.4	1	5.2
Th(IV)	3	-	1	1	11.3	1	14.3
Pa(V)	3	-	1	1	16.0	1	19.7
U(IV) ¹	3	-	1	1	5.9	1	8.1
Np(IV)	3	-	1	1	1.0	1	3.0
Pu(III) ¹	3	-	1	2.1	2.1	1	4.6
Am(III)	3	-	1	2.4	2.4	1	5.2
Cm(III) ¹	3	-	1	2.4	2.4	1	5.2

¹ Elements using chemical analogy: UF_{ILLITE} given in the 2nd column is the UF for the chemical analogue.

² If R_d is set to zero, no UF is considered.

³ An uncertainty factor of 2.6 from the pH conversion has been included in the overall uncertainty.

10 Summary

The methodology described in Bradbury et al. (2010) has been applied to the four rock types identified as being suitable host rocks for a deep radioactive waste repository, namely, Opalinus Clay (HLW, L/ILW), and 'Brauner Dogger', Effingen Member and Helvetic Marls (L/ILW) to provide sorption data bases for the reference mineralogy and a number porewater chemistries, to be used as input to the provisional safety analysis calculations required for Stage 2 of the Sectoral Plan. Sorption data bases for three lower confining units and for MX-80 bentonite have also been derived.

The selected in situ distribution ratios for the reference mineralogy and the various water compositions for each host rock, the underlying confining units and MX-80 bentonite are summarised in graphical representations in Appendix C. The variations in R_d values arising from the variation in the porewater chemistries (pH, $p\text{CO}_2$, ionic strength, speciation) are reflected by the spread in the data. An assessment of the uncertainties associated with the selected sorption values has been described in Chapter 9. The uncertainty factors summarised in Tabs. 9.3 to 9.7 are valid for each element at any chosen porewater combination, i.e. for each value given in Figs. C1 to C9.

Various earlier experimental and modelling studies have provided support for this approach (Bradbury & Baeyens 2010, 2011). Most recently, an extensive experimental study using samples of Opalinus Clay, 'Brauner Dogger', Effingen Member, Helvetic Marls and MX-80 bentonite was performed in order to further validate the methodology used to generate the sorption data bases given in the present report (Baeyens et al. 2014).

For certain rock types within a formation, the 2:1 clay mineral contents were not given in the mineralogical analyses. In these cases sorption data bases were developed based on calcite as the dominant sorbing phase and the results are summarised in Fig. C10.

In Appendix D the influence of a high pH plume on certain rock types has been evaluated.

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Appendix A: Speciation factors for the source, host rock and bentonite porewater systems

The speciation factors are calculated using the PSI/Nagra 12/07 thermodynamic database (TDB) (Thoenen et al. 2014). The following procedures have been applied:

- Speciation factors for the radionuclides for which source data ($R_{d, \text{ILLITE}}$ and $R_{d, \text{MONT}}$) are calculated at the corresponding porewater pH values in 0.1 M NaClO_4 and in the presence of 4×10^{-5} M Si_{TOT} are presented in Tabs. A1 to A4. The speciation factors in the porewaters of the host rocks and bentonite can be found in Tabs. A5 to A8.
- Silicate complexes are contained in the PSI/Nagra 12/07 TDB for Eu(III), Am(III), Sn(IV) and U(VI). They are assumed to be non-sorbing.
- For Pu(III) there are no silicate complexes in the recommended PSI/Nagra 12/07 TDB, but they are present in the supplemental data. Since Am(III) is considered as the chemical analogue for Pu(III), the speciation calculations were carried out with the supplemental data.
- The redox sensitive elements U(IV/VI) and Pu(III/IV) have been calculated in a coupled mode (see section 4.3) and for these calculations the supplemental data have been included in the calculations.
- There are no thermodynamic data in the PSI/Nagra 12/07 TDB for Mo(VI) and Po(IV). The speciation factors are taken to be unity.

A1 Speciation factors for the source clay minerals

Tab. A1: Speciation factors in 0.1 M NaClO_4 (in the presence of 4×10^{-5} M Si_{TOT}) for Opalinus Clay and 'Brauner Dogger' porewater pH values.

Element	SF_{LLITE}		
	pH = 7.0	pH = 7.2	pH = 7.5
Co(II)	1.000	1.000	1.000
Ni(II)	1.000	1.000	1.000
Tc(IV)	1.000	1.000	1.000
Sn(IV)	0.887	0.832	0.712
Eu(III)	0.322	0.240	0.157
Pb(II)	1.000	1.000	1.000
Th(IV)	1.000	1.000	1.000
Pa(V)	0.998	0.996	0.989
U(VI)	0.968	0.976	0.987
Am(III)	0.345	0.269	0.191

In the original version of this report the values for Tc(IV), Sn(IV) and Eu(III) were interchanged. This table contains the correct values.

Tab. A2: Speciation factors in 0.1 M NaClO₄ (in the presence of 4×10^{-5} M Si_{TOT}) for Effingen Member porewater pH values.

Element	SF _{LLITE}			
	Reference pH = 7.31	High SO ₄ pH = 7.25	Lowest Cl pH = 7.09	High pCO ₂ pH = 6.8
Co(II)	1.000	1.000	1.000	1.000
Ni(II)	1.000	1.000	1.000	1.000
Tc(IV)	1.000	1.000	1.000	1.000
Sn(IV)	0.793	0.815	0.864	0.926
Eu(III)	0.204	0.223	0.283	0.422
Pb(II)	1.000	1.000	1.000	1.000
Th(IV)	1.000	1.000	1.000	1.000
Pa(V)	1.000	0.995	1.000	0.996
U(VI)	0.980	0.978	0.972	0.961
Am(III)	0.235	0.253	0.308	0.439

Tab. A3: Speciation factors in 0.1 M NaClO₄ (in the presence of 4×10^{-5} M Si_{TOT}) for Helvetic Marls porewater pH values.

Element	SF _{LLITE}				
	Reference pH = 7.47	Low pε pH = 7.46	High pCO ₂ pH = 7.01	Low pCO ₂ pH = 7.95	High NaCl pH = 7.16
Co(II)	1.000	1.000	1.000	1.000	1.000
Ni(II)	1.000	1.000	1.000	1.000	1.000
Sn(IV)	0.726	0.731	0.885	0.466	0.844
Pb(II)	1.000	1.000	1.000	1.000	1.000
Th(IV)	1.000	1.000	1.000	1.000	1.000
Pa(V)	0.990	0.990	1.000	1.000	1.000
U(VI)	0.986	0.985	0.969	0.996	0.975
Am(III)	0.197	0.199	0.341	0.150	0.282

Tab. A4: Speciation factors in 0.1 M NaClO₄ (in the presence of 4×10^{-5} M Si_{TOT}) for MX-80 bentonite porewater pH values.

Element	SF _{MONT}				
	pH = 7.07	pH = 7.27	pH = 7.28	pH = 7.08	pH = 7.79
Co(II)	1.000	1.000	1.000	1.000	1.000
Ni(II)	1.000	1.000	1.000	1.000	1.000
Tc(IV)	1.000	1.000	1.000	1.000	0.999
Sn(IV)	0.870	0.808	0.804	0.867	0.559
Eu(III)	0.291	0.216	0.213	0.287	0.119
Pb(II)	1.000	1.000	1.000	1.000	1.000
Th(IV)	1.000	1.000	1.000	1.000	1.000
Pa(V)	1.000	0.994	0.994	1.000	1.000
U(VI)	0.971	0.979	0.979	0.971	0.994
Am(III)	0.316	0.247	0.244	0.312	0.155

A2 Speciation factors for the host rocks

Tab. A5: Speciation factors in the porewaters of Opalinus Clay, 'Brauner Dogger' Clay-rich sequences, 'Brauner Dogger' Limestone sequences and lower confining units (only Reference porewater).

Element	SF _{ARG ROCK}			
	Reference pH = 7.20	High pCO ₂ pH = 7.01	Low pCO ₂ pH = 7.505	High salinity pH = 7.00
Be(II)	0.717	0.615	0.733	0.808
Co(II)	0.657	0.646	0.668	0.491
Ni(II)	0.723	0.724	0.723	0.713
Zr(IV)	1.000	1.000	1.000	1.000
Tc(IV)	0.905	0.798	0.972	0.946
Pd(II)	0.979	0.949	0.994	0.083
Sn(IV)	0.824	0.882	0.700	0.883
Sm(III)	0.087	0.0907	0.081	0.198
Eu(III)	0.0344	0.0391	0.0277	0.062
Ho(III)	0.0613	0.0628	0.0589	0.168
Pb(II)	0.213	0.189	0.256	0.047
Ac(III)	0.0473	0.053	0.0392	0.0899
Th(IV)	0.271	0.129	0.595	0.795
Pa(V)	0.995	0.998	0.988	0.998
U(IV)	1.5×10^{-3}	5.4×10^{-4}	7.0×10^{-3}	1.1×10^{-2}
U(VI)	1.1×10^{-5}	5.7×10^{-6}	3.4×10^{-5}	1.1×10^{-4}
Np(IV)	1.000	1.000	1.000	1.000
Pu(III)	0.0472	0.0505	0.0423	0.0817
Pu(IV)	2.6×10^{-4}	9.1×10^{-5}	1.2×10^{-3}	1.7×10^{-4}
Am(III)	0.0473	0.0530	0.0392	0.0899
Cm(III)	0.0473	0.0530	0.0392	0.0899

Tab. A6: Speciation factors in the porewaters of Effingen Member Calcareous marl and Effingen Member Limestone sequences.

Element	$SF_{ARG\ ROCK}$			
	Reference pH = 7.31	Lowest Cl pH = 7.09	High SO_4 pH = 7.25	High pCO_2 pH = 6.80
Be(II)	0.907	0.779	0.848	0.754
Co(II)	0.562	0.748	0.583	0.557
Ni(II)	0.781	0.880	0.732	0.780
Zr(IV)	1.000	1.000	1.000	1.000
Tc(IV)	0.988	0.932	0.969	0.898
Pd(II)	0.394	0.874	0.561	0.0611
Sn(IV)	0.789	0.858	0.807	0.923
Sm(III)	0.206	0.189	0.164	0.268
Eu(III)	0.0515	0.0648	0.0494	0.0933
Ho(III)	0.180	0.143	0.138	0.225
Pb(II)	0.0738	0.213	0.106	0.0624
Ac(III)	0.0677	0.0789	0.0679	0.129
Th(IV)	0.957	0.547	0.788	0.681
Pa(V)	0.994	1.000	1.000	1.000
U(IV)	0.069	0.006	0.013	0.006
U(VI)	3.7×10^{-4}	3.7×10^{-5}	9.5×10^{-5}	7.9×10^{-5}
Np(IV)	1.0	1.0	1.0	1.0
Pu(III)	0.074	0.0840	0.0682	0.114
Pu(IV)	6.7×10^{-4}	1.9×10^{-4}	4.6×10^{-4}	6.3×10^{-5}
Am(III)	0.0677	0.0789	0.0679	0.129
Cm(III)	0.0677	0.0789	0.0679	0.129

Tab. A7: Speciation factors in the porewaters of Helvetic Marls and Helvetic Marls Limestone sequences.

Element	$SF_{\text{ARG ROCK}}$				
	Reference pH = 7.47	High pCO ₂ pH = 7.01	Low pCO ₂ pH = 7.95	Low pε pH = 7.46	High NaCl pH = 7.16
Be(II)	0.618	0.364	0.849	0.612	0.707
Co(II)	0.725	0.639	0.768	0.0375	0.611
Ni(II)	0.907	0.908	0.906	0.0018	0.844
Sn(IV)	0.719	0.879	0.457	0.724	0.840
Pb(II)	0.135	0.0913	0.218	0.134	0.0837
Ac(III)	0.017	0.0165	0.0205	0.0166	0.0556
Th(IV)	0.065	0.0094	0.378	0.0619	0.254
Pa(V)	0.990	0.998	0.961	0.990	0.996
U(IV)	1.4×10^{-3}	1.5×10^{-4}	1.5×10^{-2}	4.1×10^{-2}	4.4×10^{-3}
U(VI)	1.6×10^{-6}	3.3×10^{-7}	9.9×10^{-6}	6.0×10^{-8}	1.0×10^{-5}
Np(IV)	0.987	0.578	1.000	0.985	0.999
Pu(III)	0.020	0.019	0.0222	0.0217	0.0609
Pu(IV)	2.2×10^{-4}	1.7×10^{-5}	2.2×10^{-3}	8.1×10^{-6}	1.3×10^{-4}
Am(III)	0.017	0.0165	0.0205	0.0166	0.0556
Cm(III)	0.017	0.0165	0.0205	0.0166	0.0556

A3 Speciation factors for MX-80 bentonite

Tab. A8: Speciation factors in the porewaters of MX-80 bentonite.

Element	SF _{MX-80}				
	Reference pH = 7.27	High porosity pH = 7.28	High salinity pH = 7.08	High pCO ₂ pH = 7.07	Low pCO ₂ pH = 7.79
Be(II)	0.956	0.955	0.970	0.931	0.986
Co(II)	0.503	0.500	0.463	0.492	0.638
Ni(II)	0.535	0.525	0.676	0.531	0.679
Zr(IV)	1.000	1.000	1.000	1.000	1.000
Tc(IV)	0.901	0.901	0.945	0.791	0.986
Pd(II)	0.964	0.978	0.092	0.918	0.998
Sn(IV)	0.798	0.795	0.866	0.862	0.546
Sm(III)	0.058	0.055	0.163	0.061	0.060
Eu(III)	0.024	0.023	0.050	0.025	0.021
Ho(III)	0.046	0.044	0.136	0.046	0.043
Pb(II)	0.159	0.164	0.042	0.140	0.281
Ac(III)	0.040	0.039	0.075	0.043	0.031
Th(IV)	0.205	0.198	0.741	0.092	0.716
Pa(V)	0.994	0.994	0.997	0.997	0.974
U(IV)	9.9×10^{-4}	9.6×10^{-4}	1.04×10^{-2}	3.0×10^{-4}	1.4×10^{-2}
U(VI)	7.4×10^{-7}	7.0×10^{-6}	7.8×10^{-5}	3.6×10^{-6}	7.2×10^{-5}
Np(IV)	0.999	0.999	1.000	0.993	1.000
Pu(III)	0.033	0.032	0.069	0.033	0.032
Pu(IV)	2.5×10^{-4}	2.5×10^{-4}	2.0×10^{-4}	8.8×10^{-5}	3.6×10^{-3}
Am(III)	0.040	0.039	0.075	0.043	0.031
Cm(III)	0.040	0.039	0.075	0.043	0.031

Appendix B: Speciation calculations for the porewaters of the different host rocks and of bentonite

Speciation calculations were carried out with the code PHREEQC (Parkhurst & Appelo 1999), version 2.12.1-669 for Mac OS X, using the Davies equation for activity coefficients of charged aqueous species:

$$\log_{10} \gamma_i = -Az_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I$$

where γ_i is the activity coefficient of species i , z_i the ionic charge of species i and I the ionic strength of the aqueous solution. Activity coefficients of neutral species were assumed to be equal to one.

The speciation calculations were performed as follows: A trace amount of 10^{-8} mol/kg_{H₂O} of a specific radionuclide (the speciation of each radionuclide was calculated separately) was added to the composition of the water under consideration and the speciation was calculated.

In the case of Se, Tc, Sn, Pa, Np, and Am, which exist in more than one redox state, the speciation calculations for these elements were redox decoupled, i.e., only one redox state was considered.

For speciation calculations, PHREEQC needs an input file, which controls the calculation procedure and where information on the water composition is stored, as well as a data file, which contains the required thermodynamic data (in specific cases, thermodynamic data can also be added to the input file). The output of the calculations is directed to an output file.

Templates for generating the input files for speciation in the porewaters for Opalinus Clay and 'Brauner Dogger' (see Tab. 3.8 for the porewater compositions), for the Effingen Member (see Tab. 3.9 for the porewater compositions), for the Helvetic Marls (see Tab. 3.10 for the porewater compositions), and for MX-80 bentonite (see Tab. 8.2 for the porewater compositions) are given in Thoenen (2014a), as well as the names of the corresponding output files and compilations of the resulting radionuclide speciations.

In addition, speciation calculations were also made for radionuclides in 0.1 M NaClO₄ (in the presence of 4×10^{-5} M Si_{TOT}) at the different pH values of the hostrock and bentonite porewaters. The pH values were set by adding appropriate amounts of NaOH or HCl.

A template for generating the input files for such calculations is given in Thoenen (2014a).

The names of the output files for the calculations at the pH values of the porewaters for Opalinus Clay and 'Brauner Dogger', at the pH values of the Effingen Member porewaters, at the pH values of the porewaters for the Helvetic Marls and at the pH values of the bentonite porewaters are given in Thoenen (2014a), as well as the resulting radionuclide speciations.

The thermodynamic data and the structure of the data files are also discussed in Thoenen (2014a).

Appendix C: Graphical representation of the SDBs

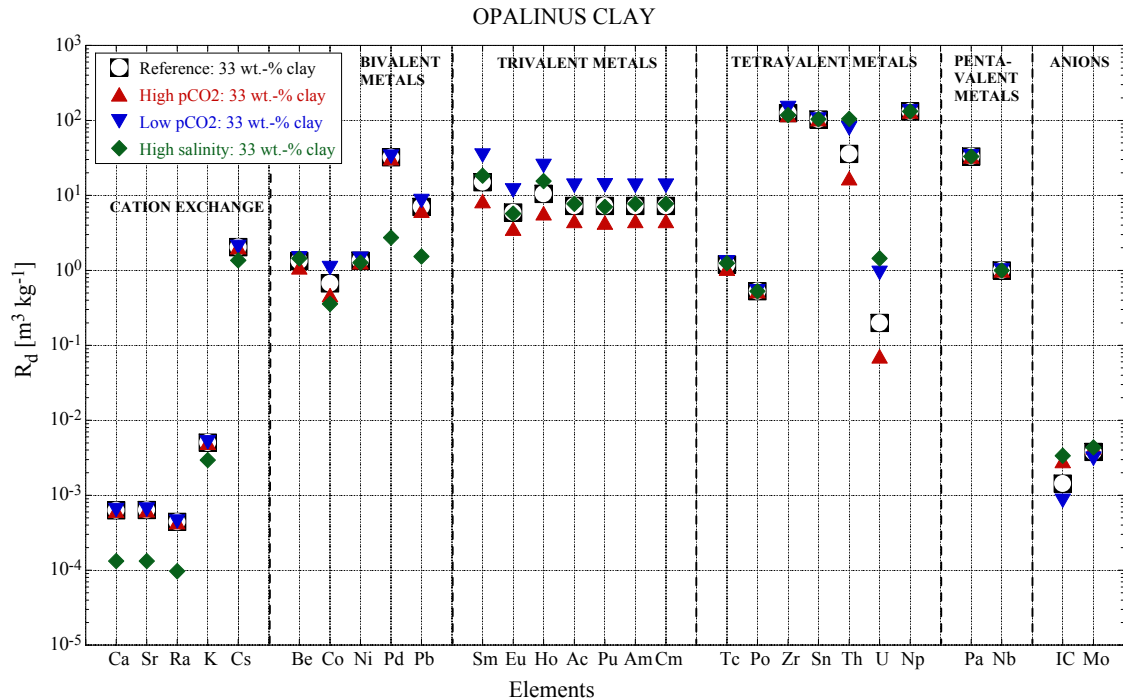


Fig. C1: Summary of SDBs for Opalinus Clay (Tab. 5.2).

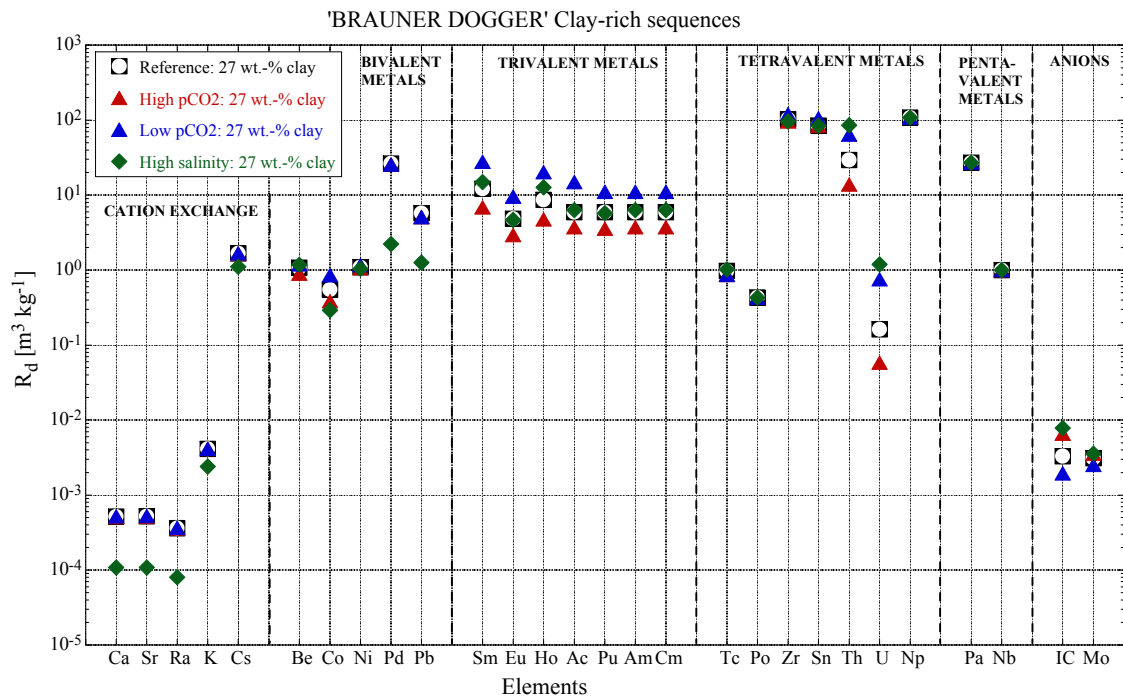


Fig. C2: Summary of SDBs for 'Brauner Dogger' Clay-rich sequences (Tab. 5.3).

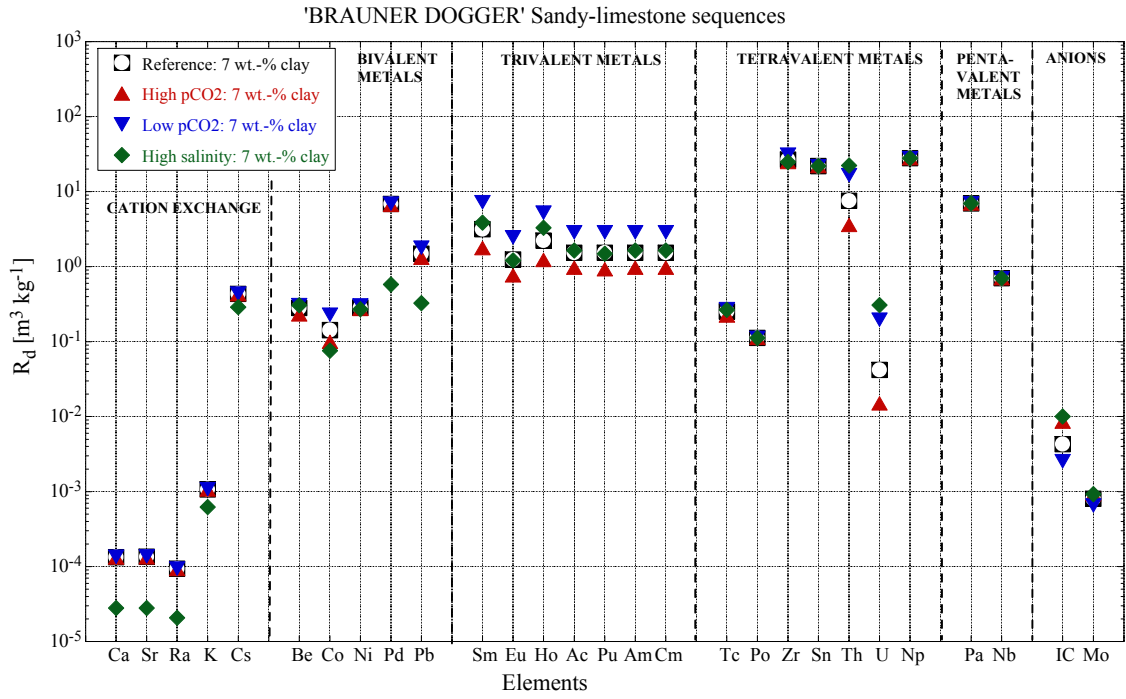


Fig. C3: Summary of SDBs for 'Brauner Dogger' Sandy limestone sequences (Tab. 5.4).

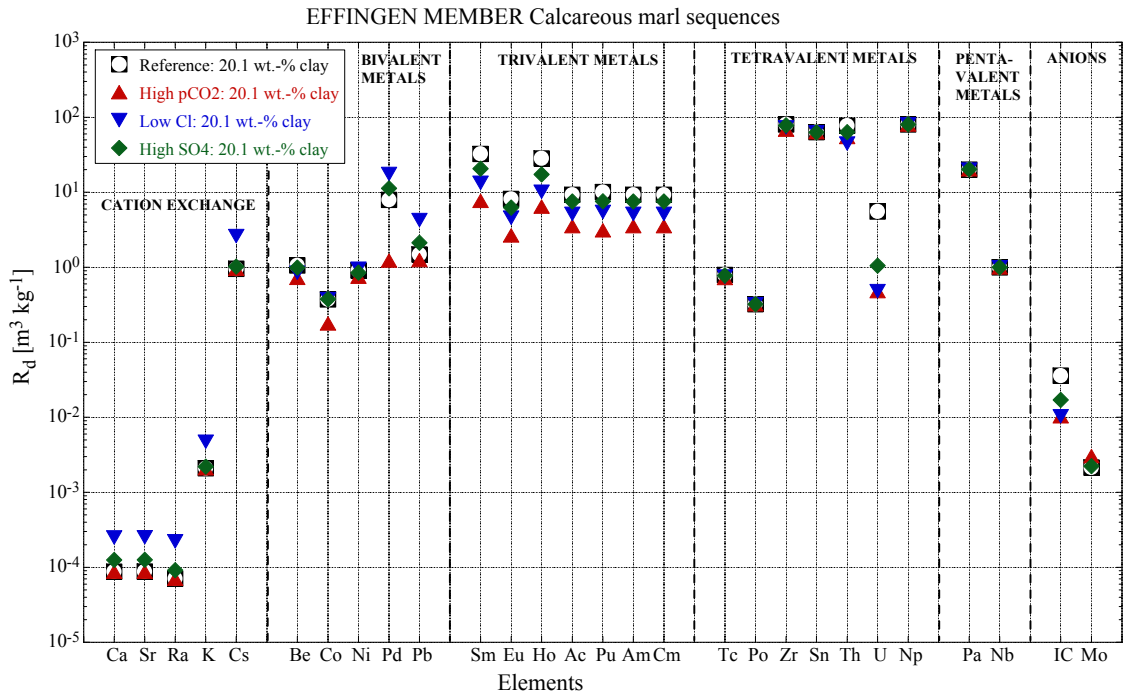


Fig. C4: Summary of SDBs for Effingen Member Calcareous marl sequences (Tab. 5.6).

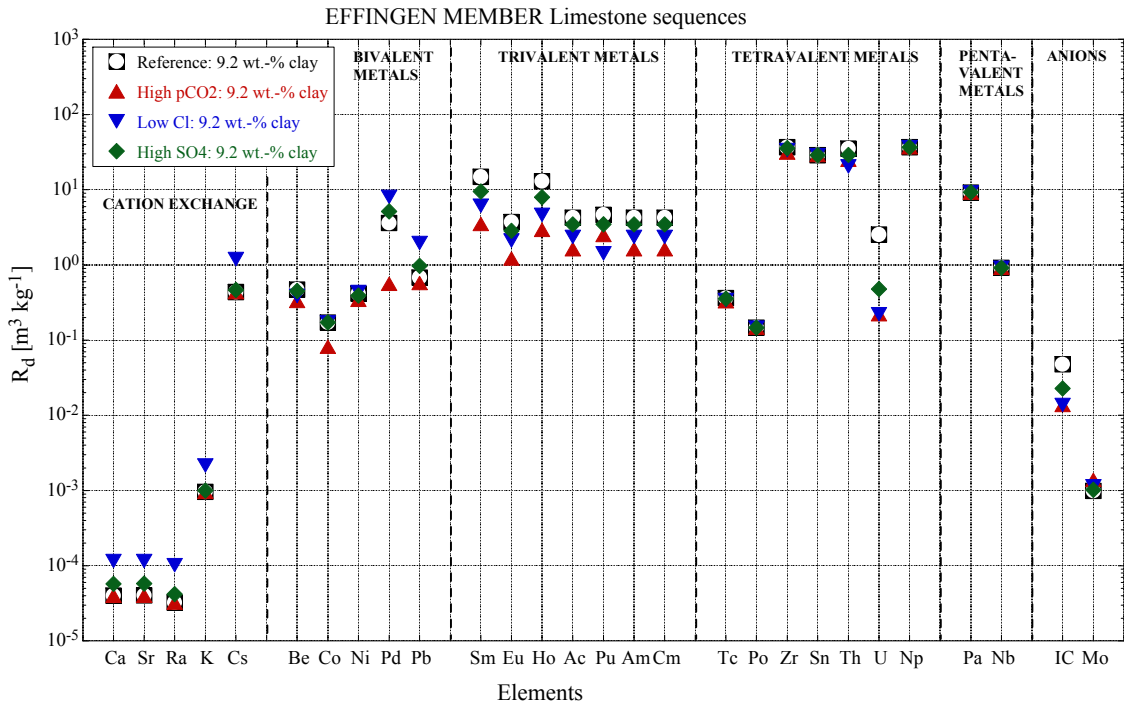


Fig. C5: Summary of SDBs for Effingen Member Limestone sequences (Tab. 5.7).

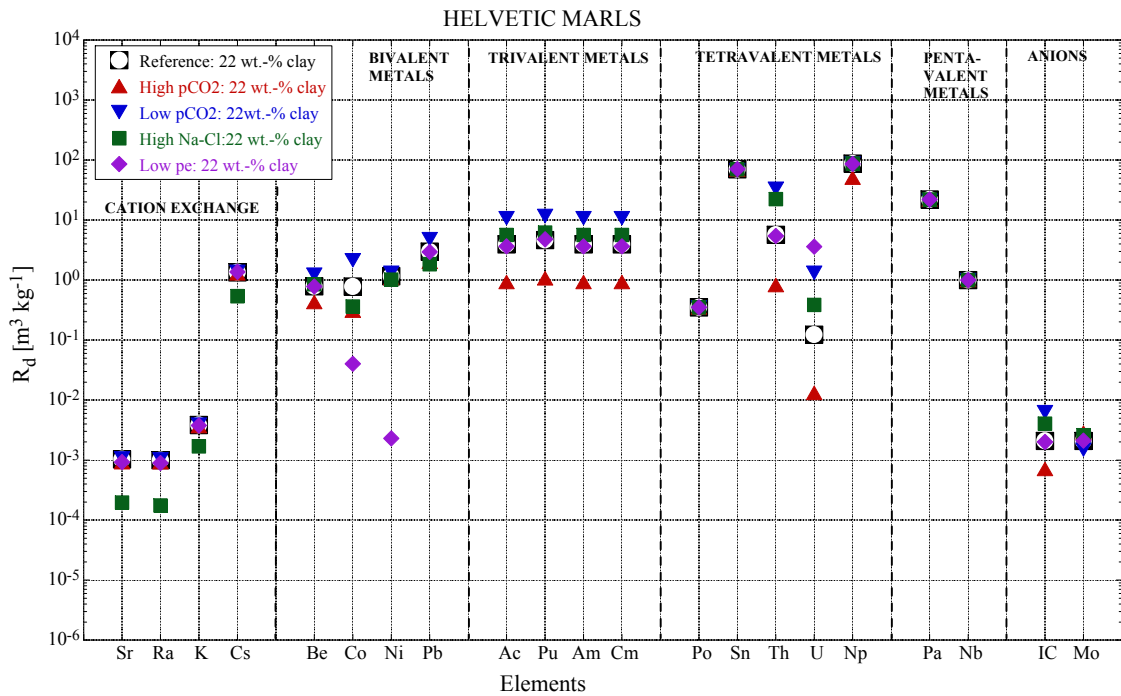


Fig. C6: Summary of SDBs for Helvetic Marls (Tab. 5.9).

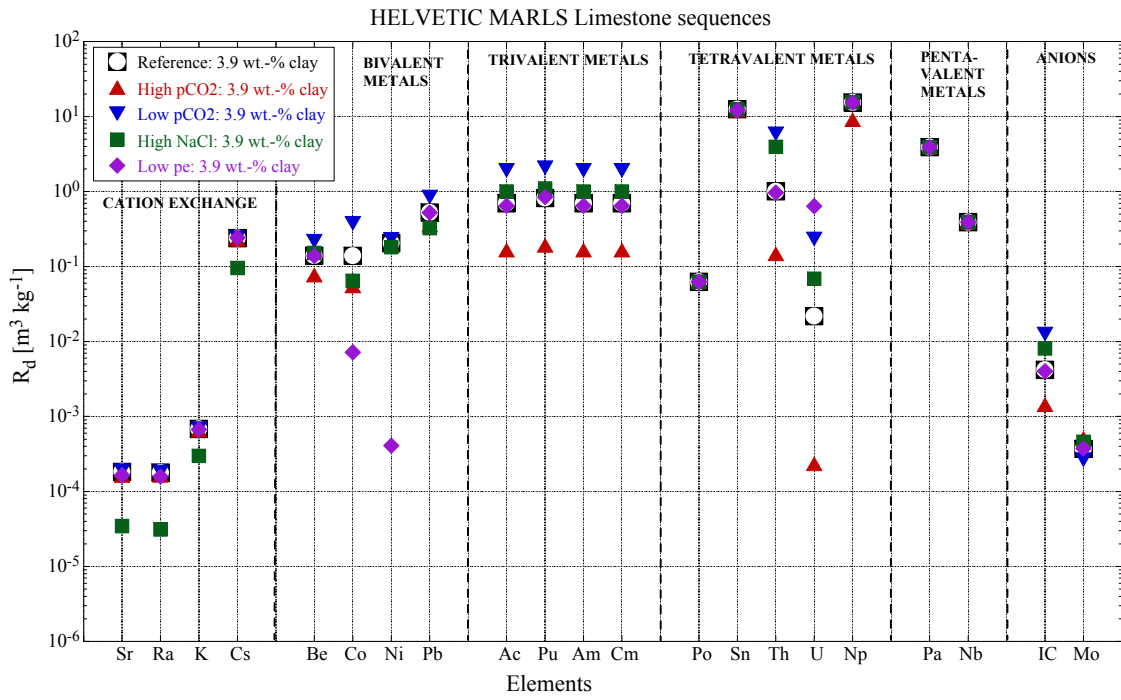


Fig. C7: Summary of SDBs for Helvetic Marls Limestone sequences (Tab. 5.10).

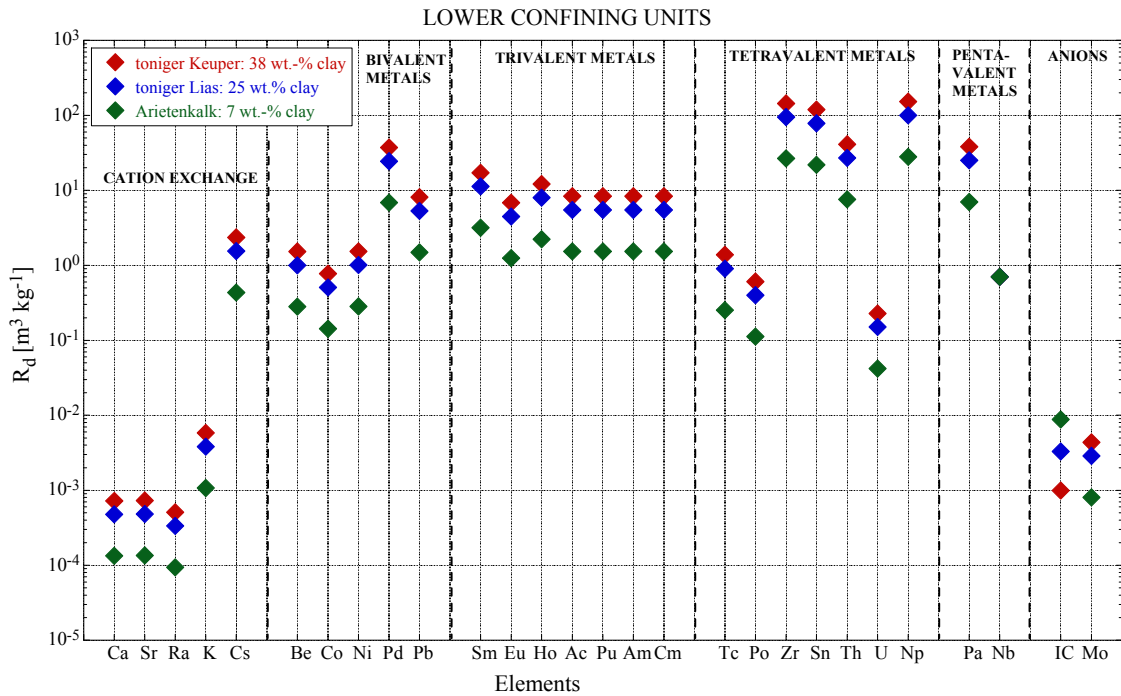


Fig. C8: Summary of SDBs for Lower confining units (Tab. 6.2).

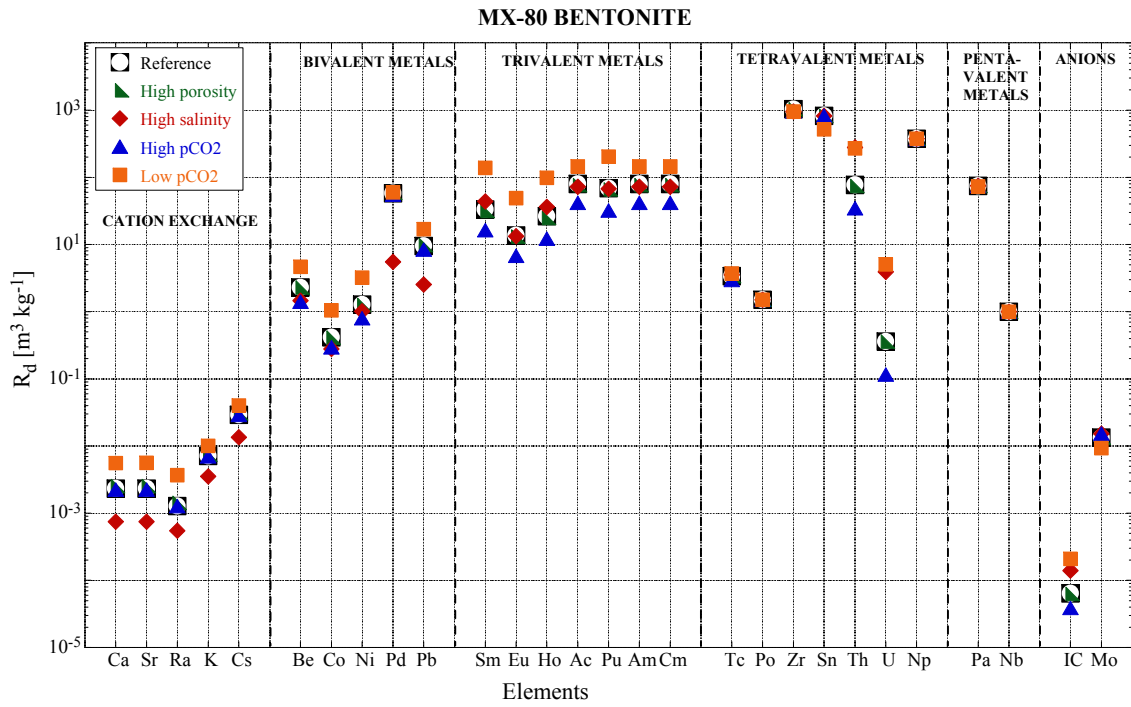


Fig. C9: Summary of SDBs for MX-80 bentonite (Tab. 8.6).

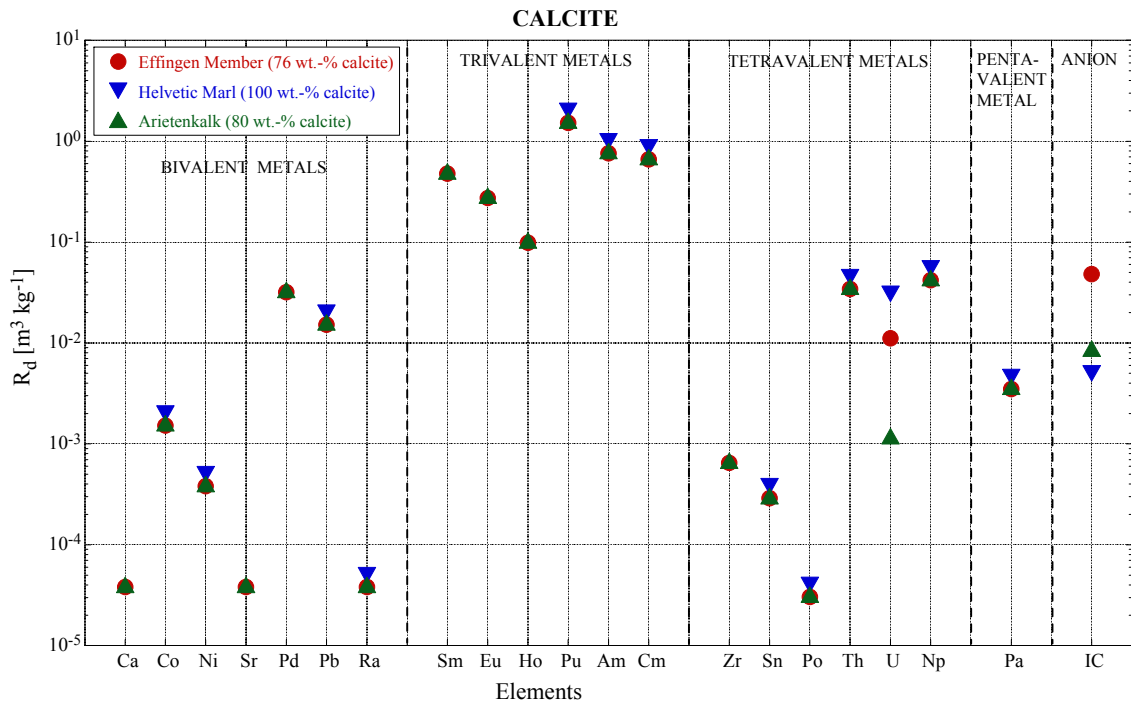


Fig. C10: Summary of SDBs for host rocks where no 2:1 type clay minerals are present (Tab. 7.3).

Appendix D: Sorption data base for pH plume altered host rocks

D1 Introduction

The main option currently under consideration by Nagra for the disposal of long-lived intermediate level radioactive waste (ILW) is to place such waste in caverns at depth in potential host rock formations (Nagra 2008).

Large quantities of cements and concretes will be used in the conditioning of the waste, waste packaging and construction. After the caverns re-saturate, interactions between the deep groundwater/porewater and the cement/concrete present in the repository will take place. The cementitious materials are unstable under the local conditions and will gradually degrade. The leaching of the hydrated cement could give rise to a pulse of hyperalkaline fluid moving out into the host rock, a so called pH plume, which could last for many thousands of years.

Under the high pH conditions predicted (Berner 1992, Neall 1994, Lagerblad & Trägårdh 1994, Bradbury et al. 2014), sheet silicate and quartz minerals in the host rocks will be unstable. (See, for example, Savage et al. 1990, 1991.) While certain minerals would dissolve, others would tend to form further out in the host rock where conditions favour the precipitation of secondary minerals.

Further, the groundwater/porewater chemistry would be significantly changed, and also possibly the hydrogeological characteristics around the repository. All of these processes would be varying in time and space along migration pathways.

New mineral phases likely to form are notably calcium silicate hydrates (C-S-H), calcium aluminium silicate hydrates (C-A-S-H) including tobermorite, jennite and hydrogarnet; chlorite, brucite ($\text{Mg}(\text{OH})_2$) and zeolites such as mordenite. A state-of-the-art study on the geochemical evolution of the L/ILW near-field has been prepared by Kosakowski et al. (2014) and confirms the formation of the mineral phases mentioned before.

Some of the considered host rocks with a clay mineral content of 40 wt.-% and below are expected to have a lower self-healing capacity against fracturing. In these host rocks, advective transport in a fracture network has to be considered, a scenario where a 'High-pH plume' could advance several meters or tens of meters into the host rock (Nagra 2014).

The following host rocks are expected to be influenced by a pH plume.

1. Effingen Member Calcareous marl sequences
2. Effingen Member Limestone sequences
3. Helvetic Marls
4. Helvetic Marls Limestone sequences

The mineralogical reaction scheme of cement/host rock interactions and its effect on pH plume buffering is not in general well known, and thus there still remain significant areas of uncertainties in the assessments given. Partly because of this, but also to cover various "what if scenarios", the aim is to consider the potential effects of a pH plume on the far-field sorption properties of Effingen Member and Helvetic Marls and to construct appropriate sorption data bases.

The methodology for the derivation of SDBs for a pH plume altered host rock is based on some previous work on a similar topic carried out for Palfris Marl (Bradbury & Baeyens 1994) and Opalinus Clay (Bradbury & Baeyens 2004).

D2 Methodology

Three scenarios on the chemical evolution within the fractures of the host rocks Effingen Member Calcareous marl sequences, Effingen Member Limestone sequences, Helvetic Marls and Helvetic Marls Limestone sequences are considered.

1. No interaction of the host rock with the pH plume. In this case the SDBs of the undisturbed host rocks are considered. These SDBs are tabulated in the 2nd column of Tabs. D1 to D4 and are taken from the reference SDBs given in Tabs. 5.6, 5.7, 5.9 and 5.10.
2. The clay minerals of the host rock are expected to be dissolved by the porlandite saturated high alkaline pH plume and converted in a 1 to 1 ratio to C-S-H phases. The SDB developed for pure C-S-H phases by Wieland (2014) is given in the 3rd column of Tabs. D1 to D4. The clay mineral contents of the host rocks are taken from the reference mineralogical composition given in Tabs. 3.4 to 3.7. For the scaling to C-S-H data all clay minerals are considered. The scaled values are given in the 4th column of Tabs. D1 to D4.
3. The final stage of the alteration process is that all C-S-H phases have been converted to their end products, i.e. calcite and quartz. For this case the SDB developed for pure calcite (Tab. 7.2, 4th column) is considered. This SDB is tabulated in the 5th column of Tabs. D1 to D4. It is very difficult to estimate the fraction of calcite formed from the degradation of the C-S-H phase which was formed from the original clay content present in the host rock. As a conservative approach, only the original calcite content in the host rocks is considered and the extra calcite from the C-S-H degradation is not taken into account. The results of the scaling to the calcite contents are tabulated in the 6th column of Tabs. D1 to D4.

From the three SDBs given in Tabs. D1 to D4 (2nd, 4th and 6th columns) the lowest sorption value is selected resulting in the most conservative SDB. These SDBs are given in the last column of Tabs. D1 to D4. With the exception of C_{inorg} , where the R_d values in the undisturbed host rocks are always the lowest, the calcite SDB are the selected values for the scenario where a pH plume has altered the host rock.

D3 Specific comments on Tables D1 to D4

1. The first column lists the elements for which a sorption value has been selected in the host rocks.
2. C_{inorg} is calculated from the calcite content originally present in the host rock.
3. The host rock SDBs list values for U(IV)/(VI) and Pu(III)/(IV) because these elements are calculated in a fully coupled mode at the redox potential of the porewater. The sorption is dominated in all cases by the highest calculated R_d value which are for these elements U(IV) and Pu(III). Only these oxidation states are considered in the pH plume altered SDBs.
4. The calcite contents of the host rocks are taken from mineralogical compositions given in Tabs. 3.4 to 3.7.
5. The calcite SDBs (column 5 in Tabs. D1 to D4) are in situ values, i.e. the Lab to Field transfer factor of 0.05 is considered.
6. The sorption values for the host rock are taken as given in Tabs. 5.6, 5.7, 5.9 and 5.10. The values derived for the CSH and calcite data are calculated to only one decimal place.

Tab. D1: Sorption values selected for altered Effingen Member Calcareous marl sequences (EFF-KMA).

All data in $\text{m}^3 \text{kg}^{-1}$.

Element	EFF-KMA: Reference SDB Tab. 5.6	C-S-H SDB Reducing*		Calcite SDB 57 wt.-% host rock		Selected values
	pH 7.31 and 20.1 wt.-% 2:1 clays	100 wt.-% CSH	27.1 wt.-% CSH (all clays)	100 wt.-% calcite	57 wt.-% calcite	
Be(II)	1.1	0	0	0	0	0
C _{inorg.}	0.036	0.30	0.082	0.063	0.036	0.036
C _{org.}	0	2.2×10^{-5}	5.9×10^{-6}	0	0	0
Cl(-I)	0	0.11	0.029	0	0	0
K(I)	2.1×10^{-3}	2.2×10^{-4}	5.9×10^{-5}	0	0	0
Co(II)	0.37	0.024	6.5×10^{-3}	2.0×10^{-3}	1.1×10^{-3}	1.1×10^{-3}
Ni(II)	0.91	0.024	6.5×10^{-3}	5.0×10^{-4}	2.9×10^{-4}	2.9×10^{-4}
Se(-II)	0	0.65	0.18	0	0	0
Sr(II)	8.8×10^{-5}	0.022	5.9×10^{-3}	5.0×10^{-5}	2.9×10^{-5}	2.9×10^{-5}
Zr(IV)	80	21	5.8	8.5×10^{-4}	4.9×10^{-4}	4.9×10^{-4}
Nb(V)	1.0	2.2	0.59	0	0	0
Mo(VI)	2.1×10^{-3}	0	0	0	0	0
Tc(IV)	0.79	2.2	0.59	0	0	0
Ag(I)	0	0	0	0	0	0
Sn(IV)	63	21	5.8	3.8×10^{-4}	2.2×10^{-4}	2.2×10^{-4}
I(-I)	0	2.2×10^{-3}	5.9×10^{-4}	0	0	0
Cs(I)	0.96	0.011	2.9×10^{-3}	0	0	0
Sm(III)	32	180	49	0.63	0.36	0.36
Eu(III)	8.1	180	49	0.36	0.21	0.21
Pb(II)	1.5	6.5	1.8	0.020	0.011	0.011
Po(IV)	0.80	0	0	4.0×10^{-5}	2.3×10^{-5}	0
Ra(II)	7.1×10^{-5}	0.11	0.029	5.0×10^{-5}	2.9×10^{-5}	2.9×10^{-5}
Ac(III)	9.3	180	49	0	0	0
Th(IV)	77	180	49	0.045	0.026	0.026
Pa(V)	20	180	49	0.046	2.6×10^{-3}	2.6×10^{-3}
U(IV)	5.6	180	49	0.095	0.054	0.054
Np(IV)	80	180	49	0.055	0.031	0.031
Pu(III)	10	180	49	2.0	1.1	1.1
Am(III)	9.3	180	49	1.0	0.57	0.57
Cm(III)	9.3	180	49	0.087	0.50	0.50

* Adapted from Table A2-3 (Reference value) in Wieland (2014) and rescaled from 46 wt.-% to 100 wt.-% CSH.

Tab. D2: Sorption values selected for altered Effingen Member Limestone sequences (EFF-KBA).

All data in $\text{m}^3 \text{kg}^{-1}$.

Element	EFF-KBA: Reference SDB Tab. 5.7	C-S-H SDB Reducing*		Calcite SDB 76 wt.-% host rock		Selected Values
	pH 7.31 and 9.2 wt.-% 2:1 clays	100 wt.-% CSH	12.0 wt.-% CSH (all clays)	100 wt.-% calcite	76 wt.-% calcite	
Be(II)	0.48	0	0	0	0	0
C _{inorg.}	0.048	0.30	0.037	0.063	0.048	0.037
C _{org.}	0	2.2×10^{-5}	2.6×10^{-6}	0	0	0
Cl(-I)	0	0.11	0.013	0	0	0
K(I)	9.6×10^{-4}	2.2×10^{-4}	2.6×10^{-5}	0	0	0
Co(II)	0.17	0.024	2.9×10^{-3}	2.0×10^{-3}	1.5×10^{-3}	1.5×10^{-3}
Ni(II)	0.42	0.024	2.9×10^{-3}	5.0×10^{-4}	3.8×10^{-4}	3.8×10^{-4}
Se(-II)	0	0.65	0.078	0	0	0
Sr(II)	4.0×10^{-5}	0.022	2.6×10^{-3}	5.0×10^{-5}	3.8×10^{-5}	3.8×10^{-5}
Zr(IV)	37	21	2.6	8.5×10^{-4}	6.5×10^{-4}	6.5×10^{-4}
Nb(V)	0.92	2.2	0.26	0	0	0
Mo(VI)	9.8×10^{-4}	0	0	0	0	0
Tc(IV)	0.36	2.2	0.26	0	0	0
Ag(I)	0	0	0	0	0	0
Sn(IV)	29	21	2.6	3.8×10^{-4}	3.2×10^{-4}	3.2×10^{-4}
I(-I)	0	2.2×10^{-3}	2.6×10^{-4}	0	0	0
Cs(I)	0.44	0.011	1.3×10^{-3}	0	0	0
Sm(III)	15	180	22	0.63	0.48	0.48
Eu(III)	3.7	180	22	0.36	0.27	0.27
Pb(II)	0.68	6.5	0.78	0.020	0.015	0.015
Po(IV)	0.15	0	0	4.0×10^{-5}	3.0×10^{-5}	0
Ra(II)	3.2×10^{-5}	0.11	0.013	5.0×10^{-5}	3.8×10^{-5}	3.2×10^{-5}
Ac(III)	4.2	180	22	0	0	0
Th(IV)	35	180	22	0.045	0.034	0.034
Pa(V)	9.1	180	22	4.6×10^{-3}	3.5×10^{-3}	3.5×10^{-3}
U(IV)	2.5	180	22	0.095	0.072	0.072
Np(IV)	37	180	22	0.055	0.042	0.042
Pu(III)	4.6	180	22	2.0	1.5	1.5
Am(III)	4.2	180	22	1.0	0.76	0.76
Cm(III)	4.2	180	22	0.87	0.66	0.66

* Adapted from Table A2-3 (Reference value) in Wieland (2014) and rescaled from 46 wt.-% to 100 wt.-% CSH.

Tab. D3: Sorption values selected for altered Helvetic Marls (MGL).

All data in $\text{m}^3 \text{kg}^{-1}$.

Element	MGL Reference SDB Tab. 5.9	C-S-H SDB Reducing*		Calcite SDB 42 wt.-% host rock		Selected Values
	pH 7.31 and 22 wt.-% 2:1 clays	100 wt.-% CSH	30.3 wt.-% CSH (all clays)	100 wt.-% calcite	42 wt.-% calcite	
Be(II)	0.79	0	0	0	0	0
C _{inorg.}	2.1×10^{-3}	0.30	0.092	5.0×10^{-3}	2.1×10^{-3}	2.1×10^{-3}
C _{org.}	0	2.2×10^{-5}	6.6×10^{-6}	0	0	0
Cl(-I)	0	0.11	0.033	0	0	0
K(I)	3.8×10^{-3}	2.2×10^{-4}	6.6×10^{-5}	0	0	0
Co(II)	0.78	0.024	7.2×10^{-3}	2.0×10^{-3}	8.4×10^{-3}	7.2×10^{-3}
Ni(II)	1.2	0.024	7.2×10^{-3}	5.0×10^{-4}	2.1×10^{-4}	2.1×10^{-4}
Se(-II)	0	0.65	0.20	0	0	0
Sr(II)	1.0×10^{-3}	0.022	6.6×10^{-3}	5.0×10^{-5}	2.1×10^{-5}	2.1×10^{-5}
Nb(V)	1.0	2.2	0.66	0	0	0
Mo(VI)	2.1×10^{-3}	0	0	0	0	0
Ag(I)	0	0	0	0	0	0
Sn(IV)	70	21	6.5	3.8×10^{-4}	1.6×10^{-4}	1.6×10^{-4}
I(-I)	0	2.2×10^{-3}	6.6×10^{-4}	0	0	0
Cs(I)	1.4	0.011	3.3×10^{-3}	0	0	0
Pb(II)	3.0	6.5	2.0	0.020	0.084	0.084
Po(IV)	0.88	0	0	4.0×10^{-5}	1.7×10^{-5}	0
Ra(II)	1.0×10^{-3}	0.11	3.3×10^{-2}	5.0×10^{-5}	2.1×10^{-5}	2.1×10^{-5}
Ac(III)	3.9	180	55	0	0	0
Th(IV)	5.7	180	55	0.045	0.019	0.019
Pa(V)	22	180	55	4.6×10^{-3}	1.9×10^{-3}	1.9×10^{-3}
U(IV)	0.12	180	55	0.095	0.040	0.040
Np(IV)	87	180	55	0.055	0.023	0.023
Pu(III)	4.6	180	55	2.0	0.84	0.84
Am(III)	3.9	180	55	1.0	0.42	0.42
Cm(III)	3.9	180	55	0.87	0.37	0.37

* Adapted from Table A2-3 (Reference value) in Wieland (2014) and rescaled from 46 wt.-% to 100 wt.-% CSH.

Tab. D4: Sorption values selected for altered Helvetic Marls Limestone sequences (MGL-KBA).

All data in $\text{m}^3 \text{kg}^{-1}$.

Element	MGL-KBA: Reference SDB Tab. 5.10	C-S-H SDB Reducing*		Calcite SDB 84 wt.-% host rock		Selected Values
	pH 7.31 and 3.9 wt.-% 2:1 clays	100 wt.-% C-S-H	5.0 wt.-% C-S-H (all clays)	100 wt.-% calcite	84 wt.-% calcite	
Be(II)	0.14	0	0	0	0	0
C _{inorg.}	4.2×10^{-3}	0.30	0.015	5.0×10^{-3}	4.2×10^{-3}	4.2×10^{-3}
C _{org.}	0	2.2×10^{-5}	1.1×10^{-6}	0	0	0
Cl(-I)	0	0.11	5.4×10^{-3}	0	0	0
K(I)	6.8×10^{-4}	2.2×10^{-4}	1.1×10^{-5}	0	0	0
Co(II)	0.14	0.024	1.2×10^{-3}	2.0×10^{-3}	1.7×10^{-3}	1.2×10^{-3}
Ni(II)	0.20	0.024	1.2×10^{-3}	5.0×10^{-4}	4.2×10^{-4}	4.2×10^{-4}
Se(-II)	0	0.65	0.033	0	0	0
Sr(II)	1.8×10^{-4}	0.022	1.1×10^{-3}	5.0×10^{-5}	4.2×10^{-5}	4.2×10^{-5}
Nb(V)	0.39	2.2	0.11	0	0	0
Mo(VI)	3.7×10^{-4}	0	0	0	0	0
Ag(I)	0	0	0	0	0	0
Sn(IV)	12	21	1.1	3.8×10^{-4}	3.2×10^{-4}	3.2×10^{-4}
I(-I)	0	2.2×10^{-3}	1.1×10^{-4}	0	0	0
Cs(I)	0.24	0.011	5.4×10^{-4}	0	0	0
Pb(II)	0.53	6.5	3.3	0.020	0.017	0.017
Po(IV)	0.16	0	0	4.0×10^{-5}	3.4×10^{-5}	0
Ra(II)	1.8×10^{-4}	0.11	5.4×10^{-3}	5.0×10^{-5}	4.2×10^{-5}	4.2×10^{-5}
Ac(III)	0.70	180	9.1	0	0	0
Th(IV)	1.0	180	9.1	0.045	0.038	0.038
Pa(V)	3.9	180	9.1	4.6×10^{-3}	3.9×10^{-3}	3.9×10^{-3}
U(IV)	0.022	180	9.1	0.095	0.080	0.022
Np(IV)	15	180	9.1	0.055	0.046	0.046
Pu(III)	0.82	180	9.1	2.0	1.7	0.82
Am(III)	0.70	180	9.1	1.0	0.84	0.70
Cm(III)	0.70	180	9.1	0.87	0.73	0.70

* Adapted from Table A2-3 (Reference value) in Wieland (2014) and rescaled from 46 wt.-% to 100 wt.-% CSH.

Appendix E Application of the sorption data in the provisional safety analyses for SGT E2

J. Mibus, Nagra

E1 Introduction

This appendix describes how the sorption data sets for host rocks, their confining units and compacted bentonite derived in this report have been selected and applied in the provisional safety analyses for Stage 2 of the Sectoral Plan for Deep Geological Repositories (SGT E2).

The sorption of radionuclides on mineral surfaces of the considered rocks or compacted bentonite, mainly surfaces of clay minerals and in some cases calcite, is one of the key processes providing the radionuclide retardation in the barrier system of a deep geological repository for radioactive waste. The term K_d value used in this appendix and in the provisional safety analyses in Nagra (2014a, b) is considered equivalent to the R_d concept used throughout this report, as both refer to sorption equilibria. The source sorption data in this report are derived from dispersed systems, i.e. from crushed rock samples dispersed in a solution at a low sorbent concentration. For some elements (e.g. Na, Cs, Sr), experiments on argillaceous rocks support the transferability from dispersed to compacted systems (Van Loon et al. 2005, 2009). For other elements (Co, Zn) experiments are in progress within the Catclay project and first results indicate that this approach to a first approximation is applicable also for strongly sorbing tracers.

E2 Reference values and uncertainties

The sorption data sets consist of a reference value and lower bounding values. The data sets are taken from Tab. 5.2 to 5.4 (OPA, BD), 5.6 and 5.7 (EFF), 5.9 and 5.10 (MGL), 6.2 (lower confining units) and 8.6 (bentonite MX-80). The reference value is always taken from the column denoted 'reference'. They refer to the reference mineralogy and the reference porewater. To estimate the uncertainties of the K_d values, an overall uncertainty factor (UF-overall) is derived in Chapter 9. This hostrock specific factor combines the individual uncertainties of the involved parameters (e.g. mineralogy, speciation etc.) by Gaussian error propagation. The overall uncertainty factor does, however, not include the variability of the porewater variants derived by Mäder (2009a,b, 2010) for which individual K_d data sets are calculated in this report besides K_d data sets for the reference porewater. Therefore, the K_d data sets of all porewater variants are divided by the corresponding overall uncertainty factor from Tab. 9.3 to 9.7. This procedure results in a set of lower bounding K_d values, one set for each porewater type.

For host rocks where a 2:1 clay mineral content of zero is given in Traber & Blaser (2013) as lower bounding value, no meaningful uncertainty factor for mineralogy can be calculated. (The numerical calculation of reference value / lower bounding value yields a divide by zero error.) In this case, the complementary approach of sorption on calcite (see Chapter 7) is employed. This concept is independent of the porewater composition. Hence, only a single data set for a generic porewater is given. This data set is considered pessimistic without further application of any uncertainty factor.

As requested in ENSI (2010), all K_d values that are below $10^{-3} \text{ m}^3\text{kg}^{-1}$ in the reference case, are set to zero in the calculation cases that address a pessimistic situation with regard to sorption. Finally, all K_d values are rounded to one significant digit.

E3 Calculation cases

According to ENSI (2010), Nagra is required to analyse a pessimistic situation concerning sorption (so-called 'ENSI case d'). The influence of the porewater composition is complex and different groups of radionuclides exhibit their minimum K_d in different porewaters. For example, radionuclides

undergoing cation exchange are sensitive to salinity whereas transition metals exhibit a strong dependence on pH. Thus, in most cases it is not possible to define a single set of pessimistic K_d values in a consistent way. Therefore, the lower bounding K_d sets of all porewater variants have to be considered in the 'ENSI case d'. For the lower confining units, the procedure is simplified and only the lower bounding value of the reference porewater is considered.

Finally, only the K_d vectors contributing to the minimum K_d of the radionuclides are chosen for the calculation cases. It turned out that the K_d data sets of the following porewaters are not needed in the safety analyses due to the special properties of the porewater variants and the conceptualization of the release pathways:

- The lower bounding values of all reference porewaters of the host rocks (the minimum is defined by the other variants) except for Effingen Member and the lower confining units
- Effingen Member 'Lowest Cl' and 'High SO₄' (the minimum is already defined by the porewater variants 'Reference porewater' and 'High pCO₂')
- Bentonite MX-80 'High porosity' (the difference to the variant with the reference porosity is not significant)
- Helvetic Marls limestone sequences, lower bounding K_d data sets are not needed as this rock unit was not considered in the 'ENSI case d'
- Helvetic Marls 'Vein infill' is eventually not used due to the conceptualization of the host rock (see Nagra 2014a)

E4 Special cases

In the bentonite system, the sorption of inorganic carbon is treated as an isotopic exchange with the calcite contained in small amounts in bentonite. The same process is considered in the calculation of the solubility limits in bentonite in Berner (2014) as so-called 'shared solubilities' between ¹⁴C and stable carbon isotopes. To avoid the consideration of the same process in two parameter sets at the same time, the K_d value of inorganic carbon for bentonite MX-80 is set to zero and only the solubility limit of C_{inorg} is applied (see also Berner 2014).

The sorption of the redox couple U(IV)/(VI) on the argillaceous rocks and on bentonite is calculated for both valence states according to their species distribution in the porewater. This procedure results in different K_d values for each valence state. However, the K_d of U(IV) is two to four orders of magnitude higher than that of U(VI). Consequently, the sorption of U(VI) is conservatively neglected and only the K_d of U(IV) is considered. The same is true for Pu(III)/(IV) where Pu(III) is sorbing stronger and Pu(IV) is being neglected.

To analyse the potential effect of a hyperalkaline fluid from a cement based L/ILW repository on a fractured host rock, a K_d data set for an alternative calculation case 'High-pH plume' is derived in Appendix D. This data set is not considered in the calculation case with pessimistic sorption parameters ('ENSI case d') as the alteration of substantial parts of the host rock by a hyperalkaline fluid is bound to higher advective flux (Kosakowski et al. 2014, Nagra 2014a) which is not part of 'ENSI case d'.

E5 Data compilation

All reference values and lower bounding values for the host rocks, confining rocks and bentonite are compiled in Tab. E1 to E5 in this appendix. Data sets that were not used in the safety analysis are indicated in italics. To facilitate the transfer of the data sets from this report to the calculation cases described in Nagra (2014a), an identification code (ID) is assigned to each K_d data set per rock unit or bentonite (consisting of 'S' for sorption and a running number). In Nagra (2014a) only the data sets used in the calculation cases are reprinted (featuring the same ID as in this appendix) and the exact allocation of a data set to a specific calculation case is explained there. In general, it was required that

host rocks and confining rocks which, according to the conceptualization of the release pathways in Nagra (2014a), are assessed in combination (e.g. Toniger Lias, Opalinus Clay, 'Brauner Dogger' and Effingen Member), are combined in a geochemically meaningful way, e.g. by a combination of all 'High pCO₂' or all 'High salinity' variants of the porewaters in one calculation case. If this is not possible, as in the case of Effingen Member where no 'Low pCO₂' porewater is defined, the corresponding lower bounding value of the reference porewater of Effingen Member is used.

E6 References

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Tab. E1: Sorption coefficients K_d [m³/kg] for Opalinus Clay and Bentonite MX-80 (reference values and lower bounding values for different porewaters).

Data sets eventually not needed in the dose calculations are indicated in *italics*.

ID	Opalinus Clay										Bentonite MX-80									
	Reference value			Lower bounding value			Reference porewater				Reference value			Lower bounding value						
	SI	S2	S3	S4	S5	SI	S1	S2	S3	S4	S5	S6	SI	S1	S2	S3	S4	S5	S6	
Be(II)	1E+00	3E-01	4E-01	4E-01	4E-01	2E+00	5E-01	2E+00	2E+00	5E-01	2E+00	5E-01	2E+00	5E-01	2E+00	2E+00	5E-01	2E+00	5E-01	2E+00
C _{inorg}	1E-03	2E-04	8E-04	9E-04	4E-04	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
C _{org}	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cl(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
K(I)	5E-03	8E-04	8E-04	4E-04	8E-04	7E-03	1E-03	2E-03	2E-03	1E-03	7E-03	1E-03	2E-03	2E-03	1E-03	2E-03	6E-04	1E-03	1E-03	1E-03
Ca(II)	6E-04	0E+00	0E+00	0E+00	0E+00	2E-03	4E-04	0E+00	0E+00	4E-04	2E-03	1E-04	1E-03	1E-03	1E-04	1E-03	1E-04	4E-04	4E-04	4E-04
Co(II)	7E-01	1E-01	3E-01	1E-01	2E-01	4E-01	1E-01	4E-01	4E-01	1E-01	4E-01	9E-02	3E-01	3E-01	9E-02	1E-01	9E-02	1E-01	1E-01	1E-01
Ni(II)	1E+00	4E-01	4E-01	3E-01	4E-01	1E+00	3E-01	1E+00	1E+00	3E-01	1E+00	3E-01	1E+00	3E-01	1E+00	1E+00	3E-01	4E-01	4E-01	4E-01
Se(-II)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sr(II)	6E-04	0E+00	0E+00	0E+00	0E+00	2E-03	4E-04	0E+00	0E+00	4E-04	2E-03	1E-04	1E-03	1E-03	1E-04	1E-03	1E-04	4E-04	4E-04	4E-04
Zr(IV)	1E+02	3E+01	4E+01	3E+01	3E+01	1E+03	3E+02	1E+03	1E+03	3E+02	1E+03	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02
Nb(V)	1E+00	2E-01	2E-01	2E-01	2E-01	1E+00	2E-01	1E+00	1E+00	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01
Mo(VI)	4E-03	9E-04	6E-04	9E-04	8E-04	1E-02	4E-03	1E-02	1E-02	4E-03	1E-02	4E-03	1E-02	1E-02	4E-03	2E-03	4E-03	3E-03	3E-03	3E-03
Tc(IV)	1E+00	3E-01	3E-01	3E-01	3E-01	3E+00	1E+00	3E+00	3E+00	1E+00	3E+00	1E+00	1E+00	1E+00	3E+00	1E+00	1E+00	1E+00	1E+00	1E+00
Pd(II)	3E+01	8E+00	9E+00	7E-01	9E+00	6E+01	2E+01	6E+01	6E+01	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01
Ag(I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sn(IV)	1E+02	3E+01	3E+01	3E+01	3E+01	8E+02	3E+02	8E+02	8E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02	3E+02
I(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cs(I)	2E+00	3E-01	3E-01	2E-01	3E-01	3E-02	5E-03	3E-02	3E-02	5E-03	3E-02	2E-03	7E-03	2E-03	2E-03	7E-03	2E-03	5E-03	5E-03	5E-03
Sm(III)	1E+01	2E+00	7E+00	4E+00	3E+00	3E+01	4E+00	3E+01	3E+01	4E+00	3E+01	1E+01	4E+01	4E+01	1E+01	4E+01	1E+01	8E+00	8E+00	8E+00
Eu(III)	6E+00	8E-01	2E+00	1E+00	1E+00	1E+01	2E+00	3E+01	3E+01	2E+00	1E+01	3E+00	1E+01	3E+00	3E+00	3E+01	3E+00	3E+00	3E+00	3E+00
Hg(III)	1E+01	1E+00	5E+00	3E+00	2E+00	3E+01	3E+00	3E+01	3E+01	2E+00	3E+01	9E+00	3E+01	9E+00	6E+00	6E+00	6E+00	6E+00	6E+00	6E+00
Pb(II)	7E+00	1E+00	2E+00	4E-01	2E+00	1E+01	4E-01	1E+01	1E+01	2E+00	1E+01	7E-01	5E+00	5E+00	3E+00	5E+00	7E-01	3E+00	3E+00	3E+00
Po(IV)	5E-01	5E-02	5E-02	5E-02	5E-02	1E+00	1E-01	1E+00	1E+00	1E-01	1E+00	1E-01	1E-01	1E-01	1E-01	1E-01	1E-01	1E-01	1E-01	1E-01
Ra(II)	4E-04	0E+00	0E+00	0E+00	0E+00	1E-03	2E-04	1E-03	1E-03	2E-04	1E-03	9E-05	6E-04	6E-04	2E-04	9E-05	2E-04	2E-04	2E-04	2E-04
Ag(III)	7E+00	8E-01	2E+00	1E+00	1E+00	8E+01	8E+00	8E+01	8E+01	8E+00	8E+01	1E+01	3E+01	3E+01	1E+01	3E+01	1E+01	1E+01	1E+01	1E+01
Th(IV)	4E+01	1E+00	5E+00	7E+00	2E+00	8E+01	2E+00	8E+01	8E+01	2E+00	2E+00	2E+01	2E+01	2E+01	2E+01	2E+01	2E+01	5E+00	5E+00	5E+00
Pa(V)	3E+01	2E+00	2E+00	2E+00	2E+00	8E+01	4E+00	8E+01	8E+01	4E+00	8E+01	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00
U(VI)	2E-01	8E-03	1E-01	2E-01	2E-02	4E-01	1E-02	4E-01	4E-01	1E-02	4E-01	5E-01	6E-01	6E-01	5E-01	6E-01	5E-01	5E-02	4E-02	4E-02
Np(IV)	1E+02	4E+01	4E+01	4E+01	4E+01	6E+01	1E+02	4E+02	4E+02	1E+02	6E+01	1E+02	1E+02	1E+02	1E+02	1E+02	1E+02	1E+02	1E+02	1E+02
Pu(III)	7E+00	8E-01	3E+00	1E+00	1E+00	8E+01	7E+00	6E+01	6E+01	7E+00	3E+01	1E+01	3E+01	3E+01	1E+01	3E+01	1E+01	1E+01	1E+01	1E+01
Am(III)	7E+00	8E-01	2E+00	1E+00	1E+00	8E+01	8E+00	8E+01	8E+01	8E+00	3E+01	1E+01	3E+01	3E+01	1E+01	3E+01	1E+01	1E+01	1E+01	1E+01
Cm(III)	7E+00	8E-01	2E+00	1E+00	1E+00	8E+01	8E+00	8E+01	8E+01	8E+00	3E+01	1E+01	3E+01	3E+01	1E+01	3E+01	1E+01	1E+01	1E+01	1E+01

Tab. E2: Sorption coefficients K_d [m^3/kg] for 'Brauner Dogger' Clay-rich sequences and Sandy limestone sequences (reference values and lower bounding values for different porewaters).

Data sets eventually not needed in the dose calculations are indicated in italics.

ID	'Brauner Dogger' Clay-rich sequences										'Brauner Dogger' Sandy limestone sequences				
	Reference value		Lower bounding value					Reference value			Lower bounding value				
	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Be(II)	1E+00	1E-01	2E-01	2E-01	2E-01	3E-01	3E-02	4E-02	4E-02	4E-02	3E-01	3E-02	4E-02	4E-02	4E-02
C_{inorg}	3E-03	3E-04	9E-04	1E-03	5E-04	4E-03	4E-04	1E-03	1E-03	1E-03	4E-04	1E-03	1E-03	1E-03	6E-04
C_{org}	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cl(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
K(I)	4E-03	4E-04	4E-04	2E-04	4E-04	1E-03	1E-04	1E-04	1E-04	1E-04	1E-04	1E-04	6E-05	1E-04	1E-04
Ca(II)	5E-04	0E+00	0E+00	0E+00	0E+00	1E-04	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Co(II)	5E-01	5E-02	1E-01	4E-02	8E-02	1E-01	1E-02	1E-02	1E-02	1E-02	3E-02	3E-02	1E-02	1E-02	2E-02
Ni(II)	1E+00	2E-01	2E-01	1E-01	2E-01	3E-01	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	4E-02
Se(-II)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sr(II)	5E-04	0E+00	0E+00	0E+00	0E+00	1E-04	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Zr(IV)	1E+02	1E+01	2E+01	1E+01	1E+01	3E+01	3E+00	3E+00	3E+00	3E+00	3E+00	4E+00	3E+00	3E+00	3E+00
Nb(V)	1E+00	1E-01	1E-01	1E-01	1E-01	7E-01	7E-02	7E-02	7E-02	7E-02	7E-02	7E-02	7E-02	7E-02	7E-02
Mo(VI)	3E-03	4E-04	3E-04	4E-04	4E-04	8E-04	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Tc(IV)	1E+00	1E-01	1E-01	1E-01	1E-01	3E-01	3E-02	3E-02	3E-02	3E-02	4E-02	4E-02	4E-02	4E-02	4E-02
Pd(II)	3E+01	4E+00	4E+00	3E-01	4E+00	7E+00	9E-01	9E-01	9E-01	9E-01	1E+00	1E+00	8E-02	1E+00	1E+00
Ag(I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sn(IV)	8E+01	1E+01	1E+01	1E+01	1E+01	2E+01	3E+00	3E+00	3E+00	3E+00	3E+00	3E+00	3E+00	3E+00	3E+00
I(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cs(I)	2E+00	2E-01	2E-01	1E-01	2E-01	4E-01	4E-01	4E-01	4E-01	4E-01	4E-01	4E-02	3E-02	4E-02	4E-02
Sm(III)	1E+01	8E-01	3E+00	2E+00	1E+01	3E+00	2E-01	2E-01	2E-01	2E-01	9E-01	9E-01	5E-01	4E-01	4E-01
Eu(III)	5E+00	4E-01	1E+00	6E-01	6E-01	1E+00	1E+00	1E+00	1E+00	1E+00	3E-01	3E-01	1E-01	2E-01	2E-01
Ho(III)	9E+00	6E-01	2E+00	2E+00	1E+00	2E+00	2E+00	2E+00	2E+00	2E+00	6E-01	6E-01	4E-01	3E-01	3E-01
Pb(II)	6E+00	7E-01	9E-01	2E-01	7E-01	1E+00	1E+00	1E+00	1E+00	1E+00	1E+00	1E+00	1E-01	2E-01	2E-01
Po(IV)	4E-01	3E-02	3E-02	3E-02	3E-02	1E-01	7E-03	7E-03	7E-03	7E-03	7E-03	7E-03	7E-03	7E-03	7E-03
Ra(II)	4E-04	0E+00	0E+00	0E+00	0E+00	9E-05	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Ac(III)	6E+00	4E-01	1E+00	6E-01	6E-01	2E+00	1E-01	1E-01	1E-01	1E-01	3E-01	3E-01	2E-01	2E-01	2E-01
Th(IV)	3E+01	6E-01	3E+00	4E+00	1E+00	8E+00	2E-01	2E-01	2E-01	2E-01	7E-01	7E-01	1E+00	3E-01	3E-01
Pa(V)	3E+01	9E-01	9E-01	9E-01	9E-01	7E+00	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01	2E-01
U(IV)	2E-01	4E-03	5E-02	9E-02	1E-02	4E-02	1E-03	1E-03	1E-03	1E-03	1E-03	1E-02	2E-02	3E-03	3E-03
Np(IV)	1E+02	2E+01	2E+01	2E+01	2E+01	3E+01	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00	4E+00
Pu(III)	6E+00	4E-01	1E+00	6E-01	6E-01	2E+00	1E-01	1E-01	1E-01	1E-01	3E-01	3E-01	2E-01	2E-01	2E-01
Am(III)	6E+00	4E-01	1E+00	6E-01	6E-01	2E+00	1E-01	1E-01	1E-01	1E-01	3E-01	3E-01	2E-01	2E-01	2E-01
Cm(III)	6E+00	4E-01	1E+00	6E-01	6E-01	2E+00	1E-01	1E-01	1E-01	1E-01	3E-01	3E-01	2E-01	2E-01	2E-01

Tab. E3: Sorption coefficients K_d [m^3/kg] for Effingen Member Calcareous marl sequences and Limestone sequences (reference values, lower bounding values for different porewaters and alternative calculation cases).

Data sets eventually not needed in the dose calculations are indicated in italics; n.a.: not applicable.

ID	Effingen Member Calcareous marl sequences						Effingen Member Limestone sequences		
	Reference porewater	Lower bounding value			Alternative calculation case 'High-pH-plume'	Reference porewater	Reference value	Lower bounding value	
		Reference porewater	High pCO_2	Low Cl				High SO_4	Generic porewater
Be(II)	1E+00	3E-01	2E-01	3E-01	0E+00	5E-01	0E+00	0E+00	0E+00
C_{inorg}	4E-02	1E-02	3E-03	5E-03	4E-02	5E-02	4E-02	5E-02	4E-02
C_{org}	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cl(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
K(I)	2E-03	3E-04	7E-04	3E-04	0E+00	1E-03	0E+00	0E+00	0E+00
Ca(II)	9E-05	0E+00	0E+00	0E+00	n.a. ¹	4E-05	0E+00	0E+00	n.a. ¹
Co(II)	4E-01	1E-01	1E-01	1E-01	1E-03	2E-01	2E-03	2E-03	2E-03
Ni(II)	9E-01	2E-01	2E-01	2E-01	3E-04	4E-01	4E-04	4E-04	4E-04
Se(-II)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sr(II)	9E-05	0E+00	0E+00	0E+00	3E-05	4E-05	0E+00	0E+00	4E-05
Zr(IV)	8E+01	2E+01	2E+01	2E+01	5E-04	4E+01	6E-04	6E-04	7E-04
Nb(V)	1E+00	2E-01	2E-01	2E-01	0E+00	9E-01	0E+00	0E+00	0E+00
Mo(VI)	2E-03	4E-04	5E-04	4E-04	0E+00	1E-03	0E+00	0E+00	0E+00
Tc(IV)	8E-01	2E-01	2E-01	2E-01	0E+00	4E-01	0E+00	0E+00	0E+00
Pd(II)	8E-00	6E-01	1E+00	8E-01	n.a. ¹	4E+00	3E-02	3E-02	n.a. ¹
Ag(I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sn(IV)	6E+01	2E+01	2E+01	2E+01	2E-04	3E+01	3E-04	3E-04	3E-04
I(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cs(I)	1E+00	1E-01	4E-01	2E-01	0E+00	4E-01	0E+00	0E+00	0E+00
Sm(III)	3E+01	6E+00	3E+00	4E+00	4E-01	1E+01	5E-01	5E-01	5E-01
Eu(III)	8E+00	2E+00	9E-01	1E+00	2E-01	4E+00	3E-01	3E-01	3E-01
Ho(III)	3E+01	5E+00	2E+00	3E+00	n.a. ¹	1E+01	1E-01	1E-01	n.a. ¹
Pb(II)	1E+00	4E-01	1E+00	6E-01	1E-02	7E-01	2E-02	2E-02	2E-02
Po(IV)	3E-01	3E-02	3E-02	3E-02	0E+00	1E-01	3E-05	3E-05	0E+00
Ra(II)	7E-05	0E+00	0E+00	0E+00	3E-05	3E-05	0E+00	0E+00	3E-05
Ac(III)	9E+00	2E+00	9E-01	1E+00	0E+00	4E+00	0E+00	0E+00	0E+00
Th(IV)	8E+01	2E+01	1E+01	2E+01	3E-02	4E+01	3E-02	3E-02	3E-02
Pa(V)	2E+01	9E-01	9E-01	9E-01	3E-03	9E+00	3E-03	3E-03	4E-03
U(IV)	6E+00	6E-01	5E-02	1E-01	5E-02	3E+00	1E-02	1E-02	7E-02
Np(IV)	8E+01	2E+01	2E+01	2E+01	3E-02	4E+01	4E-02	4E-02	4E-02
Pu(III)	1E+01	2E+00	5E-01	1E+00	1E+00	5E+00	2E+00	2E+00	2E+00
Am(III)	9E+00	1E+00	5E-01	1E+00	6E-01	4E+00	8E-01	8E-01	8E-01
Cm(III)	9E+00	1E+00	5E-01	1E+00	5E-01	4E+00	7E-01	7E-01	7E-01

Tab. E4: Sorption coefficients K_d [m^3/kg] for Helvetic Marls and Helvetic Marls Limestone sequences (reference values, lower bounding values for different porewaters and alternative calculation cases).

Data sets eventually not needed in the dose calculations are indicated in italics.

ID	Helvetic Marls						Helvetic Marls Limestone sequences									
	Reference value		Lower bounding value				Reference value		Lower bounding value				Alternative calculation case			
	Reference porewater	S1	High pCO_2	Low pCO_2	Low $p\epsilon$	High NaCl	Reference porewater	S7	S6	High pCO_2	Low pCO_2	Low $p\epsilon$	High NaCl	Reference porewater	S7	S6
Be(II)	8E-01	5E-02	1E-01	9E-02	1E-01	1E-01	1E-01	9E-03	3E-02	2E-02	2E-02	2E-02	2E-02	2E-02	2E-02	0E+00
C_{inorg}	2E-03	9E-05	8E-04	2E-04	5E-04	5E-04	4E-03	2E-04	2E-03	5E-04	1E-03	1E-03	1E-03	5E-04	5E-04	4E-03
C_{org}	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cl(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
K(I)	4E-03	3E-04	3E-04	3E-04	1E-04	1E-04	7E-04	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Co(II)	8E-01	4E-02	3E-01	5E-03	4E-02	4E-02	1E-01	7E-03	5E-02	9E-04	8E-03	2E-02	2E-02	2E-02	1E-03	1E-03
Ni(II)	1E+00	1E-01	2E-01	3E-04	1E-01	1E-01	2E-01	2E-02	3E-02	5E-05	2E-02	2E-02	2E-02	2E-02	4E-04	4E-04
Se(II)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sr(II)	1E-03	7E-05	9E-05	7E-05	2E-05	2E-05	2E-04	0E+00	0E+00	8E-05	8E-05	0E+00	0E+00	0E+00	4E-05	4E-05
Nb(V)	1E+00	9E-02	9E-02	9E-02	9E-02	9E-02	4E-01	4E-02	4E-02	4E-02	4E-02	4E-02	4E-02	4E-02	0E+00	0E+00
Mo(VI)	2E-03	3E-04	1E-04	2E-04	3E-04	3E-04	4E-04	0E+00	0E+00	2E-04	2E-04	0E+00	0E+00	0E+00	0E+00	0E+00
Ag(I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sr(IV)	7E+01	8E+00	8E+00	8E+00	8E+00	8E+00	1E+01	1E+00	1E+00	1E+00	1E+00	1E+00	1E+00	1E+00	3E-04	3E-04
I(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cs(I)	1E+00	1E-01	1E-01	1E-01	4E-02	4E-02	2E-01	2E-02	2E-02	2E-02	2E-02	2E-02	2E-02	2E-02	0E+00	0E+00
Pb(II)	3E+00	2E-01	5E-01	3E-01	2E-01	2E-01	5E-01	3E-02	8E-02	3E-01	3E-01	3E-01	3E-01	3E-01	2E-02	2E-02
Po(IV)	4E-01	2E-02	2E-02	2E-02	2E-02	2E-02	6E-02	3E-03	3E-03	3E-03	3E-03	3E-03	3E-03	3E-03	0E+00	0E+00
Ra(II)	1E-03	7E-05	8E-05	7E-05	1E-05	1E-05	2E-04	0E+00	0E+00	8E-05	8E-05	0E+00	0E+00	0E+00	4E-05	4E-05
Ac(III)	4E+00	8E-02	9E-01	3E-01	5E-01	5E-01	7E-01	1E-02	1E-02	8E-02	8E-02	8E-02	8E-02	8E-02	0E+00	0E+00
Th(IV)	6E+00	3E-02	1E+00	2E-01	8E-01	8E-01	1E+00	5E-03	2E-01	3E-02	1E-01	3E-02	1E-01	4E-02	4E-02	4E-02
Pa(V)	2E+01	8E-01	7E-01	8E-01	8E-01	8E-01	4E+00	1E-01	1E-01	1E-01	1E-01	1E-01	1E-01	1E-01	4E-03	4E-03
U(IV)	1E-01	4E-04	4E-02	1E-01	1E-02	1E-02	2E-02	7E-05	7E-03	7E-03	7E-03	7E-03	7E-03	7E-03	2E-02	2E-02
Np(IV)	9E+01	6E+00	1E+01	1E+01	1E+01	1E+01	2E+01	1E+00	2E-00	2E-00	2E-00	2E-00	2E-00	2E-00	5E-02	5E-02
Pu(III)	5E+00	1E-01	1E+00	5E-01	7E-01	7E-01	8E-01	8E-01	2E-01	9E-01	9E-01	9E-01	9E-01	9E-01	8E-01	8E-01
Am(III)	4E+00	8E-02	9E-01	3E-01	5E-01	5E-01	7E-01	1E-02	2E-01	5E-02	5E-02	5E-02	5E-02	6E-02	7E-01	7E-01
Cm(III)	4E+00	8E-02	9E-01	3E-01	5E-01	5E-01	7E-01	1E-02	2E-01	5E-02	5E-02	5E-02	5E-02	6E-02	7E-01	7E-01

Tab. E5: Sorption coefficients K_d [m^3/kg] for the lower confining units of Opalinus Clay (reference values and lower bounding values).

In rock units of the lower confining units not presented here, sorption is not considered.

ID	'Toniger Lias'		'Kalkiger Lias' and 'Arietenkalk'		'Toniger Keuper'	
	Reference value	Lower bounding value	Reference value	Lower bounding value	Reference value	Lower bounding value
	Reference porewater	Reference porewater	Reference porewater	Generic porewater	Reference porewater	Reference porewater
Be(II)	S1 1E+00	S2 3E-01	S1 3E-01	S2 0E+00	S1 2E+00	S2 4E-01
C _{inorg}	3E-03	9E-04	9E-03	9E-03	1E-03	0E+00
C _{org}	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cl(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
K(I)	4E-03	6E-04	1E-03	0E+00	6E-03	9E-04
Ca(II)	5E-04	0E+00	1E-04	0E+00	7E-04	0E+00
Co(II)	5E-01	1E-01	1E-01	2E-03	8E-01	2E-01
Ni(II)	1E+00	3E-01	3E-01	4E-04	2E+00	4E-01
Se(-II)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sr(II)	5E-04	0E+00	1E-04	0E+00	7E-04	0E+00
Zr(IV)	9E+01	2E+01	3E+01	7E-04	1E+02	3E+01
Nb(V)	1E+00	2E-01	7E-01	0E+00	1E+00	2E-01
Mo(VI)	3E-03	6E-04	8E-04	0E+00	4E-03	9E-04
Tc(IV)	9E-01	2E-01	3E-01	0E+00	1E+00	4E-01
Pd(II)	2E+01	7E+00	7E+00	3E-02	4E+01	1E+01
Ag(I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Sn(IV)	8E+01	2E+01	2E+01	3E-04	1E+02	3E+01
I(-I)	0E+00	0E+00	0E+00	0E+00	0E+00	0E+00
Cs(I)	2E+00	2E-01	4E-01	0E+00	2E+00	4E-01
Sm(III)	1E+01	2E+00	3E+00	5E-01	2E+01	4E+00
Eu(III)	4E+00	1E+00	1E+00	3E-01	7E+00	1E+00
Ho(III)	8E+00	2E+00	2E+00	1E-01	1E+01	3E+00
Pb(II)	5E+00	1E+00	1E+00	2E-02	8E+00	2E+00
Po(IV)	4E-01	4E-02	1E-01	3E-05	6E-01	5E-02
Ra(II)	3E-04	0E+00	9E-05	0E+00	5E-04	0E+00
Ac(III)	5E+00	9E-01	2E+00	0E+00	8E+00	1E+00
Th(IV)	3E+01	2E+00	8E+00	4E-02	4E+01	3E+00
Pa(V)	2E+01	1E+00	7E+00	4E-03	4E+01	2E+00
U(IV)	2E-01	2E-02	4E-02	1E-03	2E-01	3E-02
Np(IV)	1E+02	3E+01	3E+01	4E-02	2E+02	4E+01
Pu(III)	5E+00	1E+00	2E+00	2E+00	8E+00	2E+00
Am(III)	5E+00	9E-01	2E+00	8E-01	8E+00	1E+00
Cm(III)	5E+00	9E-01	2E+00	7E-01	8E+00	1E+00