

TECHNICAL REPORT 02-18

**Near-Field Sorption Data Bases
for Compacted MX-80 Bentonite
for Performance Assessment of
a High-Level Radioactive Waste
Repository in 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.

ISSN 1015-2636

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ABSTRACT

Bentonites of various types and compacted forms are being investigated in many countries as backfill materials in high-level radioactive waste disposal concepts. Nagra is currently considering an Opalinus clay (OPA) formation in the Zürcher Weinland as a potential location for a high-level radioactive waste repository. A compacted MX-80 bentonite is foreseen as a potential backfill material. Performance assessment studies will be performed for this site and one of the requirements for such an assessment are sorption data bases (SDB) for the bentonite near-field. The purpose of this report is to describe the procedures used to develop the SDB.

One of the pre-requisites for developing a SDB is a water chemistry for the compacted bentonite porewater. For a number of reasons mentioned in the report, and discussed in more detail elsewhere, this is not a straightforward task. There are considerable uncertainties associated with the major ion concentrations and in particular with the system pH and Eh. The MX-80 SDB was developed for a reference bentonite porewater (pH = 7.25) which was calculated using the reference OPA porewater. In addition, two further SDBs are presented for porewaters calculated at pH value of 6.9 and 7.9 corresponding to lower and upper bound values calculated for the range of groundwater compositions anticipated for the OPA host rock.

"In house" sorption isotherm data were measured for Cs(I), Ni(II), Eu(III), Th(IV), Se(IV) and I(-I) on the "as received" MX-80 material equilibrated with a simulated porewater composition. Complementary "in house" sorption edge and isotherm measurements on conditioned Na/Ca montmorillonites were also available for many of these radionuclides. These data formed the core of the SDB. Nevertheless, some of the required sorption data still had to be obtained from the open literature. An important part of this report is concerned with describing selection procedures and the modifications applied to the chosen values so that they are compatible with the reference mineralogy and porewater chemistries.

The SDB comprises of distribution ratios (R_d) obtained from batch sorption type measurements made on dispersed systems. It is not intrinsically evident that these values are valid for compacted systems as required in the performance assessment. Arguments justifying this Lab to Field transformation are presented in a separate report and the main conclusions are summarised here.

Finally, an attempt is made to assess the uncertainties associated with the selected distribution ratios in the SDB.

Nagra is considering a scenario where oxidising conditions exist in the near-field of the compacted bentonite surrounding spent fuel. In such a case the MX-80 porewater is considered to have the same composition as that in the reference case (pH = 7.25), but

with a redox potential (Eh) of +635 mV. Tc, Se, U, Np and Pu have been identified as the only safety relevant radionuclides which will have redox states different from those in the reference reducing case. Sorption values for the above radionuclides are presented in the Appendix.

ZUSAMMENFASSUNG

In vielen Ländern werden unterschiedliche Bentonite als Verfüllmaterialien bei derendlagerung hochradioaktiver Abfälle untersucht. Die Nagra zieht derzeit eine Opalinuston-Formation im Zürcher Weinland als potenzielles Wirtsgestein für ein Tiefenlager für hochradioaktive Abfälle in Betracht. In diesem Konzept ist ein kompakter MX-80 Bentonit als Verfüllmaterial vorgesehen. Für diesen Standort werden Sicherheitsstudien durchgeführt, für die Sorptionsdatenbanken (SDB) für das Bentonit-Nahfeld benötigt werden. In diesem Bericht wird das Vorgehen zur Erstellung der entsprechenden SDB dargestellt.

Eine Voraussetzung für die Erstellung solch einer SDB ist die Bestimmung der Porenwasserchemie im kompaktierten Bentonit. Es werden Gründe genannt, die an anderer Stelle vertieft behandelt werden und die aufzeigen, wie kompliziert diese Aufgabe ist. Die Konzentrationen der wichtigsten Ionen und insbesondere das pH/Eh System sind mit beträchtlichen Unsicherheiten behaftet. Die MX-80 SDB wurde für ein Referenz-Porenwasser des Bentonits ($\text{pH} = 7.25$) erstellt, das mit Hilfe des Referenz-Porenwassers des Opalinustons berechnet wurde. Zusätzlich werden zwei weitere SDB's für Porenwässer bei pH-Werten von 6.9 und 7.9 präsentiert. Diese pH-Werte entsprechen dem unteren und dem oberen Grenzwert der Grundwasserzusammensetzung, die für den Opalinuston erwartet werden.

Der für Sorptionsuntersuchungen am PSI verwendete MX-80 Bentonit wurde vorab mit einem synthetischen Porenwasser äquilibriert und dann für die Messungen von Sorptionsisothermen des Cs(I), Ni(II), Eu(III), Th(IV), Se(IV) und I(-I) eingesetzt. Für viele der genannten Radionuklide waren ergänzende, eigene Messergebnisse von Sorptionskanten und Sorptionsisothermen mit konditioniertem Na-/Ca-Montmorillonit vorhanden. Diese Daten bilden den Kern der Sorptionsdatenbank. Darüber hinaus mussten einige der benötigten Sorptionsdaten der offenen Literatur entnommen werden. In diesem Bericht wird das Verfahren beschrieben, das für die Auswahl dieser Daten und deren Anpassung an die Referenz-Mineralogie und -Porenwasserchemie verwendet wurde.

Die Sorptionsdatenbank besteht aus Verteilungskoeffizienten (R_d -Werten), die in Batch-Sorptionsexperimenten für disperse Systeme gemessen wurden. Es ist nicht klar, ob diese Werte auch für die kompaktierten Systeme, wie sie in den Sicherheitsanalysen betrachtet werden, gültig sind. Stichhaltige Gründe für die Labor → Feld - Übertragung werden in einem anderen Bericht vorgestellt. Hier werden nur die wichtigsten Schlussfolgerungen zusammengefasst.

Schliesslich wird versucht, die Unsicherheiten abzuschätzen, mit denen die gewählten Verteilungskoeffizienten behaftet sind.

In einem von der Nagra betrachteten Szenarium liegen oxidierende Bedingungen im Nahfeld des Bentonits vor, welche die abgebrannten Brennelemente umgibt. In diesem Fall wird angenommen, dass das MX-80 Porenwasser die gleiche Zusammensetzung hat wie im Referenzfall ($\text{pH} = 7.25$), jedoch ein Redoxpotential (Eh) von +635 mV aufweist. Tc, Se, U, Np und Pu wurden als die einzigen sicherheitsrelevanten Radionuklide identifiziert, deren Redoxzustände sich von denjenigen im reduzierenden Referenzfall unterscheiden. Sorptionswerte für die genannten Radionuklide sind im Anhang enthalten.

RÉSUMÉ

Dans plusieurs pays, des bentonites compactées de différents types et sous différentes formes font l'objet de recherches pour être utilisées comme matériel de remplissage pour les dépôts finals des déchets radioactifs de haute activité. La Nagra étudie actuellement une formation d'Argiles à Opalinus (OPA) dans le Weinland zurichois comme emplacement potentiel pour un dépôt de déchets de haute activité. Une bentonite compactée MX-80 est prévue pour le remplissage des galeries. Dans le cadre des analyses de sûreté relatives à ce site, on aura besoin de bases de données de sorption ("sorption data bases" ou SDB) pour le champ proche de la bentonite. Ce rapport décrit les procédures utilisées pour développer les SDB.

Pour développer une base de données de sorption, on doit disposer de données sur la composition chimique de l'eau interstitielle de la bentonite compactée. Pour plusieurs raisons mentionnées dans ce rapport et abordées plus en détail dans d'autres publications, ce n'est pas une tâche aisée. Des incertitudes considérables subsistent quant aux concentrations des ions principaux et en particulier aux paramètres pH et Eh du système. La SDB pour la MX-80 a été développée en se basant sur une eau interstitielle de référence pour la bentonite (pH = 7.25), calculée à partir de l'eau interstitielle de référence pour les Argiles à Opalinus. Par ailleurs, ce rapport présente deux autres SDB pour des eaux interstitielles calculées pour des pH de 6.9 et 7.9, correspondant respectivement aux valeurs les plus basses et les plus hautes que l'on s'attend à trouver dans la formation d'accueil OPA.

Des mesures d'isothermes de sorption effectuées au PSI pour Cs(I), Sr(II), Ni(II), Eu(III), Th(IV), Se(IV) et I(-I) ont porté sur le matériel MX-80 "tel quel", équilibré avec une eau interstitielle dont la composition a été simulée. Des mesures complémentaires "maison" d'isothermes de sorption, effectuées sur des montmorillonites Na/Ca conditionnées, étaient également disponibles pour plusieurs radionucléides. La SDB a été élaborée autour de ces données. Néanmoins, certaines des données de sorption nécessaires ont dû être obtenues dans les publications. Une part importante de ce rapport concerne la description des procédures de sélection et les modifications appliquées aux valeurs choisies afin de les rendre compatibles avec les compositions des minéraux de référence et de l'eau interstitielle.

La SDB comprend les valeurs de sorption (R_d) obtenues à partir de mesures de sorption de type batch effectuées sur des systèmes dispersés. Il n'est pas absolument certain que ces valeurs s'appliquent à la bentonite compactée et puissent être utilisées

dans le cadre des analyses de sûreté. Les arguments en faveur d'un tel transfert "Laboratoire – Terrain" sont présentées dans un rapport séparé et les principales conclusions sont résumées ici.

Enfin, le rapport contient une estimation des incertitudes associées aux coefficients de distribution sélectionnés dans la SDB.

La Nagra étudie actuellement un scénario où des conditions oxydantes règnent dans le champ proche de la bentonite compactée entourant les assemblages combustibles usés. Dans ce scénario, on considère que la composition chimique de l'eau interstitielle de la bentonite MX-80 est la même que dans le cas de référence ($\text{pH} = 7.25$), mais que la bentonite possède un potentiel redox (Eh) de +635 mV. On a déterminé que Tc, Se, U, Np et Pu étaient les seuls radionucléides critiques pour l'analyse de sûreté, dont les états redox seront différents de ceux établis dans le cas de référence. Les valeurs de sorption pour les radionucléides mentionnés ci-dessus sont présentées dans l'Annexe.

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1 INTRODUCTION

In order to assess the suitability of an Opalinus Clay (OPA) formation as a potential host rock for the deep disposal of high-level radioactive waste, detailed performance assessment (PA) studies are carried out (NAGRA, 2002a). The uptake of radionuclides on the immobile solids in the near- and far-fields is an important component in such safety studies. Sorption data base (SDB) reports for the specific "in situ" conditions existing in the OPA far-field have already been produced (BRADBURY & BAEYENS, 2003).

Bentonite, in the form of dry compacted blocks and/or compacted granules, is almost the universal choice as back-fill material for sealing the emplacement tunnels. This is partly because of the high swelling capacity of compacted bentonite upon re-saturation and partly because of its very low transmissivity to water movement and good sorption characteristics. Thus, compacted bentonite performs as an extremely effective near-field diffusion barrier to the movement of radionuclides.

Despite efforts extending over tens of years, it has not yet been possible to develop an internationally recognised experimental/modelling methodology for deriving porewater compositions for compacted bentonite. In common with other high clay mineral content bulk rocks, it is exceedingly difficult to obtain water samples for analysis which convincingly represent the in situ water. A consequence of this is that the calculated porewater compositions contain intrinsic uncertainties, especially with respect to pH. The procedure for calculating the compacted bentonite porewaters given briefly in Chapter 2 has been documented in CURTI & WERSIN (2002) and is essentially that due to WANNER (1986). The major assumption in these calculations is that the pH is determined over the saturation of calcite/gypsum at a PCO_2 fixed by the host rock.

Further, it is to be noted that the calculated OPA reference porewater for Benken was used as input for the calculations of the compacted MX-80 reference porewater and that there are intrinsic uncertainties associated with the former. The bentonite porewater composition used in the development of the SBDs presented here, represents a significant source of uncertainty.

The purpose of this report is to construct a SDB for compacted bentonite. The core of sorption values in the SDBs are provided by "in house" measurements:

- Sorption isotherm data for Cs(I), Ni(II), Eu(III), Th(IV), Se(IV) and I(-I) on the "as received" MX-80 material equilibrated with a simulated porewater composition.

- Sorption edge and isotherm data on conditioned Na/Ca montmorillonites for Cs(I), Ni(II), Eu(III), Sn(IV), Th(IV) and Se(IV).

Where reliable mechanistic sorption models were available, these were used.

Despite this rather extensive pool of data and knowledge, some of the required sorption values still had to be obtained from the open literature. Particular emphasis is placed on describing the procedures used to select and modify the sorption values. The former have been described and discussed in detail in BRADBURY & SAROTT (1994) and BRADBURY & BAEYENS (1997a, 2003). The approach adopted is to select the “best available laboratory sorption values” from in house and literature batch sorption measurements which are the most appropriate for the MX-80 bentonite/porewater system defined in Chapter 2. The initially selected values, chosen according to a “selection hierarchy”, section 4.1, are then modified to the specific mineralogical and porewater characteristics of the MX 80 system, section 4.2.

The SDB comprises of sorption values obtained from batch sorption type measurements made on dispersed systems. It is not intrinsically evident that these values are valid in compacted bentonite. An important consideration therefore is the so-called Lab → Field transfer factor i.e. how batch sorption data measured on dilute systems are applied to compacted bentonite. The main conclusions of a separate report dealing with this topic (BRADBURY & BAEYENS, 2002a) are summarised in Chapter 6.

Although the MX-80 SDB comprises of single distribution ratios for each element, R_d values, it will be shown that the selections made, and modifications carried out to the sorption values, are based on a broad understanding of the system and the processes taking place.

Following the practice started in BRADBURY & BAEYENS (2003), the ill-defined terminology “realistic/conservative” sorption values will be avoided wherever possible. Instead, estimated uncertainties will be assigned to the batch sorption values chosen, and to each of the modification procedures applied to these data, to yield a sorption value appropriate for the compacted MX-80. The overall error on the R_d value given is then the product of the individual errors.

2 THE REFERENCE MX-80 SYSTEM: Mineralogy and porewater chemistry

The reference MX-80 mineralogy was taken from MÜLLER-VONMOOS & KAHR (1983) and is reproduced in Table 1. The physico-chemical characterisation data, Table 2, are from BRADBURY & BAEYENS (2002b). The same source material was used for both of these sets of measurements and for the sorption investigations reported later.

Table 1: Reference MX-80 mineralogy (MÜLLER-VONMOOS & KAHR, 1983).

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

Table 2: Chloride and sulphate inventories, cation loadings and cation exchange capacity for MX-80 (BRADBURY & BAEYENS, 2002b).

Inventories (mmol kg ⁻¹)	
Cl	1.35
SO ₄	23.5
Cation fractional occupancies	
N _{Na}	0.85
N _K	0.017
N _{Ca}	0.084
N _{Mg}	0.051
Cation exchange capacity (meq kg ⁻¹)	
	787

The calculation of the MX-80 porewater requires the OPA porewater composition as input together with the assumption that equilibrium is attained with the OPA host rock PCO₂. As stated in BRADBURY & BAEYENS (2003), the pH (and hence the water composition) of the OPA system is an intrinsically uncertain quantity and this was taken into account by considering a range of pH values which bracket the selected reference value. Benken OPA porewaters derived at pH values of 6.9, 7.24 (OPA reference case) and 7.9 (Nagra, 2002b) were used by CURTI & WERSIN (2002) to calculate the

corresponding MX-80 porewater chemistries given in Table 3. (The estimated Eh value is based on the assumption that the magnetite/Fe²⁺ couple is the controlling redox reaction in compacted MX-80, see WERSIN et al., 2003)

Table 3: Reference porewater at pH = 7.25, and porewaters at the bounding pH values of 6.9 and 7.9 for compacted MX-80 bentonite having an initial dry density of 1770 kg m⁻³. (Taken from CURTI & WERSIN, 2002.)

pH	7.25	6.9	7.9
P _{CO₂} (bar)	10 ^{-2.2}	10 ^{-1.5}	10 ^{-3.5}
Eh (V)	-0.193	-0.131	-0.282
I.S. (M)	0.34	0.35	0.31
Temperature	25 °C	25 °C	25 °C
Dissolved constituents	(M)	(M)	(M)
Na	2.74 × 10 ⁻¹	2.91 × 10 ⁻¹	2.49 × 10 ⁻¹
K	1.55 × 10 ⁻³	1.67 × 10 ⁻³	1.38 × 10 ⁻³
Mg	7.64 × 10 ⁻³	8.91 × 10 ⁻³	6.15 × 10 ⁻³
Ca	1.32 × 10 ⁻²	1.33 × 10 ⁻²	1.34 × 10 ⁻²
Sr	1.90 × 10 ⁻⁵	3.68 × 10 ⁻⁵	2.92 × 10 ⁻⁶
C _{inorg.}	2.83 × 10 ⁻³	6.99 × 10 ⁻³	5.86 × 10 ⁻⁴
SO ₄ ²⁻	6.16 × 10 ⁻²	6.39 × 10 ⁻²	5.59 × 10 ⁻²
F	1.67 × 10 ⁻⁴	1.49 × 10 ⁻⁴	1.59 × 10 ⁻⁴
Cl	1.91 × 10 ⁻¹	2.03 × 10 ⁻¹	1.77 × 10 ⁻¹
Br	2.40 × 10 ⁻⁴	3.00 × 10 ⁻⁴	1.20 × 10 ⁻⁴
Fe (total)	4.33 × 10 ⁻⁵	7.74 × 10 ⁻⁵	8.00 × 10 ⁻⁶
Mn (total)	2.43 × 10 ⁻⁵	3.65 × 10 ⁻⁵	4.81 × 10 ⁻⁶
Al (total)	1.92 × 10 ⁻⁸	1.53 × 10 ⁻⁸	7.55 × 10 ⁻⁸
Si (total) as SiO ₂ aq.	1.80 × 10 ⁻⁴	1.80 × 10 ⁻⁴	1.84 × 10 ⁻⁴

3 BACKGROUND

3.1 General

In the following, the uptake of radionuclides by MX-80 bentonite at trace concentrations ($< 10^{-6}$ M) is considered to take place predominantly on the montmorillonite component and is interpreted in terms of two mechanisms: (i) cation exchange and (ii) surface complexation. Only in a very few cases are (quasi) mechanistic models considered to be sufficiently advanced to calculate sorption values in real systems. Rather, the main advantage to be gained by viewing sorption in terms of such mechanisms is that trends and insights into 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. Cation exchange reactions are commonly described by selectivity coefficients defined over mass action equations (GAINES & THOMAS, 1953).

3.3 Surface complexation

It is now widely recognised that many radionuclides can be taken up on the amphoteric hydroxyl surface functional groups ($\equiv\text{SOH}$ edge sites) of clay minerals and that this process, generally modelled in terms of the formation of surface complexes, is probably the most important sorption mechanism for heavy metals, transition metals, lanthanides and actinides in bentonite systems. Surface complexation by metals at $\equiv\text{SOH}$ type sites is normally characterised by a strong dependency on pH, a weak dependency on ionic strength and a strong dependency on concentration. Cations such as Na, K, Mg, Ca, and Sr are not generally competitive with specifically sorbing metals. Thus, the major porewater cations do not usually influence sorption by surface complexation.

Sorption of cationic and neutral 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.

Sorption of anionic species:

Anions can sorb at edge sites on clay minerals by ligand exchange with the hydroxyl surface functional groups (see for example GOLDBERG & GLAUBIG, 1986; DAVIS & KENT, 1990). The sorption behaviour shows two clear features: (i) sorption increases with decreasing pH and (ii) sorption exhibits 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 and the MX80 bentonite will be subjected to even higher temperatures.

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 PROCEDURES AND CONVERSION FACTORS

4.1 Selection procedures

In previous SDB work there was almost always the tendency to choose "conservatively" in the selection of sorption data. What is meant here is that even when very large values for R_d were measured in laboratory experiment, such values were not generally selected. Rather, a lower value was chosen without stating any particular reason for doing so. Typically values of around $5 \text{ m}^3 \text{ kg}^{-1}$ were selected on the basis that when the measured values were "very high", $5 \text{ m}^3 \text{ kg}^{-1}$ was "still high enough". This "hidden conservatism" in the selection process led to reduced transparency and traceability because measured values were often reduced by random factors which were never documented but based rather on what was felt to be "right".

The starting point in the procedure is to select the "best available sorption values" from laboratory measurements which are the most appropriate for the reference MX-80 system. (The main factors playing a role in the choices made are discussed in BRADBURY & SAROTT, 1994). The selected experimentally measured R_d values are taken directly and appear in the sorption data sheets under "selected R_d lit".

In BRADBURY & BAEYENS (2003) a "hierarchy" for the selection of laboratory sorption values was introduced based on the degree of confidence the authors had in the data from the various sources. This procedure is adopted here and follows the order given below.

4.1.1 "In house" data

First priority is given to "in house" sorption isotherm measurements carried out on MX-80 and sorption edge/isotherm determinations on Na- and Ca-montmorillonites. Almost without exception, selections of R_d values have been made at trace concentrations.

For the elements Cs(I), Ni(II), Eu(III), Th(IV), Se(IV) and I(-I) sorption isotherms were measured on MX-80 equilibrated with a synthetic bentonite porewater, SBPW, (BRADBURY & BAEYENS, unpublished data). These experiments were started long before the reference bentonite porewater was defined and as a result the SBPW composition (Table 4) was different, predominantly with respect to the ionic strength, ~0.7 M as opposed to ~0.34 M, and pH, ~7.6 as opposed to 7.25. These sorption isotherms, together with other in house measurements on montmorillonite, form an important block of data for the MX-80 SDB.

Table 4: Synthetic bentonite porewater (SBPW) composition used in the sorption isotherm determination for Cs(I), Ni(II), Eu(III), Th(IV), I(-I) and Se(IV) on MX-80.

T ~ 25 °C	
P _{CO₂} = 10 ^{-3.5} bar	
pH = 7.6	
I.S. = 0.7 M	
Dissolved constituents	Concentration (M)
Na	5.68 x 10 ⁻¹
K	2.80 x 10 ⁻³
Mg	2.30 x 10 ⁻²
Ca	3.01 x 10 ⁻²
Sr	2.67 x 10 ⁻⁴
Al	4.16 x 10 ⁻⁸
F	7.42 x 10 ⁻⁵
Cl	6.19 x 10 ⁻¹
SO ₄	2.92 x 10 ⁻²
C _{inorg.}	3.92 x 10 ⁻⁴
Si	1.82 x 10 ⁻⁴

4.1.2 Literature bentonite and montmorillonite data

The next type of preferred data are sorption isotherm and sorption edge/isotherm measurements on other bentonites and montmorillonites taken from the literature. Such measurements are normally performed under well defined conditions. This is important since it allows the data modification procedures (section 4.2) to be applied with more certainty.

4.1.3 Single point measurements

These are measurements where sorption has been determined under one set of conditions at a single concentration. Provided that the system has been well specified, such measurements can also be a useful source of data.

4.1.4 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. 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 with binding constants that are similar. Thus, it is important to take into account the redox state and aqueous speciation under the particular conditions considered when applying chemical analogy for sorption data.

4.1.5 Expert judgement

Finally, for a few elements neither measured data nor suitable chemical analogues are available. The only recourse then is to expert judgement, where the choices made must err strongly on the conservative side.

Finally, the "best available measured sorption" values selected do not go into the SDB as such, but are modified using conversion factors (see below) so that they are appropriate to the compacted MX-80 reference conditions. Uncertainties associated with the original data and the "tailoring" procedures are estimated in Chapter 5.

4.2 Conversion factors

In order to modify sorption data so that they apply to the compacted MX-80 bentonite it is important to identify the most probable dominant sorption mechanism for each radionuclide, since the influence of water chemistry on sorption is strongly linked to the mechanism. Although (quasi) mechanistic models are not yet sufficiently advanced to be used in PA calculations directly, they do enable the selection of values for SDBs to be better justified and defended through an increased understanding of the underlying processes. In any event, the transport codes used in PA still require distribution ratios as input parameters.

In the following, brief descriptions are given of how mineralogy, pH and aqueous speciation are taken into account in modifying laboratory sorption data. Note that 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.

4.2.1 Mineralogy

The major sorbing component in bentonites is montmorillonite. Scaling of the selected literature sorption values to the MX-80 mineralogy is carried out over the cation exchange capacity (CEC).

$$\text{CF-CEC} = \frac{\text{CEC}_{\text{ref}}}{\text{CEC}_{\text{lit}}} \quad (1)$$

where CF-CEC = mineralogy conversion factor
 CEC_{ref} = CEC value for the MX-80
 CEC_{lit} = CEC value of the source montmorillonite/bentonite.

The selectivity coefficients governing sorption on the planar sites of montmorillonite from different sources and in different bentonites are assumed to be the same to a first approximation. A similarly assumption is also made with respect to \equiv SOH site types and capacities and surface binding constants.

The CEC is a measure of the overall capacity of planar sites and if cation exchange is the main sorption mechanism then it is clearly a good scaling factor for sorption.

In the case where 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 exchange capacity e.g. GRIM (1953); YARIV & CROSS (1979); BAEYENS & BRADBURY (1995a). Thus the total \equiv SOH site capacities of different rocks, and thereby the sorption, should also be proportional to their respective CEC values.

4.2.2 pH

Wherever possible the sorption data were selected as close as possible to the pH of the MX-80 reference porewater (Table 3), making a correction for pH unnecessary in many cases. However, the "in house" isotherm measurements for MX-80 were carried out in the pH range ~7.6 to ~7.8, which is up to 0.5 units higher than in the reference porewater pH, necessitating a correction. For many radionuclides, sorption edge data measurements on purified montmorillonite in simple background electrolytes are available, and these were used directly to estimate the pH correction factors. The procedure is simple, and is illustrated with the aid of the schematic sorption edge given below.

The pH conversion factor (CF-pH) is 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 (see Figure 1 below), i.e. $R_{d, pH\ ref}$ and $R_{d, pH\ lit}$ respectively.

$$CF - pH = \frac{R_{d, pH\ ref}}{R_{d, pH\ lit}} \quad (2)$$

Where an adjustment for pH is necessary in the following, the rational, mainly based on sorption edge data, is given on an individual case basis.

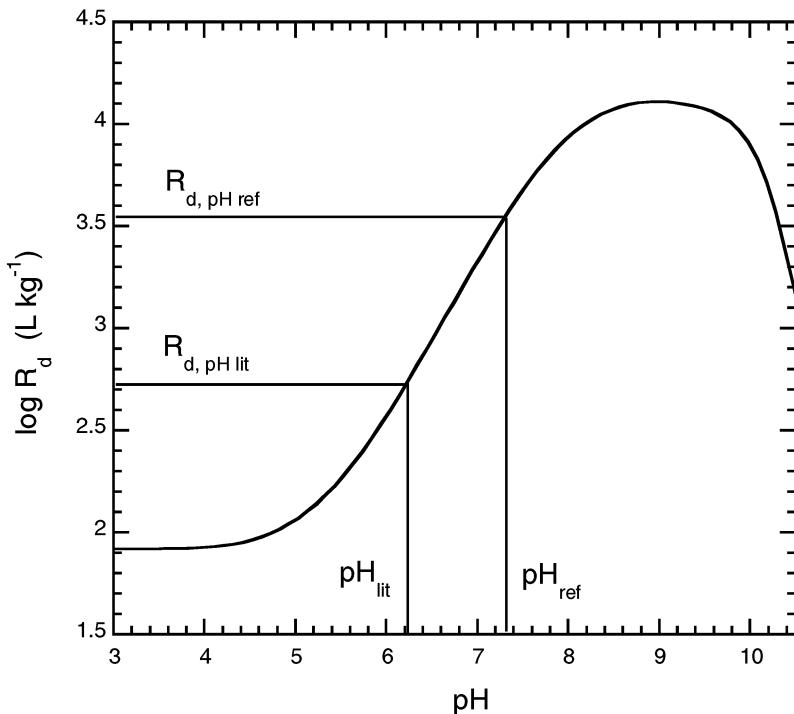


Figure 1: Schematic sorption edge indicating distribution ratios corresponding to (pH_{ref}) and (pH_{lit}) for a particular radionuclide.

4.2.3 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 for the MX-80 reference porewater are different. (This is almost always the case.) A rigorous correction is only possible when a verified sorption model is available, which 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 SCHULTHESS & HUANG, 1990; GORGEON, 1994; TURNER et al., 1998).

In order to make a correction to sorption values taking into account the differences in radionuclide speciation in different water chemistries, species which are considered to sorb, and those which do not sorb, have to be distinguished. The proposal put forward is to define free cations, positively charged and neutral hydrolysis species as sorbing. All other species are treated as being non-sorbing. (This is probably an oversimplification of reality and may not necessarily lead to conservative modifications

of the sorption data in all cases.)

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

$$CF - \text{speciation} = \frac{F_{\text{ref}}}{F_{\text{lit}}} \quad (3)$$

where 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 reference MX-80.

Attempts to correct for speciation differences in this manner are of course sensitively dependent on the quality of the stability constants in the thermodynamic data bases. The updated Nagra/PSI thermodynamic data base (HUMMEL et al., 2002) was used throughout. Ni carbonate equilibrium constants were used for Co, and the data base compilation from PEARSON et al. (1992) was used where data were missing. The results of the speciation calculations and the references to the TDBs used have been summarised by CURTI (2001).

4.2.4 Chemical analogues

In cases where chemical analogy is invoked, the reference sorption value for the analogue is taken. Since the value will have already been modified to the MX-80 reference conditions, the only further correction factor which needs to be applied to obtain the R_d ref value for the radionuclide in question is one which takes into account the differences in aqueous speciation i.e.

$$CF - \text{analogue} = \frac{F_{\text{nuclide}}}{F_{\text{analogue}}} \quad (4)$$

where

F_{nuclide} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the reference MX-80 porewater.

F_{analogue} is the fraction of the chemical analogue concentration calculated to be present in the aqueous phase as sorbing species in the MX-80 reference porewater.

4.2.5 Lab → Field transfer factors

The R_d values used to produce SDBs originate from batch tests on suspensions but are applied in performance assessment to intact rocks/compacted systems. This cannot be ignored, and means need to be found to take this into account. In the development of previous SDBs (BRADBURY & BAEYENS, 1997a, 2003) an approach was proposed based on the hypothesis that the magnitude of sorption measured at equilibrium in any system under a constant set of conditions is directly proportional to the accessible surface area. (Sorption is essentially a surface phenomenon.) Converting batch sorption data to values appropriate to intact systems would then reduce to measuring the N_2 -BET surface areas in both cases. Such data are available for MX-80 and Montigel bentonites at dry densities of 2000 kg m^{-3} (BRADBURY & BAEYENS, 1998) and imply a transfer factor of unity. (Powders and compacted bentonites were measured under "dry" conditions i.e. after heating to 200°C for 1 hour.)

However, this is certainly a too simplistic approach for compacted bentonite; in part because of its swelling characteristics, but also because of the uncertainties regarding the porewater chemistry (ionic strength (I.S.), pH and Eh in particular), as well as the question of the accessibility of the sorption sites to radionuclides. It is well established that transport through re-saturated compacted bentonite takes place via diffusion, though the mechanistic details still remain unclear. There is a relatively large pool of diffusion data for various compacted bentonite and montmorillonite systems existing in the open literature. In view of this, the approach adopted for estimating transfer factors was different. The idea was to compare and contrast the sorption values deduced from diffusion measurements with those predicted from batch sorption data. One important point here was to take into account our current understanding of sorption mechanisms. Another was to include considerations of the water chemistry. The porewater chemistry for the compacted bentonite was calculated according to a new approach described in BRADBURY & BAEYENS (2002b). A summary of the (preliminary) conclusions from this work (BRADBURY & BAEYENS, 2002a) is presented in Chapter 6. The question lying at the heart of the matter is whether it is reasonable and justifiable to produce a SDB for compacted bentonites based on sorption measurements carried out in dilute systems.

4.3 Rounding

The in situ R_d values for MX-80 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.

5 UNCERTAINTY ESTIMATES

5.1 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, $\pm 50 \{ (1/5)^2 + (3/10)^2 \}^{0.5} = \pm 18$

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.

5.2 Selected laboratory values: Uncertainty factor- R_d lit.

5.2.1 "In house" data

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. However, in cases where the sorption is either very high or very low, the uncertainty may be greater.

5.2.2 Literature sorption isotherm data on bentonites/montmorillonites

The uncertainties associated with literature sorption values originating from well defined, thorough investigations on montmorillonites/bentonites are directly comparable with "in house" measurements. Thus an uncertainty factor of 1.6 is also assigned in this case.

5.2.3 Single point measurements

If only a single point measurement is available, 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 description of the experimental methodology, system characterisation etc. It is, however, clear that single point sorption values have to be treated as being more uncertain than other data sources. Each case has to be examined individually.

5.3 Model calculations: Uncertainty factor-model

In the cases of Ca, Sr and Ra the sorption values were derived from cation exchange 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.

5.4 Mineralogy: Uncertainty factor-CEC

Conversions of sorption values for bentonites and montmorillonites with different mineralogies are carried out over the respective CEC values. (See section 5.1) The error in CEC data can be up to $\sim \pm 20\%$ which implies that an uncertainty factor of 1.3 would be associated with such a conversion.

5.5 pH: Uncertainty factor-pH

The pH conversion factors are calculated from appropriate sorption edges and defined in section 4.2 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.

5.6 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 case sensitive, and is strongly dependent on the completeness and quality of the TDB used. Also assumptions are made regarding the sorbing aqueous species and these are often poorly known.

5.7 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 (UF-speciation) factor. This is given in Table 10 as a value in parentheses.

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

See Chapter 6.

5.9 Overall uncertainty factors

The individual and overall uncertainty factors (UF) for the selected sorption values are given for each radionuclide in Table 10. The overall uncertainty factor is the product of the individual values.

For Co the overall uncertainty factor is given by

(UF-R_{dlit}) x (UF-speciation) x (UF-CEC) x (UF-pH) x (UF-Lab→Field)

For Nb, Cd, Sn, Pb, Am (Bi) the overall uncertainty factor is given by

(UF-R_{dlit}) x (UF-speciation) x (UF-CEC) x (UF-Lab→Field)

For Ni, Eu the overall uncertainty factor is given by

(UF-R_{dlit}) x (UF-speciation) x (UF-pH) x (UF-Lab→Field)

For Se(IV) the overall uncertainty factor is given by

(UF-R_{dlit}) x (UF-pH) x (UF-Lab→Field)

For Zr, 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 the overall uncertainty factor is given by

(UF-R_{dil}) x (UF-speciation) x (UF-Lab→Field)

For Ca, Sr, and Ra the overall uncertainty factor is given by

(UF-cation exchange model) x (UF-Lab→Field)

For C(org), Cl, Se(II), Mo(VI) and Ag(I) the Rd values are zero and hence the (UF-Overall) 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 (UF-Overall) equal to the maximum (UF-Overall) found for this group i.e. 10.

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

The selected sorption values in the SDB are considered to be “best estimate” values for the compacted bentonite/water 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.

$$\text{Lower bound sorption value} = \frac{\text{selected sorption value}}{\text{overall uncertainty factor}} \quad (5)$$

6 COMPARISON OF SORPTION VALUES FROM DIFFUSION AND BATCH MEASUREMENTS: A SUMMARY OF THE MAIN CONCLUSIONS

The aim of the work reported in BRADBURY & BAEYENS (2002a) was to compare sorption values derived from diffusion measurements on compacted bentonite with those measured for highly dispersed systems in batch sorption tests.

As a basis, diffusion data for Kunigel V1 presented in SATO & YUI (1997) and SATO (1998) were taken, primarily because of the breadth and completeness of the measurements. In order to extract distribution coefficients simple Fickian diffusion into a homogeneous single porosity medium was assumed in which the radionuclides either do not sorb at all or sorb rapidly, reversibly and linearly (constant K_d).

For neutral and positively charged species the effective diffusion coefficient for HTO was used and the whole of the porosity present in the original dry compacted material was considered to be available. (Radionuclide diffusive transport in performance assessment is calculated with the same simple model.)

A comparison between R_d data from intact and dispersed systems is only meaningful when it is made for the same water chemistry since pH, Eh and aqueous composition have an important influence on sorption. The methodology proposed by BRADBURY & BAEYENS (2002b) was used to calculate a porewater chemistry for compacted Kunigel V1 bentonite.

Batch sorption data were taken from a wide variety of sources where different types of purified montmorillonites were used. The selected R_d values were modified to the Kunigel V1 porewater using the methodology outlined in section 4.2.

The pathways for deriving distribution ratios for the Kunigel V1 system for the radionuclides under consideration were different, i.e.

- Sorption models were used to calculate distribution ratios for Cs(I), Ni(II) and Sm(III), using Eu(III) as chemical analogue.
- Am(III) and Np(V) sorption values were derived by modifying R_d values obtained for different purified montmorillonites to the Kunigel V1 system (section 4.2).
- In the case of Zr(IV), chemical analogy with Sn(IV) was invoked where the source data were Sn(IV) sorption measurements on a purified montmorillonite.

The important point being made here is that the “ R_d batch values” used in the comparison were derived from a mixture of different methods which are also used in

the derivation of sorption values in the SDB. The oxidation states covered the range from I to V.

When all of the above factors are taken into account, the correspondence between the sorption values derived from diffusion data and those calculated from batch sorption measurements is good to very good. The data are compared in Table 5. In this context it should be realised that a realistic uncertainty factor for batch sorption values carried out under controlled conditions in the laboratory is considered to be approximately 1.6, see section 5.1.

The preliminary conclusion drawn from the results of the above exercise is that to a first approximation suitably modified data from batch sorption type measurements on dispersed bentonite/montmorillonite systems do not differ in any significant way from R_d values derived from "in-diffusion" measurements. The proviso is that the appropriate water chemistry for the particular compacted system is considered i.e. this preliminary evidence suggests a Lab → Field transfer factor of unity. However, in view of the relatively small data set upon which this conclusion is based, an uncertainty factor of 2 is assigned to the Lab → Field transfer factor.

Finally a remark needs to be made concerning redox sensitive elements such as Np, U, Pu and Tc. Here, the agreement between deduced sorption values and those extracted from diffusion tests carried out under reducing conditions appears not to be particularly good. The D_a values calculated with the deduced sorption values tend to be smaller than those deduced from "in-diffusion" tests. Possible reasons for this discrepancy are numerous.

Diffusion measurements exist for these redox sensitive radionuclides in various compacted bentonite systems and it is claimed that the measured D_a values can be associated with a particular redox state. For oxidising conditions this may well be so, but under "reducing conditions" the situation is far from certain. Any sort of measurements at near neutral pH values and a well-defined redox state are notoriously difficult to perform. In most cases no measurements were carried out to check the redox state of the nuclide. If different oxidation states co-exist then the diffusion coefficient measured is some sort of value which is influenced by the different valence states, speciation and sorption characteristics. Claims that diffusion measurements have been carried out at a "fixed redox state" should be treated with the utmost caution. In addition, there is always the question of possible precipitation effects and whether the assumption of constant K_d is valid.

On the other hand, there are also uncertainties in the sorption values in the sorption data bases (BRADBURY & BAEYENS 2003) deduced for Np, U, Pu and Tc from batch data. The sorption mechanisms for elements in the tetravalent state are not

understood. Sorption values were based on chemical analogy with Th(IV). Assumptions had to be made concerning the sorbing species and the aqueous speciation which, especially with respect to hydroxycarbonato species (Th(IV), Np(IV), U(IV), Pu(IV)) and silicate species for the trivalent actinides, is not well established. The procedures used in the SDB work to convert lab batch sorption values to values appropriate to a given reference system are not applicable in every case, as has been noted previously (BRADBURY & BAEYENS 2003).

Making a valid comparison between sorption values originating from batch and diffusion measurements is a tricky exercise and requires a great deal of information. Situations where important information is lacking and/or where precise experimental conditions are difficult to establish, can lead to large uncertainties. This is especially so in the case of the actinides. At the moment the uncertainties are such that it is unclear which of the approaches leads to the most "correct" sorption values.

Table 5: Comparison of K_d values ($\text{m}^3 \text{ kg}^{-1}$) derived from “in-diffusion” data and K_d values modelled/predicted from batch sorption measurements as a function of dry density for Kunigel V1.

	ρ_{dry} 400 kg m^{-3}		ρ_{dry} 800 kg m^{-3}		ρ_{dry} 1400 kg m^{-3}		ρ_{dry} 1800 kg m^{-3}		ρ_{dry} 2000 kg m^{-3}	
	from diffusion data	from batch data	from diffusion data	from batch data	from diffusion data	from batch data	from diffusion data	from batch data	from diffusion data	from batch data
K_d Cs(I)	1.9×10^{-1}	2.0×10^{-1}	6.2×10^{-2}	5.4×10^{-2}	1.9×10^{-2}	4.1×10^{-2}	$9.7 \times 10^{-3}^*$	2.2×10^{-2}	6.9×10^{-3}	1.6×10^{-2}
K_d Ni(II)		9.0×10^{-1}		3.3×10^{-1}		2.9×10^{-1}	4.0×10^{-1}	4.3×10^{-1}		4.1×10^{-1}
K_d Sm(III)◊		9.2×10^{-1}	8.8	1.9	4.9	1.6	5.4	5.0		8.5
K_d Am(III)	200	25	88 175	35	17 34	33	49#	44		45
K_d Zr(IV)	6.8	16.5	8.8	21.0	11 17	22	21#	21		22
K_d Np(V)	5.5×10^{-2} 8.3×10^{-2}	$2.9 \times 10^{-2}^\ddagger$ $1.7 \times 10^{-2}^\wedge$	1.2×10^{-1}	$7.8 \times 10^{-2}^\ddagger$ $4.0 \times 10^{-2}^\wedge$	8.5×10^{-2} 1.7×10^{-1}	$7.5 \times 10^{-2}^\ddagger$ $3.8 \times 10^{-2}^\wedge$	$1.6 \times 10^{-1}^*$	$9.0 \times 10^{-2}^\ddagger$ $4.6 \times 10^{-2}^\wedge$	1.8×10^{-1}	$9.4 \times 10^{-2}^\ddagger$ $4.8 \times 10^{-2}^\wedge$

* Interpolated

Extrapolated

◊ Chemical analogue for Eu(III)

‡ GORGEON (1994)

₩ TURNER et al. (1998)

7 SELECTED SORPTION VALUES FOR THE MX-80 SYSTEM

In the following, radionuclides are grouped according to their chemical similarities and the rational behind the selection of the R_d value is briefly discussed for each radionuclide in turn. The selected laboratory/literature values ($R_{d\text{ lit}}$), conversion factors (Chapter 4) and the calculated in situ distribution ratios for most radionuclides are given in the data sheets. Sorption data sheets are presented for each of the three MX-80 porewater chemistries defined in Table 3. Summary tables of the selected sorption values and their associated uncertainty values are given in Chapter 8.

Note that it was concluded in Chapter 6 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

7.1.1 Caesium

The Cs sorption isotherm determined on MX-80 is shown in Figure 2. (BRADBURY & BAEYENS, unpublished data.) The R_d value at trace Cs equilibrium concentrations ($< 10^{-8}$ M) was measured to be $\sim 5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$, $(R_{d\text{(Cs)}})_{\text{lab}}$.

It is well established in the open literature that Cs sorbs by cation exchange on Na-montmorillonite. In the current system Na is the dominant cation and the exchange is therefore monovalent-monovalent i.e. between Cs and Na. Under these conditions the sorption of Cs is inversely proportional to the Na concentration. Hence the Cs distribution ratio at the Na concentration in the MX-80 reference water, $R_{d\text{(Cs)}}^{\text{lit}}$, is given by:

$$\frac{R_{d\text{(Cs)}}^{\text{lit}}}{R_{d\text{(Cs)}}_{\text{lab}}} = \frac{(Na)_{\text{lab}}}{(Na)_{\text{ref}}} \quad (6)$$

yielding an $R_{d\text{(Cs)}}^{\text{lit}}$ of $10^{-1} \text{ m}^3 \text{ kg}^{-1}$.

Note that Eqn. 6 takes into account the competition effect of Na on the sorption of Cs in the two water chemistries.

The above value is used in the data sheet where a speciation correction factor is applied to give $R_{d\text{(Cs)}}^{\text{ref}}$. Also, no pH correction for Cs is required since the sorption mechanism is cation exchange.

Using similar procedures to those described above, sorption values for Cs were deduced for the water chemistries at pH values of 6.9 and 7.9, see data sheets.

An in situ sorption value for Cs of $1.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $1.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $1.4 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

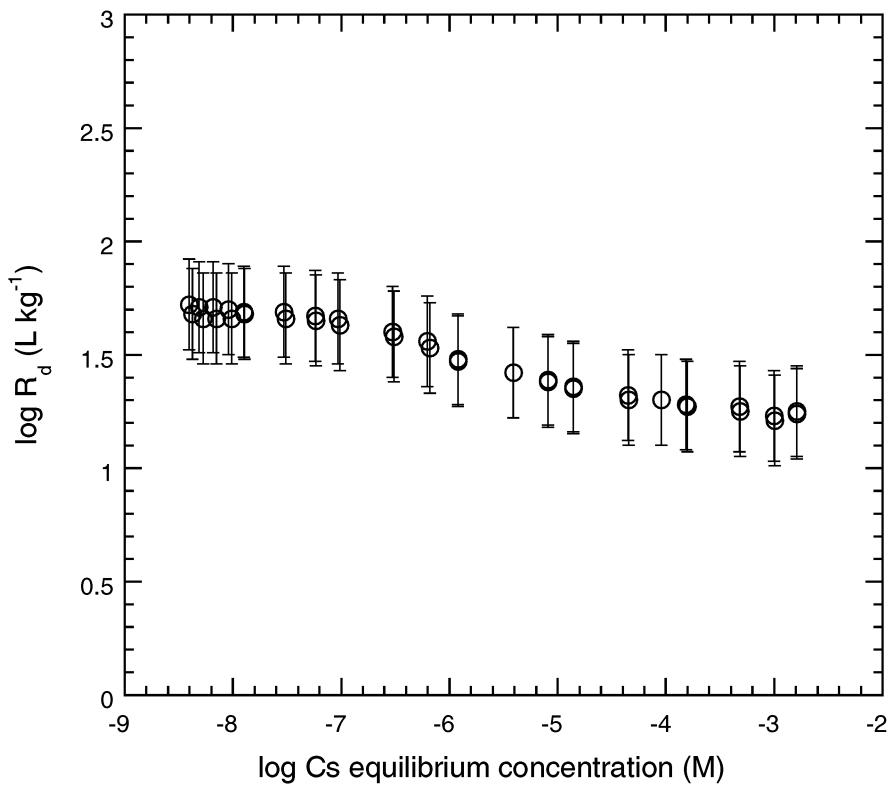


Figure 2: Cs sorption isotherm on MX-80 bentonite in SBPW, Table 4. (pH ~ 7.6, S:L = 60 g L⁻¹, equilibration time 40 days.) (BRADBURY & BAEYENS, unpublished data.)

Cs DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: $10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Corrected for the differences in Na concentration in the SBPW and MX-80 reference water; Cs equilibrium concentration: $< 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.78

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.92	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1.2	1

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
1.2×10^{-1}

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
1.2×10^{-1}

Cs DATA SHEET FOR MX-80, pH = 6.9

Literature source: BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: $9.8 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ (Corrected for the differences in Na concentration in the SBPW and MX-80 pH=6.9 water; Cs equilibrium concentration: $< 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.78

MX-80 pH = 6.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	0.92	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1.18	1

MX-80 pH = 6.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
1.2×10^{-1}

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
1.2×10^{-1}

Cs DATA SHEET FOR MX-80, pH = 7.9

Literature source: BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: $1.14 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Corrected for the differences in Na concentration in the SBPW and MX-80 pH=7.9 water; Cs equilibrium concentration: $< 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$\text{C}_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.78

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	0.93	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1.19	1

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
1.4×10^{-1}

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
1.4×10^{-1}

7.1.2 Calcium/Strontium

In a recent porewater study on MX-80 (BRADBURY & BAEYENS, 2002b) the selectivity coefficients for the major cations K, Mg and Ca with respect to Na were determined, Table 6. The selectivity coefficients in this table were used in conjunction with the MX-80 reference porewater composition, Table 3, to calculate an $R_d(\text{Ca})_{\text{ref}}$ value of $3.3 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$.

Table 6: Cation exchange equilibria and selectivity coefficients for K-Na, Mg-Na and Ca-Na on MX-80 (BRADBURY & BAEYENS, 2002b).

Exchange reaction	K_c
Na-mont + K \leftrightarrow K-mont + Na	4.0
2 Na-mont + Mg \leftrightarrow Mg-mont + 2 Na	2.2
2 Na-mont + Ca \leftrightarrow Ca-mont + 2 Na	2.6
2 Na-mont + Sr \leftrightarrow Sr-mont + 2 Na	2.6 [#]

[#]Taken to be the same as for Ca-Na exchange.

Because the Sr concentrations were very low in this study, a selectivity coefficient for Sr-Na exchange could not be determined. However, the cation exchange behaviour of Ca and Sr is very similar and normally the same value can be taken for their selectivity coefficients. (See for example BRUGGENWERT & KAMPHORST, 1982; BAEYENS, 1982.)

The following example demonstrates that this is a good assumption. GRÜTTER et al. (1992, 1994) carried out detailed studies of Sr sorption on unconsolidated glaciofluvial deposits and clay minerals. Sorption isotherm measurements were made for Sr on montmorillonite (CEC = 0.89 equiv. kg⁻¹) in a low ionic strength (I.S. = 10⁻² M) synthetic groundwater. The sorption of Sr was essentially constant over the equilibrium concentration range from $\sim 4 \times 10^{-5}$ to $\sim 10^{-7}$ M, with an average R_d value of $\sim 0.13 \text{ m}^3 \text{ kg}^{-1}$. Using the K-Na, Mg-Na and Ca-Na data in Table 6 and the code MINSORB (BRADBURY & BAEYENS, 1997b), the selectivity coefficient for Sr-Na exchange calculated from this data was ~ 2.8 i.e. close to the Ca-Na value given in Table 6. The selectivity coefficients in Table 6 were used in conjunction with the MX-80 reference porewater composition, Table 3, to calculate an $R_d(\text{Sr})_{\text{ref}}$ value of $3.3 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$. Using similar procedures to those described above, sorption values for Ca and Sr were deduced for the water chemistries at pH values of 6.9 and 7.9.

No data sheets are given for Ca or Sr.

An in situ sorption value for Ca and Sr of $3.3 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 the same in situ sorption values were chosen.

7.1.3 Radium

Literature values for the sorption of Ra on geological materials are scarce, but where reported, they are often high ($> 1 \text{ m}^3 \text{ kg}^{-1}$). The data are also associated with a large degree of scatter (see Appendix B in STENHOUSE, 1995).

The only data which could be found on Ra sorption on montmorillonite were from AMES et al. (1983a). Measurements at 25 °C were made at Ra equilibrium concentrations between 1.4×10^{-9} and $1.8 \times 10^{-11} \text{ M}$ in a 0.01 M NaCl background electrolyte. Three sorption values were measured; 3.6, 3.7 and $3 \text{ m}^3 \text{ kg}^{-1}$ i.e. over the concentration range considered the sorption was virtually constant. Ra is present in solution as the bivalent cation and is anticipated to sorb by cation exchange in analogy to other alkali-earth metals e.g. Ca, Mg, Sr and Ba. Using a cation exchange capacity of 1.2 eq. kg⁻¹ (AMES et al., 1983b) a selectivity coefficient, K_c (Ra-Na) = 0.7, for Ra-Na exchange was calculated. This value can in turn be used to calculate the Ra sorption in the reference MX-80 porewater using the code MINSORB, which yields $R_d(\text{Ra})_{\text{ref}} = 4 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$. (Note that AMES et al. (1983a) also present data for Ra sorption on nontronite, an expanding clay mineral similar to montmorillonite. In this case the selectivity coefficient K_c (Ra-Na) was 4 to 5 times higher.)

When appropriate data for Ra are not available Sr and Ba are often used as chemical analogues.

GRÜTTER et al. (1992, 1994) measured Ba sorption isotherms on montmorillonite in a synthetic groundwater. The selectivity coefficient, K_c (Ba-Na), calculated from this data in the manner described above, was 2.8 i.e. the same as for Sr (section 7.1.2), demonstrating again the close similarity between the alkali earth elements with respect to their cation exchange behaviour.

The selectivity coefficient for Ra-Na exchange deduced from the data of AMES et al. (1983a) is considered to be unusually low compared with those of Ca-Na, Sr-Na and Ba-Na. Consequently, the chemical analogy with Ba is preferred, and the sorption of Ra is calculated with a Ra-Na selectivity coefficients of 2.8 in the MX-80 reference porewater composition, Table 3, yielding a value for R_d (Ra)_{ref} of $2.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$. Using similar procedures to those described above, sorption values for Ra were deduced for the water chemistries at pH values of 6.9 and 7.9.

No data sheets are given for Ra.

An in situ sorption value for Ra of $2.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $2.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ and $2.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

7.2 Transition and heavy metals

Studies on the cation exchange behaviour of transition and heavy metals have been extensively reported in the open literature, see for example BRUGGENWERT & KAMPHORST (1982), MAES et al. (1976). Almost no use has been made of this pool of data here because for the reference MX-80 system exchange processes for this group of elements contribute little or nothing to the overall uptake.

7.2.1 Cobalt

Two sets of measurements of Co sorption on montmorillonite relevant to the MX-80 reference conditions were found: GRÜTTER et al. (1992, 1994) and TILLER & HODGSON (1960).

The study of GRÜTTER et al. (1992, 1994) included sorption and desorption kinetics for Co at different concentrations, together with a full description of the water chemistry and CEC measurements. They also present similar sorption data for Ni, and Co appears to sorb more strongly. It is worth noting that the Ni sorption value measured on SWy-1 montmorillonite at pH = 7.7-8.1 by GRÜTTER et al. (1994) at the lowest Ni concentration used, is compatible with the data of BAEYENS & BRADBURY (1997) for the same montmorillonite. From the results given, a sorption value of ~ 3.6 m³ kg⁻¹ at Co equilibrium concentrations <10⁻⁸ M was selected (pH ~ 7.9).

TILLER & HODGSON (1960) presented a sorption edge for Co (% sorbed vs. pH) up to pH ~ 8, Figure 3, but did not give the CEC of the Ca-montmorillonite used. This is not so important here since these data are used to provide a pH correction factor to convert the selected sorption value to the MX-80 reference system value of 7.25. The CF-pH is given by the ratio of the R_d values calculated from Figure 3 at pH = 7.25 and 7.9 and equals 0.37.

Using similar procedures to those described above, sorption values for Co were obtained for the water chemistries at pH 6.9 and 7.9.

Data sheets for Co are given below.

An in situ sorption value for Co of 6.4 x10⁻¹ m³ kg⁻¹ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of 4.4 x 10⁻¹ m³ kg⁻¹ and 1.8 m³ kg⁻¹ respectively were chosen.

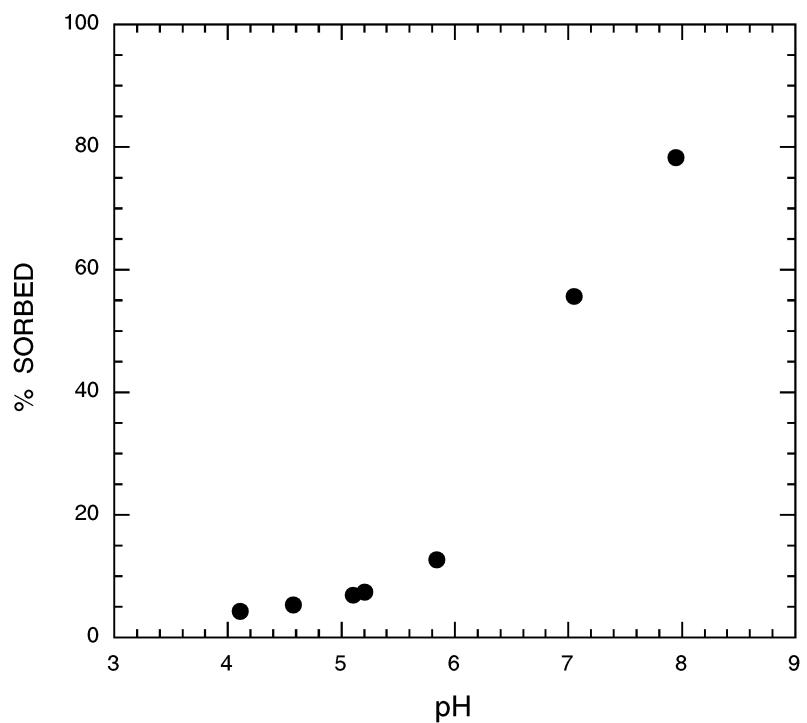


Figure 3: Co sorption edge measured on Ca-montmorillonite; 0.1 M CaCl_2 , S:L ratio = 1.66 g L⁻¹, $\text{Co}_{\text{tot}} < 10^{-6}$ M (TILLER & HODGSON, 1960).

Co DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: GRÜTTER et al. (1992, 1994)

Selected R_d lit.: $3.6 \text{ m}^3 \text{ kg}^{-1}$ (Co equilibrium concentration : $< 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.89

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.9	4.2×10^{-4}	-	6.5×10^{-3}	1

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.55	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
0.37	0.55	0.88

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
6.4×10^{-1}

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
6.4×10^{-1}

Co DATA SHEET FOR MX-80, pH = 6.9

Literature source: GRÜTTER et al. (1992, 1994)

Selected R_d lit.: $3.6 \text{ m}^3 \text{ kg}^{-1}$ (Co equilibrium concentration : $< 10^{-8} \text{ M}$)**Source data summary**

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.89

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.9	4.2×10^{-4}	-	6.5×10^{-3}	1

MX-80 pH = 6.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	0.55	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
0.25	0.55	0.88

MX-80 pH = 6.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
4.4×10^{-1}

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
4.4×10^{-1}

Co DATA SHEET FOR MX-80, pH = 7.9

Literature source: GRÜTTER et al. (1992, 1994)

Selected R_d lit.: $3.6 \text{ m}^3 \text{ kg}^{-1}$ (Co equilibrium concentration : $< 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.89

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.9	4.2×10^{-4}	-	6.5×10^{-3}	1

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	0.57	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.57	0.88

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
1.8

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

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

7.2.2 Nickel

A sorption isotherm has been measured for Ni on MX-80 in a synthetic bentonite porewater at pH = 7.6, Table 4 (BRADBURY & BAEYENS, unpublished data). The isotherm is shown in Figure 4. From these data a sorption value of $3.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was selected.

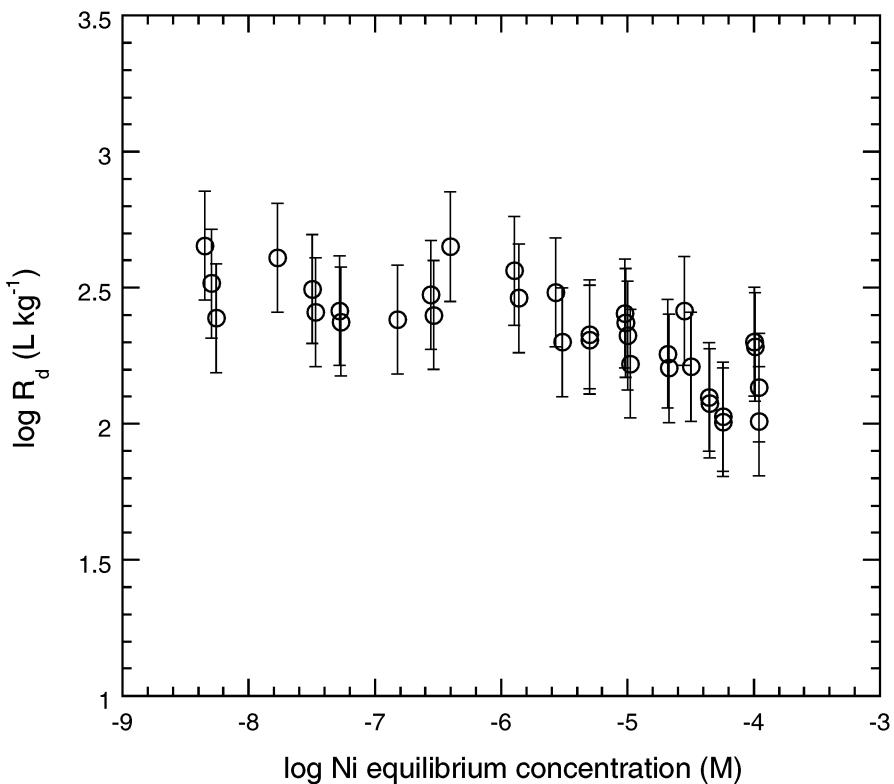


Figure 4: Ni sorption isotherm on MX-80 bentonite in SBPW, Table 4. (pH = 7.6, S:L = 1.6 g L⁻¹, equilibration time 74 days.) (BRADBURY & BAEYENS, unpublished data)

A pH correction factor to convert the selected sorption value (pH = 7.6) to the MX-80 reference system value of 7.25 was obtained from the Ni sorption edge given in Figure 5. A CF-pH factor of 0.63 was deduced.

Using similar procedures to those described above, sorption values for Ni were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Ni are given below

An in situ sorption value for Ni of $2.3 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $1.4 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $5.8 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

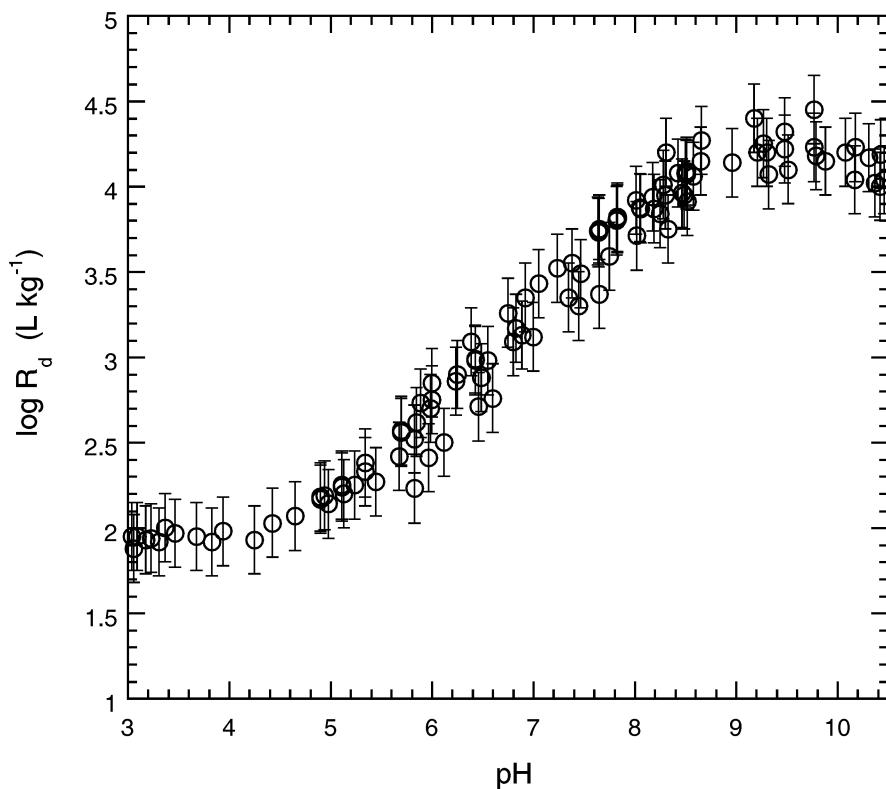


Figure 5: Ni sorption edge measured on Na- montmorillonite (SWy-1).
(0.1 M NaClO₄, S:L ratio = 1 g L⁻¹, Ni_{TOT} < 10⁻⁷ M)
(BAEYENS & BRADBURY, 1997).

Ni DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: $3.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Ni equilibrium concentrations $< 10^{-6} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.42

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.48	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
0.63	1.14	1

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
2.3×10^{-1}

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
2.3×10^{-1}

Ni DATA SHEET FOR MX-80, pH = 6.9

Literature source: BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: $3.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Ni equilibrium concentrations $< 10^{-6} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.42

MX-80 pH = 6.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	0.47	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
0.40	1.12	1

MX-80 pH = 6.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
1.4×10^{-1}

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
1.4×10^{-1}

Ni DATA SHEET FOR MX-80, pH = 7.9

Literature source: BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: $3.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Ni equilibrium concentrations $< 10^{-6} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.42

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	0.50	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1.51	1.19	1

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
5.8×10^{-1}

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
5.8×10^{-1}

7.2.3 Cadmium

A number of reports were found dealing with Cd sorption on montmorillonite e.g. ZIPER et al. (1988); SCHULTESS & HUANG (1990); ZACHARA et al. (1993); KRUSE (1993); ZACHARA & SMITH (1994) and LOTHENBACH et al. (1997). Of these, the work of ZACHARA et al. (1993) was considered to be the most appropriate because it contained a sorption edge for Cd measured on a SWy-1 Ca-montmorillonite in an 10^{-3} M $\text{Ca}(\text{ClO}_4)_2$ solution in the absence of carbonate. This edge was presented in terms of "% sorbed vs. pH" (Figure 6), but since all the ancillary data were provided, an R_d (Cd) of $1.11 \text{ m}^3 \text{ kg}^{-1}$ could be calculated at pH = 7.25.

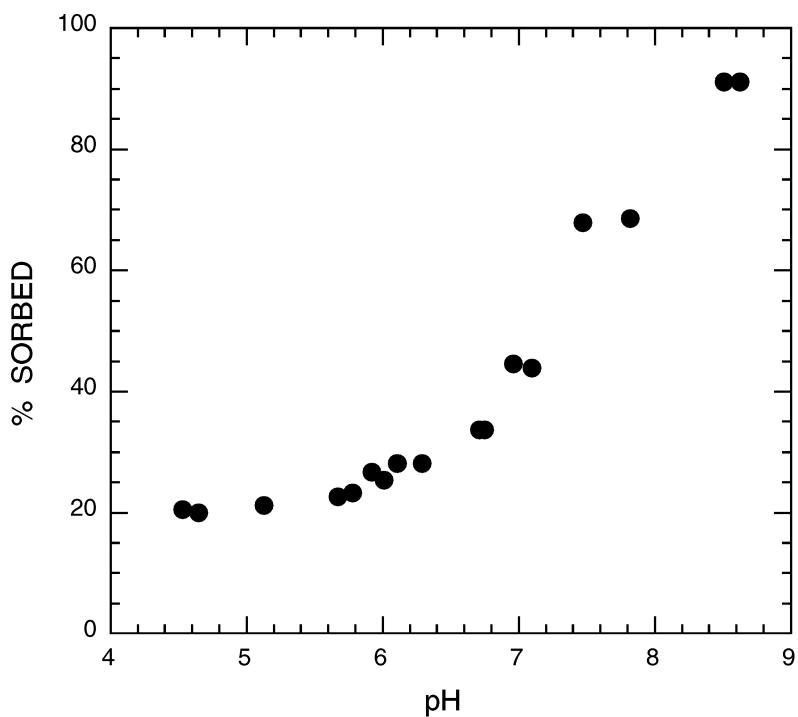


Figure 6: Cd sorption edge measured on Ca-montmorillonite (SWy-1). (Background electrolyte: 10^{-3} M $\text{Ca}(\text{ClO}_4)_2$; S:L = 1.0 g L^{-1} ; Cd_{tot} conc. $\sim 10^{-6}$ M) (Taken from ZACHARA et al., 1993).

The R_d (Cd) value of $1.11 \text{ m}^3 \text{ kg}^{-1}$, when plotted on a Ni edge measured under similar conditions (BRADBURY & BAEYENS, 1999) fell within the uncertainty band of the data. This is an indication that taking Ni as a chemical analogue for Cd (which is often done) is very reasonable. However, Cd forms significantly stronger chloro complexes than Ni, and these are assumed to be non-sorbing. Consequently, the sorption of Cd is less than Ni in the MX-80 reference system.

Using similar procedures to those described above, sorption values for Cd were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Cd are given below.

An in situ sorption value for Cd of $1.0 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $5.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ and $2.3 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Cd DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: ZACHARA et al. (1993)

Selected R_d lit.: $1.11 \text{ m}^3 \text{ kg}^{-1}$ (Cd equilibrium conc. $< 10^{-6} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.87

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	ClO_4 (M)	$F_{\text{lit. speciation}}$
7.25	-	-	2×10^{-3}	1

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.10	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.10	0.91

MX-80 reference sorption value

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

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

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

Cd DATA SHEET FOR MX-80, pH = 6.9

Literature source: ZACHARA et al. (1993)

Selected R_d lit.: $6.7 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Cd equilibrium conc. $< 10^{-6} \text{ M}$)**Source data summary**

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.87

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	ClO_4 (M)	$F_{\text{lit. speciation}}$
6.9	-	-	2×10^{-3}	1

MX-80 pH = 6.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	0.09	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.09	0.91

MX-80 pH = 6.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
5.5×10^{-2}

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
5.5×10^{-2}

Cd DATA SHEET FOR MX-80, pH = 7.9

Literature source: ZACHARA et al. (1993)

Selected R_d lit.: $2.33 \text{ m}^3 \text{ kg}^{-1}$ (Cd equilibrium conc. $< 10^{-6} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.87

$\text{pH}_{\text{lit.}}$	$\text{C}_{\text{inorg.}} (\text{M})$	$\text{SO}_4 (\text{M})$	$\text{ClO}_4 (\text{M})$	$F_{\text{lit. speciation}}$
7.9	-	-	2×10^{-3}	1

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	0.11	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.11	0.91

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
2.3×10^{-1}

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
2.3×10^{-1}

7.2.4 Palladium

No relevant sorption data could be found for Pd.

Under the anticipated in situ redox and pH conditions Pd is calculated to be fully reduced to palladium metal. The solubility is consequently exceedingly low (formally 10^{-27} M!). Under such circumstances there is little point in giving a sorption value. However, if for any reason Pd metal does not precipitate out and the solubility is considerably higher, and an estimated distribution ratio is required, then chemical analogues such as Co, Ni, Cd and Pb, for which sorption data exist, might suggest themselves. The dominant Pd species at pH = 7.25 is $\text{Pd}(\text{OH})_2^0$ (chloro complexes constitute only ~3%) and since the first hydrolysis constants for Co, Ni and Pb are significantly weaker (BAES & MESMER, 1976), such transition and heavy metals do not form neutral hydroxy species until relatively high pH. On this basis, sorption probably increases in the order Pd >> Pb > Ni ~ 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 in situ value of $5 \text{ m}^3 \text{ kg}^{-1}$, which is less than the in situ values for Pb, is almost certainly an underestimation of the real value.

At pHs of 6.9 and 7.9, Pd is still highly hydrolysed, having only ~16% and ~0.1% chloro complexes respectively present in solution, and thus no pH dependency is expected. The same value as for the MX-80 reference system at pH = 7.25 is chosen at the bounding pH values of 6.9 and 7.9.

Given the lack of almost any sort of quantitative data it is somewhat difficult to suggest an uncertainty factor. However, the rational behind the selection of a value of an overall uncertainty factor of 15 is given in section 5.8.

No data sheet is provided for Pd.

An in situ sorption value for Pd of $5 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 system at all three pH values under consideration.

7.2.5 Silver

PLEYSIER & CREMERS (1975) reported an extensive study on the cation exchange of a silver-thiourea complex onto Na-, Ca- and Al-montmorillonites. In this work the exchange of silver on a Na montmorillonite (Camp Berteau) was measured at 25 °C and a selectivity coefficient of 0.8 was reported.

The sorption of Ag on MX-80 in the reference MX-80 porewater was modelled using MINSORB and the above Ag-Na selectivity coefficient. A very low sorption value ($\sim 10^{-7} \text{ m}^3 \text{ kg}^{-1}$) was calculated, primarily due to the high Na background concentration and the strong tendency of Ag to form chloro complexes which are assumed to be non

sorbing. (Only ~0.04% of the Ag was not complexed in the reference porewater at pH = 7.25.) As a result of this, Ag is considered to be non-sorbing.

However, silver solutions are photosensitive, and it may be that in a gamma-field the Ag complexes could be reduced to Ag metal and precipitate out, thus becoming immobilised.

The sorption of Ag was taken to be zero for the MX-80 system at the three pH values under consideration.

7.2.6 Lead

RYBICKA et al. (1995) measured heavy metal sorption on montmorillonite and found the sequence of adsorption affinities to be Pb > Cd ~ Cu > Ni. The data are not particularly appropriate for the MX-80 reference system on two counts: (i) measurements were made around pH 5 where predominantly cation exchange processes will be occurring and (ii) no information was given on the water chemistries.

ULRICH & DEGUELDRÉ (1992) measured the sorption of Pb at very low concentrations ($\sim 10^{-11}$ M) on a montmorillonite (CEC = 0.76 equiv. kg⁻¹) at different ionic strengths (0.01 to 0.2 M) at pH values of 5, 6 and 7. Although the interpretation of the data is somewhat unclear, sorption values were high. These data are re-plotted as a sorption edge in Figure 7. Broadly speaking, the values obtained in 0.1 M NaClO₄ were two orders of magnitude greater than those for Ni under similar conditions.

From Figure 7 a lower bound sorption value of 63 m³ kg⁻¹ at pH = 7.25 was chosen.

Using similar procedures to those described above, sorption values for Pb were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Pb are given below.

An in situ sorption value for Pb of 7.9 m³ kg⁻¹ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of 4.7 m³ kg⁻¹ and 62.4 m³ kg⁻¹ respectively were chosen.

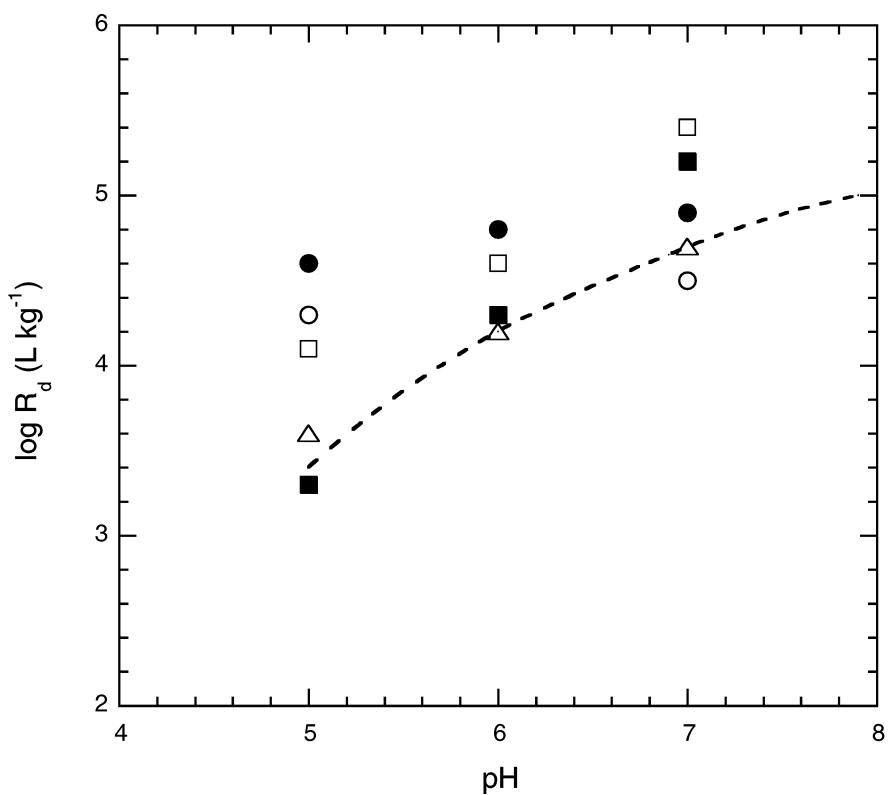


Figure 7: Data from ULRICH & DEGUELDRÉ (1992) re-plotted as a Pb sorption edge.
NaClO₄ background electrolyte at: 0.01M (○), 0.02 M (●), 0.05 M (□), 0.1 M (■), 0.2 M (Δ).

Pb DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: ULRICH & DEGUEL DRE (1992)

Selected R_d lit.: $63 \text{ m}^3 \text{ kg}^{-1}$ (Trace concentrations $\sim 10^{-11} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
montmorillonite	0.76

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	ClO_4 (M)	$F_{\text{lit. speciation}}$
7.25	1.2×10^{-4}	-	10^{-1}	0.82

Assumption: solutions are air saturated

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.10	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.12	1.04

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
7.9

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
7.9

Pb DATA SHEET THE MX-80, pH = 6.9

Literature source: ULRICH & DEGUEL DRE (1992)

Selected R_d lit.: 45 m³ kg⁻¹ (Trace concentrations ~ 10⁻¹¹ M)**Source data summary**

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

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	F _{lit. speciation}
6.9	6.1 × 10 ⁻⁵	-	10 ⁻¹	0.95

Assumption: solutions are air saturated

MX-80 pH = 6.9: data summary

pH	F _{speciation}	CEC _{ref.} (equiv. kg ⁻¹)
6.9	0.094	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.10	1.04

MX-80 pH = 6.9 sorption value

R _d (m ³ kg ⁻¹)
4.7

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
4.7

Pb DATA SHEET THE MX-80, pH = 7.9

Literature source: ULRICH & DEGUEL DRE (1992)

Selected R_d lit.: 100 m³ kg⁻¹ (Trace concentrations ~ 10⁻¹¹ M)

Source data summary

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

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	F _{lit. speciation}
7.9	5.2 × 10 ⁻⁴	-	0.1	0.25

Assumption: solutions are air saturated

MX-80 pH = 7.9: data summary

pH	F _{speciation}	CEC _{ref.} (equiv. kg ⁻¹)
7.9	0.15	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.6	1.04

MX-80 pH = 7.9 sorption value

R _d (m ³ kg ⁻¹)
62.4

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
62.4

7.3 Lanthanides

7.3.1 Europium

A sorption isotherm has been measured for Eu on MX-80 in a synthetic bentonite porewater (Table 4). The isotherm is shown in Figure 8 (BRADBURY & BAEYENS, unpublished data). From these data a sorption value of $12.6 \text{ m}^3 \text{ kg}^{-1}$ was selected.

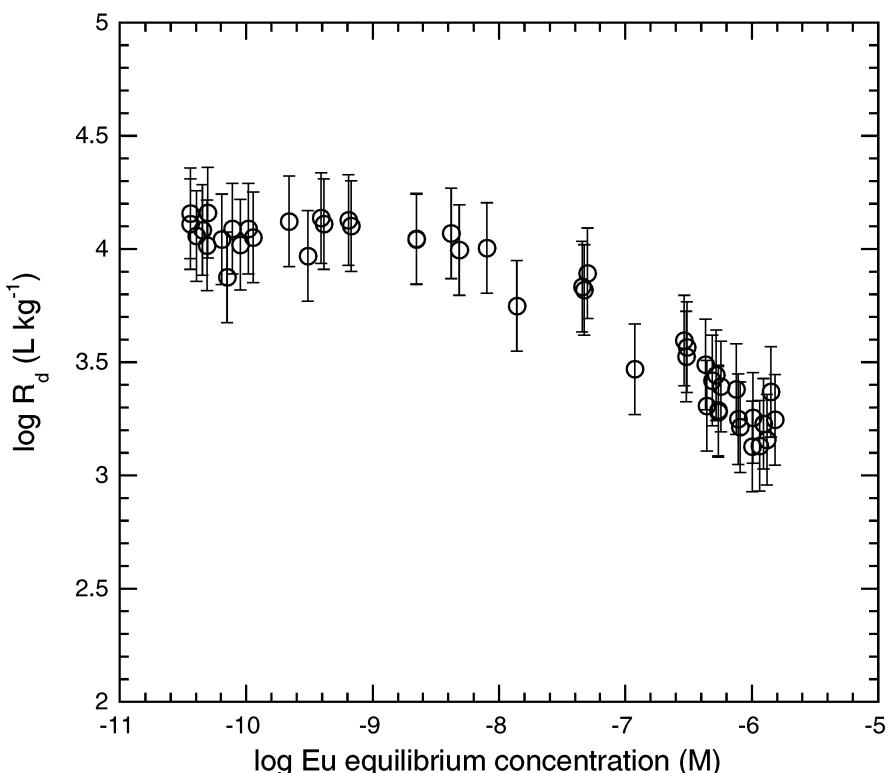


Figure 8: Eu sorption isotherm on MX-80 bentonite in SBPW, Table 4. ($\text{pH} = 7.6$, S:L ratio = $0.16 - 1.6 \text{ g L}^{-1}$, equilibration time 69 days.) BRADBURY & BAEYENS, unpublished data.

A pH correction factor to convert the selected sorption value ($\text{pH} = 7.6$) to the MX-80 reference system value of 7.25 was obtained from the Eu sorption edge in Figure 9 (BRADBURY & BAEYENS, 2002c). The CF-pH factor is 0.5. Using similar procedures to those described above, sorption values for Eu were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Eu are given below.

An in situ sorption value for Eu of $4.7 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $1.9 \text{ m}^3 \text{ kg}^{-1}$ and $14.2 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

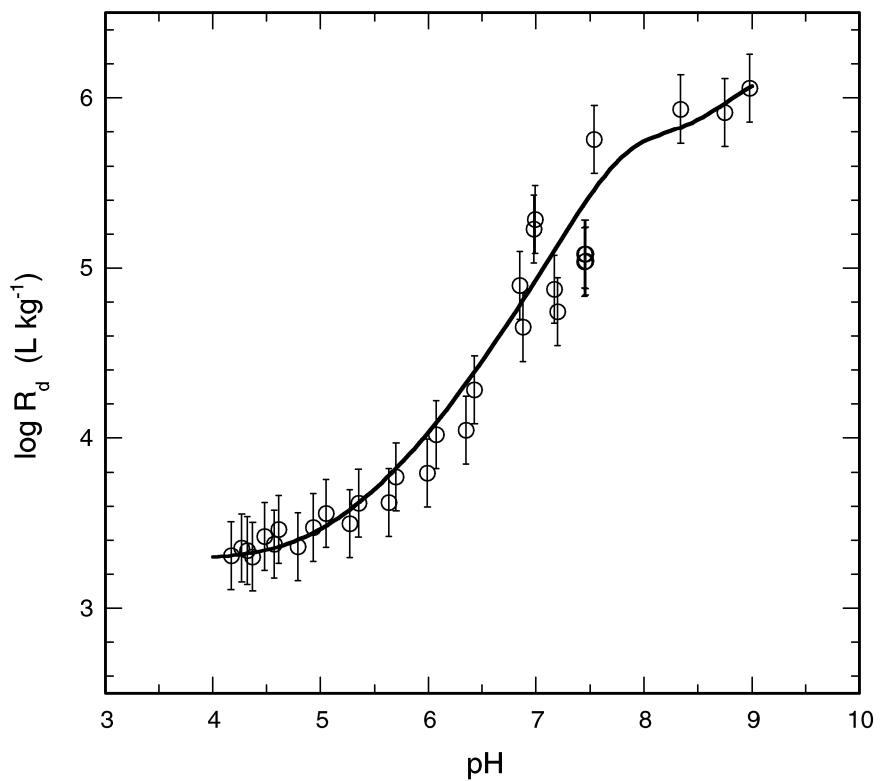


Figure 9: Eu sorption edge measured on Na-montmorillonite (SWy-1). (Background electrolyte = 0.1 M NaClO₄; S:L = 1.5 g L⁻¹; Eu_{TOT} conc. ~1.3 × 10⁻⁷ M) (Taken from BRADBURY & BAEYENS, 2002c).

Eu DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: BRADBURY & BAEYENS, unpublished data

Selected R_d lit.: $12.6 \text{ m}^3 \text{ kg}^{-1}$ (Equilibrium concentration: $\leq 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.04

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.03	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
0.5	0.75	1

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
4.7

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

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

Eu DATA SHEET MX-80, pH = 6.9

Literature source: BRADBURY & BAEYENS, unpublished data

Selected R_d lit.: $12.6 \text{ m}^3 \text{ kg}^{-1}$ (Equilibrium concentration: $\leq 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.04

MX-80 pH = 6.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	0.03	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
0.2	0.75	1

MX-80 pH = 6.9 sorption value

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

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

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

Eu DATA SHEET MX-80, pH = 7.9

Literature source: BRADBURY & BAEYENS, unpublished data

Selected R_d lit.: $12.6 \text{ m}^3 \text{ kg}^{-1}$ (Equilibrium concentration: $\leq 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	0.04

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	0.03	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1.5	0.75	1

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
14.2

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
14.2

7.3.2 Cerium, Promethium, Samarium and Holmium

No sorption data could be found for any of these elements.

No thermodynamic constants are given for the above four elements in the data base of HUMMEL et al. (2002) whereas for Ce and Sm PEARSON et al. (1992) do give some values. However, the latter are not considered to be particularly reliable. To a first approximation Ce, Pm, Sm and Ho are considered to have the same speciation as Eu, which is also taken as the chemical analogue for sorption.

No data sheets are provided for these radionuclides.

An in situ sorption value for Ce, Pm, Sm and Ho of $4.7 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $1.9 \text{ m}^3 \text{ kg}^{-1}$ and $14.2 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

7.4 Actinides

7.4.1 Americium, Actinium, Curium

7.4.1.1 Americium

GORGEOON (1994) investigated the sorption of Am on a purified homo-ionic Na-smectite from Wyoming at 1 and 0.1 M NaClO₄ as function of pH from 3 to 11 under atmospheric conditions. The equilibrium Am concentrations were low ($< 8 \times 10^{-10} \text{ M}$ from pH = 6.5 upwards). The sorption data, presented in Tables 5.17 and 5.18 in that study, are reproduced here in Figure 10.

From Figure 10 an R_d of $40 \text{ m}^3 \text{ kg}^{-1}$ was selected at pH = 7.25.

Using similar procedures to those described above, sorption values for Am were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Am are given below.

An in situ sorption value for Am of $26.8 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $6.6 \text{ m}^3 \text{ kg}^{-1}$ and $63 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

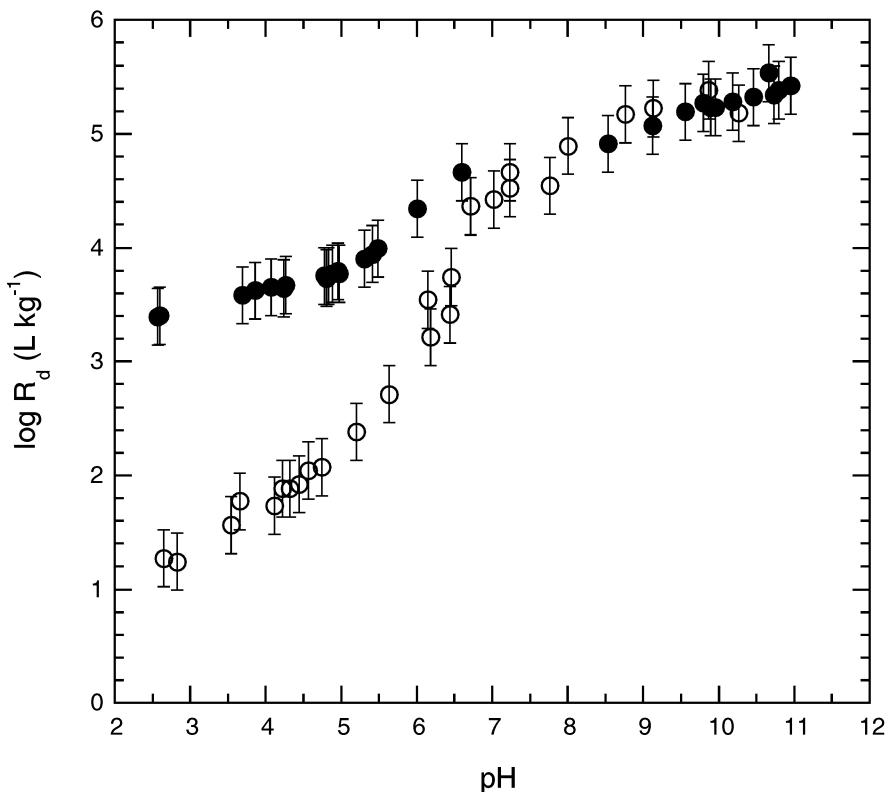


Figure 10: Am edges on montmorillonite at 2 ionic strengths: (●) 0.1 M NaClO₄, (○) 1 M NaClO₄. (Taken from GORGEON, 1994).

7.4.1.2 Actinium, Curium

No reliable sorption data for these elements was found in the open literature. Since, as far as is known, the aqueous speciation of both elements is almost identical to Am (HUMMEL, pers. comm.), the latter was taken as a chemical analogue and the same sorption values selected.

No data sheets are provided for Ac and Cm.

An *in situ* sorption value for Ac and Cm of $26.8 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 *in situ* sorption values of $6.6 \text{ m}^3 \text{ kg}^{-1}$ and $63 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Am DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: GORGEON (1994)

Selected R_d lit.: $40 \text{ m}^3 \text{ kg}^{-1}$ (Equilibrium concentration: $< 10^{-10} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
Smectite	0.79

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	SO_4 (M)	ClO_4 (M)	$F_{\text{lit. speciation}}$
7.25	1.2×10^{-4}	-	0.1	0.06

Assumption: solutions are air saturated, quartz saturated

MX-80 reference case: data summary

$\text{pH}_{\text{ref.}}$	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	0.04	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.67	1

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
26.8

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
26.8

Am DATA SHEET MX-80, pH = 6.9

Literature source: GORGEON (1994)

Selected R_d lit.: 20 m³ kg⁻¹ (Equilibrium concentration: < 10⁻¹⁰ M)**Source data summary**

Solid	$CEC_{lit.}$ (equiv. kg ⁻¹)
smectite	0.79

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	F _{lit. speciation}
6.9	6.1 × 10 ⁻⁵	-	0.1	0.12

Assumption: solutions are air saturated, quartz saturated

MX-80 pH = 6.9: data summary

pH	F _{speciation}	$CEC_{ref.}$ (equiv. kg ⁻¹)
6.9	0.04	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.33	1

MX-80 pH = 6.9 sorption value

R_d (m ³ kg ⁻¹)
6.6

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ (m ³ kg ⁻¹)
6.6

Am DATA SHEET MX-80, pH=7.9

Literature source: GORGEON (1994)

Selected R_d lit.: $63 \text{ m}^3 \text{ kg}^{-1}$ (Equilibrium concentration: $< 10^{-10} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
smectite	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	ClO_4 (M)	$F_{\text{lit. speciation}}$
7.9	5.2×10^{-4}	-	0.1	0.03

Assumption: Solutions are air saturated, quartz saturated

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	0.03	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
63

7.4.2 Thorium, Protactinium, Uranium, Neptunium, Plutonium

7.4.2.1 Actinide (IV) hydroxy-carbonato complexes

In an attempt to set up some general procedures for modifying literature sorption data to the MX-80 reference water chemistry, some broad statements regarding sorption behaviour were made. For Th, as representative for the readily hydrolysable tetravalent actinides Pa, U, Np and Pu, it was noted that the sorption edge 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. (See for example Figure 12 in the following section.) This led to the hypothesis that positive and neutral hydrolysed species sorb strongly, and that tetravalent actinides exhibit sorption plateaus between pH ~ 6 to ~ 9. Negatively charged hydrolysed species, carbonato and hydroxy-carbonato complexes for example were assumed to be non-sorbing and sorption would thus be reduced upon their formation.

In the recently completed update of the Nagra/PSI thermodynamic data base (HUMMEL et al., 2002), the solubility data for solid $\text{Th}(\text{OH})_4$ was reviewed and hydroxy-carbonato 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 (2002), the situation is far from being clear cut, and there may be large uncertainties associated with the constants given in the TDB.

Speciation calculations using the revised Th-hydroxy-carbonato stability constants indicated that under the MX-80 reference conditions these negatively charged complexes would become very important. The consequence was that " $F_{\text{speciation}}$ " factors (see section 4.2.3 and data sheets) were very small and critically dependent on the stability constant values. This in turn meant that any modifications to sorption values made using these factors may become very large and essentially determine the magnitude of the R_d value tailored to the MX-80 conditions.

In the (few) cases where comparisons were possible, tests carried out using the revised thermodynamic data and the procedures described in section 4.2 have produced anomalies between measured data and the modified sorption values.

In order to illustrate this, consider the measured Th sorption isotherm data for MX-80 (carbonate present) and the Th sorption edge data for purified/conditioned Na-montmorillonite (carbonate free) in Figures 11 and 12 respectively. If an attempt is made to calculate the sorption isotherm values from the sorption edge data at pH ~ 7.5 using the $F_{\text{speciation}}$ factors, 0.04 and unity respectively, the calculated R_d value for the isotherm is a factor of ~25 less than the corresponding R_d value for the edge. The

measured data show however that the factor is around 3. This is a significant difference and indicates that the influence of the presence of negatively charged Th-hydroxy-carbonato complexes is almost an order of magnitude less than predicted on the basis of the updated thermodynamic data and the procedures propose in section 4.2.3.

Possible explanations might be:

- (a) incorrectly measured sorption values. This seems unlikely but is not impossible.
- (b) the assumptions regarding sorption behaviour, and especially that negatively charged hydroxy-carbonato species do not sorb, is flawed. This is of course possible.
- (c) the hydroxy-carbonato complexation constants in the thermodynamic data base are far too strong.

It is clearly evident from all points of view that there is an urgent need to improve the deficit of understanding with respect to actinide sorption processes and the main geochemical factors influencing them.

However, the immediate problem is how to treat tetravalent actinides and produce credible sorption values for them in the SDB for the MX-80 reference conditions. The clear message from the above discussion is that the sorption data modification scheme with respect to the speciation as given in section 4.2.3 is not applicable for Th. Under these circumstances a decision was made to rely on the experimental measurements.

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(IV) as a chemical analogue and the data given in Figure 11. Only one element specific modification is made, and this is based on the fraction of the element present in the tetravalent oxidation state ($F_{lit\ (IV)}$ and $F_{ref\ (IV)}$).

7.4.2.2 Thorium

A sorption isotherm has been measured for Th(IV) on MX-80 in a synthetic bentonite porewater, Table 4. The isotherm is shown in Figure 11 (BRADBURY & BAEYENS, unpublished data.) and the sorption is independent of Th concentration in the range $\sim 5 \times 10^{-12}$ to $\sim 10^{-8}$ M.

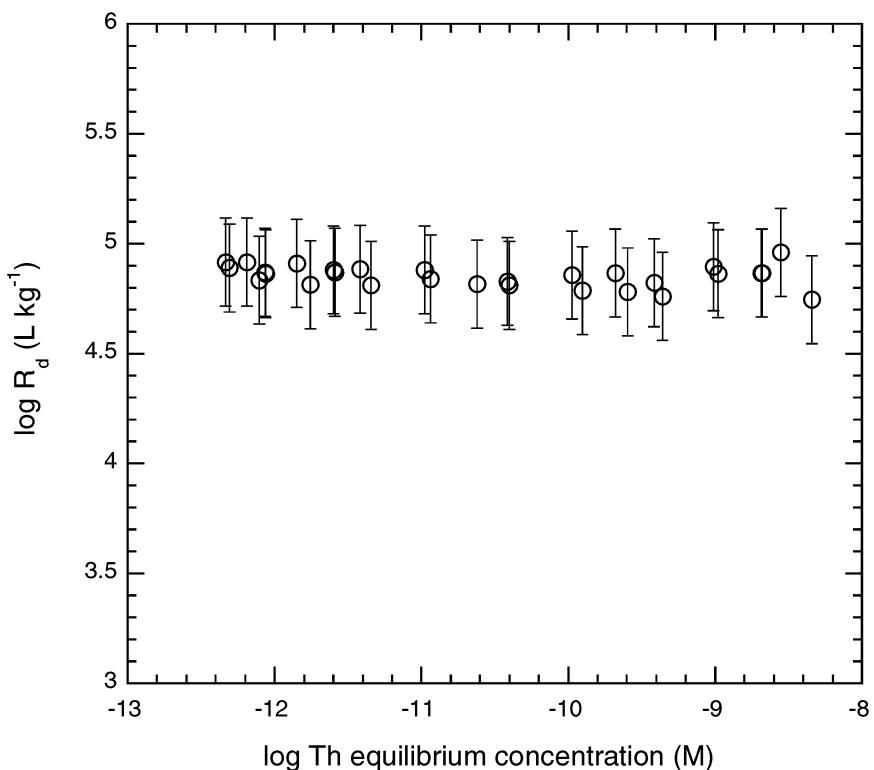


Figure 11: Th sorption isotherm on MX-80 bentonite in SBPW, Table 4. (pH = 7.2 – 7.7, S:L = 0.15 - 1.6 g L⁻¹, equilibration time = 120 days.) (BRADBURY & BAEYENS, unpublished data).

From these data a sorption value of $63 \text{ m}^3 \text{ kg}^{-1}$ was selected. Note that a pH correction factor for Th is not required since the sorption edge data indicate that sorption reaches a plateau at pH values greater than ~ 5 , Figure 12.

The modified procedure given in section 7.4.2.1 for deriving the reference sorption values for Th was applied.

Using similar procedures to those described above, sorption values for Th were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Th are given below.

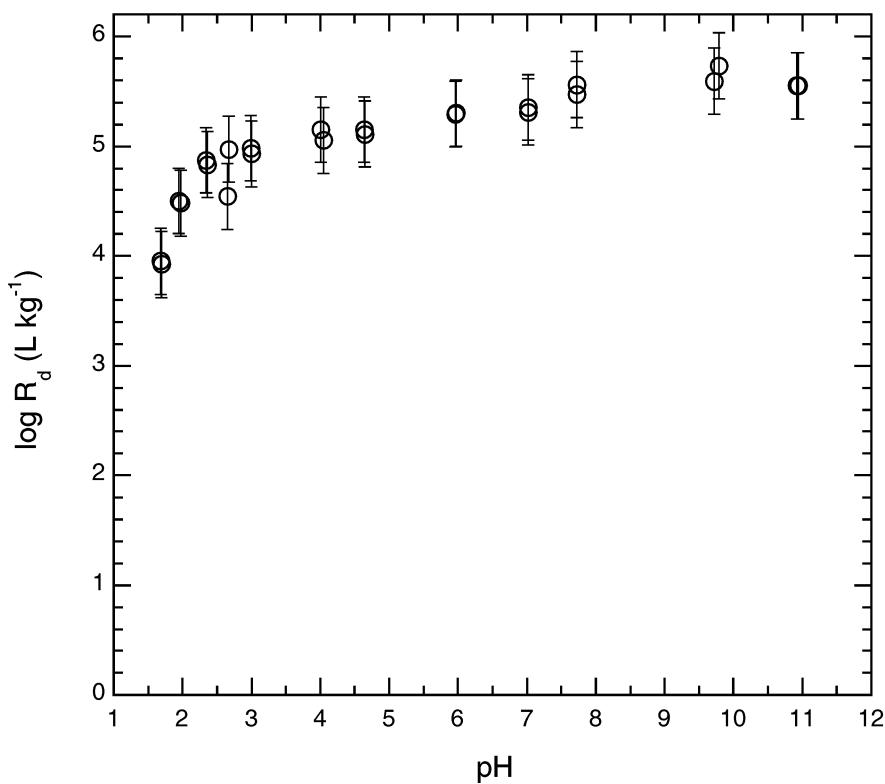


Figure 12: Th sorption edge measured on Na-SWy1montmorillonite. (0.1 M NaClO_4 , S:L ratio = 0.42 g L^{-1} , equilibration time = 7 days, $\text{Th}_{\text{TOT}} < 10^{-9}$ M) (BRADBURY & BAEYENS, unpublished data).

An in situ sorption value for Th of $63 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $63 \text{ m}^3 \text{ kg}^{-1}$ and $63 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen

Th(IV) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: BRADBURY & BAEYENS, Figure 11, unpublished data.

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

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.2 – 7.7	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	1

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
63

Th DATA SHEET FOR MX-80, pH = 6.9

Literature source: BRADBURY & BAEYENS, unpublished data.

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

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.2 – 7.7	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	1

MX-80 pH = 6.9 case: data summary

pH	F _{speciation}	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1

MX-80 pH = 6.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
63

Th DATA SHEET FOR MX-80, pH = 7.9

Literature source: BRADBURY & BAEYENS, unpublished data.

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

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.2 – 7.7	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	1

MX-80 pH = 7.9 case: data summary

pH	F _{speciation}	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
63

7.4.2.3 Protactinium

Under the anticipated in situ redox and pH conditions, Pa 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 the 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 for Th(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 and $>1000 \text{ m}^3 \text{ kg}^{-1}$. Despite the fact that working with Pa is fraught with experimental difficulties, (BAES & MESMER, 1976; BERRY et al., 1988a,b), 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 on argillaceous rocks. 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 is $>1 \text{ m}^3 \text{ kg}^{-1}$. Assuming that the sorption behaviour of Pa is similar on illite, illite-smectite mixed layers and smectite the same value selected for OPA (BRADBURY & BAEYENS, 2003) is taken here. A value of $5 \text{ m}^3 \text{ kg}^{-1}$ is given in the SDB but must be assigned a fairly high uncertainty factor. 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.

At pHs of 6.9 and 7.9, Pa speciation does not change significantly, and thus no pH dependency of the sorption is expected. The same value as for the MX-80 reference system at pH = 7.25 is chosen at the bounding pH values of 6.9 and 7.9.

No data sheets are provided for Pa.

The rational behind the selection of a value for an overall uncertainty factor of 10 is given in section 5.8.

An in situ sorption value for Pa of $5 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 system at all three pH values under consideration.

7.4.2.4 Uranium

Under the anticipated in situ redox and pH conditions, uranium is predicted to exist as U(IV) and U(VI).

Speciation calculations indicate that for the reference case at pH = 7.25 approximately ~78% of the U is in the tetravalent oxidation state. The remaining uranium is predominantly in the hexavalent state.

No relevant data on the sorption of U(IV) on montmorillonite could be found.

Sorption values for U(IV) were derived on the basis of chemical analogy with Th(IV) following the discussion and proposals given in section 7.4.2.1. (Any contribution from U(VI) to the overall sorption was not included.)

Using similar procedures to those described above, sorption values for U(IV) were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for U(IV) are given below

An in situ sorption value for U(IV) of $49.1 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $2.8 \text{ m}^3 \text{ kg}^{-1}$ and $63 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

U(IV) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 7.25

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 U(IV) data, pH = 7.25

F (U) _(IV)
0.78

Conversion

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

MX-80 sorption value, pH = 7.25

R_d (U) ($\text{m}^3 \text{ kg}^{-1}$)
49.1

MX-80 in situ sorption value, pH = 7.25

Lab → Field transfer factor (TF) = 1

R_d (U) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
49.1

U(IV) DATA SHEET FOR THE MX-80, pH = 6.9

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 6.9

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 U(IV) data, pH = 6.9

F (U) _(IV)
0.044

Conversion

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

MX-80 sorption value, pH = 6.9

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

MX-80 in situ sorption value, pH = 6.9

Lab → Field transfer factor (TF) = 1

R_d (U) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
2.8

U(IV) DATA SHEET FOR THE MX-80, pH = 7.9

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 7.9

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 U(IV) data, pH = 7.9

F (U) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 7.9

R_d (U) ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value, pH = 6.9

Lab → Field transfer factor (TF) = 1

R_d (U) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
63

7.4.2.5 Neptunium

Under the anticipated in situ redox and pH conditions, neptunium is predicted to exist almost exclusively in the tetravalent oxidation state.

No sorption values for Np(IV) on montmorillonite could be found in the open literature.

Sorption values for Np(IV) were derived on the basis of chemical analogy with Th(IV) following the discussion and proposals given in section 7.4.2.1.

Using similar procedures to those described above, sorption values for Np(IV) were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Np(IV) are given below

An in situ sorption value for Np(IV) of $63 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 the same in situ sorption values were chosen.

Np(IV) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: 63 m³ kg⁻¹ (Th equilibrium concentration: < 10⁻⁹ M)

MX-80 Th(IV) data, pH = 7.25

R_d (Th) (m ³ kg ⁻¹)	F (Th) _(IV)
63	1

MX-80 Np(IV) data, pH = 7.25

F (Np) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 7.25

R_d (Np) (m ³ kg ⁻¹)
63

MX-80 in situ sorption value, pH = 7.25

Lab → Field transfer factor (TF) = 1

R_d (Np) _{in situ} (m ³ kg ⁻¹)
63

Np(IV) DATA SHEET FOR THE MX-80, pH = 6.9

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 6.9

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 U(IV) data, pH = 6.9

F (Np) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 6.9

R_d (Np) ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value, pH = 6.9

Lab → Field transfer factor (TF) = 1

R_d (Np) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
63

Np(IV) DATA SHEET FOR THE MX-80, pH = 7.9

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 7.9

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 Np(IV) data, pH = 7.9

F (Np) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 7.9

R_d (Np) ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value, pH = 6.9

Lab → Field transfer factor (TF) = 1

R_d (Np) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
63

7.4.2.6 Plutonium

Plutonium exists to over 99% as Pu(III) under the anticipated in situ redox and pH conditions.

No relevant sorption data for Pu(III) could be found in the open literature and Am(III), section 7.4.1.1, is taken as chemical analogue.

Using similar procedures to those described above, sorption values for Pu(III) were deduced for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Pu(III) using Am(III) as a chemical analogue are given below.

An in situ sorption value for Pu of $26.8 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $6.6 \text{ m}^3 \text{ kg}^{-1}$ and $105 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Pu(III) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Selected chemical analogue: Am(III)

Source of chemical analogue sorption data: GORGEON (1994)

MX-80 reference case Am data

R_d (Am) _{ref.} ($m^3 kg^{-1}$)	F (Am) _{ref. speciation}
26.8	0.04

MX-80 reference case Pu(III) data

F (Pu) ref. speciation
0.04

Conversion

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

MX-80 reference sorption value

R_d (Pu) _{ref.} ($m^3 kg^{-1}$)
26.8

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d (Pu) _{in situ} ($m^3 kg^{-1}$)
26.8

Pu(III) DATA SHEET FOR MX-80, pH = 6.9

Selected chemical analogue: Am(III)

Source of chemical analogue sorption data: GORGEON (1994)

MX-80 pH = 6.9 Am data

R_d (Am) _{pH=6.9} ($m^3 kg^{-1}$)	F (Am) _{pH=6.9} speciation
6.6	0.04

MX-80 pH = 6.9 Pu(III) data

F (Pu) _{pH=6.9} speciation
0.04

Conversion

$$R_d (Pu)_{pH=6.9} = R_d (Am)_{pH=6.9} \times [F (Pu)_{pH=6.9} \text{ speciation} / F (Am)_{pH=6.9} \text{ speciation}]$$

MX-80 pH = 6.9 sorption value

R_d (Pu) _{pH=6.9} ($m^3 kg^{-1}$)
6.6

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d (Pu) _{in situ} ($m^3 kg^{-1}$)
6.6

Pu(III) DATA SHEET FOR MX-80, pH = 7.9

Selected chemical analogue: Am(III)

Source of chemical analogue sorption data: GORGEON (1994)

MX-80 pH = 7.9 Am data

R_d (Am) _{pH=7.9} ($m^3 kg^{-1}$)	F (Am) _{pH=7.9} speciation
63	0.03

MX-80 pH = 7.9 Pu(III) data

F (Pu) _{pH=7.9} speciation
0.05

Conversion

$$R_d (Pu)_{pH=7.9} = R_d (Am)_{pH=7.9} \times [F (Pu)_{pH=7.9} \text{ speciation} / F (Am)_{pH=7.9} \text{ speciation}]$$

MX-80 pH = 7.9 sorption value

R_d (Pu) _{pH=7.9} ($m^3 kg^{-1}$)
105

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d (Pu) _{in situ} ($m^3 kg^{-1}$)
105

7.5 Elements: Sn, Zr, Hf, Nb, and Sb

7.5.1 Tin

A sorption edge for Sn(IV) on conditioned SWy-1 Na montmorillonite was measured in 0.1 M NaClO₄ and is shown below, Figure 13 (BRADBURY & BAEYENS, unpublished data). Kinetic studies for up to 60 days indicated that the sorption of Sn was rapid, and certainly complete within one day.

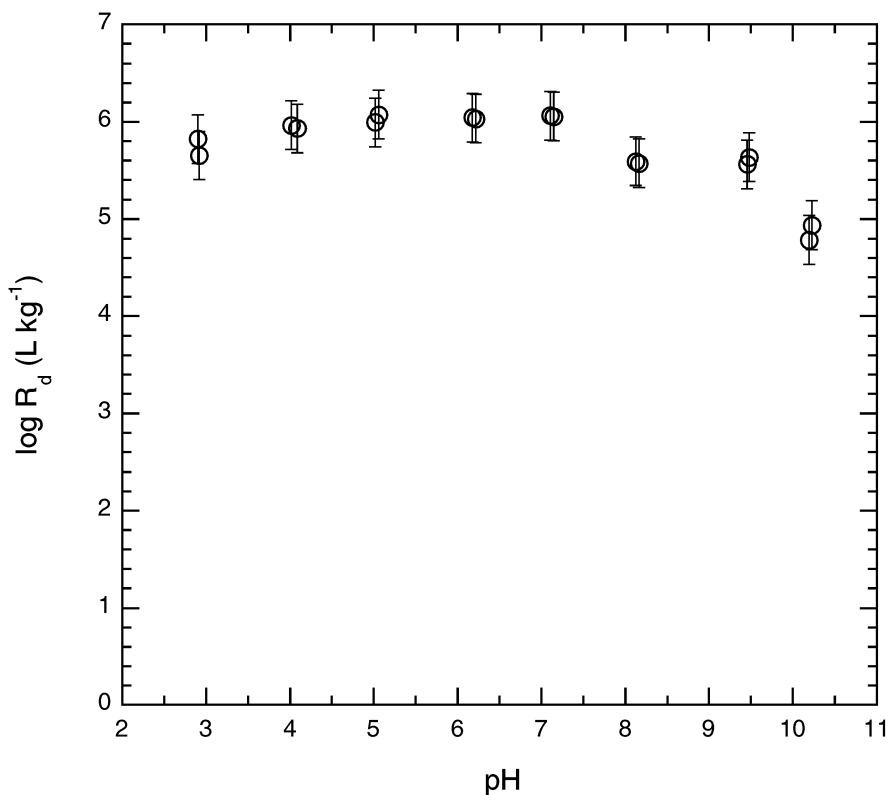


Figure 13: Sn(IV) sorption edge on conditioned SWy-1 Na montmorillonite in 0.1 M NaClO₄. (S:L = 0.54 g L⁻¹, equilibration time 21 days.) BRADBURY & BAEYENS, unpublished data.

According to AMAYA et al. (1997), Sn(IV) is present below a pH of ~ 8 predominantly as the neutral tetrahydroxy complex. Figure 13 shows clearly that the sorption of Sn is high and constant in the pH range ~4 to ~8, where the Sn(OH)₄⁰ species is dominant. Above pH ~ 8 the sorption begins to decrease, presumably due to the influence of the formation of Sn(OH)₅⁻.

At pH = 7.25, an R_d(Sn) of 890 m³ kg⁻¹ is selected from the above figure.

Because the sorption of Sn is constant in the pH range of interest i.e. 6.9 to 7.9, and the speciation is dominated by hydrolysed species, only a correction factor for the mineralogy is applied.

In view of the very high sorption values measured for Sn(IV) a UF-R_d lit of 5 was assigned to the distribution ratio.

The data sheets for Sn at the three pH values are the same and only one is given for the reference case as an example.

An in situ sorption value for Sn of 810 m³ kg⁻¹ was chosen for the MX-80 system at all three pH values under consideration.

Sn DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: BRADBURY & BAEYENS, unpublished data

Selected R_d lit.: $890 \text{ m}^3 \text{ kg}^{-1}$ (Sn equilibrium conc. $< 5 \times 10^{-8} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
SWy-1	0.87

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	ClO_4 (M)	$F_{\text{lit. speciation}}$
7.25	-	-	0.1	1

MX-80 reference case: data summary

pH _{ref.}	$F_{\text{ref. speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	0.91

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
810

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
810

7.5.2 Zirconium and Hafnium

For Zr(IV) and Hf(IV) no reliable and/or relevant sorption data under well defined conditions are available.

Zr and Hf are tetravalent elements and have a similar hydrolysis behaviour to Sn(IV) except that the negatively charged hydroxy species begin to become significant at $\text{pH} \leq 6$. (For the MX-80 reference conditions, hydroxy-carbonato complexes would not be present at any significant levels, CURTI, pers. comm.)

The Sn sorption data in Figure 13 indicate that sorption is reduced when the negatively charged hydroxy species form. The conservative assumption is made here that only the neutral hydroxy species sorb and that Sn is an appropriate chemical analogue for both elements.

Using similar procedures to those described above, sorption values for Zr and Hf deduced for the water chemistries at pH values of 6.9 and 7.9.

Only data sheets for Zr are given since Hf is assumed to have the same speciation and sorption.

An in situ sorption value for Zr and Hf of $81 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $135 \text{ m}^3 \text{ kg}^{-1}$ and $33.1 \text{ m}^3 \text{ kg}^{-1}$ respectively for both elements were chosen.

Zr DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Selected chemical analogue: Sn

Source of chemical analogue sorption data: BRADBURY & BAEYENS, unpublished data.

MX-80 reference case Sn data

R_d (Sn) _{ref.} ($m^3 kg^{-1}$)	F (Sn) _{ref. speciation}
810	0.80

MX-80 reference case Zr data

F (Zr) _{ref. speciation}
0.08

Conversion

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

MX-80 reference sorption value

R_d (Zr) _{ref.} ($m^3 kg^{-1}$)
81

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d (Zr) _{in situ} ($m^3 kg^{-1}$)
81

Zr DATA SHEET FOR MX-80, pH = 6.9

Selected chemical analogue: Sn

Source of chemical analogue sorption data: BRADBURY & BAEYENS, unpublished data.

MX-80 pH = 6.9 Sn data

R_d (Sn) _{pH=6.9} ($m^3 kg^{-1}$)	F (Sn) _{pH=6.9} speciation
810	0.90

MX-80 pH = 6.9 Zr data

F (Zr) _{pH=6.9} speciation
0.15

Conversion

$$R_d (Zr)_{pH=6.9} = R_d (Sn)_{pH=6.9} \times [F (Zr)_{pH=6.9} \text{ speciation} / F (Sn)_{pH=6.9} \text{ speciation}]$$

MX-80 pH = 6.9 sorption value

R_d (Zr) _{pH=6.9} ($m^3 kg^{-1}$)
135

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d (Zr) _{in situ} ($m^3 kg^{-1}$)
135

Zr DATA SHEET FOR MX-80, pH = 7.9

Selected chemical analogue: Sn

Source of chemical analogue sorption data: BRADBURY & BAEYENS, unpublished data.

MX-80 pH = 7.9 Sn data

R_d (Sn) $_{pH=7.9}$ ($m^3 kg^{-1}$)	F (Sn) $_{pH=7.9}$ speciation
810	0.49

MX-80 pH = 7.9 Pu(III) data

F (Zr) $_{pH=7.9}$ speciation
0.02

Conversion

$$R_d (Zr)_{pH=7.9} = R_d (Sn)_{pH=7.9} \times [F (Zr)_{pH=7.9} \text{ speciation} / F (Sn)_{pH=7.9} \text{ speciation}]$$

MX-80 pH = 7.9 sorption value

R_d (Zr) $_{pH=7.9}$ ($m^3 kg^{-1}$)
33.1

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d (Zr) $_{\text{in situ}}$ ($m^3 kg^{-1}$)
33.1

7.5.3 Niobium

No sorption data for Nb on montmorillonite could be found.

LEGOUX et al. (1992) measured Nb sorption values between 1.5 and 2.6 m³ 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. (No significant trend with pH was observed.)

BERRY et al. (1988b) report a single R_d value of > 6 m³ 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 Nb(OH)₅⁰ in the pH/Eh conditions in these experiments.

If the assumption is made that the only sorbents in the sediments are the clay minerals, an estimate for the sorption of Nb as a function of pH in MX-80 can be made over the cation exchange conversion factor, Table 10.

Table 7: Sorption data for Nb(V) in a synthetic groundwater on various sediments. (Nb equilibrium concentration: < 10⁻¹⁰ M). Taken from LEGOUX et al. (1992).

Solid phase	CEC (equiv. kg ⁻¹)	pH	R _d lit (m ³ kg ⁻¹)	R _d in situ (m ³ kg ⁻¹)
Sediment A	0.03	7.6	2.6	68.5
Sediment B	0.043	5.9	1.5	27.6
Sediment C	0.047	6.6	1.7	28.6
Sediment D	0.026	8	2.1	63.8

From pH = 6.6 to 8 the Nb sorption values only vary by a factor of about 2. The sorption of Nb can be considered to be approximately constant over this pH range and a value of 30 m³ kg⁻¹ is selected near the lower end of the calculated values.

In view of the differences in the two systems and the somewhat indirect approach, a UF-R_d lit value of 5 is assigned to the chosen sorption value.

No data sheet is given for Nb(V).

An in situ sorption value for Nb of 30 m³ kg⁻¹ was chosen for the MX-80 reference system for all three pH values under consideration.

7.5.4 Antimony

Antimony exists to over 99% as the neutral hydroxy complex $\text{Sb}(\text{OH})_3^0$ under the anticipated in situ redox and pH conditions.

No data could be found for Sb(III) sorption on montmorillonite.

Bismuth might be considered to be a reasonable chemical analogue for Sb, but only one sorption data set due to ULRICH & DEGUELDRÉ (1992) could be found. This data is re-plotted as a sorption edge in Figure 14. The R_d values are generally high and although the pH range is rather limited, it appears that at $\text{pH} > 7$ the sorption is levelling off. This is what might be expected since Bi is predominantly present as the neutral hydroxy complex.

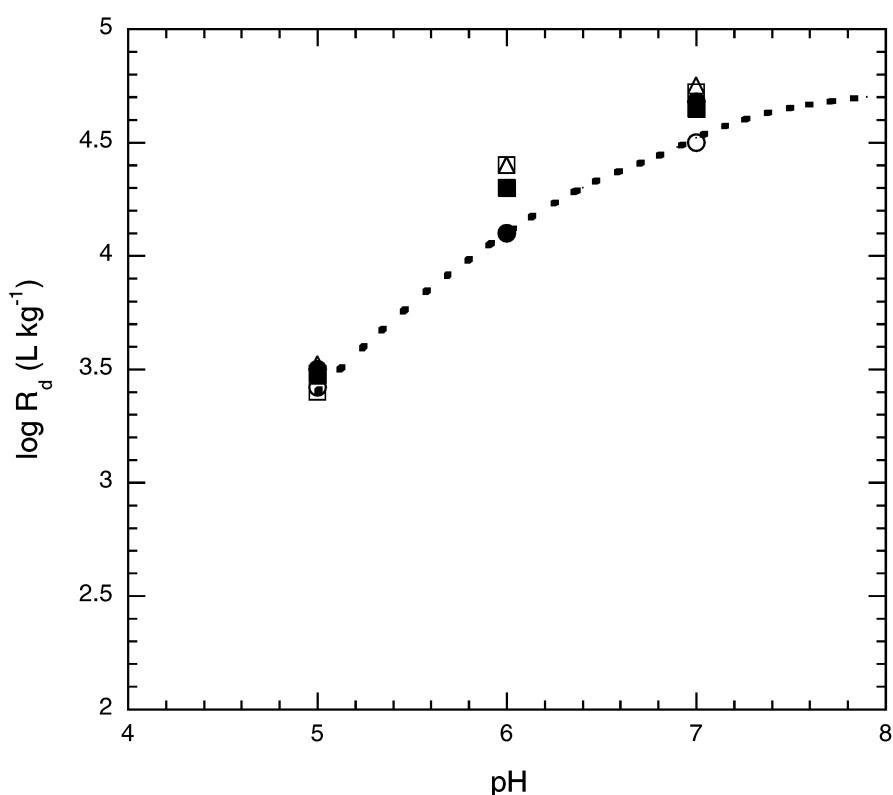


Figure 14: Data from ULRICH & DEGUELDRÉ (1992) re-plotted as a Bi sorption edge. NaClO₄ background electrolyte at: 0.01M (○), 0.02 M (●), 0.05 M (□), 0.1 M (■), 0.2 M (△).

From Figure 14 a lower bound sorption value of $40 \text{ m}^3 \text{ kg}^{-1}$ at $\text{pH} = 7.25$ was chosen for Bi(III).

Similar procedures to those described above were used to deduced sorption values for Sb for the water chemistries at pH values of 6.9 and 7.9.

Data sheets for Bi are given. Since the speciation factors for Bi and Sb are equal to unity in all cases the same sorption values are taken for Sb as chosen for Bi. No data sheets are given for Sb.

An overall uncertainty factor of 5.8 is assigned to Bi, see section 5.8.

Since Bi is used as the chemical analogue for Sb, the overall uncertainty factor for Sb is greater by the speciation uncertainty factor i.e. greater by a factor of 1.4.

An in situ sorption value for Sb of $41.6 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $29.1 \text{ m}^3 \text{ kg}^{-1}$ and $52 \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

Bi(III) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: ULRICH & DEGUELDRÉ (1992)

Selected R_d lit.: $40 \text{ m}^3 \text{ kg}^{-1}$ ($< 10^{-11} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
montmorillonite	0.76

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	F _{lit. speciation}
7.25	3.3×10^{-4}	-	0.1	1

Assumption: solutions are air saturated

MX-80 reference case: data summary

pH _{ref.}	F _{ref. speciation}	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.25	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1.04

MX-80 reference sorption value

R_d ref. ($\text{m}^3 \text{ kg}^{-1}$)
41.6

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
41.6

Bi(III) DATA SHEET FOR MX-80, pH = 6.9

Literature source: ULRICH & DEGUELDRÉ (1992)

Selected R_d lit.: $28 \text{ m}^3 \text{ kg}^{-1}$ ($< 10^{-11} \text{ M}$)

Source data summary

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

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	F _{lit. speciation}
6.9	6.1×10^{-5}	-	0.1	1

Assumption: solutions are air saturated

MX-80 pH = 6.9: data summary

pH	F _{speciation}	CEC _{ref.} (equiv. kg ⁻¹)
6.9	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1.04

MX-80 pH = 6.9 sorption value

R _d (m ³ kg ⁻¹)
29.1

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
29.1

Bi(III) DATA SHEET FOR MX-80, pH = 7.9

Literature source: ULRICH & DEGUELDRÉ (1992)

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

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

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	ClO ₄ (M)	F _{lit. speciation}
7.9	5.2×10^{-4}	-	0.1	1

Assumption: solutions are air saturated

MX-80 pH = 7.9: data summary

pH	F _{speciation}	CEC _{ref.} (equiv. kg ⁻¹)
7.9	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1.04

MX-80 pH = 7.9 sorption value

R _d (m ³ kg ⁻¹)
52

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
52

7.6 Elements: Po, Mo, Tc, Ru

7.6.1 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 for the MX-80 system. Po is in group 6a of the Periodic Table, as is Se, which also forms a similar anionic species, SeO_3^{2-} .

For Se(IV), 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 is in accord with the modelling of Se(IV) uptake on other sorbents. (See for example STUMM et al., 1980; DZOMBAK & MOREL, 1990, DAVIS & KENT, 1990).

DAVIS & KENT (1990) present a Se(IV) sorption edge on ferrihydrite which shows that the uptake 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).

The sorption isotherm for Se(IV) measured at pH = 7.8 (BRADBURY & BAEYENS, unpublished data) is presented in Figure 15. At Se equilibrium concentrations below $\sim 10^{-7}$ M the sorption is constant and exhibit values of $4 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$. The Se(IV) sorption edge given in Figure 16 shows strong similarities to those presented by DAVIS & KENT (1990) and DZOMBAK & MOREL (1990) on HFO. Data sheets for Se(IV) are given. It should be noted that at pH = 7.8 the dominant aqueous Se species are HSeO_3^- and SeO_3^{2-} . (These species are also dominant at 6.9 and 7.25.) 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) exists 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.

No data sheets are given for Po(IV).

An overall uncertainty factor of 8.3 is assigned to Se, see section 5.8.

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.

An in situ sorption value for Po of $6.8 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ was selected for the MX-80 reference system at pH = 7.25. At the bounding pH values of 6.9 and 7.9 sorption values of $1.0 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ and $4.0 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

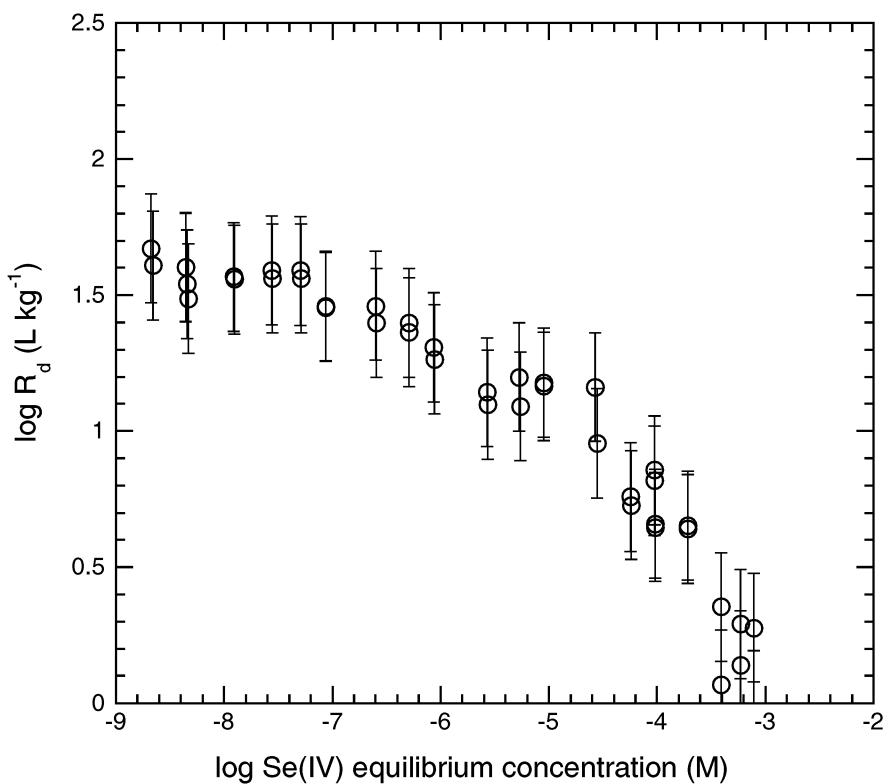


Figure 15 Se(IV) sorption isotherm on MX-80 bentonite in SBPW, Table 4. (pH = 7.8, S:L = 7.5 g L⁻¹, equilibration time ~90 days.) (BRADBURY & BAEYENS, unpublished data).

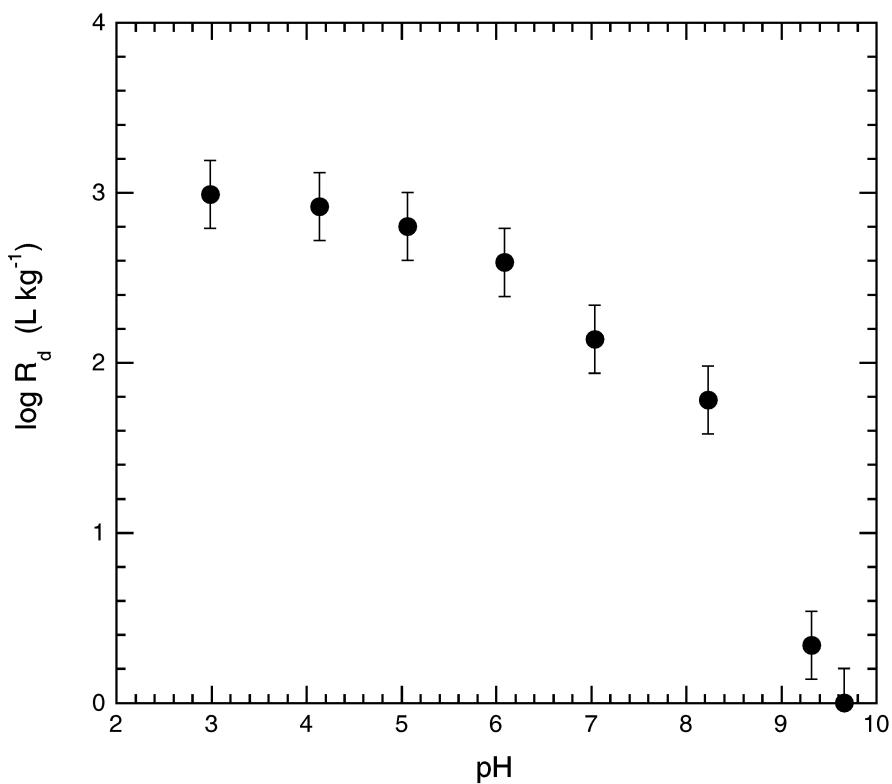


Figure 16: Se(IV) sorption edge measured on Na-Swy-1. (0.1 M NaClO₄; S:L = 1 g L⁻¹; S_{tot} ~ 9.5 x 10⁻⁹ M; equilibration time = 21 days.) (BRADBURY & BAEYENS, unpublished data).

Se(IV) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Literature source: BRADBURY & BAEYENS , unpublished data.

Selected R_d lit.: $4 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$, (Se(IV) equilibrium concentration: $< 10^{-7} \text{ M}$)

Source data summary

Solid	CEC _{lit.} (equiv. kg ⁻¹)
MX-80	0.79

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	Cl (M)	F _{lit. speciation}
7.8	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	1

MX-80 reference case: data summary

pH _{ref.}	F _{ref. speciation}	CEC _{ref.} (equiv. kg ⁻¹)
7.25	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1.7	1	1

MX-80 reference sorption value

R _d ref. (m ³ kg ⁻¹)
6.8×10^{-2}

MX-80 in situ sorption value

Lab→Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
6.8×10^{-2}

Se(IV) DATA SHEET FOR MX-80, pH = 6.9

Literature source: BRADBURY & BAEYENS , unpublished data.

Selected R_d lit.: $4 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$, (Se(IV) equilibrium concentration: $< 10^{-7} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	1

MX-80 pH = 6.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
6.9	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
2.5	1	1

MX-80 pH = 6.9 sorption value

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

MX-80 pH = 6.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

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

Se(IV) DATA SHEET FOR MX-80, pH=7.9

Literature source: BRADBURY & BAEYENS , unpublished data.

Selected R_d lit.: $4 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$, (Se(IV) equilibrium concentration: $< 10^{-7} \text{ M}$)

Source data summary

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
MX-80	0.79

pH _{lit.}	$C_{\text{inorg.}}$ (M)	SO_4 (M)	Cl (M)	$F_{\text{lit. speciation}}$
7.6	3.92×10^{-4}	2.92×10^{-2}	6.19×10^{-1}	1

MX-80 pH = 7.9: data summary

pH	$F_{\text{speciation}}$	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
7.9	1	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	1	1

MX-80 pH = 7.9 sorption value

R_d ($\text{m}^3 \text{ kg}^{-1}$)
4.0×10^{-2}

MX-80 pH = 7.9 in situ sorption value

Lab→Field transfer factor (TF) = 1

R_d in situ ($\text{m}^3 \text{ kg}^{-1}$)
4.0×10^{-2}

7.6.2 Molybdenum

No relevant data could be found for Mo sorption on montmorillonite and as aqueous speciation calculations indicate that Mo exists entirely as the MoO_4^{2-} anion under the MX-80 reference conditions, Mo is treated as being non-sorbing at all three pH values.

The sorption of Mo was taken to be zero for the MX-80 system at pH values of 6.9, 7.25 and 7.9.

7.6.3 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 ruthenium metal with a consequently exceedingly 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 analogues present themselves for Ru. Considering of it's 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 rational behind the selection of a value for an overall uncertainty factor of 15 is given in section 5.8.

An in situ sorption value for Ru of $5 \text{ m}^3 \text{ kg}^{-1}$ is proposed for the MX-80 system at pH values of 6.9, 7.25 and 7.9.

7.6.4 Technetium

Under the Eh/pH conditions corresponding to the MX-80 system, technetium is tetravalent and exists predominantly as the neutral complex TcO(OH)_2^0 ($= \text{Tc(OH)}_4^0$)

No sorption values for Tc(IV) on montmorillonite could be found in the open literature.

Sorption values for Tc were derived on the basis of chemical analogy with Th(IV) following the discussions and proposals given in section 7.4.2.1.

Data sheets for Tc(IV) are provided.

An in situ sorption value for Tc(IV) of $63 \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 system at the three pH values under consideration.

Tc(IV) DATA SHEET FOR THE MX-80 REFERENCE CASE, pH = 7.25

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

Selected R_d lit.: 63 m³ kg⁻¹ (Th equilibrium concentration: < 10⁻⁹ M)

MX-80 Th(IV) data, pH = 7.25

R_d (Th) (m ³ kg ⁻¹)	F (Th) _(IV)
63	1

MX-80 Tc(IV) data, pH = 7.25

F (Tc) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 7.25

R_d (Tc) (m ³ kg ⁻¹)
63

MX-80 in situ sorption value, pH = 7.25

Lab → Field transfer factor (TF) = 1

R_d (Tc) _{in situ} (m ³ kg ⁻¹)
63

Tc(IV) DATA SHEET FOR THE MX-80, pH = 6.9

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 6.9

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 Tc(IV) data, pH = 6.9

F (Tc) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 6.9

R_d (Tc) ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value, pH = 6.9

Lab → Field transfer factor (TF) = 1

R_d (Tc) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
63

Tc(IV) DATA SHEET FOR THE MX-80, pH = 7.9

Selected chemical analogue: Th(IV), BRADBURY & BAEYENS, unpublished data.

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

MX-80 Th(IV) data, pH = 7.9

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 Tc(IV) data, pH = 7.9

F (Tc) _(IV)
1

Conversion

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

MX-80 sorption value, pH = 7.9

R_d (Tc) ($\text{m}^3 \text{ kg}^{-1}$)
63

MX-80 in situ sorption value, pH = 6.9

Lab → Field transfer factor (TF) = 1

R_d (Tc) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
63

7.7 Anions

7.7.1 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 MX-80 would be swamped by the high chloride concentrations in the reference porewater (~0.32 M). For these reasons Cl⁻ is unlikely to sorb at all on MX-80.

The sorption of Cl was taken to be zero

7.7.2 Iodide

LIU & VON GUNten (1988) carried out an extensive review of the sorption behaviour of iodide on geological substrates. Although iodide may exhibit very low sorption under certain circumstances, they nevertheless conclude that the data are so uncertain that it is not justifiable to use even such low values in SDBs for PA.

However, a series of careful “in house” measurements at high solid to liquid ratios (150 and 300 g L⁻¹) on MX-80 at equilibrium concentrations of ~10⁻⁷, 10⁻⁵ and 10⁻³ M yielded a small but definite sorption of ~5 x 10⁻⁴ m³ kg⁻¹ at pH ~ 7.5 (BRADBURY & BAEYENS, unpublished data) and this value is used in the SDB.

In view of the very low sorption values measured for I⁻, a UF-R_d lit uncertainty factor of 5 was assigned to the distribution ratio.

No data sheet is provided for I⁻.

A sorption value of 5 x 10⁻⁴ m³ kg⁻¹ for I⁻ was taken for the MX-80 system at all three pH values considered.

7.7.3 Selenium

Under the Eh/pH conditions prevailing in situ in the MX-80, Se is expected to be present almost entirely as HSe⁻ (>99.9%).

In view of the lack of relevant sorption data, and the dominance of the HSe⁻ species in the MX-80 reference porewater, the sorption of Se is taken to be zero.

The sorption for Se (as HSe⁻) was taken to be zero for the MX-80 system at all three pH values considered.

7.8 ^{14}C Carbon

7.8.1 ^{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., 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.

The sorption of ^{14}C containing organic molecules was taken to be zero for the MX-80 system at all three pH values considered.

7.8.2 ^{14}C in inorganic molecules

The most likely removal mechanism for any ^{14}C existing in solution as $\text{H}^{14}\text{CO}_3^-/\text{H}^{14}\text{CO}_3^{2-}$, 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 difficult question to answer is how much of the calcite present is available to take part in this exchange. BRADBURY & BAEYENS (1997a) gave a very 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 $\text{H}^{14}\text{CO}_3^-/\text{H}^{14}\text{CO}_3^{2-}$, then the total moles of exchangeable CO_3^{2-} in the solid phase is ~ 1.9×10^{-4} moles per kg of MX-80. Thus, the $\text{H}^{14}\text{CO}_3^-/\text{H}^{14}\text{CO}_3^{2-}$ sorption values in the reference MX-80 porewater can be readily obtained using the aqueous concentration given in Table 3, 2.83×10^{-3} M, and the above value. At equilibrium, the R_d value is estimated to be $6.7 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$. This is a small, but significant, sorption. Using similar procedures to those described above, sorption values for $\text{H}^{14}\text{CO}_3^-/\text{H}^{14}\text{CO}_3^{2-}$ were deduced for the water chemistries at pH values of 6.9 and 7.9. Note that the assumptions used to derive the above sorption values are considered to be so conservative that an overall uncertainty value has not been assigned.

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

An in situ sorption value for $\text{H}^{14}\text{CO}_3^-/\text{H}^{14}\text{CO}_3^{2-}$ of $6.7 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$ was chosen for the MX-80 reference system. At the bounding pH values of 6.9 and 7.9 in situ sorption values of $2.7 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$ and $3.2 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ respectively were chosen.

8 SELECTED R_d VALUES CORRESPONDING TO THE IN SITU CONDITIONS IN COMPACTED MX-80 AND ASSOCIATED UNCERTAINTIES: SUMMARY TABLES

The selected in situ distribution ratios for the mineralogy and the reference water chemistry defined in Tables 1 and 3 respectively are summarised in Table 8, together with the sources of the data used. Table 9 summarises the sorption data for the bounding pH values of 6.9 and 7.9.

The uncertainties associated with the selected R_d values defined in Chapter 7 are summarised in Table 10.

Table 11 summarises all of the selected sorption values and the overall uncertainties for each element.

Table 8: In situ R_d values ($\text{m}^3 \text{ kg}^{-1}$) for the MX-80 reference conditions at pH = 7.25.

Radionuclide	R_d	Data source
C(inorg.)	6.7 E-5	Isotopic exchange with calcite
C(org.)	0	
Cl(-I)	0	
Ca(II)	3.3 E-3	BRADBURY & BAEYENS (2002b)
Co(II)	6.4 E-1	GRUETTER et al (1992, 1994)
Ni(II)	2.3 E-1	BRADBURY & BAEYENS (unpublished data)
Se(-II)	0	
Sr(II)	3.3 E-3	GRÜTTER et al (1992, 1994)
Zr(IV)	81	Sn(IV) analogue
Nb(V)	30	LEGOUX et al. (1992)
Mo(VI)	0	
Tc(IV)	63	Th(IV) analogue
Ru(III/IV)	5	Expert judgement
Pd(II)	5	Expert judgement
Ag(I)	0	
Cd(II)	1.0 E-1	ZACHARA & SMITH (1994)
Sn(IV)	810	BRADBURY & BAEYENS (unpublished data)
Sb(III)	41.6	Bi(III) analogue, ULRICH & DEGUELDRÉ (1992)
I(-I)	5.0 E-4	BRADBURY & BAEYENS (unpublished data)
Cs(I)	1.2 E-1	BRADBURY & BAEYENS (unpublished data)
Ce(III)	4.7	Eu(III) analogue
Pm(III)	4.7	Eu(III) analogue
Sm(III)	4.7	Eu(III) analogue
Eu(III)	4.7	BRADBURY & BAEYENS (unpublished data)
Ho(III)	4.7	Eu(III) analogue
Hf(IV)	81	Sn(IV) analogue
Pb(II)	7.9	ULRICH & DEGUELDRÉ (1992)
Po(IV)	6.8 E-2	Se(IV) analogue, BRADBURY & BAEYENS (unpub. data)
Ra(II)	2.1 E-3	Ba(II) analogue, GRÜTTER et al (1992, 1994)
Ac(III)	26.8	Am(III) analogue
Th(IV)	63	BRADBURY & BAEYENS (unpublished data)
Pa(V)	5	Expert judgement
U(IV)	49.1	Th(IV) analogue
Np(IV)	63	Th(IV) analogue
Pu(III)	26.8	Am(III) analogue
Am(III)	26.8	GORGEOON (1994)
Cm(III)	26.8	Am(III) analogue

Table 9: In situ R_d values ($m^3 \text{ kg}^{-1}$) for the MX-80 at pH = 6.9 and 7.9.

Radionuclide	R_d (pH = 6.9)	R_d (pH = 7.9)	Data source
C(inorg.)	2.7 E-5	3.2 E-4	Isotopic exchange with calcite
C(org.)	0	0	
Cl(-I)	0	0	
Ca(II)	3.3 E-3	3.3 E-3	BRADBURY & BAEYENS (2002b)
Co(II)	4.4 E-1	1.8	GRUETTER et al (1992, 1994)
Ni(II)	1.4 E-1	5.8 E-1	BRADBURY & BAEYENS (unpublished data)
Se(-II)	0	0	
Sr(II)	3.3 E-3	3.3 E-3	GRÜTTER et al (1992, 1994)
Zr(IV)	135	33.1	Sn(IV) analogue
Nb(V)	30	30	LEGOUX et al. (1992)
Mo(VI)	0	0	
Tc(IV)	63	63	Th(IV) analogue
Ru(III/IV)	5	5	Expert judgement
Pd(II)	5	5	Expert judgement
Ag(I)	0	0	
Cd(II)	5.5 E-2	2.3 E-1	ZACHARA & SMITH (1994)
Sn(IV)	810	810	BRADBURY & BAEYENS (unpublished data)
Sb(III)	29.1	52	Bi(III) analogue, ULRICH & DEGUELDR (1992)
I(-I)	5.0 E-4	5.0 E-4	BRADBURY & BAEYENS (unpublished data)
Cs(I)	1.2 E-1	1.4 E-1	BRADBURY & BAEYENS (unpublished data)
Ce(III)	1.9	14.2	Eu(III) analogue
Pm(III)	1.9	14.2	Eu(III) analogue
Sm(III)	1.9	14.2	Eu(III) analogue
Eu(III)	1.9	14.2	BRADBURY & BAEYENS (unpublished data)
Ho(III)	1.9	14.2	Eu(III) analogue
Hf(IV)	135	33.1	Sn(IV) analogue
Pb(II)	4.7	62.4	ULRICH & DEGUELDR (1992)
Po(IV)	1.0 E-1	4.0 E-2	Se(IV) analogue, BRADBURY & BAEYENS (unpub. data)
Ra(II)	2.1 E-3	2.1 E-3	Ba(II) analogue, GRÜTTER et al (1992, 1994)
Ac(III)	6.6	63	Am(III) analogue
Th(IV)	63	63	BRADBURY & BAEYENS (unpublished data)
Pa(IV)	5	5	Expert judgement
U(IV)	2.8	63	Th(IV) analogue
Np(IV)	63	63	Th(IV) analogue
Pu(III)	6.6	105	Am(III) analogue
Am(III)	6.6	63	GORGEO (1994)
Cm(III)	6.6	63	Am(III) analogue

Table 10: 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-spec.	UF-CEC	UF-Lab->Field	UF-Overall
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)			25.5
Nb(V)		5		1.4	1.3	2	18.2
Mo(VI)							-
Tc(IV)				(1.4)			6.3
Ru(III/IV)							15
Pd(II)							15
Ag(I)							-
Cd(II)		1.6		1.4	1.3	2	5.8
Sn(IV)		5		1.4	1.3	2	18.2
Sb(III)				(1.4)			8.2
I(-I)		5		1.4		2	14
Cs(I)		1.6		1.4		2	4.5
Ce(III)				(1.4)			16.3
Pm(III)				(1.4)			16.3
Sm(III)				(1.4)			16.3
Eu(III)		1.6	2.6	1.4		2	11.6
Ho(III)				(1.4)			16.3
Hf(IV)				(1.4)			25.5
Pb(II)		1.6		1.4	1.3	2	5.8
Po(IV)				(1.4)			11.6
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

Bi(III): Overall UF = 5.8, Se(IV): Overall UF = 8.3

Table 11: Summary of in situ R_d values ($\text{m}^3 \text{ kg}^{-1}$) for the MX-80 at pH = 6.9, 7.9 and 7.25 with the overall uncertainty factors.

Radionuclide	R_d (pH = 6.9)	R_d (pH = 7.9)	R_d (pH = 7.25)	UF-Overall
C(inorg.)	2.7 E-5	3.2 E-4	6.7 E-5	-
C(org.)	0	0	0	-
Cl(-I)	0	0	0	-
Ca(II)	3.3 E-3	3.3 E-3	3.3 E-3	6
Co(II)	4.4 E-1	1.8	6.4 E-1	15.1
Ni(II)	1.4 E-1	5.8 E-1	2.3 E-1	11.6
Se(-II)	0	0	0	-
Sr(II)	3.3 E-3	3.3 E-3	3.3 E-3	6
Zr(IV)	135	33.1	81	25.5
Nb(V)	30	30	30	18.2
Mo(VI)	0	0	0	-
Tc(IV)	63	63	63	6.3
Ru(III/IV)	5	5	5	15
Pd(II)	5	5	5	15
Ag(I)	0	0	0	-
Cd(II)	5.5 E-2	2.3 E-1	1.0 E-1	5.8
Sn(IV)	810	810	810	18.2
Sb(III)	29.1	52	41.6	8.2
I(-I)	5.0 E-4	5.0 E-4	5.0 E-4	14
Cs(I)	1.2 E-1	1.4 E-1	1.2 E-1	4.5
Ce(III)	1.9	14.2	4.7	16.3
Pm(III)	1.9	14.2	4.7	16.3
Sm(III)	1.9	14.2	4.7	16.3
Eu(III)	1.9	14.2	4.7	11.6
Ho(III)	1.9	14.2	4.7	16.3
Hf(IV)	135	33.1	81	25.5
Pb(II)	4.7	62.4	7.9	5.8
Po(IV)	1.0 E-1	4.0 E-2	6.8 E-2	11.6
Ra(II)	2.1 E-3	2.1 E-3	2.1 E-3	6
Ac(III)	6.6	63	26.8	8.2
Th(IV)	63	63	63	4.5
Pa(IV)	5	5	5	10
U(IV)	2.8	63	49.1	6.3
Np(IV)	63	63	63	6.3
Pu(III)	6.6	105	26.8	8.2
Am(III)	6.6	63	26.8	5.8
Cm(III)	6.6	63	26.8	8.2

9 ACKNOWLEDGEMENTS

We would like to express our gratitude to Drs. D. Pellegrini, D. Stammose and F. Besnus, (Institute for Radioprotection and Nuclear Safety, Fontenay-aux Roses, France) for their constructive and detailed review of the report. Special thanks are due to Dr. E. Curti (PSI) for performing geochemical speciation calculations. Dr. J. Hadermann (PSI) and Drs. I. Hagenlocher and B. Schwyn (Nagra) are thanked for their numerous helpful discussions, and B. Gschwend (PSI) for the final layout of the report. The work was partially financed by Nagra.

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APPENDIX**MX-80 SDB FOR OXIDISING CONDITIONS**

The possibility that oxidising conditions could exist in the near-field of compacted bentonite surrounding spent fuel is a scenario being evaluated by Nagra. In such a case the MX-80 porewater is considered to have the same composition as that in the reference case (pH = 7.25), Table 3, but with a redox potential (Eh) of +635 mV. Solubility/speciation calculations (BERNER, 2002) have identified Tc, Se, U, Np and Pu as the only safety relevant radionuclides which will have redox states under such oxidising conditions different from those in the reference reducing case (Eh = -193 mV).

The radionuclide speciation used to calculate speciation conversion factors in the data sheets can be found in CURTI (2002).

In the following, sorption values for Tc(VII), Se(VI), U(VI), Np(V) and PU(IV/V) are given for MX-80 bentonite.

A1 Se(VI)

Under the Eh/pH conditions corresponding to the oxidising MX-80 bentonite system, selenium exists as the hexavalent selenate anion. No sorption data of SeO_4^{2-} on montmorillonite could be found in the open literature. The sorption of SeO_3^{2-} on Na-montmorillonite has been studied, see section 7.5.2.1.

The uptake of Se(IV) and Se(VI) has been investigated on hydrous ferric oxide (DZOMBAK & MOREL, 1990) and the pH dependent sorption behaviour indicates that a ligand exchange mechanism is taking place (see also DAVIS & KENT, 1990). The data show that Se(IV) sorbs more strongly than Se(VI). In the modelling studies by DZOMBAK & MOREL (1990) the intrinsic surface complexation constants of Se(VI) sorption on the amphoteric surface sites are 4 to 5 orders of magnitude weaker than those for Se(IV). Since the sorption of Se(IV) on montmorillonite at pH = 7.25 is already weak (see Figure 16), it is anticipated that Se(VI) will not be taken up by montmorillonite clay at this pH, and Se(VI) is treated here as being non sorbing.

No data sheet is provided for Se(VI).

An in situ sorption value for Se(VI) of zero was selected for the oxidising MX-80 bentonite system.

A2 Tc(VII)

Under the Eh/pH conditions corresponding to the oxidising MX-80 bentonite system, technetium exists as the pertechnetate anion.

The sorption of TcO_4^- is very weak on virtually all geological substrates, $< 10^{-3} \text{ m}^3 \text{ kg}^{-1}$. (See for example WINKLER et al., 1988; LEGOUX et al., 1992; LIESER & BAUSCHER, 1987.) Sorption measurements on bentonites and montmorillonites (e.g. SERNE et al., 1977; SATO et al., 1993) confirm the very poor sorption characteristics of the pertechnetate anion and a value of zero is selected in most SDBs (e.g. BRANDBERG & SKAGIUS, 1991).

The sorption of TcO_4^- is certainly very low and is treated here as being non-sorbing.

No data sheet is provided for technetium.

An in situ sorption value for Tc(VII) of zero was selected for the oxidising MX-80 bentonite system.

A3 Pu(IV/V)

Under the Eh/pH conditions corresponding to the oxidising MX-80 bentonite system, plutonium is predicted to exist as Pu(IV), ~27%, and Pu(V), ~71%. The remaining ~2 % is calculated to be in the hexavalent oxidation state.

No relevant data on the sorption of Pu(IV) on montmorillonite could be found.

Sorption values for Pu(IV) were derived on the basis of chemical analogy with Th(IV) following the discussion and proposals given in section 7.4.2.1. (Only tetravalent Pu is assumed to sorb.)

A data sheet is given for Pu(IV).

An in situ sorption value for Pu(IV) of $16.8 \text{ m}^3 \text{ kg}^{-1}$ was selected for the oxidising MX-80 bentonite system.

Pu(IV) DATA SHEET FOR MX-80, pH=7.25, OXIDISING CONDITIONS

Selected analogue: Th(IV) Figure 11, BRADBURY & BAEYENS, unpublished data.

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

Th source data summary, pH = 7.25

R_d (Th) ($\text{m}^3 \text{ kg}^{-1}$)	F (Th) _(IV)
63	1

MX-80 Pu(IV) data summary, pH = 7.25

F (Pu) _(IV)
0.266

Conversion

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

MX-80 sorption value, oxidising conditions

R_d (Pu) ($\text{m}^3 \text{ kg}^{-1}$)
16.8

MX-80 in situ sorption value, oxidising conditions

Lab → Field transfer factor (TF) = 1

R_d (Pu) _{in situ} ($\text{m}^3 \text{ kg}^{-1}$)
16.8

A4 U(VI)

Under the Eh/pH conditions corresponding to the oxidising MX-80 bentonite system, uranium exists as the hexavalent uranyl ion.

PABLAN & TURNER (1997) investigated the sorption of U(VI) on a purified homo-ionic Na-montmorillonite (SAz-1) in 0.1 M NaNO₃ as function of pH from 2 to 11 under atmospheric conditions, P_{CO₂} = 10^{-3.5} bar. The equilibrium U(VI) concentrations were low (~7.5 × 10⁻⁹ M at pH = 7.25). The sorption data are reproduced here in Figure A1.

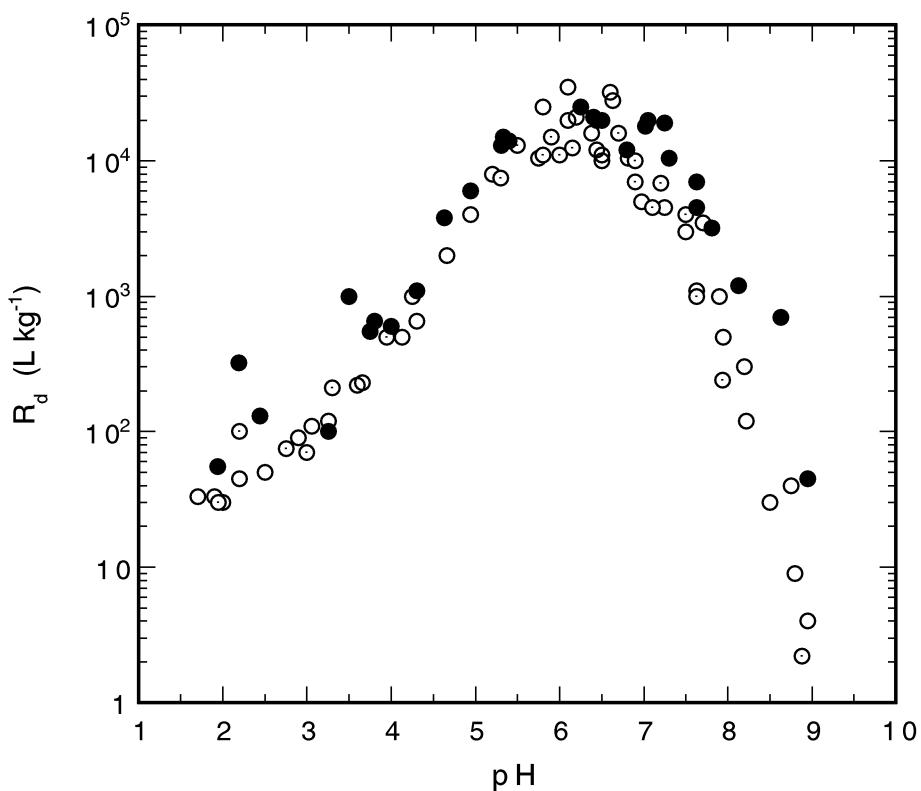


Figure A1: Sorption of U(VI) at trace concentrations on Na-montmorillonite (SAz-1) in 0.1 M NaNO₃ as a function of pH under atmospheric conditions, P_{CO₂} = 10^{-3.5} bar. (○) S:L ratio ~3.2 g L⁻¹; (◎) S:L ratio ~0.27 g L⁻¹ and (●) S:L ratio ~0.028 g L⁻¹.

A sorption value for U(VI) of 5 m³ kg⁻¹ at pH = 7.25 was chosen from this data.

A data sheet for U(VI) is given.

An in situ sorption value for U(VI) of 10⁻² m³ kg⁻¹ was selected for the oxidising MX-80 bentonite system.

U(VI) DATA SHEET FOR MX-80, pH = 7.25, OXIDISING CONDITIONS

Literature source: PABLAN & TURNER (1997).

Selected R_d lit.: $5 \text{ m}^3 \text{ kg}^{-1}$, (U(VI) equilibrium concentration : $\sim 7.5 \times 10^{-9} \text{ M}$)

Source data summary

Solid	#CEC _{lit.} (equiv. kg ⁻¹)
Saz-1 Montmorillonite	1.2

#VAN OLPHEN & FRIPIAT (1979)

pH _{lit}	C _{inorg.} (M)	SO ₄ (M)	NaNO ₃ (M)	F _{lit. speciation}
7.25	1.2×10^{-4}	-	0.1	0.068

MX-80 reference case: data summary

pH _{ref.}	F _{ref. speciation}	CEC _{ref.} (equiv. kg ⁻¹)
7.25	2.2×10^{-4}	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	3.2×10^{-3}	0.66

MX-80 sorption value, oxidising conditions

R _d ref. (m ³ kg ⁻¹)
10^{-2}

MX-80 in situ sorption value, oxidising conditions

Lab → Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
10^{-2}

A5 Np(V)

Under the Eh/pH conditions corresponding to the oxidising MX-80 bentonite system, neptunium exists as the pentavalent neptunium ion.

TURNER et al. (1998) investigated the sorption of Np(V) on a purified homo-ionic Na-montmorillonite (SAz-1) in 0.1 M NaNO₃ as function of pH from 5 to 11 in the absence of CO₂. The equilibrium Np concentrations were low (~ 7.5 × 10⁻⁷ M at pH = 7.25). The sorption data are reproduced here in Figure A2.

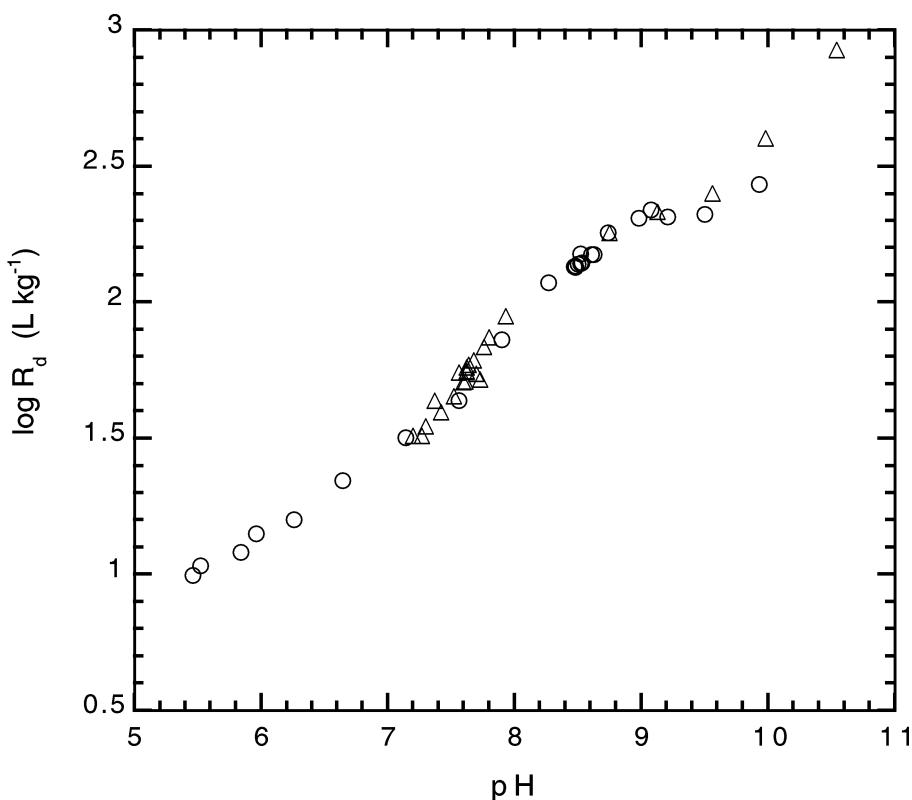


Figure A2: Sorption of Np(V) at trace concentrations on Na-montmorillonite (SAz-1) in 0.1 M NaNO₃ as a function of pH in the absence of CO₂.

From Figure A2 an R_d of 3.2 × 10⁻² m³ kg⁻¹ was selected at pH = 7.25.

A data sheet for Np(V) is given.

An in situ sorption value for Np(V) of 1.8 × 10⁻² m³ kg⁻¹ was selected for the oxidising MX-80 bentonite system.

Np(V) DATA SHEET FOR MX-80, pH = 7.25, OXIDISING CONDITIONS

Literature source: TURNER et al. (1998)

Selected R_d lit.: $3.2 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ (Np(V) equilibrium concentration: $\sim 7.5 \times 10^{-7} \text{ M}$)

Source data summary

Solid	#CEC _{lit.} (equiv. kg ⁻¹)
Montmorillonite (Na-SAz-1)	1.2

#VAN OLPHEN & FRIPIAT (1979)

pH _{lit.}	C _{inorg.} (M)	SO ₄ (M)	NaNO ₃ (M)	F _{lit. speciation}
7.25	-	-	0.1	1

MX-80 data summary, pH = 7.25

pH	F _{speciation}	CEC _{ref.} (equiv. kg ⁻¹)
7.25	0.86	0.79

Conversion factors

CF-pH	CF-speciation	CF-CEC
1	0.86	0.66

MX-80 sorption value, oxidising conditions

R _d (m ³ kg ⁻¹)
1.8×10^{-2}

MX-80 in situ sorption value, oxidising conditions

Lab → Field transfer factor (TF) = 1

R _d in situ (m ³ kg ⁻¹)
1.8×10^{-2}

A6 Summary of sorption values and uncertainties

Selected sorption values for those safety relevant radionuclides identified as having different redox states from the reference case under oxidising conditions, namely Se(VI) Tc(VII) U(VI) Np(V) Pu(IV/V), are given in Table A1.

The estimated uncertainties for these sorption values are presented in Table A2.

Table A1: In situ R_d values ($\text{m}^3 \text{ kg}^{-1}$) for MX-80 under oxidising conditions.
($\text{pH} = 7.25$, $\text{Eh} = +635 \text{ mV}$).

Element	R_d	Data source
Se(VI)	0	Expert judgement
Tc(VII)	0	Expert judgement
U(VI)	1.0 E-2	PABLAN & TURNER (1997)
Np(V)	1.8 E-2	TURNER et al. (1998)
Pu(IV/V)	16.8	Th(IV) analogue; BRADBURY & BAEYENS (unpublished data)

Table A2: Estimated uncertainties in the selected in situ sorption values.
($\text{pH} = 7.25$, $\text{Eh} = +635 \text{ mV}$).

Element	Lab R_d UF	Mineralogy UF	pH UF	Speciation UF	Lab → Field UF	Total UF
Se(IV)	-	-	-	-	-	-
Tc(VII)	-	-	-	-	-	-
U(VI)	1.6	1.3		1.4	2	5.8
Np(V)	1.6	1.3		1.4	2	5.8
Pu(IV/V)				(1.4)		6.3

A7 References

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ADDENDUM

Sorption values (K_d), effective diffusion coefficients (D_e) and accessible porosities (ε) for bentonite used in safety assessment calculations within the Project Opalinus Clay (Entsorgungsnachweis)

B. Schwyn (Nagra)

Table AD-1 of this addendum presents the parameters used to calculate radionuclide transport in the bentonite near-field of a high-level waste / spent fuel (HLW/SF) repository within the safety assessment of the Project Opalinus Clay. Table AD-1 corresponds to Table A2.6 in Nagra (2002a). This addendum explains the origin of the data and their documentation.

In a diffusive dominated system like compacted bentonite the spreading of radionuclides is 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:

$$D_a = \frac{D_e}{\varepsilon + K_d \rho_d} \quad (\text{AD-1})$$

D_e : effective diffusion coefficient [m² s⁻¹]

ρ_d : dry density of bentonite [kg m⁻³]

K_d : distribution coefficient [m³ kg⁻¹]

ε : accessible porosity [-]

As discussed in Nagra (2002a) the latter approach is used in the 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 bentonite and in Bradbury & Baeyens (2003) for Opalinus Clay, respectively.
- Although the direct measurement of D_a values may be straightforward, obtaining good data for strongly sorbing elements on a laboratory time scale is difficult.
- 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.

It cannot be taken for granted that complete consistency will be observed between apparent diffusivities derived from batch K_d values and those directly determined in diffusion experiments, because of differences in porewater chemistry between highly compacted bentonite and more dilute systems. For Cs(I), Ni(II), Sm(III), Am(III), Zr(IV), and Np(V), however, Bradbury & Baeyens (2002) found a good agreement of K_d values obtained from diffusion experiments in compacted Kunigel V1 bentonite with the ones obtained from batch sorption experiments on montmorillonite and benonite (see also chapter 6 of this report).

A comparison with a broader spectrum of elements and diffusion experiments reveals reasonable agreement between the K_d values derived using the two different approaches, considering the rather scattered data from diffusion experiments. For some elements, however, K_d values listed in Table 11 of this report are either lower or higher than the ones derived from diffusion experiments in compacted bentonite. In particular, Table 11 presents higher K_d values for Tc and U under reducing conditions than values derived from diffusion experiments.

For technetium Kuroda, et al. (1997) report apparent diffusivities between 1×10^{-13} and $5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ measured in Kunigel V1 at a dry density between 1620 and 1830 kg m⁻³ in contact with a corroded carbon steel plate; they assign the values to Tc(IV). In Table AD-1 a pessimistic K_d of 0.5 m³ kg⁻¹ is proposed which is in accordance with the findings by Kuroda, et al. (1997). However, their values may represent an unwanted mixture of oxidation states. Corresponding evidence comes from a diffusion experiment by Albinsson et al. (1991) on MX-80 at a dry density of 1600 kg m⁻³. In the presence of Fe(0) they measured an apparent diffusivity of $1 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$.

Similar considerations apply to U but the lower limit value of 2 m³ kg⁻¹ derived by the regular procedure, described below, covers the resulting uncertainty.

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.

Cations, typically sorbing by an ion exchange mechanism, appear to diffuse faster through compacted bentonite than their K_d values, measured in dilute systems, would predict (Eq. AD-1). Interpretation of this phenomenon by "surface diffusion" (see Yu & Neretnieks 1997, Ochs et al. 1998) is, however, not uniformly supported by experimental evidence, some of which suggests the effect is negligible when the

porewater composition is carefully adapted to the in-situ conditions of compacted bentonite (Bradbury & Baeyens 2002).

The following parameters were used for safety assessment calculations:

Non-anionic species:

The effective diffusion coefficient $D_e = 2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ was taken from the Kristallin-I safety assessment study (Nagra 1994). This is double the value proposed by Yu & Neretnieks (1997) for species not affected by ion exclusion or surface diffusion effects. It therefore includes a potential effect of the elevated in-situ temperature which is thought to be 50°C, maximum.

The full porosity of 0.36 is assumed to be accessible for non-anionic species. The full porosity is determined by the compaction degree of the bentonite after a tunnel convergence process which is assumed to lead to a balance between the external stress field and swelling pressure of the resaturated bentonite (Nagra 2002a). An ε of 0.36 together with a bentonite solid density of 2760 kg m⁻³ results in a dry density of $\rho_d = 1760 \text{ kg m}^{-3}$. The latter value is used in the above equation (AD-1) for non-anionic and anionic species.

Anionic species:

The effective diffusion coefficient D_e and the accessible porosity ε were taken from Yu & Neretnieks (1997). To be on the conservative side, the value for iodine ($D_e = 3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$) was selected, although a three times lower value is reported for chloride. An ε of 0.05 is used as porosity accessible to anions.

For both groups of species the sorption values K_d were mainly taken from Table 11 in the main part of this report (reducing conditions) and from Table A1 in the Appendix (oxidising conditions). 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 the ones used in other recent safety assessments. 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 and in Appendix A of this report the symbol R_d is used for the distribution ratio between bentonite 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 slightly differs 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 (2002b) 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 (Co, Ru, Cd, Sb, Ce, Pm, Eu and Hf) were dropped in Table AD-1, hydrogen (HTO) and beryllium were added.

A K_d of zero was assumed for hydrogen, 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 = 7.25 and Eh = -194 mV were taken from Table 11.
- The lower limit (pessimistic) K_d value for an element was derived from Table 11 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 (6.9) porewater conditions, the best estimate for high pH (7.9) 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 (6.9) pore water conditions, the best estimate for high pH (7.9) pore water 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 11 (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 according to the comments made above on the comparison of batch sorption measurements with diffusion experiments.

- The extraordinary high K_d value of $800 \text{ m}^3 \text{ kg}^{-1}$ for Sn in Table AD-1 is based on batch sorption measurements by Bradbury & Baeyens (unpublished data, see section 7.5.1 in the main part of this report). This value is much higher than those used in other safety assessment studies. No data are available from diffusion experiments. To account for this extra uncertainty the lower limit K_d value in Table AD-1 was overwritten with $1 \text{ m}^3 \text{ kg}^{-1}$.
- Since iodine is an important safety relevant element a "What if?"¹ 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 7.7.2 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.
- After geochemical data were frozen for safety assessment calculations in July 2002 the assumed oxidation state of selenium for oxidising conditions was changed from IV to VI. Indeed, model calculations by Berner (2002) reveal that Se(VI) becomes dominant above a redox potential of +400 mV. The K_d value of $0.06 \text{ m}^3 \text{ kg}^{-1}$ in Table AD-1 may therefore be too optimistic for the "what if?" case of oxidising conditions since the corresponding redox potential is assumed to be 635 mV. Table A1 of this report proposes a K_d value of $0 \text{ m}^3 \text{ kg}^{-1}$.
- Values were truncated (reference case and lower limit) or rounded (upper limit) to one significant figure.

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¹Defined in Appendix 5 of Nagra (2002a)

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Table AD-1: Sorption values (K_d), effective diffusion coefficients (D_e) and accessible porosities (ε) in compacted bentonite: Reference Case (pH = 7.25, Eh = -194 mV) incl. lower (pessimistic) and upper (optimistic) limits, and "what if?" case for oxidising conditions.

This table corresponds to Table A2.6 of Nagra (2002a).

Element	Reducing conditions					Oxidising conditions ²			Remarks
	K_d		D_e	ε	K_d	D_e	ε		
	Ref. case [m ³ kg ⁻¹]	Lower limit (pessimistic) [m ³ kg ⁻¹]	Upper limit (optimistic) [m ³ kg ⁻¹]	[m ² s ⁻¹]	[-]	[m ³ kg ⁻¹]	[m ² s ⁻¹]	[-]	
H	0	0	0	2×10 ⁻¹⁰	0.36				
Be	0.2	0.009	5	2×10 ⁻¹⁰	0.36				
C _{inorg}	6×10 ⁻⁵	2×10 ⁻⁵	3×10 ⁻⁴	3×10 ⁻¹²	0.05				Anion
C _{org}	0	0	0	2×10 ⁻¹⁰	0.36				
Cl	0	0	0	3×10 ⁻¹²	0.05				Anion
Ca	0.003	5×10 ⁻⁴	0.02	2×10 ⁻¹⁰	0.36				
Ni	0.2	0.009	5	2×10 ⁻¹⁰	0.36				
Se	0	0	0	3×10 ⁻¹²	0.05	0.06			Anion
Sr	0.003	5×10 ⁻⁴	0.02	2×10 ⁻¹⁰	0.36				
Zr	80	1	4000	2×10 ⁻¹⁰	0.36				
Nb	30	1	900	2×10 ⁻¹⁰	0.36				
Mo	0	0	0	3×10 ⁻¹²	0.05				Anion
Tc	60	0.5	600	2×10 ⁻¹⁰	0.36	0	3×10 ⁻¹²	0.05	ox: Anion
Pd	5	0.2	100	2×10 ⁻¹⁰	0.36				
Ag	0	0	0	2×10 ⁻¹⁰	0.36				
Sn	800	1	10000	2×10 ⁻¹⁰	0.36				
I ³	5×10 ⁻⁴	5×10 ⁻⁵	0.005	3×10 ⁻¹²	0.05				Anion
Cs	0.1	0.03	0.3	2×10 ⁻¹⁰	0.36				
Sm	4	0.1	100	2×10 ⁻¹⁰	0.36				
Ho	4	0.1	100	2×10 ⁻¹⁰	0.36				
Pb	7	0.5	100	2×10 ⁻¹⁰	0.36				
Po	0.06	0.008	0.5	3×10 ⁻¹²	0.05				Anion
Ra	0.002	3×10 ⁻⁴	0.01	2×10 ⁻¹⁰	0.36				
Ac	20	1	300	2×10 ⁻¹⁰	0.36				
Th	60	10	200	2×10 ⁻¹⁰	0.36				
Pa	5	0.2	100	2×10 ⁻¹⁰	0.36				
U	40	2	400	2×10 ⁻¹⁰	0.36	0.01			
Np	60	6	600	2×10 ⁻¹⁰	0.36	0.01			
Pu	20	1	300	2×10 ⁻¹⁰	0.36	10			
Am	20	1	300	2×10 ⁻¹⁰	0.36				
Cm	20	1	300	2×10 ⁻¹⁰	0.36				

² Only given when different from reducing conditions.

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 11) 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				
Ni	25	11.6	0.009	0.01	5	2
Se						
Sr	6	6				
Zr	45	25.5	1	3	4000	2000
Nb	30	18.2			900	500
Mo						
Tc	9.6	6.3			600	400
Pd	20	15	0.2	0.3	100	80
Ag						
Sn	15	18.2				
I	10	14	5×10^{-5}	3×10^{-5}	0.005	0.007
Cs	3.2	4.5	0.03	0.02	0.3	0.5
Sm	25	16.3	0.1	0.2	100	70
Ho	25	16.3	0.1	0.2	100	70
Pb	14.4	5.8	0.5	1	100	60
Po	8.3	11.6	0.008	0.005	0.5	0.7
Ra	6	6				
Ac	14.4	8.2	1	3	300	200
Th	3.2	4.5			200	300
Pa	20	10	0.2	0.5	100	50
U	9.6	6.3			400	300
Np	9.6	6.3	6	10	600	400
Pu	14.4	8.2	1	3	300	200
Am	14.4	5.8	1	4	300	100
Cm	14.4	8.2	1	3	300	200

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