



TECHNICAL REPORT 02-19

Far-Field Sorption Data Bases for Performance Assessment of a High-Level Radioactive Waste Repository in an Undisturbed Opalinus Clay Host Rock

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

PREFACE

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra).

The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

NOTE: The Nagra Technical Report contains in addition an addendum.

Therein the parameters are presented which were used for radionuclide transport calculations in Opalinus Clay within the safety assessment of the Project Opalinus Clay (Entsorgungsnachweis). The origin of the data and their documentation are explained.

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ABSTRACT

An Opalinus Clay formation in the Zürcher Weinland is under consideration by Nagra as a potential location for a high-level and long-lived intermediate-level radioactive waste repository. Performance assessment studies will be performed for this site and the purpose of this report is to describe the procedures used to develop sorption data bases appropriate for an undisturbed Opalinus Clay host rock which are required for such safety analysis calculations.

In tight, low water content argillaceous rock formations such as Opalinus Clay, there is uncertainty concerning the in situ pH/ P_{CO_2} . In order to take this intrinsic uncertainty into account porewater chemistries were calculated for a reference case, pH = 7.24, and for two other pH values, 6.3 and 7.8. Sorption data bases are given for the three cases.

The basis for the sorption data bases is “in-house” sorption measurements for Cs(I), Sr(II), Ni(II), Eu(III), Sn(IV), Se(IV), Th(IV) and I(-I) carried out on Opalinus Clay samples from Mont Terri (Canton Jura) since at the time the experiments were performed no core samples from the Benken borehole (Zürcher Weinland) were available. The Opalinus Clay at Mont Terri and Benken are part of the same geological formation.

Despite having directly measured data for the above key radionuclides, some of the required distribution ratios (R_d) used to generate the sorption data bases still came from the open literature. An important part of this report is concerned with describing the procedures whereby these selected literature R_d values were modified so as to apply to the Benken Opalinus Clay mineralogy and groundwater chemistries calculated at the three pH values given above. The resulting R_d values were then further modified using so-called Lab→Field transfer factors to produce sorption values which were appropriate to the in situ bulk rock for the selected range of water chemistry conditions.

Finally, it is important to have some appreciation of the uncertainties associated with the selected R_d values in the sorption data bases. An attempt has been made in the report to move away from the unsatisfactory “realistic/conservative” terminology and to develop a procedure for estimating uncertainty in a transparent and traceable manner.

ZUSAMMENFASSUNG

Eine Opalinuston-Formation im Zürcher Weinland wird von der Nagra als potentieller Standort für ein geologisches Tiefenlager für verglaste hochradioaktive Abfälle sowie langlebige mittelradioaktive Abfälle in Betracht gezogen. Hierzu werden standortspezifische Sicherheitsanalysen durchgeführt, für deren Berechnungen Sorptionsdatenbanken benötigt werden. In diesem Bericht werden die Verfahren beschrieben, die für die Erstellung einer geeigneten Sorptionsdatenbank für ein ungestörtes Opalinuston-Wirtsgestein angewendet wurden.

In dichten Tongesteinen mit niedrigem Wassergehalt, wie zum Beispiel dem Opalinuston, besteht eine systembedingte Unsicherheit bezüglich der in-situ pH/PCO₂-Bedingungen. Um diese zu berücksichtigen, wird die Porenwasserchemie bei verschiedenen pH-Werten gerechnet. Neben einem Referenzfall mit einem pH-Wert von 7.24 werden zwei weitere pH-Werte von 6.3 und 7.8 betrachtet. Für alle drei Fälle wird jeweils eine Sorptionsdatenbank erstellt.

Als Grundlage für die Sorptionsdatenbanken dienen am PSI durchgeführte Sorptionsmessungen für Cs(I), Sr(II), Ni(II), Eu(III), Sn(IV), Th(IV) und I(-I). Sie wurden an Opalinuston-Gesteinsproben aus dem Felslabor Mont Terri (Kanton Jura) durchgeführt, da zur Zeit der Experimente noch keine Bohrkerne aus Benken (Zürcher Weinland) vorhanden waren. Der Opalinuston an beiden Standorten ist jedoch Teil der gleichen geologischen Formation.

Trotz der direkt gemessenen Daten für die oben erwähnten Schlüssel-Radionuklide musste ein Teil der benötigten Verteilungskoeffizienten (R_d) aus der offenen Literatur entnommen werden, um die Sorptionsdatenbank zu erstellen. Dieser Bericht beschreibt das Vorgehen, mit welchem die ausgewählten Literaturwerte an die Mineralogie und Grundwasserchemie des Opalinustons von Benken angepasst wurden. Die resultierenden R_d -Werte wurden durch sogenannte Labor→Feld Transferfaktoren weiter modifiziert, um Sorptionswerte zu liefern, die für das "in-situ" Gestein und für den gewählten Bereich der hydrochemischen Bedingungen gelten.

Die gewählten R_d -Werte in den Sorptionsdatenbanken sind mit Unsicherheiten behaftet, die es schlüssig zu beurteilen gilt. Im vorliegenden Bericht wird versucht, von der Terminologie "realistisch/konservativ" insofern abzurücken, als dass ein Verfahren entwickelt wird, welches eine Abschätzung der Unsicherheiten auf transparente und nachvollziehbare Weise erlaubt.

RÉSUMÉ

La formation d'Argiles à Opalinus située dans le Weinland zurichoïse, est actuellement étudiée par la Nagra dans le cadre de ses recherches relatives à un site de dépôt pour les assemblages combustibles usés, les déchets de haute activité vitrifiés et les déchets de moyenne activité à vie longue. Des études d'évaluation de la sûreté seront réalisées pour ce site. Ce rapport décrit les procédures suivies pour développer les bases de données de sorption nécessaires pour évaluer la sûreté de la formation non perturbée d'Argiles à Opalinus en tant que roche d'accueil.

Dans des formations argileuses denses, à faible teneur en eau, telles que les Argiles à Opalinus, des incertitudes subsistent quant au rapport $\text{pH}/\text{P}_{\text{CO}_2}$ *in situ*. Afin de prendre en compte cette incertitude intrinsèque, la composition chimique des eaux interstitielles a été calculée pour une situation de référence où le $\text{pH} = 7.24$, et pour deux autres pH , à savoir 6.3 et 7.8. Les bases de données de sorption sont fournies pour les trois hypothèses.

Les bases de données reposent sur des mesures effectuées "en interne" pour Cs(I), Sr(II), Ni(II), Eu(III), Sn(IV), Se(IV), Th(IV) et I(-I) sur des échantillons d'Argiles à Opalinus provenant du Mont Terri (canton du Jura), du fait que les échantillons de Benken dans le Weinland zurichoïse n'étaient pas encore disponibles au moment où les expériences ont été réalisées. Les Argiles à Opalinus du Mont Terri et de Benken appartiennent à la même formation géologique.

Pour les principaux radionucléides énumérés ci-dessus, les mesures ont été effectuées directement; toutefois, dans d'autres cas, des mesures issues de publications existantes ont dû être utilisées pour générer les bases de données. Une part importante de ce rapport est consacrée à la description des procédures utilisées pour ajuster ces données à la minéralogie et à la composition chimique de l'eau interstitielle des Argiles à Opalinus du Weinland zurichoïse, pour les trois pH mentionnés ci-dessus. Les valeurs de R_d obtenues ont elles-mêmes été modifiées par le biais de facteurs de transfert dits "Laboratoire→Terrain" afin d'obtenir des données de sorption appropriées pour la formation *in situ*, pour la gamme choisie de conditions hydrochimiques.

Enfin, il est important de pouvoir mettre en perspective les incertitudes associées aux coefficients de distribution définis dans les bases de données de sorption. Ce rapport se distancie de la terminologie "hypothèse réaliste / hypothèse conservatrice", qui n'est pas vraiment satisfaisante, et tente de mettre au point une procédure qui permette d'évaluer les incertitudes d'une manière transparente et vérifiable.

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1 INTRODUCTION

An Opalinus Clay (OPA) formation is under consideration as a potential host rock for the deep disposal of high-level radioactive waste and spent fuel. In order to be able to assess their suitability, detailed performance assessment (PA) studies are carried out (NAGRA, 2002a,b). Sorption data bases (SDBs) which provide values for the uptake of radionuclides on the immobile solids in the near- and far-field are an important component in such safety studies. This report documents the procedure whereby sorption values for the OPA far-field are derived.

A series of selection procedures and methodologies were developed and described in some earlier SDB work for the Palfris marl formation at Wellenberg (BRADBURY & BAEYENS, 1997a). Much of this methodology will be taken over here and applied to OPA. Common topics, discussed in detail in the above mentioned report will only be referred to, but key features of the process will be given for completeness. A number of differences and refinements to the previous work have been introduced in the case of OPA and these are discussed in detail.

In argillaceous rock formations, in situ water samples representative of those in tight intact rock are exceedingly difficult to obtain. Consequently, there is an intrinsic uncertainty in the system pH/P_{CO₂} and hence in any reference water chemistry proposed. In order to take this inherent uncertainty into account, sorption values for each element under consideration are given for two pH values (and corresponding water chemistries) which are approximately one pH unit above and below that in the chosen reference case.

Briefly, the approach adopted is to select the “best available laboratory sorption values” from “in-house” and literature data which are the most appropriate for the OPA/groundwater systems given in Chapter 2. Many factors play a role in the choices made and the main ones are discussed in BRADBURY & SAROTT (1994). An additional consideration, a “selection hierarchy”, is discussed in Chapter 4. The initial selected values are then modified to the mineralogical and groundwater characteristics of the OPA system, see Chapter 5, to provide “in situ sorption values”.

Although SDBs are composed of simple solid/liquid distribution ratios, R_d values:

$$R_d = \frac{\text{quantity of a radionuclide sorbed per unit mass}}{\text{equilibrium concentration of radionuclide}} \quad [\text{m}^3 \text{ kg}^{-1}] \quad (1)$$

the processes of selection often involve considerations of, for example, sorption mechanisms, isotherm data and trace element concentrations in the groundwater. That

is to say, the selections are based on a broad understanding of the system and the processes taking place. In many cases the choice of a single sorption value can be justified on the basis of the prevailing conditions even though the particular radionuclide may well exhibit complex and generally non-linear sorption characteristics.

A SDB consists of distribution ratios and it is important to have some appreciation of the uncertainty associated with the selected values. This point is one which is almost never addressed directly. It is mostly circumvented by the "realistic/conservative" terminology. These terms have never been quantitatively defined anywhere, which leaves them open to almost any interpretation and can lead to misunderstandings. If previous SDBs are examined, it turns out in practice that "conservative values" are about a factor of five.. or ten.. or twenty.. less than "realistic values" (see for example MCKINLEY & HADERMANN, 1984; STENHOUSE, 1995, ANDERSSON & GRUNDTEKNIK, 1999). Satisfactory explanations are never given as to where these factors come from and why they are different for different radionuclides. An attempt has been made in this report to develop a procedure for estimating uncertainty in a transparent and traceable manner although, it is freely admitted, a fully consistent overall methodology has not yet been achieved.

Finally, one part of the repository is designed to take long-lived intermedium level waste (ILW) and transuranic contaminated (TRU) wastes and will contain large quantities of cements and concretes. The interaction of these cementitious materials with the groundwater could give rise to a pulse of hyperalkaline fluid moving into the host rock. The potential influence of this "pH plume" on the radionuclide retention characteristics of the OPA is not considered here but is treated separately in another report (BRADBURY & BAEYENS, 2003).

2 THE REFERENCE OPA SYSTEM

2.1 Mineralogy and groundwater chemistry

The reference Benken OPA mineralogy is given in NAGRA (2002a) and is reproduced in Table 1. A reference mineralogy for OPA from Mont Terri previously defined by WABER et al. (1998) is also included in this table for comparative reasons. The in-house sorption measurements were carried out on OPA samples from Mont Terri. As can be seen from this table the mineral modal compositions in both OPA sediments are similar but variations do exist in the wt. % values.

Table 1: Reference mineralogies for Opalinus Clay from Benken NAGRA (2002a) and Mont Terri (WABER et al., 1998).

Minerals	Benken OPA (wt. %)	Mont Terri OPA (wt. %)
Calcite	16	11
Dolomite/Ankerite	1	0.6
Siderite	4	2.7
Quartz	20	18
K-Feldspar	2	1.2
Albite	1	1.4
Pyrite	1.1	1.8
Illite	18	28
Illite/Smectite ML	14	8
Kaolinite	17	17
Chlorite	5	10
Organic Carbon	0.6	0.9

Table 2 (first column with figures) gives the Benken OPA reference groundwater chemistry as defined by NAGRA (2002a). As stated in the Introduction, the pH (and hence the water composition) of the OPA system is an intrinsically uncertain quantity and this is taken into account in the development of SDBs by considering a range of pH values, 6.8 to 8.2, which bracket the selected reference value, 7.24 (NAGRA, 2002a). The in-house sorption measurements were carried out on the Mont Terri system (LAUBER et al., 2000) and were completed long before the Benken reference water chemistry became available in April 2001. The in-house experimental data were generated at pH = 6.3 and 7.8 and the water chemistries given in Table 2 (second and

third column) are calculated for the Benken OPA system at the above pH values (PEARSON, 2002). The distribution ratios given in the SDBs are derived for these three water chemistries.

Table 2: Reference OPA groundwater composition at pH = 7.24 (NAGRA, 2002a), and groundwater compositions calculated at pH = 6.3 and 7.8 (PEARSON, 2002).

pH	7.24	6.3	7.8
P _{CO₂} (bar)	10 ^{-2.20}	10 ^{-0.37}	10 ^{-3.31}
Eh (V)	-0.167	-0.104	-0.205
I.S. (M)	0.23	0.24	0.23
Temperature (°C)	25	25	25
Dissolved constituents (M)			
Na	1.69 x 10 ⁻¹	1.79 x 10 ⁻¹	1.67 x 10 ⁻¹
K	5.65 x 10 ⁻³	5.98 x 10 ⁻³	5.61 x 10 ⁻³
Mg	7.48 x 10 ⁻³	8.67 x 10 ⁻³	7.36 x 10 ⁻³
Ca	1.05 x 10 ⁻²	1.23 x 10 ⁻²	1.03 x 10 ⁻²
Sr	3.04 x 10 ⁻⁴	3.59 x 10 ⁻⁴	2.98 x 10 ⁻⁴
Alkalinity as HCO ₃ ⁻	2.50 x 10 ⁻³	1.96 x 10 ⁻²	7.25 x 10 ⁻⁴
C _{inorg.}	2.70 x 10 ⁻³	3.41 x 10 ⁻²	7.18 x 10 ⁻⁴
S(VI) as SO ₄ ²⁻	2.40 x 10 ⁻²	2.40 x 10 ⁻²	2.40 x 10 ⁻²
S(-II) as H ₂ S	1.41 x 10 ⁻¹¹	3.12 x 10 ⁻¹¹	1.36 x 10 ⁻¹¹
F	1.67 x 10 ⁻⁴	1.63 x 10 ⁻⁴	1.67 x 10 ⁻⁴
Cl	1.60 x 10 ⁻¹	1.60 x 10 ⁻¹	1.60 x 10 ⁻¹
Br	2.40 x 10 ⁻⁴	2.40 x 10 ⁻⁴	2.40 x 10 ⁻⁴
Fe (total)	4.33 x 10 ⁻⁵	6.53 x 10 ⁻⁵	4.14 x 10 ⁻⁵
Mn (total)	2.42 x 10 ⁻⁵	3.55 x 10 ⁻⁵	2.32 x 10 ⁻⁵
Al (total)	1.78 x 10 ⁻⁸	4.86 x 10 ⁻⁸	7.28 x 10 ⁻⁸
U (total)	6.96 x 10 ⁻⁹	6.82 x 10 ⁻⁷	1.32 x 10 ⁻⁹
Si (total) as SiO ₂ aq.	1.78 x 10 ⁻⁴	1.77 x 10 ⁻⁴	1.80 x 10 ⁻⁴

2.2 Cation exchange capacity

From a large number of cation exchange capacity (CEC) measurements carried out on OPA samples from Benken, NAGRA (2002a) proposed a reference CEC value of 0.106 eq. kg⁻¹. In comparison, a value of 0.12 eq. kg⁻¹ for OPA samples from Mont Terri has been measured (LAUBER et al., 2000).

2.3 Redox

The estimated redox potentials for the Benken OPA reference systems are given in Table 2, NAGRA (2002a). The minerals controlling the redox are considered to be pyrite and siderite.

2.4 Organics

WABER et al. (1998) report that dissolved organic carbon (DOC) contents varied considerably in water samples taken at Mont Terri and that they tended to decrease with time after the drilling of the bore hole. It appears therefore that part of the DOC most probably arises from contamination but these authors do raise the issue of the presence of humic substances, which are strong complexants, particularly with trivalent rare earth and actinide metals (GLAUS et al., 1997, 2000; HUMMEL et al., 2000). GLAUS et al. (2001) carried out a series of experiments with aqueous extracts from OPA samples from Mont Terri and Benken containing DOC. The sorption of Ni(II), Eu(III) and Th(IV) on a cation exchange medium in the absence and presence of these extracts was measured. The conclusion drawn was that the dissolved organic substances did not have any significant effect on sorption for the investigated radionuclides. In some previous work on OPA samples from Mont Terri LAUBER et al. (1998) came to the same conclusions.

2.5 Colloids

From "in situ" measurements made at the Mont Terri rock laboratory DEGUELDRE et al. (1997) estimated colloid concentrations in groundwater samples to range from 2 to 200 ng L⁻¹. Such low colloid concentrations are compatible with the high salinity of the OPA groundwater which tends to enhance particle coagulation and increase the sticking probability on the rock.

3 BACKGROUND

3.1 General

When setting up a SDB for any host rock formation, it is never the case that all of the sorption values required have been measured on that particular rock/groundwater system. Some specific "in-house" measurements may be available, but much of the data will inevitably come from the open literature.

The rock mineralogies and water chemistries used in experiments to generate the sorption data reported in the literature will not generally be the same as those defined for the reference OPA system, Chapter 2. Some means is therefore required to either justify the use of literature sorption data directly for OPA or a chemically reasonable procedure needs to be defined by which the literature data can be modified to correspond to OPA conditions. Before discussing this topic in detail in Chapter 5, some background information is required regarding sorption mechanisms, "data selection hierarchy" and the use of chemical analogues in selecting sorption values.

In the following, the uptake of radionuclides onto the OPA surfaces at (generally) trace concentrations ($<10^{-6}$ M) is interpreted in terms of one of two mechanisms: (i) cation exchange and (ii) surface complexation. Sorption values are selected at trace concentrations since under these conditions the uptake of sorbate tends to a Langmuir type behaviour, i.e. at low enough concentration the sorption becomes linear. Further, it is proposed that the clay mineral components are essentially responsible for the sorption characteristics of OPA. Even with these assumptions the majority of (quasi) mechanistic models are not yet sufficiently advanced to calculate sorption values directly in real systems nor can the influence of water chemistry changes and variations in mineralogy be calculated specifically. Rather, by viewing sorption in terms of these uptake models, trends and insights into the important processes can be identified which in turn allow deductions to be made concerning how sorption depends on some key system parameters.

3.2 Cation exchange

Cation exchange on clay minerals has been extensively studied (see for example BOLT, 1982; BRUGGENWERT & KAMPHORST, 1982) and can contribute significantly to radionuclide sorption depending on the conditions. Sorption by this mechanism is characterised by a strong dependency on ionic strength/solution composition and a weak dependency on pH and is usually of the Langmuir type. A cation exchange sorption model has been developed to describe the sorption of Cs on argillaceous rock types where the major sorbing mineral component is illite, BRADBURY & BAEYENS

(2000). Selectivity coefficient data have also been deduced for K-Na, Ca-Na and Mg-Na exchange equilibria from experimental data on marls and OPA rocks (BAEYENS & BRADBURY, 1991, 1994; BRADBURY & BAEYENS, 1997b, 1998a). A high degree of confidence exists in these models and parameters since they have been tested over a wide range of different conditions. Thus, sorption values on OPA for the alkaline and alkaline-earth metals can be calculated specifically for the reference water compositions using sorption models, taking into account natural background element concentrations where necessary.

3.3 Surface complexation

Many radionuclides can be taken up on the amphoteric hydroxyl surface functional groups ($\equiv\text{SOH}$) of iron, silica and alumina phases (see for example STUMM et al., 1970; SCHINDLER et al., 1976; SPOSITO, 1984; DAVIS & KENT, 1990; DZOMBAK & MOREL, 1990). Considerably less is known about the uptake of radionuclides on the edge sites of clay minerals. Sorption studies of Ni, Zn and Eu on montmorillonite (BAEYENS & BRADBURY, 1995a,b, 1997; BRADBURY & BAEYENS, 1995, 1997c, 2002), or Mo on clay minerals (MOTTA & MIRANDA, 1989), however, clearly showed that under certain conditions (pH, ionic strength) these nuclides are taken up by the surface via a surface complexation or a ligand exchange mechanism. Surface complexation by a radionuclide at such sites is normally characterised by a strong dependency on pH, a weak dependency on ionic strength and a strong dependency on sorbate concentration. Cations such as Ca, Sr, Mg, Na, K are not generally competitive with the specifically sorbing heavy metals, transition metals, lanthanides and actinides for the surface sites. Thus major groundwater cations do not usually influence sorption by surface complexation.

3.3.1 Sorption of cationic species

Generally speaking, pH is probably the single most important parameter influencing the uptake of aqueous metal species via a surface complexation mechanism and can have a very significant influence on the magnitude of sorption. Exactly how sorption varies with pH is strongly dependent on sorbent and sorbate (see BRADBURY & BAEYENS (1995) and section 5.2.1 in this report for more details).

3.3.2 Sorption of anionic species

Anions can sorb at edge sites on clay minerals by ligand exchange with the hydroxyl surface functional groups (GOLDBERG & GLAUBIG, 1986; DAVIS & KENT, 1990). The sorption behaviour shows two clear features: (i) sorption increases with decreasing pH

and (ii) sorption exhibits a Langmuir type behaviour (MOTTA & MIRANDA, 1989). Again, the parameter of most importance is the pH.

3.4 Temperature

The temperature considered in this work is 25 °C. That is to say, the sorption values in the SDB and the constants in the TDB used in speciation calculations refer to this temperature. The OPA formation temperature is 38 °C.

There is little or no information available in the open literature on temperature effects and their potential influence was not considered in the report.

4 SELECTION AND SELECTION PRIORITIES

4.1 Background

In the past when sorption data were selected for inclusion in SDBs there was almost always the tendency to choose "conservatively". For example, when very large values for R_d were measured in laboratory experiments, say $100 \text{ m}^3 \text{ kg}^{-1}$, such a value was not generally selected. Rather, a lower value was chosen without stating any particular reason for doing so (see for example ALLARD, 1985). This immediately introduces a "hidden conservatism" into the selection process. In the above example a value of $5 \text{ m}^3 \text{ kg}^{-1}$ might typically have been selected on the basis that the measured values are "very high" and $5 \text{ m}^3 \text{ kg}^{-1}$ is "still high enough". Clearly, transparency and traceability are lost in this procedure because measured values were often reduced by random factors which were never stated but based rather on what was felt to be "right".

In this report, the "best available sorption values" are selected and these measured R_d values appear in the sorption data sheets under "selected $R_{d \text{ lit}}$ ". However, these measured data do not go into the SDB directly, but are only a starting point for a process which converts them to new values corresponding to the OPA "in situ" conditions, see Chapter 5. Uncertainties associated with the original data and the "tailoring" procedures used are estimated in Chapter 6.

4.2 Data sources and selection hierarchy

The first step in the procedure is to select the "best available" sorption data from laboratory measurements which are the most appropriate for the reference OPA/groundwater system. As discussed in BRADBURY & SAROTT (1994) many factors play a role in the choices made, but "expert judgement" remains an important component. Documentation of the sources of sorption data used and the processes by which data selections were made ("transparency" and "traceability") are particularly relevant since this allows the quality of the expert judgement to be independently assessed and evaluated. A "hierarchy" for the selection of laboratory sorption values has been introduced in this report which is based on the degree of confidence the authors had in the data from the various sources.

"In-house" data

Clearly first priority is given to "in-house" sorption isotherm measurements carried out under chemically similar conditions to those believed to exist "in situ". Isotherm determinations which yield a consistent picture of sorption over a range of concentrations bring with them a confidence in the measurements which cannot be

there to the same degree when only single point values are measured. Further, isotherm data allow different sorption behaviour in different concentration ranges to be identified (linear Langmuir type; non-linear Freundlich type) which can in principle be linked up with the source term radionuclide concentrations. In most cases selections of R_d values have been made at "trace concentrations" (generally $< 10^{-6}$ M) in the linear part of the sorption isotherm.

A programme of sorption measurements (kinetics, isotherms) was carried out at PSI on OPA samples from Mt. Terri for 7 key radionuclides (Cs(I), Sr(II), Ni(II), Eu(III), Th(IV), Sn(IV) and Se(IV)) in synthetic high ionic strength (I.S. = 0.3 M) NaCl-type porewaters at pH = 6.3 (± 0.1) and 7.8 (± 0.2) (Table 3). These data sets form a very important component in the following part of the report describing the derivation of a SDB for OPA.

Table 3: Synthetic OPA porewater compositions used in the sorption measurements for Cs(I), Sr(II), Ni(II), Eu(III), Sn(IV), Th(IV), I(-I) and Se(IV) on OPA from Mont Terri.

	T ~ 25 °C pH = 6.3 $P_{CO_2} = 10^{-0.68}$ bar I.S. = 0.27 M	T ~ 25 °C pH = 7.8 $P_{CO_2} = 10^{-3.97}$ bar I.S. = 0.38 M
Element	Concentration (M)	Concentration (M)
Na	1.82×10^{-1}	2.46×10^{-1}
K	4.10×10^{-3}	5.80×10^{-3}
Mg	1.40×10^{-2}	2.14×10^{-2}
Ca	1.85×10^{-2}	2.85×10^{-2}
Sr	2.10×10^{-4}	2.50×10^{-4}
F	1.10×10^{-4}	1.10×10^{-4}
Cl	1.86×10^{-1}	3.00×10^{-1}
SO ₄	2.80×10^{-2}	2.60×10^{-2}
C _{inorg.}	1.70×10^{-2}	1.78×10^{-4}
Si	1.77×10^{-4}	1.79×10^{-4}

Illite data

The next type of preferred data are sorption isotherm measurements on illite, which is a major clay mineral component of OPA (see Table 1). The measurement conditions for such single mineral investigations are often well defined, which is important, since it allows the tailoring procedures to be applied with more certainty.

Argillaceous rock systems

Sorption measurements on argillaceous rock systems geochemically similar to that of OPA are also a good source of data if the experimental system is well defined. Unfortunately, the uncertainties associated with such data are often much larger than in the case of studies on illites. In many cases incomplete sets of water chemistry, mineralogies and/or CEC values are given which makes it difficult to modify the sorption to the OPA conditions. Also, sorption isotherms are seldom measured. Additional sources of uncertainty concern the organic matter often present in argillaceous rocks. A portion is normally soluble and in most cases the influence of this on the experimental sorption data remains unquantified.

Single point measurements

Finally, there are single point measurements in which sorption has been determined under one set of conditions at a single concentration. From the point of view of selecting sorption values for a SDB, such data must be viewed as being considerably less useful than isotherm data and must be assigned considerably greater uncertainties. Sometimes the system has been well characterised and the experimental conditions well specified, and in these cases the data can be used. Often, however, the reverse is true and the sorption data can only be taken to give a qualitative idea of whether the sorption is strong or weak.

4.3 Chemical Analogues

Sometimes reliable sorption data for a particular radionuclide are not available at all. The only option then is to select a chemical analogue for which sorption data are available and make a selection on this basis. However, it is necessary to define clearly how chemical analogy is applied in practice for this purpose.

Radionuclide sorption depends on many factors, but the principal ones are:

- site capacity of the sorbing sites on the solid,
- the affinity of these sites for the radionuclide. (This is usually expressed in terms of a selectivity coefficient or an intrinsic surface complexation constant.),
- aqueous speciation, since this can effect the concentration of the sorbing species in solution,
- water composition e.g. concentration of inactive isotopes of the radionuclide; concentration of competing species,
- pH/Eh,
- radionuclide concentration.

Generally, two nuclides are taken to be chemically analogous because they belong to the same group in the periodic table and exhibit similar aqueous speciation behaviour. This is then taken to imply that they exhibit the same sorption behaviour.

However, such an assumption is not necessarily valid.

Chemical analogy as far as sorption is concerned implies that under the same chemical conditions the same types of aqueous species are taken up by the same solid surface. This is distinctly different from saying that the sorption is the same, because even when sorbing species and binding constants are similar, the aqueous speciation can still have a strong influence on the R_d values and must be taken into account. In other words it is important to consider aqueous speciation under the particular reference case conditions when applying chemical analogy for sorption data.

5 CONVERSION FACTORS

In setting up SDBs, literature data are always required. The following sections describe proposals for modifying literature sorption data so that they apply to the in situ OPA. Note that in the following the subscript “lit.” is used as a general designation referring to the source data whether they be “in house” data “, literature data, chemical analogue data etc.

In general, it is important to try to identify the most probable dominant sorption mechanism for each particular radionuclide, since the influence of water chemistry on sorption is strongly linked to the mechanism. A mechanistic approach and the development of thermodynamic sorption models are used (at the moment) predominantly to interpret laboratory experiments, gain insights into the processes occurring and as a tool to better understand sorption and the main factors which influence it. The models are not yet sufficiently advanced to be used in PA calculations directly. (In any event, the transport codes used in PA still require distribution ratios, though they may be radionuclide dependent, as input parameters.) A (quasi) mechanistic approach to sorption enables the selection of values for SDBs to be better justified and defended through an increased understanding of the underlying processes.

5.1 Mineralogy

The major mineral components in OPA are clay minerals (notably illite, illite/smectite mixed layers, kaolinite and chlorite) and carbonates, see Chapter 2. For sorption occurring by cation exchange and/or surface complexation, the uptake of radionuclides is most likely to be dominated by the clay minerals. Selected literature sorption values, whether measured on illites, or sediments/ argillaceous rocks are scaled to the OPA mineralogy over their respective CEC values. The reasons are as follows.

The selectivity coefficients governing sorption on the planar sites of different clay minerals of the “tetrahedral-octahedral-tetrahedral” (TOT or 2:1) type such as illite and smectite, or illite/smectite mixed layers are very similar to a first approximation (BRUGGENWERT & KAMPHORST, 1982). The CEC is a measure of the overall capacity of such sites and if cation exchange is the main sorption mechanism then it is also a good measure of the magnitude of sorption (BOLT et al., 1976).

In the case when sorption is dominated by surface complexation, the scaling is still done over the CEC. It has been generally observed that the surface complexation site capacity for many clay minerals is approximately 10 % of the CEC e.g. GRIM (1953);

YARIV & CROSS (1979); BAEYENS & BRADBURY (1995a). Thus the total $\equiv\text{SOH}$ site capacities of different rocks, and thereby the sorption, should also be proportional to their respective CEC values.

However, it is not known a priori which particular $\equiv\text{SOH}$ type sites associated with which clay mineral are predominantly responsible for the radionuclide uptake. If the modal clay mineral compositions of the argillaceous rocks from which the sorption data are taken are similar to that of OPA, then this is not a major problem since the radionuclides will distribute themselves in a similar manner between the available sites in both cases. However, if the clay mineral modal compositions are very different, then scaling over the CEC may be less defensible.

Thus, where cation exchange is the main uptake mechanism, it is helpful but not imperative that the clay mineral modal compositions are similar, whereas for sorption via a surface complexation mechanism it is much more relevant.

In the cases where the sorption data were taken from measurements on illite scaling was carried out over the OPA CEC. (Scaling over the illite mass fraction (with the exception of Cs, see section 7.1) was considered to be overly conservative since this would ignore the contribution from the other clay minerals). The assumption here is that the other clay minerals behave similarly to illite with respect to sorption. The other important clay mineral component is illite-smectite mixed layers and this exhibits generally stronger sorption characteristics than illite.

The conversion factor which takes into account the differences in mineralogy between the reference OPA and the literature solid phase is given by an equation of the form:

$$CF_{\text{CEC}} = \frac{\text{CEC}_{\text{ref}}}{\text{CEC}_{\text{lit}}} \quad (2)$$

where,

CF_{CEC} = mineralogy conversion factor

CEC_{ref} = CEC value for the OPA reference mineralogy

CEC_{lit} = CEC value of the source material.

5.2 Water chemistry

5.2.1 pH

When cation sorption at trace concentrations is investigated at high ionic strength as a function of pH in clay mineral systems it is almost invariably observed, except for

alkaline and alkaline-earth metals, that a strong increase in sorption occurs somewhere in the pH range from approximately 5 to 10. For clay minerals such as illite and montmorillonite it has been experimentally observed that the slope of this “sorption edge”, expressed in the form of $\log R_d$ versus pH, has a value of approximately unity i.e. the distribution coefficient within the sorption edge increases (decreases) by about one order of magnitude for each unit increase (decrease) in pH (see for example O’CONNOR & KESTER, 1975; BANGASH et al., 1992; GORGEON, 1994; BAEYENS & BRADBURY, 1997, POINSSOT et al., 1999a).

For the OPA, in cases where the uptake of radionuclides is via surface complexation on clay minerals, it is proposed to modify sorption values for differences in pH using a pH conversion factor (CF_{pH}) defined as the ratio of distribution coefficients at the reference pH (pH_{ref}) and the measurement pH (pH_{lit}) as read off from the appropriate sorption edge on illite (see Figure 1 below), i.e. $R_{d, pH\ ref}$ and $R_{d, pH\ lit}$ respectively.

$$CF_{pH} = \frac{R_{d, pH\ ref}}{R_{d, pH\ lit}} \quad (3)$$

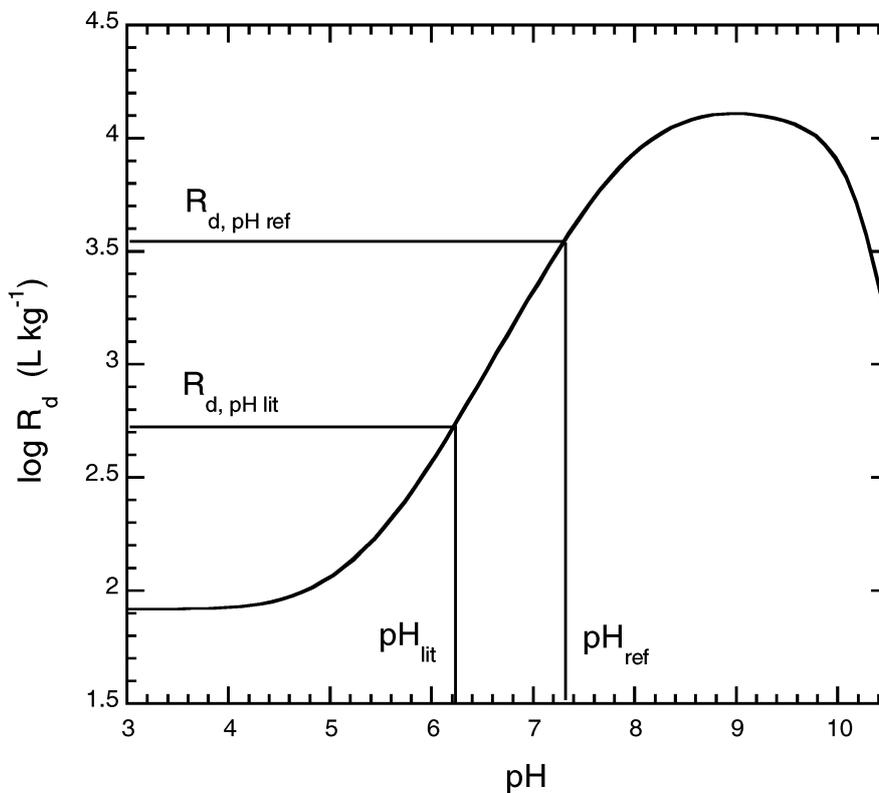


Figure 1: Schematic sorption edge indicating distribution ratios corresponding to (pH_{ref}) and (pH_{lit}) for a particular radionuclide.

In cases where no appropriate sorption edges on illite are available pH correction is carried out by using the principle of chemical analogy. There are examples in the literature of sorption edges of transition metals and heavy metals on calcite (ZACHARA et al., 1991), oxides (DZOMBAK & MOREL, 1990) and clay minerals (BAEYENS & BRADBURY, 1995b) which show that the slope of the edges are similar, but they are displaced from each other. It is thus possible to use the slope of a sorption edge of a certain transition metal for making pH corrections for an other transition element according to the method described above. In the case of Co and Pb a sorption edge of Ni on illite was used.

Although there is good experimental evidence to support the general trends in sorption behaviour with pH given above, the influence of pH on sorption is strongly system dependent and pH conversion factors can be large. In general, it is better to avoid the need for such a conversion factor altogether. Hence, sorption data measured at or near to the three pH values of interest (7.24, 6.3 and 7.8) were selected wherever possible.

5.2.2 Speciation

The complexation of radionuclides with inorganic and organic ligands can influence sorption and therefore corrections need to be made which reflect this when the water chemistries used in the literature measurements and the OPA reference water are different. (This is almost always the case.) A rigorous correction is only possible when a verified sorption model is available, and as stated previously, this is generally not the case. Nevertheless some attempt should be made to correct for different water chemistries.

In oxide and clay mineral systems it is widely observed that the formation of positively charged or neutral hydrolysed species does not adversely influence sorption behaviour. Indeed, very high metal sorption is often measured in regions where neutral hydroxy species dominate. (See for example SCHULTESS & HUANG, 1990; GORGEON, 1994; TURNER et al., 1998.) (Whether other neutral and positively charged complexes can also be taken up by sorbents is less clear, but must remain 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 is to define free cation, positively charged and neutral hydrolysed species as being sorbing. All other species are treated as being non-sorbing.

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

$$CF_{\text{speciation}} = \frac{F_{\text{ref}}}{F_{\text{lit}}} \quad (4)$$

where

$CF_{\text{speciation}}$ is the speciation conversion factor.

F_{lit} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the source sorption measurements.

F_{ref} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the OPA groundwater at the reference pH, and at the upper or lower bound pH values considered.

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 new updated Nagra/PSI thermodynamic data base (HUMMEL et al., 2002) has been used throughout this report. A compilation of the results of all the speciation calculations is given in a separate technical report (THOENEN, 2002).

5.2.3 Chemical analogues

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

$$CF_{\text{analogue}} = \frac{F_{\text{nuclide}}}{F_{\text{analogue}}} \quad (5)$$

where

CF_{analogue} is the chemical analogue conversion factor.

F_{nuclide} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the OPA groundwater at the reference pH, and at the upper or lower bound pH values considered.

F_{analogue} is the fraction of the chemical analogue concentration calculated to be present in the aqueous phase as sorbing species in the OPA groundwater at the reference pH, and at the upper or lower bound pH values considered.

5.3 Lab→Field

The general applicability of batch sorption data to intact rock systems and proposals how to modify measurements on crushed rock so that they are applicable to the "in situ" case have been fully addressed in BRADBURY & BAEYENS (1997a, Chapter 7) and in BRADBURY & BAEYENS (1998b). In this work the Lab→Field transfer factor was calculated from N₂-BET surface area data measured on intact rock and then again on the same sample but in a crushed state and the transfer factor defined as:

$$\text{Lab} \rightarrow \text{Field} = \frac{(\text{N}_2 - \text{BET area})_{\text{intact rock}}}{(\text{N}_2 - \text{BET area})_{\text{crushed rock}}} \quad (6)$$

Since then no new information on this topic has been published which changes the general conclusions given there. Consequently a Lab→Field conversion factor of unity was chosen for OPA.

5.4 Rounding

The in situ R_d values for OPA are the product of the individual selected R_d values and their respective conversion factors. For transparency and traceability reasons these calculated values have not been rounded.

6 UNCERTAINTY FACTORS

6.1 General

It is common practice to present errors in data as a plus/minus fraction of a value, $X \pm \Delta X$, i.e. a symmetric uncertainty. However, in the following uncertainties are given in terms of factors, e.g. Y . A best estimate value, X , with an uncertainty factor Y , implies that the range of values for this parameter varies from $X \cdot Y$ to X/Y . The uncertainty in this representation is non-symmetric. The reason for choosing this form of presentation is that the authors believe that it gives a better "feel" for the limits within which a certain value is to be viewed. Also, it is immediately apparent from where the major uncertainty arises. For example, if

$A = B \times C \times D$, with uncertainty factors f_B, f_C, f_D , then the uncertainty in A, f_A , is simply

$$f_A = f_B \times f_C \times f_D$$

Thus it is easy to see which terms are contributing the most to the overall uncertainty.

The above also implies that where symmetric errors in data are given, these have to be converted to non-symmetric uncertainty factors, and an approximation has to be made. The procedure is best illustrated by an example.

Let $A = B \times C$

$B = 5 \pm 1$ and $C = 10 \pm 3$

Error in A is then, $\pm 50 \times \{(1/5)^2 + (3/10)^2\}^{1/2} = \pm 18$

i.e. $A = 50 \pm 18$

Thus the extreme values of A are 68 and 32, which is approximately 50 within a factor of 1.4.

6.2 Selected laboratory values: Uncertainty factor- $R_{d \text{ lit}}$

"In-house" data

The uncertainties associated with "in-house" data 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. An experimental study in which Ni sorption on Na-montmorillonite was measured as a function of pH at trace concentrations under nominally similar conditions at intervals over an 18 month period produced an uncertainty in the $\log R_d$ values of ± 0.2 log units (BAEYENS & BRADBURY, 1995b). This latter estimate is considered to be realistic and therefore an uncertainty factor of 1.6 is assigned to "in-house" measurements.

Model calculations

In the cases of Cs, Ca, Sr and Ra the sorption values were derived from model calculations. In the original publications 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 in situ R_d values for the above elements.

Literature: Sorption isotherm data on illite

The uncertainties associated with sorption values originating from well defined, thorough investigations on illite are most probably comparable with "in-house" measurements. Thus an uncertainty factor of 1.6 is also assigned in this case.

Literature: Sorption data on argillaceous/sedimentary rocks

In the remaining case where sorption data are deduced from similar argillaceous rock systems, estimates of uncertainties are much more difficult to define in a logical manner. The quality of the measurements themselves is one thing. Their appropriateness to the OPA system is another. In these two cases in particular, other information may have to be considered.

When the reported measurements are carried out on a well-characterised system, experimental procedures are fully described and values for key parameters are given, then this is usually an indication that the data have been well measured. If in addition sorption has been measured as a function of concentration then there is no reason to believe that the measurements are more uncertain than the "in-house" ones.

Such data are therefore assigned an uncertainty factor of 1.6. (Considerations such as whether natural organics, for example, might be exerting an (unknown) influence on literature data is not a consideration in this context since if this were to be suspected, then the data would not have been selected.)

If only single point measurements have been made it is difficult to put the datum into a context. In the case of isotherms for example, each measured value stands in the context of the other measured values and can, at least in part, be judged from the scatter of the data and the form of the overall curve. Thus the quality of single point R_d values are very difficult to judge and only a qualitative impression can be gained from the write up of the experimental methodology, system characterisation etc. It is however clear that single point sorption values have to be treated as being significantly more uncertain than other data sources.

As always, each case has to be examined individually.

6.3 Mineralogy: Uncertainty factor-CEC

Conversions of sorption values to systems with different mineralogies are carried out over the respective CEC values (see section 5.1). The error in CEC data can be up to $\pm 20\%$ which implies that an uncertainty factor of ~ 1.3 would be associated with such a conversion. In the cases where sorption measurements are carried out on OPA from Mont Terri, no mineralogical uncertainty factor is considered because of the very similar mineralogy. OPA from Mont Terri and Benken are part of the same formation.

6.4 Speciation: Uncertainty factor-speciation

HUMMEL & BERNER (2002) have tried to evaluate the potential uncertainty in the speciation conversion factor, and came to the conclusion that to a first approximation a factor of 2 exists between the highest and lowest value. This implies an uncertainty factor of 1.4 in the speciation conversion factor. However, it should be realised that the assessment of an uncertainty associated with this conversion factor is very difficult, and is strongly dependent on the completeness and quality of the TDB used.

6.5 pH: Uncertainty factor-pH

The pH conversion factors are calculated from appropriate sorption edges and defined in section 5.2.1 as the quotient of the distribution ratios at the literature pH and reference pH respectively. As the uncertainty factor in each of the R_d values was estimated to be 1.6 (see above), then it follows that the overall error in the pH conversion factor is a factor of 2.6.

6.6 Lab→Field transfer factor: Uncertainty factor-Lab→Field

N_2 -BET measurements on crushed and intact OPA samples indicate a Lab→Field transfer factor (TF) of approximately unity (see BRADBURY & BAEYENS, 1998b).

However all surfaces accessible to N_2 may not be accessible to radionuclides. What then is the uncertainty?

Some first hand knowledge comes from the Grimsel migration tests and the associated laboratory experiments on granitic rock material. From the "in situ" measurements, the best estimates for the TF corresponding to the intact granodiorite was approximately 0.1 (BRADBURY & BAEYENS, 1997a). This is in good agreement with the estimate from the N_2 -BET measurements (see the discussion in Chapter 7 in BRADBURY & BAEYENS 1997a, and BRADBURY & BAEYENS, 1998b).

For the fracture infill, the best estimate for the TF from the migration experiments was 0.2 to 0.4 (HADERMANN, pers. comm.). This slightly higher value can be rationalised in terms of the more disaggregated nature of this material compared with granodiorite and that the porosity is ~10 % instead of ~1 %.

A TF of approximately 0.25 was derived from laboratory CEC measurements (BAEYENS et al., 1989) and estimated CEC values for the in situ material (EIKENBERG et al., 1991). The laboratory CEC data were determined on crushed material < 63 μm whereas the material in the migration fracture is very heterogeneous in size, with biotite and muscovite grains having dimensions of millimetres. This probably explains the differences in CEC values in the two cases.

The situation for OPA is somewhat different. For example, the material from Benken has relatively high porosities (10 to 15 %) and high clay mineral contents (18 wt. % illite, 14 wt. % mixed layers, 17 wt.% kaolinite, and 5 wt.% chlorite) for which the platelet sizes are of the order of microns. For OPA, crushing is not likely to lead to any significant change in areas nor to any significant changes in the clay mineral surfaces which are essentially responsible for the uptake of radionuclides. The N_2 -BET measurements indicate that the clay mineral external surface areas available in the intact OPA are very much the same as in the crushed material (BRADBURY & BAEYENS, 1998b). The lowest TF measured for an argillaceous rock was 0.4 for a Valanginian marl sample. This low value may be related to a combination of low porosity and a high quartz and carbonate content of ~ 65 wt. %.

The external surfaces within argillaceous rocks are certainly more accessible than those in granodiorite because of their general mineralogy, particularly their high clay mineral content, structure and higher porosities (BRADBURY & BAEYENS, 1998b) i.e. the TF for OPA must be significantly greater than for granodiorite/fracture infill material. The N_2 -BET measurements on OPA yield a value of unity, which represents the best currently available estimate. The uncertainty on this value is difficult to

quantify but on the basis of the above discussion the TF is unlikely to be less than 0.5. Consequently the latter value is taken as a lower bound, and the uncertainty factor for the Lab→Field transfer factor is taken to be 2.

6.7 Chemical analogues

Where chemical analogy is invoked for a particular radionuclide, the same overall uncertainty factor as that given for the chemical analogue is taken multiplied by the speciation UF.

6.8 Overall uncertainty factors

Four conversion factors are proposed to scale the selected literature sorption values to sorption values appropriate for the in situ OPA conditions. The equation used to scale the literature sorption data to the OPA in situ sorption data is given by the following relationship:

$$R_{d \text{ in situ}} = R_{d \text{ lit.}} \times CF_{\text{CEC}} \times CF_{\text{pH}} \times CF_{\text{speciation}} \times CF_{\text{Lab} \rightarrow \text{Field}} \quad (7)$$

The individual and overall uncertainty factors (UF) for the selected sorption values are given for each radionuclide in Table 9. The overall uncertainty factor is the product of the individual values.

For Co, Mo and Pb the overall uncertainty factor is given by
(UF- $R_{d \text{ lit.}}$) x (UF-speciation) x (UF-CEC) x (UF-pH) x (UF- Lab→Field)

For Nb, Bi and Am the overall uncertainty factor is given by
(UF- $R_{d \text{ lit.}}$) x (UF-speciation) x (UF-CEC) x (UF-Lab→Field)

For Ni the overall uncertainty factor is given by
(UF- $R_{d \text{ lit.}}$) x (UF-speciation) x (UF-pH) x (UF-Lab→Field)

For Se(IV) the overall uncertainty factor is given by
(UF- $R_{d \text{ lit.}}$) x (UF-Lab->Field)

For I, Eu, Sn and Th the overall uncertainty factor is given by
(UF- $R_{d \text{ lit.}}$) x (UF-speciation) x (UF-Lab→Field)

For Zr, Cd, Tc, Sb, Ce, Pm, Sm, Ho, Hf, Po, Ac, U(IV), Np(IV), Pu(III) and Cm, the overall uncertainty factor is given by
(Overall-UF)_{analogue} x (UF-speciation)

For Cs, Ca, Sr, and Ra the overall uncertainty factor is given by
(UF-cation exchange model) x (UF-Lab→Field)

For H(HTO), C(org), Cl, Se(-II) and Ag(I) the R_d values are zero and hence the overall-UF values are also zero.

For Pa, Pd and Ru, sorption values are selected on the basis of expert judgement alone.

Pa belongs to the actinides and is assigned an overall UF equal to the maximum overall UF found for this group i.e. 10.

Pd and Ru belong to the transition elements and are assigned an overall UF equal to the maximum overall UF found for this group i.e. 15.

The selected sorption values in the SDB are considered to be “best estimate” values for the OPA/groundwater system. The overall uncertainty factor should be used in the sense of estimating a lower bound for the sorption of any individual radionuclide i.e.

$$\text{Lower bound sorption value} = \frac{\text{selected sorption value}}{\text{overall uncertainty factor}} \quad (8)$$

It should be noted that in the selection of sorption values, and in the estimation of uncertainties, the potential influence of competitive effects from other sorbing species present in the repository, has not been included.

7 SELECTED SORPTION VALUES FOR THE IN SITU OPA SYSTEM

In this chapter the radionuclides are treated in groups selected according to their chemical similarities. Each radionuclide is taken in turn and the rationale behind the selection of the R_d value is briefly discussed. The selected laboratory values ($R_{d \text{ lit}}$) together with the conversion factors (Chapter 5) and the calculated in situ distribution ratios for most radionuclides are given in the data sheets.

Summary tables with the selected sorption values and their associated uncertainty values are given in Chapter 8.

Note that it was concluded in Chapter 5 that the best estimate for the Lab→Field transfer factor was unity, which implies that the $R_{d \text{ ref}}$ and $R_{d \text{ in situ}}$ values are the same.

7.1 Alkali and alkaline-earth metals: Cs, Ca, Sr, Ra

7.1.1 Caesium

It is well established in the open literature that Cs sorbs predominantly by cation exchange (see for example COLEMAN et al., 1963). In addition, practically all measurements of Cs uptake as a function of concentration in systems containing a significant illite component indicate that the sorption is non-linear (BROUWER et al., 1983; DE PRETER, 1990; POINSSOT et al., 1999b). Because Cs has such a simple aqueous chemistry, only being present as the hydrated monovalent cation, Freundlich sorption characteristics imply that sorption is occurring on at least two different sorption sites with different affinities and probably different site capacities. Further, monovalent cations with low hydration energies such as K, Rb and NH_4 can compete strongly with Cs for the available sorption sites (see for example SAWHNEY, 1972; CREMERS et al., 1988).

A relatively simple three site cation exchange sorption model for Cs, based on selectivity coefficient and site capacity data derived from the open literature on illite, has been developed for argillaceous rocks (BRADBURY & BAEYENS, 2000). Sorption is calculated first on a “reference illite” which has fixed site capacities for each of the three sites considered, and the result is then scaled to the illite content present in the natural rock. The model was tested against four Cs isotherm data sets determined on the argillaceous rocks Boom Clay, Palfris marl, Oxford Clay and Opalinus Clay. It was concluded from this study that the Cs sorption model, in which there are no free parameters, can be used to predict the uptake of Cs as a function of equilibrium

concentrations $< 10^{-3}$ M to within a factor of 2 to 3 in natural argillaceous rock systems.

Table 4 summarises the cation exchange reactions and respective selectivity coefficients for the “reference illite”. Figure 1 presents the calculated Cs sorption isotherms for the reference Benken OPA mineralogy (see Table 1), and the groundwater compositions given in Table 2. The calculations were performed with the geochemical speciation code MINSORB (BRADBURY & BAEYENS, 1997c). The competition from K on the high affinity sites (frayed edge sites) is the most important factor in the sorption behaviour of Cs. Since the concentrations of K in the 3 groundwaters are almost the same, the calculated Cs sorption isotherms in the three groundwaters are very similar. Figure 2 shows that at Cs concentrations below $<10^{-8}$ M the sorption becomes constant at $\sim 5.5 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$. The Cs background concentration for Benken OPA is not known and so the data obtained at the Mt. Terri site were considered. DEGUELDRE et al. (2001) measured Cs concentrations which were $\sim 4 \times 10^{-9}$ M.

An in situ sorption value for Cs of $5.5 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 the sorption values were the same as in the reference case.

Table 4: Summary of cation exchange reactions and selectivity coefficients for Cs sorption on the reference illite (BRADBURY & BAEYENS, 2000). Site capacity values are also given.

Exchange reaction	log K_c
Na-PS + $\text{K}^+ \rightleftharpoons \text{K-PS} + \text{Na}^+$	1.1
Na-PS + $\text{Cs}^+ \rightleftharpoons \text{Cs-PS} + \text{Na}^+$	1.6
Na-II + $\text{K}^+ \rightleftharpoons \text{K-II} + \text{Na}^+$	2.1
K-II + $\text{Cs}^+ \rightleftharpoons \text{Cs-II} + \text{K}^+$	1.5
K-FES + $\text{Cs}^+ \rightleftharpoons \text{Cs-FES} + \text{K}^+$	4.6
<u>Site types and capacities:</u>	
Planar sites (PS): $1.6 \times 10^{-1} \text{ eq. kg}^{-1}$	
Type II sites (II): $4.0 \times 10^{-2} \text{ eq. kg}^{-1}$	
Frayed edge sites (FES): $5.0 \times 10^{-3} \text{ eq. kg}^{-1}$	

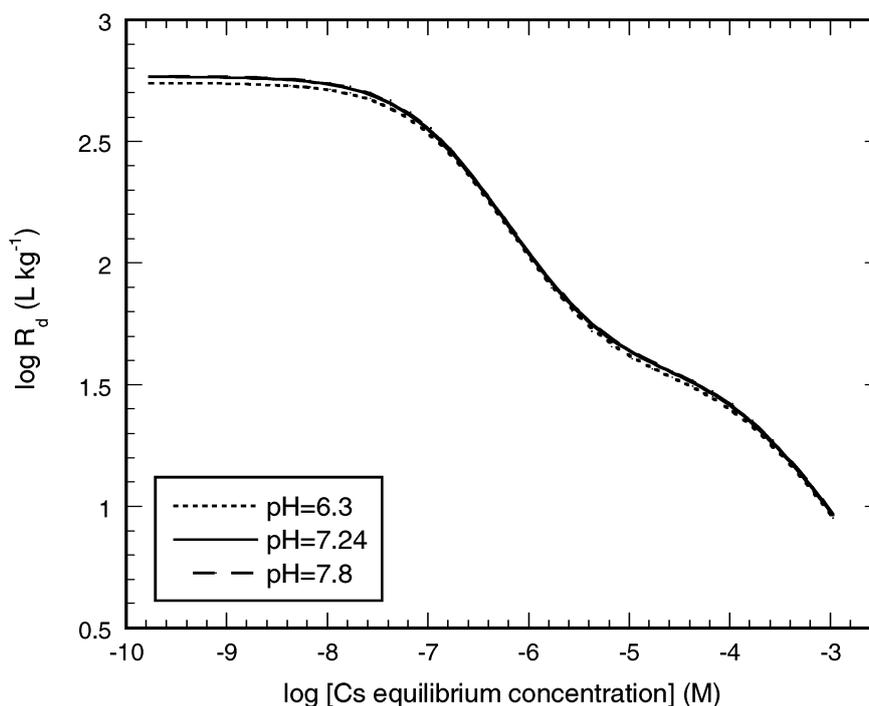


Figure 2: Cs sorption isotherms predicted for the reference OPA mineralogy using the model and model parameters as given in Table 4 (taken from BRADBURY & BAEYENS, 2000), and the 3 groundwater compositions given in Table 2.

7.1.2 Calcium/Strontium

The physico-chemical characteristics of OPA have been determined in connection with experimental work on porewater chemistry (BRADBURY & BAEYENS, 1998a) and sorption investigations (LAUBER et al., 2000). Thus OPA specific data for cation exchange reactions and selectivity coefficients, K_C values, are available and are given in Table 5.

Table 5: Selectivity coefficients for K-Na, Mg-Na and Ca-Na exchange on OPA derived from data obtained from core sample BGP-1-C11 (LAUBER et al., 2000) and BWS-A1-C12 (BRADBURY & BAEYENS, 1998a).

Exchange reaction	Core sample BGP-1-C11	Core sample BWS-A1-C12	Mean value
$\text{Na-OPA} + \text{K}^+ \rightleftharpoons \text{K-OPA} + \text{Na}^+$	5.3 (± 0.4)	5.0 (± 0.7)	5.2
$2\text{Na-OPA} + \text{Mg}^{2+} \rightleftharpoons \text{Mg-OPA} + 2\text{Na}^+$	3.4 (± 0.5)	3.9 (± 1.5)	3.7
$2\text{Na-OPA} + \text{Ca}^{2+} \rightleftharpoons \text{Ca-OPA} + 2\text{Na}^+$	3.7 (± 0.4)	4.7 (± 1.8)	4.2

Using the mean values of the selectivity coefficient data from Table 5, the reference CEC value of $0.106 \text{ eq. kg}^{-1}$, and the reference groundwater composition given in Table 2, a sorption value of $1.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ for Ca was calculated in the reference Benken OPA system. At the bounding pHs of 6.3 and 7.8 sorption values of $9.3 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $1.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ were calculated. These calculations were performed with the geochemical speciation code MINSORB.

It was not possible to determine the selectivity coefficient for Sr-Na exchange independently because the Sr concentrations were too low. However, the cation exchange behaviour of Ca and Sr is very similar and the same value can be taken for their selectivity coefficients (see for example BRUGGENWERT & KAMPHORST, 1982). Note also in this context that BAEYENS (1982) measured a linear Sr isotherm on Boom clay with a Ca-Sr selectivity coefficient of unity. Using the same method as given above for Ca, the calculated sorption values for Sr are equal to those obtained for Ca for the reference Benken OPA system and for the bounding pHs of 6.3 and 7.8.

LAUBER et al. (2000) measured some single point Sr sorption measurements on OPA in synthetic porewaters given in Table 3. Isotherms could not be measured since the Sr equilibrium concentration at a fixed pH is governed by saturation with celestite. The measured R_d values were higher than the values calculated with the K_c data. This is not well understood but could be due to a contribution of Sr isotopic exchange with celestite. For the Benken systems the model calculations for Sr are preferred rather than converting the R_d values measured by Lauber et al. (2000).

No data sheets are provided.

An in situ sorption value for Ca and Sr of $1.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $9.3 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $1.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

7.1.3 Radium

Literature values for the sorption of Ra on geological materials are often high ($> 1 \text{ m}^3 \text{ kg}^{-1}$) and associated with a large degree of scatter (see Appendix B in STENHOUSE, 1995). Also, in some reported data, Ra sorption values tend to exhibit trends which are not compatible with sorption processes. For example, AMES et al. (1983a) present values for the quantities of Ra taken up by illite as a function of initial and equilibrium concentrations which increase with increasing concentration. These data can clearly not be regarded as being representative of Ra sorption but rather are indicative of other processes; precipitation for example.

BASTON et al. (1990) investigated the sorption of Ra at initial concentrations of 10^{-8} M on Caithness flags and London clay in contact with "equilibrated cement water". The solution pH was adjusted to ~ 8 before batch sorption experiments were performed at different S:L ratios, (pH range 7.5 to 8.2). Although mineralogies and "equilibrated cement water compositions" were given, it was not clear from their text what the effect of the pH adjustment was and what the water composition in the batch tests was. Because of the above, these measurements can only be taken as a rough guide as to what sorption values might be expected. Values for Caithness flags varied between >0.7 and $4.5 \text{ m}^3 \text{ kg}^{-1}$ and for London clay between 0.14 and $0.85 \text{ m}^3 \text{ kg}^{-1}$.

When appropriate data for Ra are not available Sr is often taken as chemical analogue. However, it is considered that Ba is probably more appropriate because of its closer proximity to Ra in the Periodic Table.

GRÜTTER et al. (1992, 1994) carried out detailed studies of Sr and Ba sorption on unconsolidated glaciofluvial deposits and clay minerals. Sorption isotherm measurements were made for Sr and Ba on an illite (CEC = 0.36 eq. kg^{-1}) in a low ionic strength (I.S. = 10^{-2} M) synthetic groundwater.

The sorption of Sr on illite and montmorillonite was essentially constant in both cases over the equilibrium concentration range 4×10^{-5} and 1.6×10^{-7} M with R_d values of $0.05 \text{ m}^3 \text{ kg}^{-1}$ and $0.13 \text{ m}^3 \text{ kg}^{-1}$ respectively. The data indicates that Sr is sorbing via a cation exchange mechanism on both clay minerals.

The sorption of Ba on montmorillonite was also constant as a function of concentration but exhibited strongly non-linear behaviour on illite. (Concentration ranges of 4×10^{-5} to 4×10^{-8} M.) At the lowest Ba equilibrium concentration of 1.7×10^{-7} M an R_d value of $1.3 \text{ m}^3 \text{ kg}^{-1}$ was measured for illite i.e. a factor of ~ 25 higher than Sr.

It appears from the above data that Ba sorbs distinctly stronger on illite than Sr and by a different mechanism. However, the Ba data set is very limited, only having been measured under one set of conditions. Consequently no conclusions can be made regarding the sorption mechanism of Ba on illite and for this reason a conservative approach is adopted and Sr taken as the chemical analogue for Ra.

The sorption of Ra in the Benken OPA reference system was calculated in the same way as for Sr assuming $\frac{S_r}{S_a} K_c$ equals unity. Taking the mean selectivity coefficient data from Table 5, the reference CEC value of $0.106 \text{ eq. kg}^{-1}$, and the reference groundwater composition given in Table 2, a sorption value of $7.6 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ was calculated for Ra in the reference Benken OPA system. At the bounding pH values of

6.3 and 7.8 sorption values of $6.9 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $7.6 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ respectively were calculated in the corresponding groundwater chemistries, Table 2.

No data sheets are given for Ra.

An in situ sorption value for Ra of $7.6 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $6.9 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $7.6 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

7.2 Transition and heavy metals

7.2.1 Cobalt

Two data sets on the sorption of Co were found which were potentially relevant to the OPA system.

The first is the Co sorption isotherm data measured on Oxford clay and presented in MCKINLEY & WEST (1982, 1984). A full mineralogy and water chemistry are given but a CEC value for Oxford clay was not measured. In addition, no accurate pH values were given, only a range between 7 and 7.5 was reported. The influence of dissolved organic carbon, present in the groundwater at $4 \mu\text{g ml}^{-1}$, on the sorption of Co is also an unknown. For these reasons these data were not considered further.

The second is the sorption measurements of Co on illite reported by GRÜTTER et al. (1994). This detailed study included the time dependence of sorption and desorption at different concentrations together with a full description of the water chemistry and CEC measurements (GRÜTTER et al. 1992, 1994). From the results given a sorption value of $5 \text{ m}^3 \text{ kg}^{-1}$, corresponding to trace concentration levels ($<10^{-8} \text{ M}$), was selected.

No appropriate Co sorption edge data on illite could be found. The data from O'CONNOR & KESTER (1975) on illite, and BANGASH et al. (1992) on an illitic soil, only indicate that there is a clear pH dependency. A Ni edge on illite in 0.1 M NaClO_4 has been measured by POINSSOT et al. (1999a) and this data is reproduced in Figure 3. The edge data are used for the pH conversion factor according to the method described in section 5.2.1.

Data sheets for Co are given.

An in situ sorption value for Co of $4.9 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $1.6 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $9.5 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

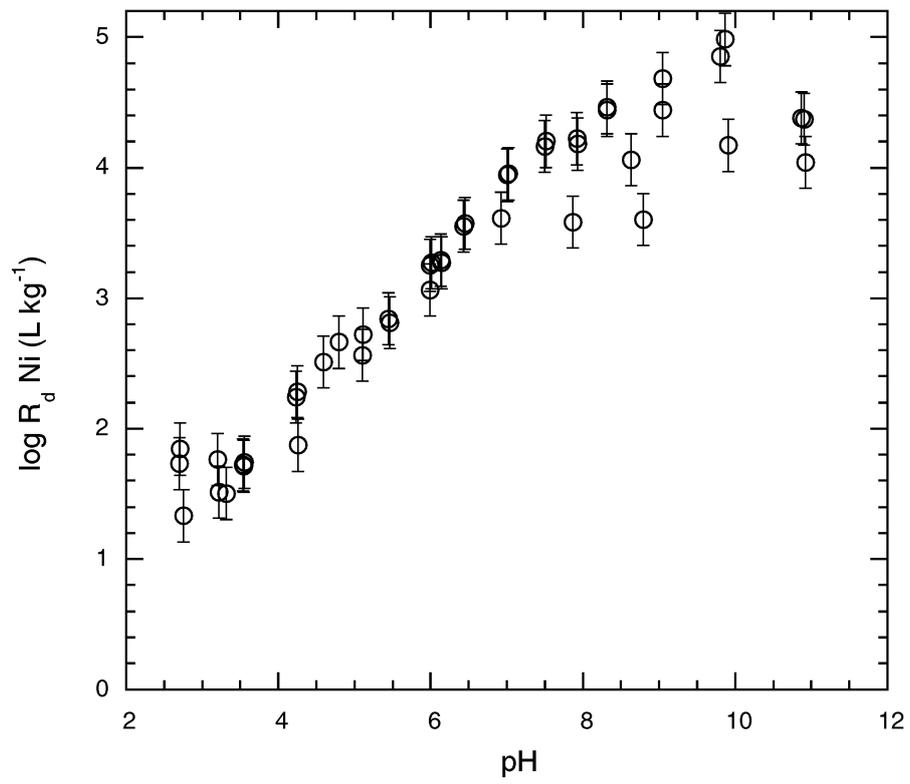


Figure 3: Ni sorption edge measurements on Na-illite in 0.1 M NaClO_4 . (Taken from POINSSOT et al., 1999a)

Co DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: GRÜTTER et al. (1994)

Selected $R_{d \text{ lit.}}$: $5 \text{ m}^3 \text{ kg}^{-1}$ (Co equilibrium concentration: $< 10^{-8} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (eq. kg ⁻¹)
Illite	0.36

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.9	4.2×10^{-4}	-	6.5×10^{-3}	0.98

Opalinus Clay reference case: data summary

pH _{ref.}	F _{ref. speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.24	0.72	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
0.46	0.73	0.29

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ (m ³ kg ⁻¹)
4.9×10^{-1}

Opalinus Clay in situ sorption value

Lab → Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
4.9×10^{-1}

Co DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: GRÜTTER et al. (1994)

Selected $R_{d \text{ lit.}}$: $5 \text{ m}^3 \text{ kg}^{-1}$ (Co equilibrium concentration: $< 10^{-8} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (eq. kg ⁻¹)
Illite	0.36

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.9	4.2×10^{-4}	-	6.5×10^{-3}	0.98

Opalinus Clay pH = 6.3: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
6.3	0.71	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
0.15	0.72	0.29

Opalinus Clay pH = 6.3 sorption value

R_d (m ³ kg ⁻¹)
1.6×10^{-1}

Opalinus Clay, pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

R_d in situ (m ³ kg ⁻¹)
1.6×10^{-1}

Co DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: GRÜTTER et al. (1994)

Selected $R_{d \text{ lit.}}$: $5 \text{ m}^3 \text{ kg}^{-1}$ (Co equilibrium concentration: $< 10^{-8} \text{ M}$)**Source data summary**

Solid	CEC _{lit.} (eq. kg ⁻¹)
Illite	0.36

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.9	4.2×10^{-4}	-	6.5×10^{-3}	0.98

Opalinus Clay pH = 7.8: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.8	0.72	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
0.9	0.73	0.29

Opalinus Clay pH = 7.8 sorption value

R_d (m ³ kg ⁻¹)
9.5×10^{-1}

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

R_d in situ (m ³ kg ⁻¹)
9.5×10^{-1}

7.2.2 Nickel

The primary source of Ni sorption data is the "in-house" measurements of LAUBER et al. (2000) on OPA from Mont Terri as a function of concentration in synthetic OPA porewater compositions at pH 6.3 and 7.8. The isotherms are presented in Figure 4.

No background Ni concentration data are available for the Benken OPA porewater. Trace metal concentrations were monitored in the groundwaters at the Mont Terri site (DEGUELDRE et al., 1997). However, in these high Cl^- groundwaters the detection limit for Ni is $\sim 10^{-7}$ M. For conservative reasons this concentration is taken as the lower limit for the choice of Ni sorption data from the isotherms given in Figure 4. Sorption values of $2 \text{ m}^3 \text{ kg}^{-1}$ (pH = 7.8; Ni concentration = 10^{-7} M) and $0.32 \text{ m}^3 \text{ kg}^{-1}$ (pH = 6.3; Ni conc. = 3×10^{-7} M) were selected from Figures 4a and 4b, respectively. Since the in-house Ni sorption data were measured on OPA from Mont Terri in porewater compositions which are different from the Benken OPA system, the selected values need to be converted.

For the reference Benken system at pH = 7.24 the Ni sorption value at pH = 7.8 was selected, and the pH conversion factor was obtained from the Ni sorption edge on illite, Figure 3, following the procedure described in section 5.2.1.

Data sheets for Ni are given.

An in situ sorption value for Ni of $9.3 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $2.9 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $1.9 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

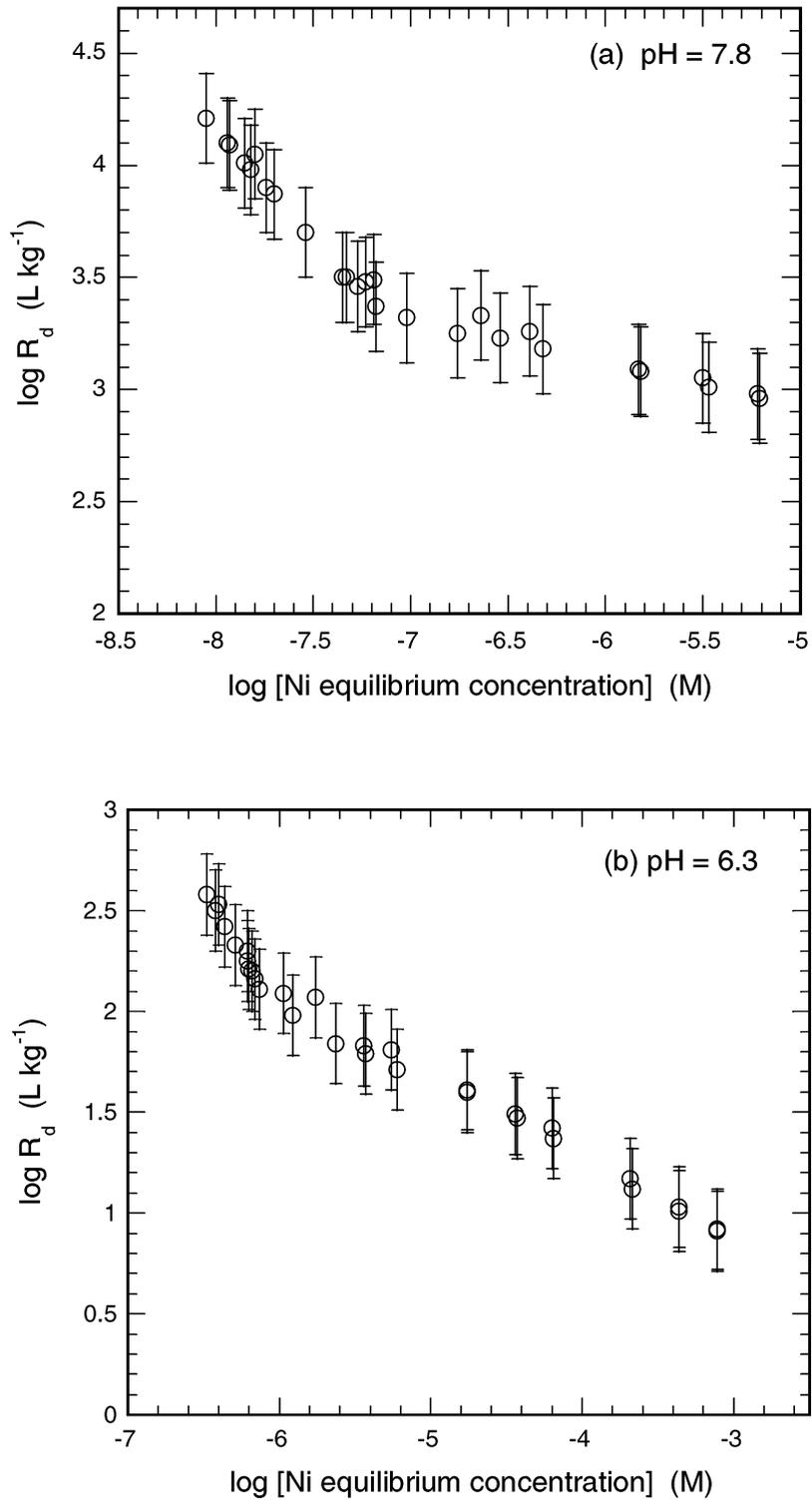


Figure 4: Ni sorption isotherms on OPA from Mont Terri at (a) pH = 7.8 and (b) pH = 6.3 from LAUBER et al. (2000).

Ni DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $2 \text{ m}^3 \text{ kg}^{-1}$ (Ni equilibrium concentration: $= 10^{-7} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.8	1.8×10^{-4}	2.6×10^{-2}	3×10^{-1}	0.63

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.24	0.67	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
0.50	1.06	0.88

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
9.3×10^{-1}

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
9.3×10^{-1}

Ni DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $3.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Ni equilibrium concentration: $= 3 \times 10^{-7} \text{ M}$)

Source data summary

Solid	$CEC_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$pH_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
6.3	1.7×10^{-2}	2.8×10^{-2}	1.9×10^{-1}	0.65

Opalinus Clay pH = 6.3: data summary

pH	$F_{\text{speciation}}$	$CEC_{\text{ref.}}$ (eq. kg^{-1})
6.3	0.66	0.106

Conversion factors

CF_{pH}	$CF_{\text{speciation}}$	CF_{CEC}
1	1.02	0.88

Opalinus Clay pH = 6.3 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
2.9×10^{-1}

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ in situ}$ ($\text{m}^3 \text{ kg}^{-1}$)
2.9×10^{-1}

Ni DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $2 \text{ m}^3 \text{ kg}^{-1}$ (Ni equilibrium concentration: $= 10^{-7} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.8	1.8×10^{-4}	2.6×10^{-2}	3×10^{-1}	0.63

Opalinus Clay pH = 7.8: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.8	0.67	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	1.06	0.88

Opalinus Clay pH = 7.8 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
1.9

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ in situ}$ ($\text{m}^3 \text{ kg}^{-1}$)
1.9

7.2.3 Cadmium

No relevant sorption data for the OPA system could be found for Cd.

Ni is taken as chemical analogue. However, Cd forms significantly stronger chloro-complexes than Ni and in the OPA groundwaters, Table 2, most of the total Cd concentration exists as chloro complexes which are assumed to be non-sorbing. Consequently, the sorption of Cd is significantly less than Ni in the corresponding OPA systems.

Data sheets for Cd are given below.

An in situ sorption value for Cd of $1.8 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $5.7 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ and $3.7 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Cd DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Selected chemical analogue: Ni

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay reference case Ni data

$R_d(\text{Ni})_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$	$F(\text{Ni})_{\text{ref. speciation}}$
9.3×10^{-1}	0.67

Opalinus Clay reference case Cd data

$F(\text{Cd})_{\text{ref. speciation}}$
0.13

Conversion

$$R_d(\text{Cd})_{\text{ref.}} = R_d(\text{Ni})_{\text{ref.}} \times [F(\text{Cd})_{\text{ref. speciation}} / F(\text{Ni})_{\text{ref. speciation}}]$$

Opalinus Clay reference sorption value

$R_d(\text{Cd})_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
1.8×10^{-1}

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ in situ } \text{ (m}^3 \text{ kg}^{-1}\text{)}$
1.8×10^{-1}

Cd DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Selected chemical analogue: Ni

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 6.3 Ni data

$R_d(\text{Ni})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Ni})_{\text{pH}=6.3} \text{ speciation}$
2.9×10^{-1}	0.66

Opalinus Clay pH = 6.3 Cd data

$F(\text{Cd})_{\text{pH}=6.3} \text{ speciation}$
0.13

Conversion

$$R_d(\text{Cd})_{\text{pH}=6.3} = R_d(\text{Ni})_{\text{pH}=6.3} \times [F(\text{Cd})_{\text{pH}=6.3} \text{ speciation}] / F(\text{Ni})_{\text{pH}=6.3} \text{ speciation}]$$

Opalinus Clay pH = 6.3 sorption value

$R_d(\text{Cd})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$
5.7×10^{-2}

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ in situ} (\text{m}^3 \text{kg}^{-1})$
5.7×10^{-2}

Cd DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Selected chemical analogue: Ni

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 7.8 Ni data

$R_d(\text{Ni})_{\text{pH}=7.8} \text{ (m}^3 \text{ kg}^{-1}\text{)}$	$F(\text{Ni})_{\text{pH}=7.8} \text{ speciation}$
1.9	0.67

Opalinus Clay pH = 7.8 Cd data

$F(\text{Cd})_{\text{pH}=7.8} \text{ speciation}$
0.13

Conversion

$$R_d(\text{Cd})_{\text{pH}=7.8} = R_d(\text{Ni})_{\text{pH}=7.8} \times [F(\text{Cd})_{\text{pH}=7.8} \text{ speciation}] / F(\text{Ni})_{\text{pH}=7.8} \text{ speciation}]$$

Opalinus Clay pH = 7.8 sorption value

$R_d(\text{Cd})_{\text{pH}=7.8} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
3.7×10^{-1}

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ in situ (m}^3 \text{ kg}^{-1}\text{)}$
3.7×10^{-1}

7.2.4 Palladium

The speciation calculations for Pd, under the redox conditions of the OPA systems at the reference pH and at the lower and upper pH values predict metallic Pd at an extremely low solubility ($< 10^{-27}$ M). This means in principle that Pd in the OPA systems is totally immobilized. However, if this should not prove to be the case for any reason, and Pd concentrations are considerably higher than expected, a sorption value is estimated below based on expert judgement.

Pd forms extremely stable hydroxy complexes (see Figure 18.4 in BAES & MESMER, 1976), and this is an important indicator that it can bind strongly to mineral surfaces (see for Table 10.5 in DZOMBAK & MOREL, 1990), although the mechanism is unclear.

Chemical analogues for Pd such as Co, Ni, Cd and Pb, for which sorption data exist, might suggest themselves. However, the dominant Pd species at pH 7.24 is the neutral $\text{Pd}(\text{OH})_2^0$, (chloro complexes constitute only $\sim 2\%$), and since the first hydrolysis constants for Co, Ni, Cd and Pb are significantly weaker, such transition and heavy metals do not form neutral hydroxy species until relatively high pH values. On this basis, sorption probably increases in the order $\text{Pd} \gg \text{Pb} > \text{Ni} \sim \text{Co}$ (see for example DZOMBAK & MOREL, 1990). Thus Pd is likely to sorb considerably more strongly than Co, Ni, Cd and Pb and choosing an $R_{d \text{ in situ}}$ value of $5 \text{ m}^3 \text{ kg}^{-1}$, which is similar to Pb (at pH = 7.8), is almost certainly a significant underestimation of the real value.

At pH 7.8, Pd is still highly hydrolysed, having only $\sim 0.1\%$ chloro complexes present in solution, and thus no pH dependency is expected. At pH 6.3 the chloro complexes become more important and the speciation calculations indicate that $\sim 57\%$ of the total Pd are chloro complexes, and $\sim 43\%$ are the neutral $\text{Pd}(\text{OH})_2^0$ species (THOENEN, 2002). The application of a speciation factor for pH = 6.3 would result in a reduction in the selected sorption value by about a factor of 2. However considering that the selection of the $R_{d \text{ in situ}}$ value was anyway conservative, and that an overall uncertainty factor of 15 is given, a speciation factor was not applied. The selected sorption value at pH = 6.3 was therefore the same as at the other two pHs.

Given the lack of almost any sort of quantitative data it is somewhat difficult to suggest an uncertainty factor. However, the rationale behind the selection of a value of an overall uncertainty factor of 15 is given in section 6.8.

No data sheets are provided for Pd.

An in situ sorption value for Pd of $5 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA systems.

7.2.5 Silver

Literature sorption data for Ag on minerals of interest are scarce, and the only sorption values found were those given in LEGOUX et al. (1992). In the pH range from ~6.5 to 8, and at an initial Ag concentration of 1.8×10^{-7} M, measured R_d values between 1.8 and $17 \text{ m}^3 \text{ kg}^{-1}$ are reported. These values are very high, and since silver solutions are photosensitive, the values are probably more representative of precipitation processes and are therefore deemed to be inappropriate. In addition, Ag forms strong complexes with chloride, and in the three OPA groundwater systems silver would only be present as neutral and anionic chloro complexes. As outlined in section 5.2.3, these are assumed to be non-sorbing.

No data sheets are provided for Ag.

The sorption of Ag was taken to be zero for the OPA systems.

7.2.6 Lead

With the exception of Pb sorption studies in soils (see for example HIGGO, 1988) where "organics" in the solid and liquid phases are likely to play an important but unquantified role, almost no reliable sorption data are available in the literature (STENHOUSE, 1995, Appendix B).

LIESER & AMENT (1993) present R_d values for Pb in three different groundwater/sediment systems from Gorleben. The water chemistries are available, but no detailed rock mineralogy or CEC values were reported. The values measured by these authors were high (20 to $> 50 \text{ m}^3 \text{ kg}^{-1}$).

RYBICKA et al. (1995) measured heavy metal (Cd, Cu, Pb, Zn and Ni) sorption on illite at pH 5.5. Unfortunately the data cannot be used since no information was given on the water chemistries. The only semi-quantitative conclusion which could be drawn from this study was the sequence of adsorption affinities for illite i.e. $\text{Pb} > \text{Cd} \sim \text{Cu} > \text{Ni} > \text{Zn}$.

KOSS et al. (1992) determined Pb sorption values in a natural groundwater/sediment system from Pb concentrations in the groundwater and Pb extractions from the solid phase. Water chemistry and a CEC value for the sediment were given but the mineralogy was not described. Nevertheless, an R_d value for Pb of $1.5 \text{ m}^3 \text{ kg}^{-1}$ at pH 6.7 was selected from the data given in this work. However, these data were the only

ones found, and the reliability of such measurements is difficult to assess. An uncertainty factor of 5 is assigned to the Pb sorption data to reflect this.

Since no appropriate sorption edge of Pb on illite is available the Ni sorption edge given in Figure 2 is used for the pH conversion factor according to the method described in section 5.2.1.

Data sheets for Pb are given.

An in situ sorption value for Pb of $2.7 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at $\text{pH} = 7.24$. At the bounding pH values of 6.3 and 7.8 sorption values of $8.0 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $6.7 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Pb DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: KOSS et al. (1992)

Selected $R_{d \text{ lit.}}$: $1.5 \text{ m}^3 \text{ kg}^{-1}$ (Pb equilibrium concentration: $= 1.5 \times 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Sediment	0.036

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
6.7	10^{-3}	7×10^{-3}	3.3×10^{-3}	0.40

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.24	0.14	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1.8	0.35	2.9

Opalinus Clay reference sorption value

$R_{d \text{ ref}}$ ($\text{m}^3 \text{ kg}^{-1}$)
2.7

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
2.7

Pb DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: KOSS et al. (1992)

Selected $R_{d \text{ lit.}}$: $1.5 \text{ m}^3 \text{ kg}^{-1}$ (Pb equilibrium concentration: $= 1.5 \times 10^{-8} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (eq. kg ⁻¹)
Sediment	0.036

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
6.7	10 ⁻³	7 x 10 ⁻³	3.3 x 10 ⁻³	0.40

Opalinus Clay pH = 6.3: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
6.3	0.13	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
0.56	0.33	2.9

Opalinus Clay pH = 6.3 sorption value

R_d (m ³ kg ⁻¹)
8.0 x 10 ⁻¹

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
8.0 x 10 ⁻¹

Pb DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: KOSS et al. (1992)

Selected $R_{d \text{ lit.}}$: $1.5 \text{ m}^3 \text{ kg}^{-1}$ (Pb equilibrium concentration: $= 1.5 \times 10^{-8} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (eq. kg ⁻¹)
Sediment	0.036

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
6.7	10 ⁻³	7 x 10 ⁻³	3.3 x 10 ⁻³	0.40

Opalinus Clay pH = 7.8: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.8	0.17	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
3.6	0.43	2.9

Opalinus Clay pH = 7.8 sorption value

R_d (m ³ kg ⁻¹)
6.7

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
6.7

7.3 Lanthanides

7.3.1 Europium

The primary source for Eu sorption data are the measurements of LAUBER et al. (2000) on OPA as a function of concentration in synthetic OPA porewater compositions at pHs of 7.8 and 6.3. From the isotherm data presented in Figures 5a and 5b sorption values of 80 and 8 m³ kg⁻¹ were selected at pH = 7.8 and 6.3 respectively. At equilibrium concentrations below ~ 10⁻⁹ M, the sorption of Eu is linear.

The aqueous speciation calculations indicate that the Eu carbonate and sulphate complexes dominate at pH = 6.3, whereas at pH = 7.8 Eu hydroxy-silicate complexes are dominant. These complexes are assumed to be non sorbing, and hence the speciation factors for Eu in both the OPA laboratory and references systems are very small.

For the reference Benken system at pH = 7.24 the Eu sorption edge on illite from POINSSOT et al. (1999a), Figure 6 was used for the pH conversion factor. As can be seen from these data, above pH ~ 7 the Eu sorption on illite is constant.

Data sheets for Eu are given.

An in situ sorption value for Eu of 59.8 m³ kg⁻¹ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of 5 m³ kg⁻¹ and 50 m³ kg⁻¹ respectively were chosen.

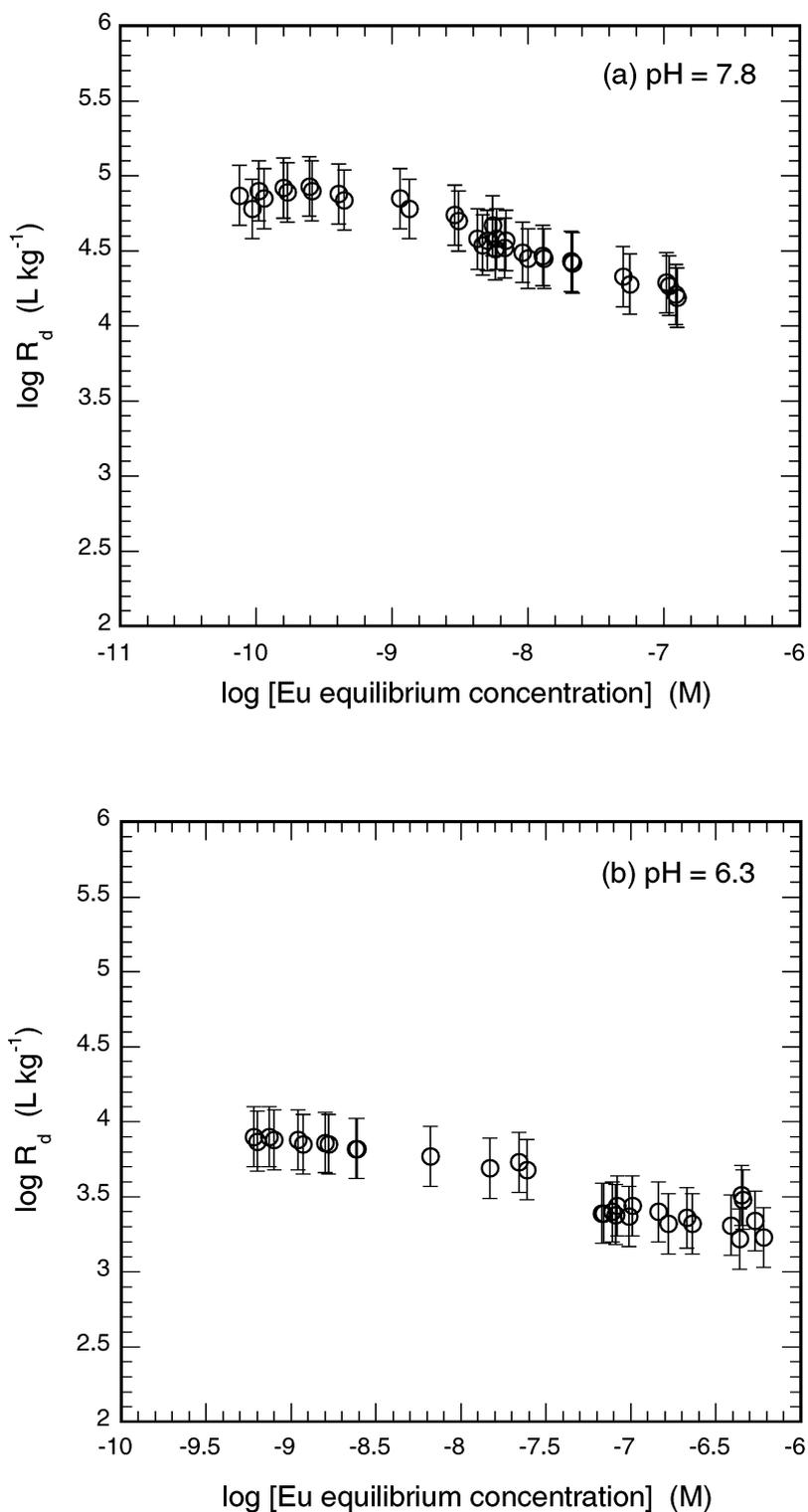


Figure 5: Eu sorption isotherms on OPA from Mont Terri at (a) pH = 7.8 and (b) pH = 6.3 in synthetic OPA porewaters.

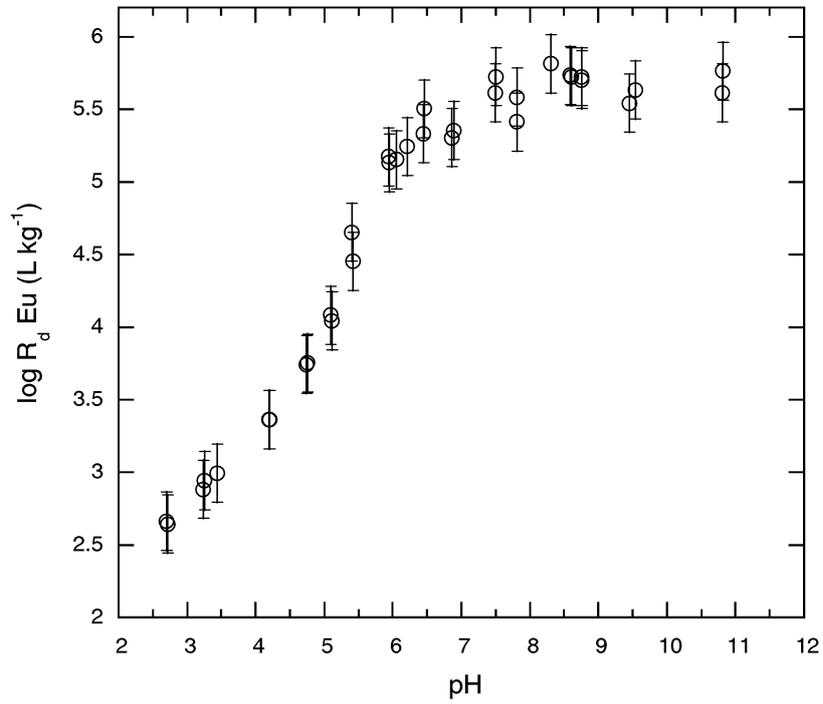


Figure 6: Eu sorption edge measurements on Na-illite in 0.1 M NaClO_4 . (Taken from POINSSOT et al., 1999a)

Eu DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $80 \text{ m}^3 \text{ kg}^{-1}$ (Eu equilibrium concentration: $< 10^{-9} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.8	1.8×10^{-4}	2.6×10^{-2}	3×10^{-1}	0.041

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.24	0.035	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	0.85	0.88

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
59.8

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
59.8

Eu DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $8 \text{ m}^3 \text{ kg}^{-1}$ (Eu equilibrium concentration: $< 10^{-9} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
6.3	1.7×10^{-2}	2.8×10^{-2}	1.86×10^{-1}	0.07

Opalinus Clay pH = 6.3: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
6.3	0.05	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	0.71	0.88

Opalinus Clay pH = 6.3 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
5.0

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
5.0

Eu DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $80 \text{ m}^3 \text{ kg}^{-1}$ (Eu equilibrium concentration: $< 10^{-9} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.8	1.8×10^{-4}	2.6×10^{-2}	3×10^{-1}	0.041

Opalinus Clay pH = 7.8: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.8	0.029	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	0.71	0.88

Opalinus Clay pH = 7.8 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
50.0

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
50.0

7.3.2 Cerium, Promethium, Samarium and Holmium

No relevant sorption data for these lanthanides could be found.

There are no thermodynamic data for these elements contained in the updated Nagra/PSI TDB, and where data is reported (e.g. PEARSON et al., 1992) it is not very reliable.

Because of the chemical similarity of lanthanides, Eu is taken as an analogue for these trivalent radionuclides.

No data sheets are provided for Ce, Pm, Sm and Ho.

An in situ sorption value for Ce, Pm, Sm and Ho of $59.8 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $5 \text{ m}^3 \text{ kg}^{-1}$ and $50 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

7.4 Actinides

7.4.1 Americium

Sorption of Am on illite has been reported by MUCCIARDI et al. (1978), DEGUELDRE et al. (1994) & GORGEON (1994). LEGOUX et al. (1992) report single point sorption values for Am on quartz rich sediments in low ionic strength groundwaters.

GORGEON (1994) thoroughly investigated the sorption behaviour of Am on a purified homo-ionic Na-illite du Puy at 1 and 0.1 M NaClO_4 as function of pH from 3 to 10 under atmospheric conditions. The equilibrium Am concentrations were low ($< 8 \times 10^{-10}$ M from pH 6.5 upwards). The raw data, presented in the tables in that study, are reproduced here in Figure 7.

The measurements clearly show that the sorption of Am on illite is pH dependent. Below pH ~ 6 , Am sorption is dependent on the NaClO_4 concentration whereas above this pH the ionic strength dependency disappears. This behaviour can be very satisfactorily interpreted in terms of two main sorption mechanisms, namely, cation exchange and surface complexation (see for example BRADBURY & BAEYENS, 2002).

Similar behaviour of Am sorption on other clay minerals has been described in the literature; see for example BEALL & ALLARD (1979, 1981) for montmorillonite, GORGEON (1994) for kaolinite and smectite and STAMMOSE & DOLO (1990) for kaolinite/smectite mixed layer.

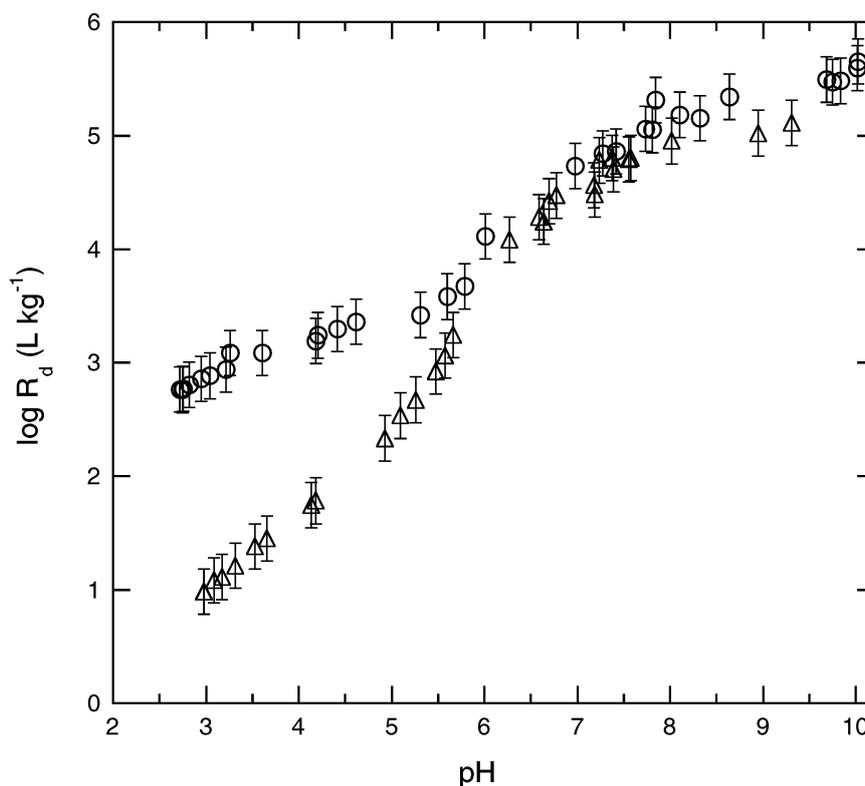


Figure 7: Am sorption edges on illite du Puy at two ionic strengths GORGEON (1994)
(O): 0.1 M NaClO₄; (Δ) 1 M NaClO₄.

The measurements of GORGEON (1994) are considered to be the most relevant and R_d values of $50 \text{ m}^3 \text{ kg}^{-1}$ (pH = 7.24), $10 \text{ m}^3 \text{ kg}^{-1}$ (pH = 6.3) and $126 \text{ m}^3 \text{ kg}^{-1}$ (pH = 7.8) were selected from her data.

The aqueous speciation calculations indicate that in the pH range from 6.3 to 7.8 the Am carbonate and hydroxy-silicate complexes are dominant. These complexes are assumed to be non-sorbing. As in the case of Eu, the speciation factors for Am in the OPA groundwater systems are therefore very small.

Data sheets for Am are given.

An in situ sorption value for Am of $17 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $1.2 \text{ m}^3 \text{ kg}^{-1}$ and $63 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Am DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: GORGEON (1994)

Selected $R_{d \text{ lit.}}$: $50 \text{ m}^3 \text{ kg}^{-1}$ (Am equilibrium concentration: $< 10^{-10} \text{ M}$)**Source data summary**

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Illite du Puy	0.212

$\text{pH}_{\text{lit.}}$	$\#C_{\text{inorg.}}$ (M)	SO_4 (M)	NaClO_4 (M)	$\$F_{\text{lit. speciation}}$
7.24	1.2×10^{-4}	-	10^{-1}	0.066

#Assumption: solutions are air saturated.

\$Calculated with quartz saturation.

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.24	0.045	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	0.68	0.5

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
17.0

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
17.0

Am DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: GORGEON (1994)

Selected $R_{d \text{ lit.}}$: $10 \text{ m}^3 \text{ kg}^{-1}$ (Am equilibrium concentration: $< 10^{-10} \text{ M}$)**Source data summary**

Solid	CEC _{lit.} (eq. kg ⁻¹)
Illite du Puy	0.212

pH _{lit.}	#C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	\$F _{lit. speciation}
6.3	2.3×10^{-5}	-	10^{-1}	0.34

#Assumption: solutions are air saturated.

\$Calculated with quartz saturation.

Opalinus Clay pH = 6.3: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
6.3	0.08	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
1	0.24	0.5

Opalinus Clay pH = 6.3 sorption value

R_d (m ³ kg ⁻¹)
1.2

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
1.2

Am DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: GORGEON (1994)

Selected $R_{d \text{ lit.}}$: $126 \text{ m}^3 \text{ kg}^{-1}$ (Am equilibrium concentration: $< 10^{-10} \text{ M}$)**Source data summary**

Solid	CEC _{lit.} (eq. kg ⁻¹)
Illite du Puy	0.212

pH _{lit.}	#C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	\$F _{lit. speciation}
7.8	2.6×10^{-4}	-	10^{-1}	0.031

#Assumption: solutions are air saturated.

\$Calculated with quartz saturation.

Opalinus Clay pH = 7.8: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.8	0.031	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
1	1	0.5

Opalinus Clay pH = 7.8 sorption value

R_d (m ³ kg ⁻¹)
63

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

R_d in situ (m ³ kg ⁻¹)
63

7.4.2 Actinium, Curium

The lack of reliable sorption data for these elements available in the open literature (see for example STENHOUSE, 1995, Appendix I) precluded the selection of distribution ratios specific for Ac or Cm. Instead, since both elements are chemically very similar to Am, the same sorption values were selected.

No data sheets are provided for Ac and Cm.

An in situ sorption value for Ac and Cm of $17 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $1.2 \text{ m}^3 \text{ kg}^{-1}$ and $63 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

7.4.3 Actinide carbonate complexes

In the recently completed update of the Nagra/PSI thermodynamic data base (TDB) (HUMMEL et al., 2002), the solubility data for solid $\text{Th}(\text{OH})_4$ was reviewed and hydroxy-carbonate complexes were included for the first time. The available solubility data for tetravalent U, Np and Pu suggested that for these actinides such complexes (if they form) would have much weaker constants than in the case of Th. However, as pointed out by HUMMEL & BERNER (2001), the situation is far from being clear cut, and there may be large uncertainties associated with the constants given in the TDB.

In an attempt to set up some general procedures for modifying literature sorption data to the OPA reference water chemistry, some broad statements regarding sorption behaviour were made. In the case of the readily hydrolysable actinides Th, Pa, U, Np and Pu it was noted that where data were available sorption edges on clay minerals tended to occur already at relatively low pH values. Thereafter the sorption remained virtually constant over a broad pH range where positively charged and neutral hydroxy species dominated. This led to the hypothesis that positive and neutral hydrolysed species sorb strongly and that tetravalent actinides, especially, exhibit sorption plateaus between pH ~ 6 to ~ 9. Negatively charged hydrolysed species, carbonate, and hydroxy-carbonate complexes were assumed to be non-sorbing and sorption would thus be reduced upon their formation. However, some anomalies in this simplified picture of sorption became apparent.

For the experimental conditions used to measure the Th sorption data given later in Figure 8, speciation calculations with the new Th-hydroxy-carbonate stability constants indicated that these negatively charged complexes become very important. The consequence is that corrections for speciation (see section 5.2.2) become dominant

and critically dependent on the stability constant values. The $F_{\text{lit. speciation}}$ values for Th calculated at pHs 6.3 and 7.8 were 0.001 and 0.07 respectively. In other words only 0.1% and 7% of the Th in the aqueous phase consisted of sorbing species. If the sorption of Th in this pH range is approximately constant (no pH effect) in the absence of complexants, then, in the presence of carbonate it would be expected that the difference in sorption values at pH = 6.3 and pH = 7.8 in the above approach should be a factor of ~70.

The measurements however tell a rather different story. First, the measured sorption at both pH values is very high and secondly the difference between the values at pH = 6.3 ($25 \text{ m}^3 \text{ kg}^{-1}$) and pH = 7.8 ($63 \text{ m}^3 \text{ kg}^{-1}$) is only a factor of ~2.5. The simple general approach suggested in section 5.2.2 fails in this example for Th. There are however others.

AMES et al. (1983b) investigated U(VI) sorption on illite in 0.01 M NaCl (pH = 7) and 0.01 M NaHCO_3 solutions (pH ~ 8.5) and measured values of 0.5 and $0.1 \text{ m}^3 \text{ kg}^{-1}$ respectively at equilibrium concentrations of $< 10^{-8} \text{ M}$. In the latter case speciation calculations indicate that all of the U(VI) should be present as $\text{UO}_2(\text{CO}_3)_2^{2-}$. MEYER et al. (1988) carried out very similar measurements with U(VI) and illite in diluted brine solutions (I.S. = 0.03 M) and measured sorption reduction factors of 5 to 15 whereas on the basis of speciation calculations no sorption would be expected.

Further, in the uranyl sorption modelling studies of HSI & LANGMUIR (1985) on iron oxides, PAYNE & WAITE (1991) on natural rocks and BOND et al. (1990) on London clay, all authors had to include the uptake of the negatively charged uranyl carbonate complexes on the various solids in order to obtain respectable fits to the data.

Also, in the Am/illite system the measurements of MUCCIARDI et al. (1978) and DEGUELDRE et al. (1994) appear to indicate that inorganic carbon concentrations up to 0.1 M at pH = 8 do not influence the sorption behaviour of Am to any significant extent. However, there is substantial evidence in the open literature that Am can form strong carbonate and hydroxy-carbonate complexes (SILVA et al., 1995) which should lead to decreased sorption.

Possible explanations might be:

- (a) incorrectly measured sorption values. This seems highly unlikely. Large sorption values would have to be measured in systems where there should be no sorption.

- (b) the assumptions regarding sorption behaviour, and especially that negatively charged hydroxy-carbonate and carbonate species do not sorb, are flawed. This is a real issue.
- (c) the hydroxy-carbonate and carbonate complexation constants in the thermodynamic data base are too strong. This is also plausible.

Thus there are (often) large uncertainties in actinide speciation (especially for the tetravalent state) and almost no information on the species which sorb and their sorption mechanisms and the corresponding surface complexes which form. The overriding conclusion is that the uptake of actinides on clay minerals and argillaceous rocks is poorly understood and it is clearly important from all points of view to improve this deficit of understanding for this important group of safety relevant radionuclides.

With respect to the selection of sorption values for tetravalent actinides, the example of Th indicates clearly that the decrease in sorption as a result of the formation of negatively charged complexes (particularly hydroxy-carbonate complexes) is much less than the speciation calculations and the general approach suggested in section 5.2.2 would indicate. On the other hand, because of the lack of system understanding, we do not have any clearly defined procedures for modifying literature data to correspond with the reference conditions for OPA for these elements.

The clear message from the above discussion is that the sorption data modification scheme with respect to the speciation as given in section 5.2.2 is not applicable for Th. Under these circumstances a decision was made to rely on the experimental evidence.

The same general uncertainties in the TDB also apply to other tetravalent actinides and Tc(IV). The procedure proposed for these elements is to use Th as a chemical analogue and the data given in Figure 8. Only one element specific modification is made and this is based on the fraction of the element present in the tetravalent oxidation state ($F_{\text{lit (IV)}}$ and $F_{\text{ref (IV)}}$).

7.4.4 Thorium

The primary source for Th sorption data are the measurements of LAUBER et al. (2000) on OPA as a function of concentration in synthetic OPA porewater compositions at pH values of 7.8 and 6.3. From the isotherm data presented in Figures 8a and 8b sorption values of 63 and 25 m³ kg⁻¹ were selected at pH ~7.8 and 6.3 respectively. The sorption of Th in the measured concentration range is linear.

For the reference OPA conditions (pH = 7.24) it is anticipated that the sorption of Th is independent of pH in the range between 7.24 and 7.8. In addition, the aqueous speciation of Th is very similar in the reference Benken porewater at pH = 7.24 and the synthetic OPA porewater at pH = 7.8. For the reference case, the Th sorption value at pH = 7.8 is selected, i.e. 63 m³ kg⁻¹.

The modified procedure given in section 7.4.3 for deriving the sorption values were applied for Th.

Data sheets are given for Th.

An in situ sorption value for Th of 55.4 m³ kg⁻¹ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of 22 m³ kg⁻¹ and 55.4 m³ kg⁻¹ respectively were chosen.

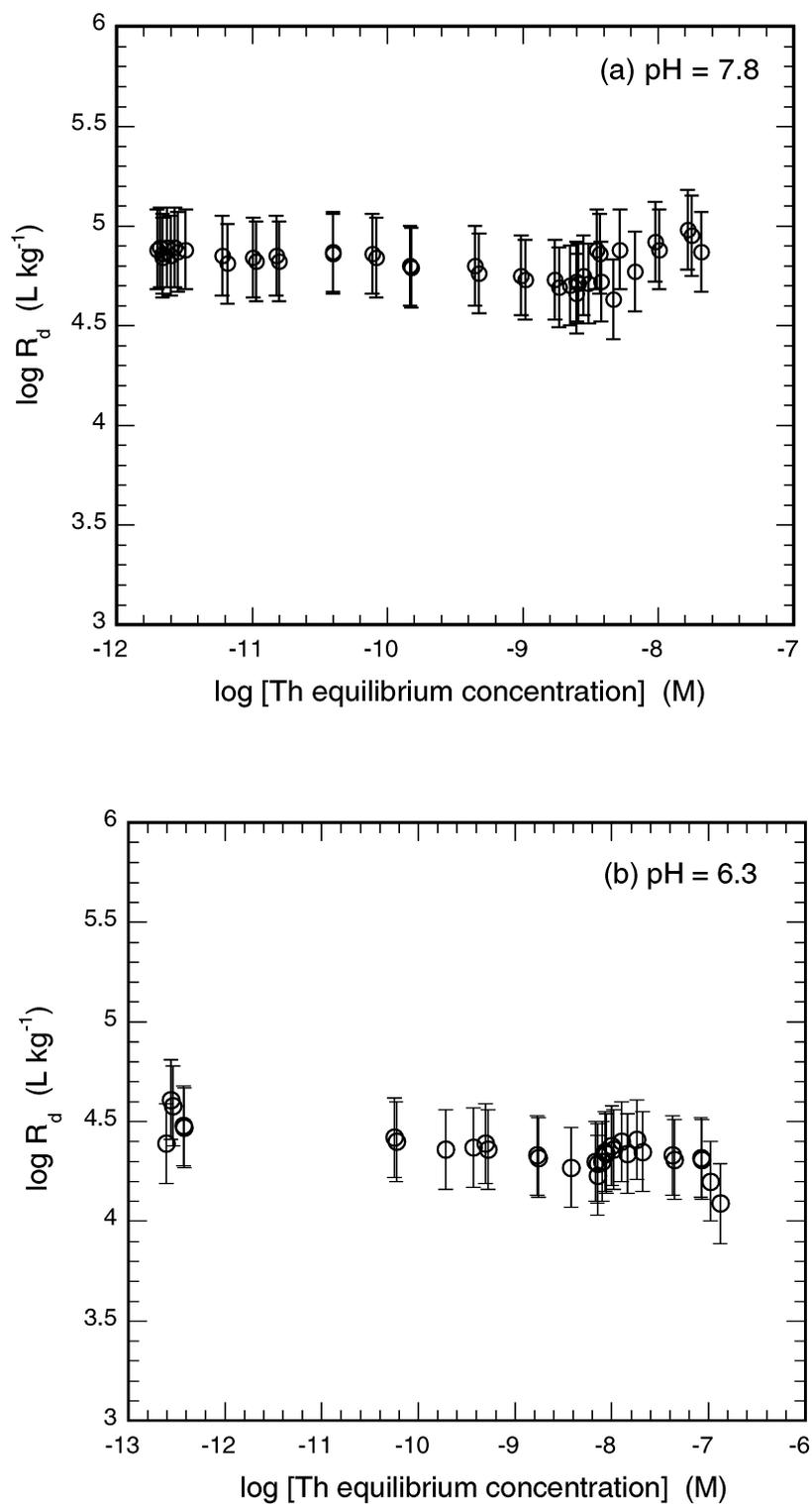


Figure 8: Th(IV) sorption isotherms on OPA from Mont Terri at (a) pH = 7.8 and (b) pH = 6.3 in synthetic OPA porewaters.

Th(IV) DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $63 \text{ m}^3 \text{ kg}^{-1}$ (Th equilibrium concentration: $< 10^{-9} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$F_{\text{lit. (IV)}}$
7.8	1

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. (IV)}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.24	1	0.106

Conversion factors

CF_{pH}	$\text{CF}_{(\text{IV})}$	CF_{CEC}
1	1	0.88

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
55.4

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
55.4

Th(IV) DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $25 \text{ m}^3 \text{ kg}^{-1}$ (Th equilibrium concentration: $< 10^{-9} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$F_{\text{lit. (IV)}}$
6.3	1

Opalinus Clay pH = 6.3: data summary

pH	$F_{\text{(IV)}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
6.3	1	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{(IV)}}$	CF_{CEC}
1	1	0.88

Opalinus Clay pH = 6.3 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
22.0

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ in situ}$ ($\text{m}^3 \text{ kg}^{-1}$)
22.0

Th(IV) DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $63 \text{ m}^3 \text{ kg}^{-1}$ (Th equilibrium concentration: $< 10^{-9} \text{ M}$)**Source data summary**

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$F_{\text{lit. (IV)}}$
7.8	1

Opalinus Clay pH = 7.8: data summary

pH	$F_{\text{(IV)}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.8	1	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{(IV)}}$	CF_{CEC}
1	1	0.88

Opalinus Clay pH = 7.8 sorption value

R_{d} ($\text{m}^3 \text{ kg}^{-1}$)
55.4

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_{\text{d in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
55.4

7.4.5 Protactinium

Under the anticipated in situ redox and pH conditions, protactinium exists predominantly in the pentavalent oxidation state. At first sight Np(V) might be considered as a suitable chemical analogue for Pa(V). Upon closer inspection however it can be seen that Np(V) is inappropriate. Under the in situ OPA conditions Pa exists as PaO_2OH^0 species whereas Np is predominantly present as NpO_2^+ ; two completely different sorbing species.

Because Pa exists as the neutral hydroxy species, high sorption values would be expected (see section 5.2.1); probably of the same order of magnitude as Th(IV), Np(IV) and Pu(IV). However, to claim chemical analogy with any of these nuclides would also be inappropriate.

BERRY et al. (1988a) measured the sorption of Pa(V) under reducing conditions on six rock types in the pH range 6 to 9.5 and measured values between 1 - >1000 $\text{m}^3 \text{kg}^{-1}$. The values for London clay, selected as being the most similar of the six materials to OPA, lay between ~3 and >1000 $\text{m}^3 \text{kg}^{-1}$; pH = 8.8 to 9.1, initial Pa concentration $\sim 5 \times 10^{-11}$ M. Despite the fact that working with Pa is fraught with experimental difficulties, (BAES & MESMER, 1976; BERRY et al., 1988a), there is a clear indication that Pa sorbs extremely strongly on almost all rock types under neutral to slightly alkaline conditions. This is entirely in keeping with Pa existing as the neutral hydroxy species and the discussion given in section 5.2.1.

The selection of a sorption value for Pa is somewhat difficult because of the wide range of values measured. From the work of BERRY et al. (1988a) on different rock types it can be said with a reasonably high degree of certainty that the sorption value for Pa on OPA is $>1 \text{ m}^3 \text{kg}^{-1}$. Further, using the comparison with London clay, the sorption is probably $\geq 3 \text{ m}^3 \text{kg}^{-1}$. A value of $5 \text{ m}^3 \text{kg}^{-1}$ is given in the SDB. However, from the above, the expectation is that Pa will sorb orders of magnitude more strongly than the value given but at the moment such high sorption values cannot be justified.

The rationale behind the selection of a value for an overall uncertainty factor of 10 is given in section 6.8.

No data sheets are provided for Pa.

An in situ sorption value for Pa of $5 \text{ m}^3 \text{kg}^{-1}$ was chosen for the OPA reference system. The same value is chosen for the bounding pH values of 6.3 and 7.8.

7.4.6 Uranium

BERRY et al. (1989, 1991) and BASTON et al. (1991, 1992) investigated the sorption of U(IV) on Caithness flagstones, St. Bees sandstone and London clay rocks in contact with "equilibrated cement water". Solution pH values were adjusted to ~ 8 before batch sorption experiments were performed at different S:L ratios. Although mineralogies and "equilibrated cement water compositions" were given, it was not clear from their text what the effect of the pH adjustment was and what the water composition in the batch tests became. Also it is not sure whether the tetravalent redox state of U was maintained during their experiments. Because of the above, these single point measurements were not further considered.

Speciation calculations indicate that at pH = 6.3 U is predominantly in the hexavalent oxidation state. Only 2.5 % is present in the tetravalent state. At higher pH values, tetravalent U is dominant.

Sorption values for U(IV) were derived on the basis of chemical analogy with Th(IV) following the discussion and proposals given in section 7.4.3. Note that the fraction of U present in the hexavalent state is not taken into account as being sorbing.

Data sheets for U(IV) are given.

An in situ sorption value for U(IV) of $20.5 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $5.5 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $48.2 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

U DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay reference case Th data

$R_d(\text{Th})_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$	$F(\text{Th})_{(\text{IV})}$
55.4	1

Opalinus Clay reference case U data

$F(\text{U})_{(\text{IV})}$
0.37

Conversion

$$R_d \text{ U(IV)}_{\text{ref}} = R_d \text{ Th(IV)}_{\text{ref}} \times [F(\text{U})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay reference sorption value

$R_d \text{ U(IV)}_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
20.5

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{ U(IV)}_{\text{in situ}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
20.5

U DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 6.3 Th data

$R_d(\text{Th})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Th})_{(\text{IV})}$
22.0	1

Opalinus Clay pH = 6.3 U data

$F(\text{U})_{(\text{IV})}$
0.025

Conversion

$$R_d(\text{U})_{\text{pH}=6.3} = R_d(\text{Th})_{\text{pH}=6.3} \times [F(\text{U})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay pH = 6.3 sorption value

$R_d(\text{U})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$
5.5×10^{-1}

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{U})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
5.5×10^{-1}

U DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 7.8 Th data

$R_d(\text{Th})_{\text{pH}=7.8} \text{ (m}^3 \text{ kg}^{-1}\text{)}$	$F(\text{Th})_{(\text{IV})}$
55.4	1

Opalinus Clay pH = 7.8 U data

$F(\text{U})_{(\text{IV})}$
0.87

Conversion

$$R_d(\text{U})_{\text{pH}=7.8} = R_d(\text{Th})_{\text{pH}=7.8} \times [F(\text{U})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay pH = 7.8 sorption value

$R_d(\text{U})_{\text{pH}=7.8} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
48.2

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{U})_{\text{in situ}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
48.2

7.4.7 Neptunium

Speciation calculations indicate that Np is present in the tetravalent oxidation state under the Eh/pH conditions in both OPA reference groundwaters.

HENRION et al. (1985) studied Np sorption on Boom clay under reducing conditions. However, because strong complexation with humic substances essentially determined the Np sorption, the results from this work are not relevant for the OPA system.

The only other potentially relevant data found were those from BARNEY (1982) where Np was measured under reducing conditions (0.05 M hydrazine) on a sandstone (CEC = 0.099 eq. kg⁻¹) in a synthetic groundwater at pH values between 8.7 to 9.4. The R_d values determined in this study for Np ranged from 0.1 to 0.7 m³ kg⁻¹. The Np equilibrium concentration was $\sim 3 \times 10^{-7}$ M. The mean value of 10 independent measurements was 0.4 (± 0.3) m³ kg⁻¹. Because of the uncertainties with respect to the influence of hydrazine and the scatter in the data, these measurements were not considered further.

Sorption values for Np(IV) were derived on the basis of chemical analogy with Th(IV) following the discussion and proposals given in section 7.4.3.

Data sheets for Np(IV) are provided.

An in situ sorption value for Np(IV) of 55.4 m³ kg⁻¹ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of 22 m³ kg⁻¹ and 55.4 m³ kg⁻¹ respectively were chosen.

Np DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay reference case Th data

$R_d(\text{Th})_{\text{ref.}} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Th})_{(\text{IV})}$
55.4	1

Opalinus Clay reference case Np data

$F(\text{Np})_{(\text{IV})}$
1

Conversion

$$R_d \text{Np(IV)}_{\text{ref}} = R_d \text{Th(IV)}_{\text{ref}} \times [F(\text{Np})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay reference sorption value

$R_d \text{Np(IV)}_{\text{ref.}} (\text{m}^3 \text{kg}^{-1})$
55.4

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_d \text{Np(IV)}_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
55.4

Np DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 6.3 Th data

$R_d(\text{Th})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Th})_{(\text{IV})}$
22.0	1

Opalinus Clay pH = 6.3 Np data

$F(\text{Np})_{(\text{IV})}$
1

Conversion

$$R_d(\text{Np})_{\text{pH}=6.3} = R_d(\text{Th})_{\text{pH}=6.3} \times [F(\text{Np})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay pH = 6.3 sorption value

$R_d(\text{Np})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$
22.0

Opalinus Clay, pH = 6.3: in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Np})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
22.0

Np DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 7.8 Th data

$R_d(\text{Th})_{\text{pH}=7.8} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Th})_{(\text{IV})}$
55.4	1

Opalinus Clay pH = 7.8 Np data

$F(\text{Np})_{(\text{IV})}$
1

Conversion

$$R_d(\text{Np})_{\text{pH}=7.8} = R_d(\text{Th})_{\text{pH}=7.8} \times [F(\text{Np})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay pH = 7.8 sorption value

$R_d(\text{Np})_{\text{pH}=7.8} (\text{m}^3 \text{kg}^{-1})$
55.4

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Np})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
55.4

7.4.8 Plutonium

The speciation of Pu in the reference OPA groundwater under the Eh/pH conditions given in Table 2 indicates that the redox state of Pu is trivalent at pH = 6.3. At pH = 7.24 and 7.8 the total Pu present in the trivalent oxidation state is 93.5% and 73.2 % respectively.

No relevant sorption data for Pu(III) could be found in the open literature and Am(III) is taken as chemical analogue. The chemical analogue speciation correction as described in section 5.2.3 was applied to Pu(III). Note that the fraction of Pu present in the tetravalent state is not taken into account as being sorbing, resulting in conservative R_d values.

Data sheets for Pu(III) are given.

An in situ sorption value for Pu(III) of $22.6 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $1.1 \text{ m}^3 \text{ kg}^{-1}$ and $75.2 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Pu(III) DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Selected chemical analogue: Am(III)

Source of chemical analogue sorption data: GORGEON (1994)

Opalinus Clay reference case Am(III) data

$R_d(\text{Am})_{\text{ref.}} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Am})_{\text{ref.}} \text{speciation}$
20.8	0.045

Opalinus Clay reference case Pu data

$F(\text{Pu})_{\text{ref.}} \text{speciation}$
0.049

Conversion

$$R_d(\text{Pu})_{\text{ref.}} = R_d(\text{Am})_{\text{ref.}} \times [F(\text{Pu})_{\text{ref.}} \text{speciation}] / F(\text{Am})_{\text{ref.}} \text{speciation}]$$

Opalinus Clay reference sorption value

$R_d(\text{Pu})_{\text{ref.}} (\text{m}^3 \text{kg}^{-1})$
22.6

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Pu})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
22.6

Pu(III) DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Selected chemical analogue: Am(III)

Source of chemical analogue sorption data: GORGEON (1994)

Opalinus Clay pH = 6.3 Am(III) data

$R_d (\text{Am})_{\text{pH}=6.3} (\text{m}^3 \text{ kg}^{-1})$	$F (\text{Am})_{\text{pH}=6.3} \text{ speciation}$
1.2	0.08

Opalinus Clay pH = 6.3 Pu data

$F (\text{Pu})_{\text{pH}=6.3} \text{ speciation}$
0.07

Conversion

$$R_d (\text{Pu})_{\text{pH}=6.3} = R_d (\text{Am})_{\text{pH}=6.3} \times [F (\text{Pu})_{\text{pH}=6.3} \text{ speciation}] / F (\text{Am})_{\text{pH}=6.3} \text{ speciation}]$$

Opalinus Clay pH = 6.3 sorption value

$R_d (\text{Pu})_{\text{pH}=6.3} (\text{m}^3 \text{ kg}^{-1})$
1.1

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d (\text{Pu})_{\text{in situ}} (\text{m}^3 \text{ kg}^{-1})$
1.1

Pu(III) DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Selected chemical analogue: Am(III)

Source of chemical analogue sorption data: GORGEON (1994)

Opalinus Clay pH = 7.8 Am(III) data

$R_d (\text{Am})_{\text{pH}=7.8} (\text{m}^3 \text{kg}^{-1})$	$F (\text{Am})_{\text{pH}=7.8} \text{ speciation}$
63	0.031

Opalinus Clay pH = 7.8 Pu data

$F (\text{Pu})_{\text{pH}=7.8} \text{ speciation}$
0.037

Conversion

$$R_d (\text{Pu})_{\text{pH}=7.8} = R_d (\text{Am})_{\text{pH}=7.8} \times [F (\text{Pu})_{\text{pH}=7.8} \text{ speciation}] / F (\text{Am})_{\text{pH}=7.8} \text{ speciation}]$$

Opalinus Clay pH = 7.8 sorption value

$R_d (\text{Pu})_{\text{pH}=7.8} (\text{m}^3 \text{kg}^{-1})$
75.2

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d (\text{Pu})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
75.2

7.5 Other elements: Sn, Zr, Hf, Nb, Sb, Tc

7.5.1 Tin

Reliable sorption data for Sn on relevant geological substrates are extremely rare in the open literature. Data exist for soils (see for example the review of MORGAN & BEETHAN, 1990), for suspended particles in seawater (LI et al., 1984; NYFFELER et al., 1984) and for deep-sea interfacial sediment in seawater at pH 7.8 (BALISTRIERI & MURRAY, 1984). None of these data are appropriate because in all cases the presence of organic matter is most probably playing a significant, but unquantified, role in the experiments.

LAUBER et al. (2000) measured the sorption kinetics at trace concentrations of Sn(IV) on OPA from Mont Terri at pH values of 6.3 and 8.1. Because of the limited solubility of Sn(IV) in this pH range ($\sim 5 \times 10^{-8}$ M), sorption isotherms could not be determined. The R_d values obtained from this study were $145 \text{ m}^3 \text{ kg}^{-1}$ and $125 \text{ m}^3 \text{ kg}^{-1}$ at pH = 8.1 and 6.3 respectively. Clearly, Sn(IV) sorption under these conditions is very high and, within experimental error, does not apparently vary in any significant way with pH.

Data measured by LEGOUX et al. (1992) on 4 similar sedimentary rocks (CEC range between 0.026 to 0.047 eq. kg^{-1}) in the pH range 5.9 to 8 yielded R_d values from $10 \text{ m}^3 \text{ kg}^{-1}$ to $45 \text{ m}^3 \text{ kg}^{-1}$. This data indicate again that there is no clear trend in the sorption behaviour of Sn(IV) as function of pH.

A sorption edge for Sn on conditioned Na illite was measured in 0.1 M NaClO_4 and is presented in Figure 9 (BRADBURY & BAEYENS, unpublished data). These data show clearly that the sorption of Sn(IV) is high and constant in the pH range ~ 4 to ~ 9.5 . Above pH = 9.5 the sorption begins to decrease, presumably due to the influence of the formation of $\text{Sn}(\text{OH})_5^-$. According to AMAYA et al. (1997), see Figure 10, below pH ~ 8 Sn(IV) is present pre-dominantly as the neutral tetrahydroxy complex.

In view of the above considerations, it is assumed that between pH 6.3 and 7.8 the sorption is not dependent on pH. In addition speciation calculations in the synthetic laboratory waters and under the OPA reference conditions using the Nagra/PSI TDB (HUMMEL et al., 2002) indicate that only hydroxy species are present. In view of this only one sorption value is taken for the reference OPA system at pH = 7.24 and the bounding pHs of 6.3 and 7.8, and, the lower bound value of $125 \text{ m}^3 \text{ kg}^{-1}$ is selected.

In view of the very high sorption values measured for Sn(IV) a laboratory uncertainty factor of 5 was assigned to the distribution ratio.

Given the above considerations, the only conversion factor that applies is the one correcting for the difference in mineralogies. The CF_{CEC} for the OPA system is 0.88 and this value has been applied to the selected data.

No data sheets for Sn are given.

An in situ sorption value for Sn of $110 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at $\text{pH} = 7.24$. At the bounding pH values of 6.3 and 7.8 the sorption values were the same as in the reference case.

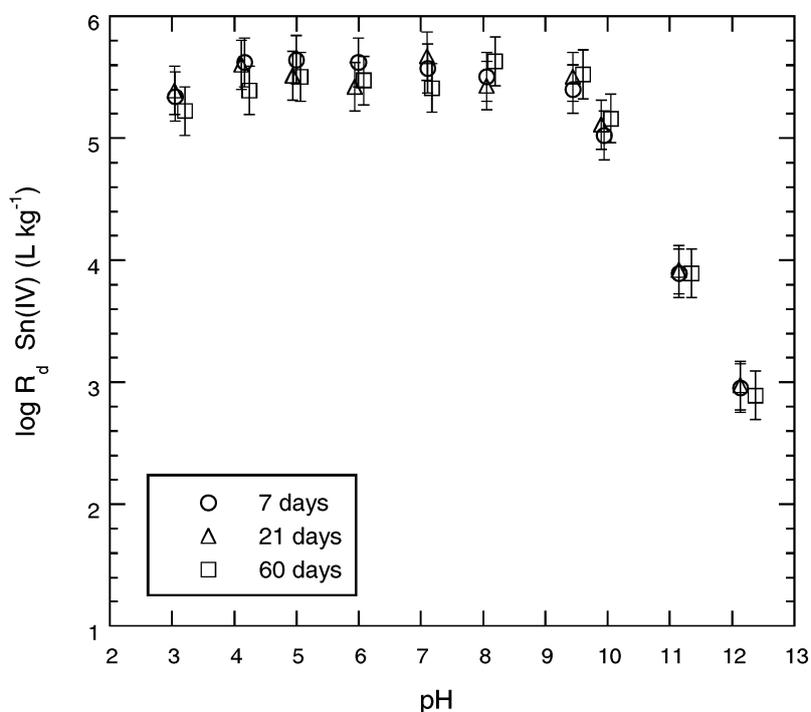


Figure 9: Sn sorption edge measurements on Na-illite in 0.1 M NaClO_4 . (BRADBURY & BAEYENS, unpublished data)

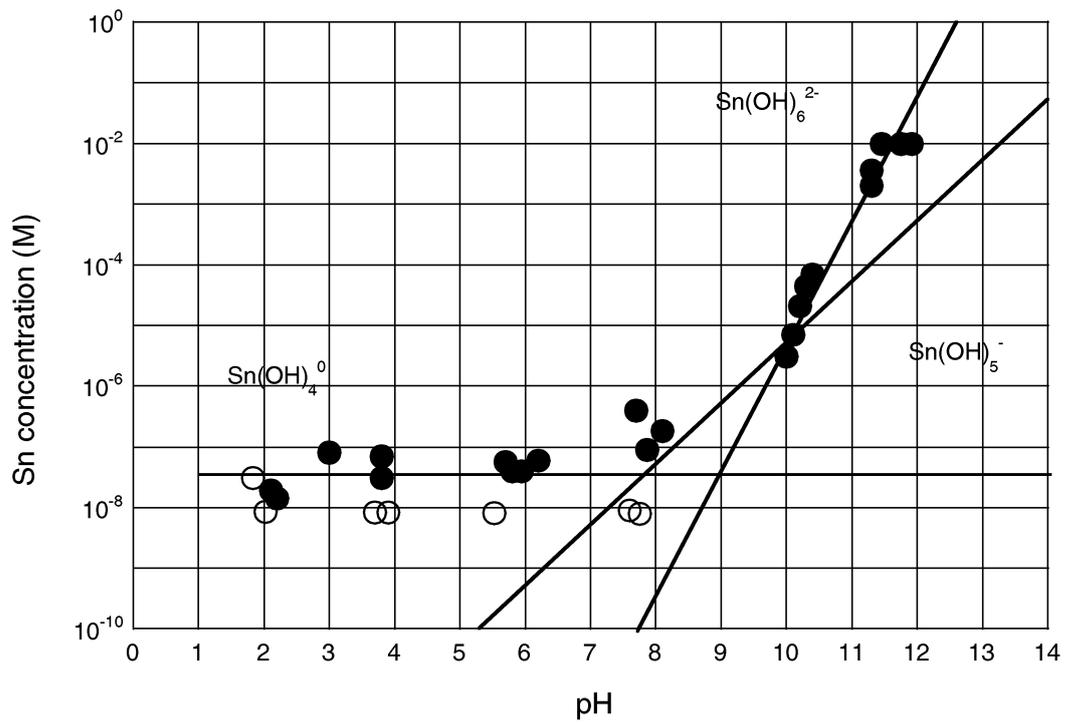


Figure 10: Solubility and speciation of Sn(IV) as a function of pH. Open symbols refer to crystalline SnO_2 , closed symbols refer to amorphous SnO_2 . (Taken from AMAYA et al., 1997)

7.5.2 Zirconium and Hafnium

For Zr and Hf no relevant sorption data could not be found in the open literature (see HIGGO, 1988 and Appendix B in STENHOUSE, 1995).

Zr and Hf are tetravalent elements which have a similar hydrolysis behaviour to Sn(IV) except that the negatively charged hydroxy species begin to become significant at $\text{pH} \leq 6$. Although it is clear that uncharged hydroxy species sorb strongly, the mechanism is not known, and it is not clear to what extent the formation of negatively charged hydroxy species reduce the sorption. The conservative assumption is made here that only the neutral hydroxy species sorb. Thus Sn is taken as the chemical analogue for both elements and a conversion factor, calculated over the speciation at pH 7.24, 6.3 and 7.8, is applied to obtain the sorption values.

The updated Nagra/PSI TDB does not contain thermodynamic data for Hf. Because the hydrolysis behaviour of Hf is very similar to Zr (BAES & MESMER, 1976) the same sorption values are selected.

Data sheets for Zr are given. No data sheets for Hf are given.

An in situ sorption value for Zr and Hf of $10.9 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at $\text{pH} = 7.24$. At the bounding pH values of 6.3 and 7.8 sorption values of $39.7 \text{ m}^3 \text{ kg}^{-1}$ and $4.7 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Zr DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Selected chemical analogue: Sn(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay reference case Sn data

$R_d(\text{Sn})_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$	$F(\text{Sn})_{\text{ref. speciation}}$
110	0.81

Opalinus Clay reference case Zr data

$F(\text{Zr})_{\text{ref. speciation}}$
0.08

Conversion

$$R_d(\text{Zr})_{\text{ref.}} = R_d(\text{Sn})_{\text{ref.}} \times [F(\text{Zr})_{\text{ref. speciation}} / F(\text{Sn})_{\text{ref. speciation}}]$$

Opalinus Clay reference sorption value

$R_d(\text{Zr})_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
10.9

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Zr})_{\text{in situ}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
10.9

Zr DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Selected chemical analogue: Sn(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 6.3 Sn data

$R_d(\text{Sn})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Sn})_{\text{pH}=6.3} \text{ speciation}$
110	0.97

Opalinus Clay pH = 6.3 Zr data

$F(\text{Zr})_{\text{pH}=6.3} \text{ speciation}$
0.35

Conversion

$$R_d(\text{Zr})_{\text{pH}=6.3} = R_d(\text{Sn})_{\text{pH}=6.3} \times [F(\text{Zr})_{\text{pH}=6.3} \text{ speciation}] / F(\text{Sn})_{\text{pH}=6.3} \text{ speciation}]$$

Opalinus Clay pH = 6.3 sorption value

$R_d(\text{Zr})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$
39.7

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Zr})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
39.7

Zr DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Selected chemical analogue: Sn(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 7.8 Sn data

$R_d(\text{Sn})_{\text{pH}=7.8} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Sn})_{\text{pH}=7.8} \text{ speciation}$
110	0.54

Opalinus Clay pH = 7.8 Zr data

$F(\text{Zr})_{\text{pH}=7.8} \text{ speciation}$
0.023

Conversion

$$R_d(\text{Zr})_{\text{pH}=7.8} = R_d(\text{Sn})_{\text{pH}=7.8} \times [F(\text{Zr})_{\text{pH}=7.8} \text{ speciation}] / F(\text{Sn})_{\text{pH}=7.8} \text{ speciation}]$$

Opalinus Clay pH = 7.8 sorption value

$R_d(\text{Zr})_{\text{pH}=7.8} (\text{m}^3 \text{kg}^{-1})$
4.7

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Zr})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
4.7

7.5.3 Niobium

Only two sources of Nb sorption data were found for which both water chemistries and mineralogies were described.

LEGOUX et al. (1992) measured single point Nb sorption values between 1.5 and 2.6 $\text{m}^3 \text{kg}^{-1}$ on four similar quartz rich sediments containing ~10 wt.% illite and smectite clay minerals in the pH range from 5.9 to 8. (CEC values were also given.). BERRY et al. (1988b) report a single R_d value of $> 6 \text{ m}^3 \text{kg}^{-1}$ for London clay at pH ~ 8. The measurements of BERRY et al. (1988b) and LEGOUX et al. (1992) both show high Nb sorption, and speciation calculations indicate that a substantial fraction of Nb exists as $\text{Nb}(\text{OH})_5^0$ in the pH/Eh conditions used in these experiments. Following the comments given in section 5.2.1 on the high sorptivity often associated with neutral hydroxy species, the presence of $\text{Nb}(\text{OH})_5^0$ in the aqueous phase might explain the strong sorption of Nb.

Following the same arguments as given for Sn, no pH conversion factors and speciation factors are applied to the measured data to obtain in situ R_d values. Only the conversion factor for mineralogy is used. The results of the data are summarised in Table 6. Only one value covering the pH range of 6.3 and 7.8 is considered for Nb and from Table 6 the lower bound R_d value of $4 \text{ m}^3 \text{kg}^{-1}$ is selected for the reference OPA system at pH = 7.24 and for the bounding pH values of 6.3 and 7.8.

Table 6: Sorption data for Nb(V) in a synthetic groundwater on various sediments. (Nb equilibrium concentration $< 10^{-10} \text{ M}$). Taken from LEGOUX et al. (1992).

Solid phase	CEC (eq. kg^{-1})	pH	R_d lit ($\text{m}^3 \text{kg}^{-1}$)	R_d in situ ($\text{m}^3 \text{kg}^{-1}$)
Sediment A	0.03	7.6	2.6	9.2
Sediment B	0.043	5.9	1.5	3.7
Sediment C	0.047	6.6	1.7	3.8
Sediment D	0.026	8	2.1	8.6

Because of the lack of understanding of the sorption process, the fact that the quartz rich sediments/water chemistries are so different from the OPA reference case and only single point measurements are available, a higher R_d uncertainty factor is considered for this value, i.e. $R_d\text{-UF} = 5$.

No data sheets for Nb are given.

An in situ sorption value for Nb of $4 \text{ m}^3 \text{kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 the sorption values were the same as in the reference case.

7.5.4 Antimony

The speciation calculations for Sb under the pH/Eh conditions of the 3 OPA groundwater systems, Table 2, indicate that Sb is solely present in the trivalent oxidation state as the neutral trihydroxy complex, $\text{Sb}(\text{OH})_3^0$. Antimony belongs to the group V-A elements, and according to BAES & MESMER (1976), the usual trend of increasing cationic behaviour in this group is exhibited by the heavier elements such as Sb(III) and Bi(III).

No relevant sorption data for the OPA system of Sb(III) could be found in the literature.

As already discussed in section 5.2.1, it is known that hydrolysed cationic species such as trivalent lanthanides and actinides sorb very strongly on a large number of sorbents. However, in view of the above, it is not clear whether these elements are appropriate chemical analogues for Sb(III).

ENDERS (1996) studied the adsorption of Sb(III) on hydrous ferric iron oxide and observed constant and very high sorption values ($R_d \sim 220 \text{ m}^3 \text{ kg}^{-1}$) in the pH range 4 to 10. These results are in agreement with the expected high sorptivity of the neutral trihydroxy Sb(III) species and the fact that only this species is present in the pH range between ~ 3 and 10 (see Figure 16.1 in BAES & MESMER, 1976).

Since no relevant data for Sb(III) could be found Bi(III) was considered to be a good chemical analogue. Figure 16.6 in BAES & MESMER (1976) indicates that only positively charged and neutral hydroxy species are present up to pH ~ 10 . No sorption data of Bi on argillaceous rocks or illite could be found in the open literature. ULRICH & DEGUELDRE (1992) measured the sorption of Bi(III) on montmorillonite clay between pH = 5 and 7 in different NaClO_4 background concentrations. These results are re-plotted in Figure 11 and show a typical sorption edge between pH 5 and 7. No clear effects of ionic strengths are observed. This sorption behaviour indicates that the uptake mechanism is likely to be surface complexation.

Although there is some evidence, albeit limited, that the uptake of hydrolysable trivalent cations on various clay minerals shows a similar surface complexation behaviour in terms of magnitude of sorption. Examples are Am(III) sorption on kaolinite, illite and montmorillonite (GORGEON, 1994); Eu(III) sorption on montmorillonite (BRADBURY & BAEYENS, 2002) and illite (POINSSOT et al., 1999a). The sorption values taken from the montmorillonite data are conservatively converted to the OPA system by applying a mineralogical conversion factor.

In view of the above, the data set of Bi(III) on montmorillonite from ULRICH & DEGUELDRE (1992) is considered, and lower bound sorption values of $40 \text{ m}^3 \text{ kg}^{-1}$, $18 \text{ m}^3 \text{ kg}^{-1}$ and $50 \text{ m}^3 \text{ kg}^{-1}$ at pH 7.24, 6.3 and 7.8 respectively are selected from Figure 11.

Data sheets for Bi(III) are given.

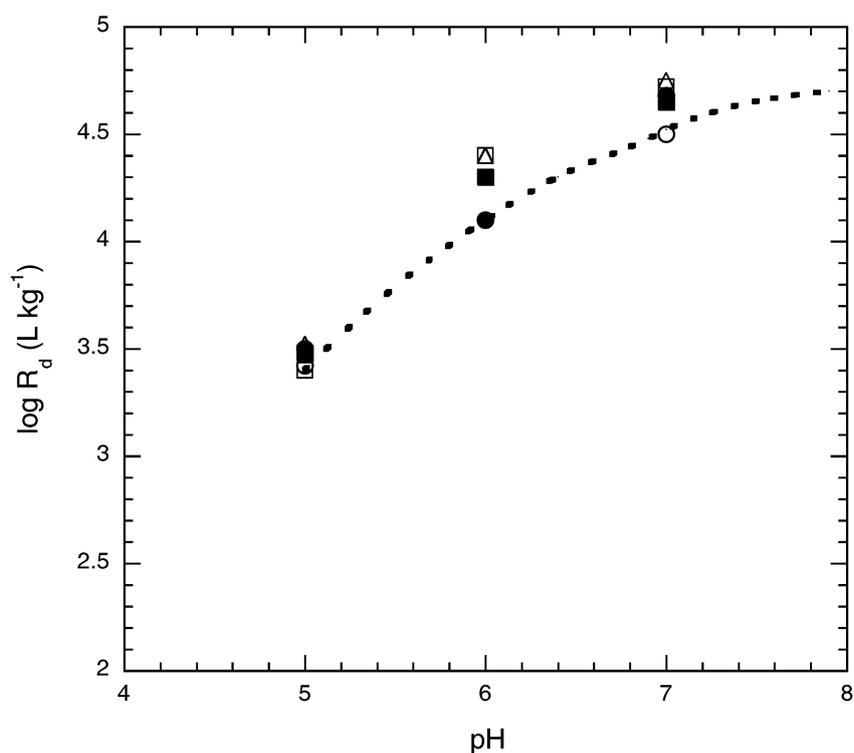


Figure 11: Bi(III) sorption data from ULRICH & DEGUELDRE (1992) re-plotted as a sorption edge. NaClO_4 background electrolyte at 0.01 M (O); 0.02 M (●); 0.05 M (□); 0.1 M (■) and 0.2 M (Δ).

Bi(III) is taken as a chemical analogue for Sb(III). The speciation for pH values of 6.3, 7.24 and 7.8 predict only the neutral trihydroxyantimony complex, hence the speciation conversion factor is 1 and the same R_d values are selected for Sb(III) as for Bi(III). In view of the sparseness of the data and the uncertainties associated with the Bi sorption values for montmorillonite applied to illite, a higher laboratory UF of 5 was assigned to the selected R_d values. This results in an overall UF for Bi of 18.2, see section 6.8.

No data sheets for Sb(III) are given.

An in situ sorption value for Sb of $5.6 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $2.5 \text{ m}^3 \text{ kg}^{-1}$ and $7.0 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Bi(III) DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: ULRICH & DEGUELDRE (1992)

Selected $R_{d \text{ lit.}}$: $40 \text{ m}^3 \text{ kg}^{-1}$ (Bi equilibrium concentration $< 10^{-11} \text{ M}$)**Source data summary**

Solid	CEC _{lit.} (eq. kg ⁻¹)
Montmorillonite	0.76

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.24	1.2×10^{-4}	-	0.1	1

Opalinus Clay reference case: data summary

pH _{ref.}	F _{ref. speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.24	1	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
1	1	0.14

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ (m ³ kg ⁻¹)
5.6

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
5.6

Bi(III) DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: ULRICH & DEGUELDRE (1992)

Selected $R_{d \text{ lit.}}$: $18 \text{ m}^3 \text{ kg}^{-1}$ (Bi equilibrium concentration: $< 10^{-11} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (eq. kg ⁻¹)
montmorillonite	0.76

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
6.3	2.3×10^{-5}	-	0.1	1

Opalinus Clay pH = 6.3: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
6.3	1	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
1	1	0.14

Opalinus Clay pH = 6.3 sorption value

R_d (m ³ kg ⁻¹)
2.5

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

R_d in situ (m ³ kg ⁻¹)
2.5

Bi(III) DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: ULRICH & DEGUELDRE (1992)

Selected $R_{d \text{ lit.}}$: $50 \text{ m}^3 \text{ kg}^{-1}$ (Bi equilibrium concentration: $< 10^{-11} \text{ M}$)**Source data summary**

Solid	CEC _{lit.} (eq. kg ⁻¹)
Montmorillonite	0.76

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.8	4.1×10^{-4}	-	0.1	1

Opalinus Clay pH = 7.8: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.8	1	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
1	1	0.14

Opalinus Clay pH = 7.8 sorption value

R_d (m ³ kg ⁻¹)
7.0

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
7.0

7.5.5 Polonium

No relevant sorption data were found for Po.

Po(II) oxidises easily to Po(IV) by self-irradiation (FALBE & REGITZ, 1992) and probably exists as PoO_3^{2-} under the Eh/pH conditions envisaged to exist in the OPA formation. Po is in group VI-A of the periodic table as is Se which also forms a similar anionic species. Since no sorption data for Po(IV) could be found, Se(IV) is taken as chemical analogue.

The sorption characteristics are those which would be anticipated from a ligand exchange mechanism on the amphoteric $\equiv\text{SOH}$ edge sites on clay minerals. This assumption is in accord with the modelling of Se(IV) uptake on other sorbents by a surface ligand exchange mechanism (see for example STUMM et al., 1980; DZOMBAK & MOREL, 1990, DAVIS & KENT, 1990).

DAVIS & KENT (1990) present a Se(IV) sorption edge on ferrihydrate and show that the uptake of selenite is constant between pH 4 and 6, and decreases from pH 6 to 10. This sorption behaviour indicates that in addition to SeO_3^{2-} , the protonated HSeO_3^- is also a sorbing species. This is in agreement with the modelling approach presented by DZOMBAK & MOREL (1990) for the uptake of Se(IV) and other anionic species on hydrous ferric oxide (HFO). In their sorption model the free and protonated anions are sorbing on HFO via a surface complexation mechanism.

The sorption isotherms for Se(IV) measured at pH = 7.8 and 6.3 (LAUBER et al., 2000) are presented in Figure 12. At Se equilibrium concentrations below $\sim 10^{-7}$ M the sorption is constant and exhibit values of 0.32 and 0.08 $\text{m}^3 \text{kg}^{-1}$ at pH = 7.8 and 6.3 respectively. The sorption value for the OPA reference system at pH = 7.24 certainly lies between these values and an R_d of 0.2 $\text{m}^3 \text{kg}^{-1}$ is selected. The data given in Figure 12 indicate that the sorption of Se(IV) is higher at pH = 7.8 compared to pH = 6.3. This behaviour is not in agreement if a ligand exchange mechanism is taking place. The reasons are unclear and may be due to measurement error. A higher uncertainty factor for the laboratory sorption value is considered for Se(IV).

Data sheets for Se(IV) are given. It should be noted that at pH = 7.24, 6.3 and 7.8 the dominant aqueous Se species are HSeO_3^- and SeO_3^{2-} . In the calculation of the speciation conversion factors in the data sheet for Se(IV), see below, these species were taken to be sorbing.

Selenite is taken as a chemical analogue for polonite. Po(IV) exist solely as PoO_3^{2-} and thus its speciation factor is 1. Since the speciation factor for Se(IV) is also 1 the same sorption values for Po can be taken as for Se.

An overall uncertainty factor of 10 is assigned to Se, see section 6.8.

Since SeO_3^{2-} is used as the chemical analogue for PoO_3^{2-} , the overall uncertainty factor for Po is greater than for Se by the speciation uncertainty factor even though the speciation factor is unity for Po.

No data sheets are given for Po(IV).

An in situ sorption value for Po of $1.8 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $7.0 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ and $2.8 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

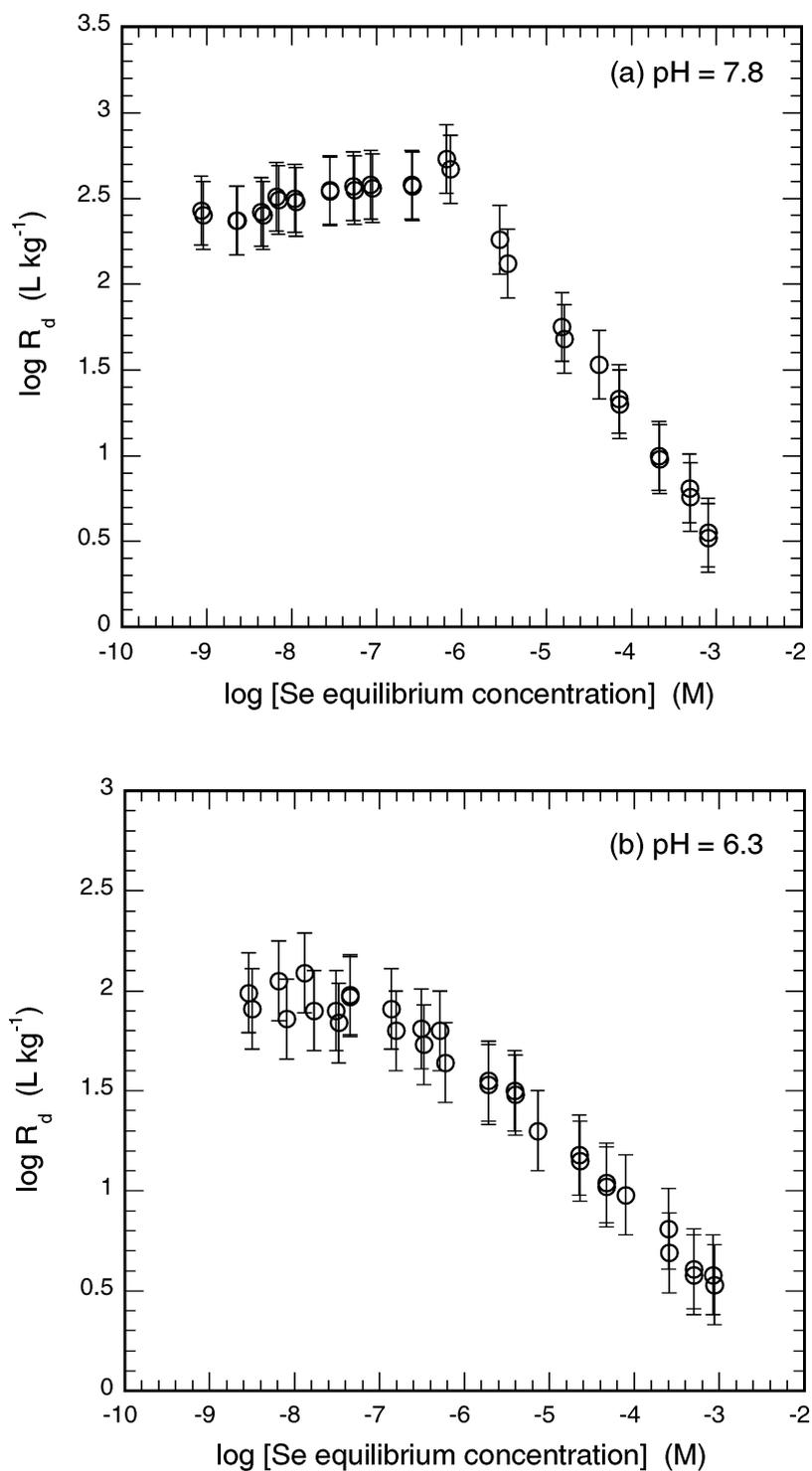


Figure 12: Se(IV) sorption isotherms on OPA from Mont Terri at (a) pH = 7.8 and (b) pH = 6.3 in synthetic OPA porewaters.

Se(IV) DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $0.2 \text{ m}^3 \text{ kg}^{-1}$ (Se equilibrium concentration: $< 10^{-6} \text{ M}$)**Source data summary**

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.8	1.8×10^{-4}	2.8×10^{-2}	3×10^{-1}	1

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.24	1	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	1	0.88

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
1.8×10^{-1}

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
1.8×10^{-1}

Se(IV) DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $0.08 \text{ m}^3 \text{ kg}^{-1}$ (Se equilibrium concentration: $< 10^{-6} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
6.3	1.7×10^{-2}	2.8×10^{-2}	1.86×10^{-1}	1

Opalinus Clay pH = 6.3: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
6.3	1	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	1	0.88

Opalinus Clay pH = 6.3 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
7.0×10^{-2}

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
7.0×10^{-2}

Se(IV) DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: LAUBER et al. (2000)

Selected $R_{d \text{ lit.}}$: $0.32 \text{ m}^3 \text{ kg}^{-1}$ (Se equilibrium concentration: $< 10^{-6} \text{ M}$)**Source data summary**

Solid	$\text{CEC}_{\text{lit.}}$ (eq. kg^{-1})
Mont Terri OPA	0.12

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.8	1.8×10^{-4}	2.8×10^{-2}	3×10^{-1}	1

Opalinus Clay, pH = 7.8: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (eq. kg^{-1})
7.8	1	0.106

Conversion factors

CF_{pH}	$\text{CF}_{\text{speciation}}$	CF_{CEC}
1	1	0.88

Opalinus Clay, pH = 7.8: sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
2.8×10^{-1}

Opalinus Clay, pH = 7.8: in situ sorption value

Lab→Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
2.8×10^{-1}

7.5.6 Molybdenum

Mo only exists in the valence state VI and above pH ~ 4 the dominant aqueous species is the anionic molybdate (MoO_4^{2-}) (BAES & MESMER, 1976).

Sorption data for MoO_4^{2-} on geological substrates are scarce. MOTTA & MIRANDA (1989) studied MoO_4^{2-} adsorption on illite in 0.01 M NaCl under well-defined conditions. They modelled the sorption using a constant capacitance surface complexation model and interpreted the data in terms of a ligand exchange mechanism with the reactive hydroxy groups located at the edges of clay mineral particles. The sorption was of the Langmuir type and isotherms at pH 8.9 and 8.2 were presented. MOTTA & MIRANDA (1989) did not measure a sorption edge and so other sources are required to provide information on the pH dependency.

Adsorption of molybdate by soils has been extensively studied within the framework of its mobility and availability to plants (e.g. PARFITT, 1978; GONZALES et al., 1974; THENG, 1971). From the results presented by THENG (1971), who measured the effects of pH on MoO_4^{2-} retention by soil clays, it appears that sorption increases as the pH decreases, reaching a maximum at pH = 4. The sorption increases by a factor of approximately 2 for each unit decrease in pH and this is taken as the basis for the pH correction for the OPA groundwater systems.

MOTTA & MIRANDA (1989) do not give a CEC value for the illite. A typical value of 0.2 eq. kg^{-1} is taken and used to calculate conversion factors.

Data sheets for Mo(VI) are given.

An in situ sorption value for Mo of $1.7 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $3.2 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ and $1.2 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Mo(VI) DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Literature source: MOTTA & MIRANDA (1989)

Selected $R_{d \text{ lit.}}$: $0.016 \text{ m}^3 \text{ kg}^{-1}$ (Mo equilibrium concentration: $< 5 \times 10^{-4} \text{ M}$)

Source data summary

Solid	$CEC_{\text{lit.}}$ (eq. kg^{-1})
illite	0.2

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
8.2	-	-	10^{-2}	1

Opalinus Clay reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$CEC_{\text{ref.}}$ (eq. kg^{-1})
7.24	1	0.106

Conversion factors

CF_{pH}	$CF_{\text{speciation}}$	CF_{CEC}
2*	1	0.53

*sorption increases by a factor of 2 for each pH unit decrease (8.2 -> 7.24)

Opalinus Clay reference sorption value

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
1.7×10^{-2}

Opalinus Clay in situ sorption value

Lab → Field transfer factor = 1

$R_{d \text{ in situ}}$ ($\text{m}^3 \text{ kg}^{-1}$)
1.7×10^{-2}

Mo(VI) DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Literature source: MOTTA & MIRANDA (1989)

Selected $R_{d \text{ lit.}}$: $0.016 \text{ m}^3 \text{ kg}^{-1}$ (Mo equilibrium concentration: $< 5 \times 10^{-4} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (eq. kg ⁻¹)
illite	0.2

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
8.2	-	-	10 ⁻²	1

Opalinus Clay pH = 6.3: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
6.3	1	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
3.8*	1	0.53

*sorption increases by a factor of 2 for each pH unit decrease (8.2 → 6.3)

Opalinus Clay pH = 6.3 sorption value

R_d (m ³ kg ⁻¹)
3.2×10^{-2}

Opalinus Clay, pH = 6.3: in situ sorption value

Lab → Field transfer factor = 1

$R_{d \text{ in situ}}$ (m ³ kg ⁻¹)
3.2×10^{-2}

Mo(VI) DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Literature source: MOTTA & MIRANDA (1989)

Selected $R_{d \text{ lit.}}$: $0.016 \text{ m}^3 \text{ kg}^{-1}$ (Mo equilibrium concentration: $< 5 \times 10^{-4} \text{ M}$)**Source data summary**

Solid	CEC _{lit.} (eq. kg ⁻¹)
illite	0.2

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
8.2	-	-	10 ⁻²	1

Opalinus Clay pH = 7.8: data summary

pH	F _{speciation}	CEC _{ref.} (eq. kg ⁻¹)
7.8	1	0.106

Conversion factors

CF _{pH}	CF _{speciation}	CF _{CEC}
1.4*	1	0.53

*sorption increases by a factor of 2 for each pH unit decrease (8.2 -> 7.8)

Opalinus Clay pH = 7.8 sorption value

R_d (m ³ kg ⁻¹)
1.2×10^{-2}

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

R_d in situ (m ³ kg ⁻¹)
1.2×10^{-2}

7.5.7 Technetium

Under the Eh/pH conditions corresponding to the reference OPA systems at the reference conditions and at both the upper and lower pH values, the predicted redox state of Tc is tetravalent.

No relevant sorption data could be found for tetravalent Tc and sorption values for Tc were derived on the basis of chemical analogy with Th(IV) following the discussions and proposals given in section 7.4.3.

Data sheets for Tc(IV) are provided.

An in situ sorption value for Tc of $55.4 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at pH = 7.24. At the bounding pH values of 6.3 and 7.8 sorption values of $22 \text{ m}^3 \text{ kg}^{-1}$ and $55.4 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Tc DATA SHEET FOR THE OPALINUS CLAY REFERENCE CASE, pH = 7.24

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay reference case Th data

$R_d(\text{Th})_{\text{ref.}} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Th})_{(\text{IV})}$
55.4	1

Opalinus Clay reference case Tc data

$F(\text{Tc})_{(\text{IV})}$
1

Conversion

$$R_d(\text{Tc})_{\text{ref.}} = R_d(\text{Th})_{\text{ref.}} \times [F(\text{Tc})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay reference sorption value

$R_d(\text{Tc})_{\text{ref.}} (\text{m}^3 \text{kg}^{-1})$
55.4

Opalinus Clay in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Tc})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
55.4

Tc DATA SHEET FOR OPALINUS CLAY, pH = 6.3

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 6.3 Th data

$R_d(\text{Th})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$	$F(\text{Th})_{(\text{IV})}$
22.0	1

Opalinus Clay, pH = 6.3: Tc data

$F(\text{Tc})_{(\text{IV})}$
1

Conversion

$$R_d(\text{Tc})_{\text{pH}=6.3} = R_d(\text{Th})_{\text{pH}=6.3} \times [F(\text{Tc})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay pH = 6.3 sorption value

$R_d(\text{Tc})_{\text{pH}=6.3} (\text{m}^3 \text{kg}^{-1})$
22.0

Opalinus Clay pH = 6.3 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Tc})_{\text{in situ}} (\text{m}^3 \text{kg}^{-1})$
22.0

Tc DATA SHEET FOR OPALINUS CLAY, pH = 7.8

Selected chemical analogue: Th(IV)

Source of chemical analogue sorption data: LAUBER et al. (2000)

Opalinus Clay pH = 7.8 Th data

$R_d(\text{Th})_{\text{pH}=7.8}$ ($\text{m}^3 \text{kg}^{-1}$)	$F(\text{Th})_{(\text{IV})}$
55.4	1

Opalinus Clay pH = 7.8 Tc data

$F(\text{Tc})_{(\text{IV})}$
1

Conversion

$$R_d(\text{Tc})_{\text{pH}=7.8} = R_d(\text{Th})_{\text{pH}=7.8} \times [F(\text{Tc})_{(\text{IV})} / F(\text{Th})_{(\text{IV})}]$$

Opalinus Clay pH = 7.8 sorption value

$R_d(\text{Tc})_{\text{pH}=7.8}$ ($\text{m}^3 \text{kg}^{-1}$)
55.4

Opalinus Clay pH = 7.8 in situ sorption value

Lab→Field transfer factor = 1

$R_d(\text{Tc})_{\text{in situ}}$ ($\text{m}^3 \text{kg}^{-1}$)
55.4

7.5.8 Ruthenium

No relevant sorption data could be found for Ru.

Ru belongs to the platinum group of metals and the thermodynamic data available are sparse and uncertain.

Under the anticipated in situ redox and pH conditions Ru is most likely to be present as Ru metal with a very low solubility.

The dominant aqueous species are probably the neutral hydroxy species of Ru(III) and Ru(IV) based on the Eh/pH diagrams given in POURBAIX (1974) and BAES & MESMER (1976).

No obviously appropriate chemical analogue presents themselves for Ru. Considering its position in the Periodic Table it is proposed to treat Ru similarly to Pd i.e. a sorption value of $5 \text{ m}^3 \text{ kg}^{-1}$ is suggested.

The rationale behind the selection of a value for an overall uncertainty factor of 15 is given in section 6.8.

No data sheets for Ru are given.

An in situ sorption value for Ru of $5 \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA systems.

7.5.9 Tritium

Tritium will be present in the aqueous phase as tritiated water (HTO). Water sorption onto surfaces of clay minerals takes place via two mechanisms: (1) hydrogen bonding between the water molecules and exposed hydroxyls or oxygen atoms and (2) hydration of exchangeable ions (YARIV & CROSS, 1979). Tritiated water can undergo isotopic exchange reactions with such "adsorbed water". Although some (low) sorption of tritium is likely, its magnitude is very difficult to quantify.

No data sheets are provided for H(HTO).

The sorption of H(HTO) was taken to be zero for the OPA systems.

7.6 Anions: Cl, I and Se

7.6.1 Chloride

The sorption of Cl^- on soils and clays is observed to be low, and occurs predominantly under acidic conditions (PARFITT, 1978); presumably by ligand exchange. Also, any anion exchange capacity which could be attributed to the OPA would be swamped by the high chloride concentrations in the reference OPA porewater ($\sim 0.3 \text{ M}$). For these reasons Cl^- is unlikely to sorb at all on OPA.

No data sheets are provided for chloride.

The sorption of chloride was taken to be zero for the OPA systems.

7.6.2 Iodide

In-house sorption measurements of iodide on OPA from Mont Terri have been made and the distribution coefficients determined varied between $\sim 3 \times 10^{-5}$ and $4 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$. The measurements were carried out at a very high S:L ratio (1 kg L^{-1}) because low sorption values were expected. The equilibrium pH was 7.5.

KAPLAN et al. (2000) measured iodide sorption on illite and illite containing sediments and their results confirm the very low sorption values measured on OPA.

Speciation calculations in both reference groundwaters indicate that only iodide is present.

The mechanism of iodide sorption is unknown, but it is anticipated that a ligand exchange process may explain the uptake and hence a lower pH would lead to an increase in sorption. Therefore, taking the same iodide R_d value for the upper and lower pH values of the OPA reference systems is considered to be conservative.

In view of the very low sorption values measured for I an $\text{UF-R}_{d \text{ lit}}$ of 5 was assigned to the distribution ratio.

No data sheets are provided for iodide.

In situ sorption values for iodide of $3.5 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$ were selected for the OPA systems.

7.6.3 Selenium

Under the Eh/pH conditions prevailing in situ in the OPA, Se is predicted to be present predominantly as HSe^- (see also for example NEAL et al., 1987, BROOKINS, 1988).

In view of the lack of relevant sorption data, and the fact that HSe^- is the dominant species in both OPA reference groundwaters, the sorption of Se is taken to be zero.

No data sheets are provided for Se(-II).

The sorption for Se(-II) was taken to be zero for the OPA systems.

7.7 ^{14}C Carbon

^{14}C in organic molecules

It is generally well known that dissolved organic ligands interact with mineral surfaces (see for example THENG, 1974, RAUSSELL-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., 1976, 1978 and PEIGNEUR et al., 1979). However, since no specific information on the types and inventories of " ^{14}C containing organics" in the repository was available, it has been assumed that they are non-sorbing.

No data sheets are provided for " ^{14}C containing organics".

The sorption of ^{14}C containing organic molecules was taken to be zero for the OPA systems.

^{14}C in inorganic molecules

For any ^{14}C existing as $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$, the most likely removal mechanism from solution is isotopic exchange with the surface layers of carbonate minerals, particularly CaCO_3 (see section 9.4.2 in BRADBURY & BAEYENS, 1997a and the references therein). The most critical (and difficult) question to answer is how much of the intact calcite present is available to take part in this exchange. BRADBURY & BAEYENS (1997a) give a conservative estimate of ~ 0.27 % of the total calcite.

If 0.27 % of the bulk calcite (Table 1) 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 CO_3^{2-} in the solid phase is ~ 4.3×10^{-3} mol per kg of OPA. Thus, the $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$ sorption values in the reference OPA groundwater and for the two bounding pHs of 6.3 and 7.8 can be

readily obtained using the aqueous concentrations given in Table 2 ($C_{\text{inorg.}}$) and the above value. At equilibrium the R_d values are estimated to be $1.6 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$, $1.3 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $6.0 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ at $\text{pH} = 7.24$, 6.3 and 7.8 respectively.

Since a very conservative approach was followed to estimate a sorption value for $\text{H}^{14}\text{CO}_3^-/\text{}^{14}\text{CO}_3^{2-}$, no uncertainty factors are considered.

No data sheet are provided for ^{14}C existing as $\text{H}^{14}\text{CO}_3^-/\text{}^{14}\text{CO}_3^{2-}$.

An in situ sorption value for $\text{H}^{14}\text{CO}_3^-/\text{}^{14}\text{CO}_3^{2-}$ of $1.6 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was selected for the OPA reference system at $\text{pH} = 7.24$. At the bounding pH values of 6.3 and 7.8 sorption values of $1.3 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $6.0 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

8 SELECTED R_d VALUES CORRESPONDING TO IN SITU CONDITIONS IN OPALINUS CLAY AND ASSOCIATED UNCERTAINTIES: SUMMARY TABLES

The selected in situ distribution ratios for the OPA mineralogy and water chemistry data defined in Tables 1 and 2, respectively, are summarised in Tables 7 and 8 together with the source references.

The uncertainties associated with the selected R_d values for the reference case, discussed in Chapter 5, are summarised in Table 9.

Table 10 presents all of the selected sorption values and the associated overall uncertainties for each element.

In all of these tables the radionuclides are ordered according to atomic numbers.

Table 7: In situ R_d values for the Opalinus Clay reference conditions at pH=7.24.

Radionuclide	R_d ($m^3 kg^{-1}$)	Source
H(HTO)	0	
C(inorg.)	1.6 E-3	isotopic exchange with calcite
C(org.)	0	
Cl(-I)	0	
Ca(II)	1.1 E-3	Model calculations; BRADBURY & BAEYENS (1998a)
Co(II)	4.9 E-1	GRÜTTER et al. (1994)
Ni(II)	9.3 E-1	LAUBER et al. (2000)
Se(-II)	0	
Sr(II)	1.1 E-3	Model calculations; BRADBURY & BAEYENS (1998a)
Zr(IV)	10.9	Sn(IV) analogue
Nb(V)	4	LEGOUX et al. (1992)
Mo(VI)	1.7 E-2	MOTTA & MIRANDA (1989)
Tc(IV)	55.4	Th(IV) analogue
Ru(III/IV)	5	Expert judgement
Pd(II)	5	Expert judgement
Ag(I)	0	
Cd(II)	1.8 E-1	Ni(II) analogue
Sn(IV)	110	LAUBER et al. (2000)
Sb(III)	5.6	Bi(III) analogue; ULRICH & DEGUELDRE (1992)
I(-I)	3.5 E-5	In-house (this work)
Cs(I)	5.5 E-1	Model calculations; BRADBURY & BAEYENS (2000)
Ce(III)	59.8	Eu(III) analogue
Pm(III)	59.8	Eu(III) analogue
Sm(III)	59.8	Eu(III) analogue
Eu(III)	59.8	LAUBER et al. (2000)
Ho(III)	59.8	Eu(III) analogue
Hf(IV)	10.9	Sn(IV) analogue
Pb(II)	2.7	Koss et al (1992)
Po(IV)	1.8 E-1	Se(IV) analogue; LAUBER et al. (2000)
Ra(II)	7.6 E-4	Sr(II) analogue, model calculations
Ac(III)	17.0	Am(III) analogue
Th(IV)	55.4	LAUBER et al. (2000)
Pa(IV)	5	Expert judgement
U(IV)	20.5	Th(IV) analogue
Np(IV)	55.4	Th(IV) analogue
Pu(III)	22.6	Am(III) analogue
Am(III)	17.0	GORGEON (1994)
Cm(III)	17.0	Am(III) analogue

Table 8: In situ R_d values ($\text{m}^3 \text{kg}^{-1}$) for the Opalinus Clay for pH = 6.3 and 7.8.

Radionuclide	R_d (pH = 6.3)	R_d (pH = 7.8)	Source
H(HTO)	0	0	
C(inorg.)	1.3 E-4	6.0 E-3	isotopic exchange with calcite
C(org.)	0	0	
Cl(-I)	0	0	
Ca(II)	9.3 E-4	1.1 E-3	Model calculations; BRADBURY & BAEYENS (1998a)
Co(II)	1.6 E-1	9.5 E-1	GRÜTTER et al. (1994)
Ni(II)	2.9 E-1	1.9	LAUBER et al. (2000)
Se(-II)	0	0	
Sr(II)	9.3 E-4	1.1 E-3	Model calculations; BRADBURY & BAEYENS (1998a)
Zr(IV)	39.7	4.7	Sn(IV) analogue
Nb(V)	4	4	LEGOUX et al. (1992)
Mo(VI)	3.2 E-2	1.2 E-2	MOTTA & MIRANDA (1989)
Tc(IV)	22	55.4	Th(IV) analogue
Ru(III/IV)	5	5	Expert judgement
Pd(II)	5	5	Expert judgement
Ag(I)	0	0	
Cd(II)	5.7 E-2	3.7 E-1	Ni(II) analogue
Sn(IV)	110	110	LAUBER et al. (2000)
Sb(III)	2.5	7.0	Bi(III) analogue; ULRICH & DEGUELDRE (1992)
I(-I)	3.5 E-5	3.5 E-5	In-house (this work)
Cs(I)	5.5 E-1	5.5 E-1	Model calculations; BRADBURY & BAEYENS (2000)
Ce(III)	5.0	50.0	Eu(III) analogue
Pm(III)	5.0	50.0	Eu(III) analogue
Sm(III)	5.0	50.0	Eu(III) analogue
Eu(III)	5.0	50.0	LAUBER et al. (2000)
Ho(III)	5.0	50.0	Eu(III) analogue
Hf(IV)	39.7	4.7	Sn(IV) analogue
Pb(II)	8.0 E-1	6.7	Koss et al (1992)
Po(IV)	7.0 E-2	2.8 E-1	Se(IV) analogue; LAUBER et al. (2000)
Ra(II)	6.9 E-4	7.6 E-4	Sr(II) analogue, model calculations
Ac(III)	1.2	63	Am(III) analogue
Th(IV)	22	55.4	LAUBER et al. (2000)
Pa(IV)	5	5	Expert judgement
U(IV)	5.5 E-1	48.2	Th(IV) analogue
Np(IV)	22	55.4	Th(IV) analogue
Pu(III)	1.1	75.2	Am(III) analogue
Am(III)	1.2	63	GORGEON (1994)
Cm(III)	1.2	63	Am(III) analogue

Table 9: Uncertainty estimates associated with the selected R_d in situ values and the individual conversion steps involved in obtaining the overall uncertainty factor.

Radionuclide	UF-model	UF- R_d lit.	UF-pH	UF-speciation	UF-CEC	UF-Lab→Field	UF-overall
H(HTO)							
C(inorg.)		-					
C(org.)		-					
Cl(-I)		-					
Ca(II)	3					2	6
Co(II)		1.6	2.6	1.4	1.3	2	15.1
Ni(II)		1.6	2.6	1.4		2	11.6
Se(-II)							
Sr(II)	3					2	6
Zr(IV)				(1.4)			19.6
Nb(V)		5		1.4	1.3	2	18.2
Mo(VI)		1.6	2.6	1.4	1.3	2	15.1
Tc(IV)				(1.4)			6.3
Ru(III/IV)							15
Pd(II)							15
Ag(I)							
Cd(II)				(1.4)			16.4
Sn(IV)		5		1.4		2	14
Sb(III)				(1.4)			25.5
I(-I)		5		1.4		2	14
Cs(I)	3					2	6
Ce(III)				(1.4)			6.3
Pm(III)				(1.4)			6.3
Sm(III)				(1.4)			6.3
Eu(III)		1.6		1.4		2	4.5
Ho(III)				(1.4)			6.3
Hf(IV)				(1.4)			19.6
Pb(II)		5	2.6	1.4	1.3	2	47.3
Po(IV)				(1.4)			14
Ra(II)	3					2	6
Ac(III)				(1.4)			8.2
Th(IV)		1.6		1.4		2	4.5
Pa(V)							10
U(IV)				(1.4)			6.3
Np(IV)				(1.4)			6.3
Pu(III)				(1.4)			8.2
Am(III)		1.6		1.4	1.3	2	5.8
Cm(III)				(1.4)			8.2

Se(IV): UF-overall = 10, Bi(III): UF-overall = 18.2

Table 10: Summary of in situ R_d values ($m^3 kg^{-1}$) for OPA at pH = 6.3, 7.24 and 7.8 together with the associated overall uncertainty factors.

Radionuclide	R_d (pH = 6.3)	R_d (pH = 7.24)	R_d (pH = 7.8)	UF-overall
H(HTO)	0	0	0	
C(inorg.)	1.3 E-4	1.6 E-3	6.0 E-3	
C(org.)	0	0	0	
Cl(-I)	0	0	0	
Ca(II)	9.3 E-4	1.1 E-3	1.1 E-3	6
Co(II)	1.6 E-1	4.9 E-1	9.5 E-1	15.1
Ni(II)	2.9 E-1	9.3 E-1	1.9	11.6
Se(-II)	0	0	0	
Sr(II)	9.3 E-4	1.1 E-3	1.1 E-3	6
Zr(IV)	39.7	10.9	4.7	19.6
Nb(V)	4	4	4	18.2
Mo(VI)	3.2 E-2	1.7 E-2	1.2 E-2	15.1
Tc(IV)	22	55.4	55.4	6.3
Ru(III/IV)	5	5	5	15
Pd(II)	5	5	5	15
Ag(I)	0	0	0	
Cd(II)	5.7 E-2	1.8 E-1	3.7 E-1	16.4
Sn(IV)	110	110	110	14
Sb(III)	2.5	5.6	7.0	25.5
I(-I)	3.5 E-5	3.5 E-5	3.5 E-5	14
Cs(I)	5.5 E-1	5.5 E-1	5.5 E-1	6
Ce(III)	5.0	59.8	50.0	6.3
Pm(III)	5.0	59.8	50.0	6.3
Sm(III)	5.0	59.8	50.0	6.3
Eu(III)	5.0	59.8	50.0	4.5
Ho(III)	5.0	59.8	50.0	6.3
Hf(IV)	39.7	10.9	4.7	19.6
Pb(II)	8.0 E-1	2.7	6.7	47.3
Po(IV)	7.0 E-2	1.8 E-1	2.8 E-1	14
Ra(II)	6.9 E-4	7.6 E-4	7.6 E-4	6
Ac(III)	1.2	17.0	63	8.2
Th(IV)	22	55.4	55.4	4.5
Pa(V)	5	5	5	10
U(IV)	5.5 E-1	20.5	48.2	6.3
Np(IV)	22	55.4	55.4	6.3
Pu(III)	1.1	22.6	75.2	8.2
Am(III)	1.2	17.0	63	5.8
Cm(III)	1.2	17.0	63	8.2

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ADDENDUM

Sorption values (K_d), effective diffusion coefficients ($D_{e\perp}$) and accessible porosities (ε) for Opalinus Clay used in safety assessment calculations within Project Opalinus Clay (Entsorgungsnachweis)

B. Schwyn (Nagra)

Table AD-1 of this addendum presents the parameters used to calculate radionuclide transport in Opalinus Clay within the safety assessment of the Project Opalinus Clay. Table AD-1 corresponds to Table A2.8 in Nagra (2002a). This addendum explains the origin of the data and their documentation.

In a diffusion dominated system like Opalinus Clay the spreading of radionuclides is mainly determined by the element specific apparent diffusion coefficient D_a . D_a can either be measured directly or it can be derived using K_d values from batch sorption experiments in dilute systems using the equation, below:

$$D_a = \frac{D_e}{\varepsilon + K_d \rho_d} = \frac{D_e}{\varepsilon R}$$

D_e :	effective diffusion coefficient	[m ² s ⁻¹]
ρ_d :	dry density of Opalinus Clay	[kg m ⁻³]
ε :	accessible porosity	[-]
K_d :	distribution coefficient	[m ³ kg ⁻¹]
R:	retardation factor ¹	[-]

As discussed in Nagra (2002a) the latter approach is used for both, bentonite and Opalinus Clay in Project Opalinus Clay for the following reasons:

- A representative set of batch sorption measurements is available to derive a comprehensive K_d data base. The method, including the adjustment to in-situ mineralogy and porewater chemistry, is described in the main part of this report for Opalinus Clay and in Bradbury & Baeyens (2003) for bentonite, respectively.
- Diffusion experiments in Opalinus Clay have been performed only for weakly sorbing elements; nonetheless, a consistent treatment of diffusive transport in the bentonite barrier and the Opalinus Clay had to be achieved.

¹ The retardation factor R also affects the advective part of radionuclide transport in Opalinus Clay.

Concerning the element specific effective diffusivity D_e and porosity ε the radioelements were divided into two groups, non-anionic and anionic species.

Dynamic anions, e.g., negatively charged carbonate complexes of radioelements, were conservatively neglected. The corresponding elements, independent of their speciation in the porewater, were assigned to the group of non-anionic species.

The following parameters are used for safety assessment calculations:

Non-anionic species:

Effective diffusion coefficients ($D_{e\perp}$, reference case and upper limit; $D_{e=}$) are taken from Nagra (2002b). Important for radionuclide release calculations is the effective diffusivity perpendicular to bedding $D_{e\perp}$ with a reference value of $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

The full porosity of 0.12, as reported in Nagra (2002b) is assumed to be accessible for non-anionic species. An ε of 0.12 together with an Opalinus Clay solid density of 2720 kg m^{-3} results in a dry density of $\rho_d = 2390 \text{ kg m}^{-3}$. The latter value is used in the above equation for non-anionic and anionic species.

Anionic species:

Effective diffusion coefficients ($D_{e\perp}$, reference case and upper limit; $D_{e=}$) and the accessible porosity ε of 0.06 are taken from Nagra (2002b). The reference value for the effective diffusivity perpendicular to bedding is $1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

For both groups of species the sorption values K_d were mainly taken from Table 10 in the main part of this report. The values were carefully checked in terms of their use in safety assessment calculations. Plausibility checks were carried out by using independent information, in particular by comparing the data set, presented here, with those used in other clay systems. This work will be presented in a separate report (Schwyn & Wersin, 2003). K_d values in Table AD-1 were compiled taking into account the comments below:

- In the main part of this report the symbol R_d is used for the distribution ratio between Opalinus Clay and porewater. For safety assessment purposes R_d is renamed to K_d indicating that equilibrium conditions are assumed in transport calculations.
- The list of nuclides discussed in this report differs slightly from the list of safety-relevant nuclides considered in the safety assessment calculations. This is because the simple screening analysis for the derivation of the list of safety-relevant nuclides described in Appendix 5 of Nagra (2002c) was modified at a later stage in Project Opalinus Clay; i.e. after the bulk of the work described in this

report was undertaken. Therefore, some elements (Ru, Cd, Sb, Ce, Pm, Hf) were dropped in Table AD-1, beryllium was added.

For beryllium, nickel was used as a chemical analogue since the chemical properties of Be(II) resemble more the ones of the bivalent transition metals rather than the rest of the alkaline-earth metals (see Schwyn & Wersin, 2003).

- For the reference case (bold in Table AD-1) values for pH = 7.24 and Eh = -167 mV were taken from Table 10.
- The lower limit (pessimistic) K_d value for an element was derived from Table 10 in the main part of this report and Table AD-2, below. The minimum of the following three values was taken: The reference case K_d value divided by the corresponding uncertainty factor UF' in Table AD-2, the best estimate for low pH (6.3) porewater conditions, the best estimate for high pH (7.8) porewater conditions.
- In a similar way upper limit (optimistic) K_d values were derived. The maximum of the following three values was taken: The reference case K_d value multiplied by the corresponding uncertainty factor UF' in Table AD-2, the best estimate for low pH (6.3) porewater conditions, the best estimate for high pH (7.8) porewater conditions.
- After the geochemical data were frozen for safety assessment calculations in July 2002 the treatment of uncertainties in this report was improved, i.e., the uncertainty factors in Table 10 (UF) differ slightly from the ones used in safety assessment calculations (UF'). Affected lower and upper limit K_d values are presented in Table AD-2, below. Changes are too small to be significant for the safety assessment.
- Lower limits, determined by the above procedure, were overwritten for the elements Tc and Sn:
 - For technetium a lower limit K_d value of $0.5 \text{ m}^3 \text{ kg}^{-1}$ was used. This is consistent with the lower limit K_d value used for bentonite (addendum in Bradbury & Baeyens, 2003). For bentonite the results of a diffusion experiment were taken into account.
 - The high K_d value of $100 \text{ m}^3 \text{ kg}^{-1}$ for Sn in Table AD-1 is based on batch sorption measurements by Lauber et al. (2000) (see section 7.5.1 in the main part of this report). To be consistent with the bentonite sorption database (addendum in Bradbury & Baeyens, 2003) the lower limit K_d value in Table AD-1 was overwritten with $0.2 \text{ m}^3 \text{ kg}^{-1}$.

- Since iodine is an important safety relevant element a "What if?"² case with $K_d = 0$ was also included in the safety assessment calculations. In fact a retention of iodide was observed in clays (see section 7.6.2 in the main part of this report) but a "What if?" case with $K_d = 0$ should reflect the uncertainty concerning the retention mechanism; e.g., an oxidation of iodide traces cannot be totally ruled out.
- Values were truncated (reference case and lower limit) or rounded (upper limit) to one significant figure.

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²Defined in Appendix 5 of Nagra (2002a).

Table AD-1: Sorption values (K_d), effective diffusion coefficients ($D_{e\perp}$) and accessible porosities (ε) in Opalinus Clay.

Reference case (pH = 7.3, Eh = -167 mV) incl. lower (pessimistic) and upper (optimistic) limits for K_d s and upper (pessimistic) limits for $D_{e\perp}$ (perpendicular to bedding). In addition, diffusion coefficients parallel to bedding ($D_{e\parallel}$) are given. This table corresponds to Table A2.8 in Nagra (2002a).

Element	K_d			$D_{e\perp}$		$D_{e\parallel}$	ε	Remarks
	Ref. case [m ³ kg ⁻¹]	Lower limit (pessimistic) [m ³ kg ⁻¹]	Upper limit (optimistic) [m ³ kg ⁻¹]	Ref. case [m ² s ⁻¹]	Upper limit (pessimistic) [m ² s ⁻¹]	[m ² s ⁻¹]	[-]	
H	0	0	0	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Be	0.9	0.03	20	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
C _{inorg}	0.001	1×10^{-4}	0.006	1×10^{-12}	3×10^{-12}	5×10^{-12}	0.06	Anion
C _{org}	0	0	0	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Cl	0	0	0	1×10^{-12}	3×10^{-12}	5×10^{-12}	0.06	Anion
Ca	0.001	1×10^{-4}	0.007	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Co	0.4	0.01	20	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Ni	0.9	0.03	20	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Se	0	0	0	1×10^{-12}	3×10^{-12}	5×10^{-12}	0.06	Anion
Sr	0.001	1×10^{-4}	0.007	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Zr	10	0.3	300	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Nb	4	0.1	100	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Mo	0.01	0.001	0.2	1×10^{-12}	3×10^{-12}	5×10^{-12}	0.06	Anion
Tc	50	0.5	500	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Pd	5	0.2	100	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Ag	0	0	0	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Sn	100	0.2	1000	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
I ³	3×10^{-5}	3×10^{-6}	4×10^{-4}	1×10^{-12}	3×10^{-12}	5×10^{-12}	0.06	Anion
Cs	0.5	0.09	3	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Sm	50	5	600	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Eu	50	5	600	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Ho	50	5	600	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Pb	2	0.02	300	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Po	0.1	0.04	0.7	1×10^{-12}	3×10^{-12}	5×10^{-12}	0.06	Anion
Ra	7×10^{-4}	1×10^{-4}	0.005	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Ac	10	1	200	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Th	50	10	200	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Pa	5	0.2	100	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
U	20	0.5	200	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Np	50	5	500	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Pu	20	1	300	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Am	10	1	200	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	
Cm	10	1	200	1×10^{-11}	1×10^{-10}	5×10^{-11}	0.12	

³ The possibility of $K_d(I) = 0 \text{ m}^3 \text{ kg}^{-1}$ is considered in a "what if?" case.

Table AD-2: Uncertainty factors UF and UF' and resulting lower and upper limits.
 UF: Uncertainty factor derived in the main part of this report (Table 10) after freezing of the data in Table AD-1.
 UF': Uncertainty factor used to derive lower and upper limit K_d values in Table AD-1.

Element	UF' used in Table AD-1	UF derived in this report	Lower limit ⁴ from Table AD-1	Lower limit ⁴ resulting from UF	Upper Limit ⁴ from Table AD-1	Upper Limit ⁴ resulting from UF
H						
Be						
Cinorg						
Corg						
Cl						
Ca	6	6				
Co	37.4	15.1	0.01	0.03	20	7
Ni	25	11.6	0.03	0.08	20	10
Se						
Sr	6	6				
Zr	30	19.6	0.3	0.5	300	200
Nb	30	18.2	0.1	0.2	100	70
Mo	12.5	15.1			0.2	0.3
Tc	9.6	6.3			500	300
Pd	20	15	0.2	0.3	100	70
Ag						
Sn	10	14			1000	2000
I	10	14	3×10^{-6}	2×10^{-6}	4×10^{-4}	5×10^{-4}
Cs	6	6				
Sm	9.6	6.3			600	400
Eu	9.6	4.5			600	300
Ho	9.6	6.3			600	400
Pb	117	47.3	0.02	0.05	300	100
Po	4	14	0.04	0.01	0.7	3
Ra	6	6				
Ac	14.4	8.2			200	100
Th	3.2	4.5				
Pa	20	10	0.2	0.5	100	50
U	9.6	6.3			200	100
Np	9.6	6.3	5	8	500	300
Pu	14.4	8.2			300	200
Am	14.4	5.8			200	100
Cm	14.4	8.2			200	100

⁴ Only given when upper or lower limits are changed by UF compared to Table AD-1.