

TECHNICAL REPORT 03-12

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Sorption Data Bases for Opalinus Clay Influenced by a High pH Plume

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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.

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Abstract

The interaction of groundwater with the large quantities of cement/concrete used in the construction and backfilling of emplacement tunnels containing long-lived intermediate level radioactive waste may give rise to the release of a pulse of hyperalkaline fluid (pH plume) into the surrounding rock. Since the pH of this plume could remain in excess of 12.5 for tens of thousands of years, many minerals in a sedimentary host rock would be unstable leading to dissolution reactions, secondary mineral precipitation and changes in groundwater chemistry.

An Opalinus clay formation in the Zürcher Weinland, is under consideration by Nagra as a potential host rock for a repository of spent fuel (SF), vitrified high-level waste (HLW) from reprocessing of spent fuel and long-lived intermediate-level radioactive waste (ILW). The purpose of this report is to assess the effects of the interactions between a pH plume and Opalinus clay on the sorption properties of the formation and to provide appropriate sorption data bases.

Zusammenfassung

Die Wechselwirkung zwischen Grundwasser und Zement, der sowohl zum Bau als auch zur Verfüllung der Tunnels eingesetzt wird, die zur Aufnahme langlebiger, mittelaktiver Abfälle vorgesehen sind, kann zu einer Hoch-pH-Fahne im umgebenden Wirtgestein führen. Dieser hohe pH Wert (grösser als 12.5), der über mehrere Zehntausend Jahre vorherrschen kann, wird zur Auflösung von Mineralien des Sedimentgesteins, zur Ausfällung von Sekundärmineralien und zu einer geänderten Grundwasserchemie führen.

Eine Opalinustonformation im Zürcher Weinland ist von der Nagra als potentielles Wirtgestein für ein geologisches Tiefenlager für abgebrannte Brennelemente (BE), hochaktive verglaste Abfällen aus der Wiederaufarbeitung (HAA) und langlebige mittelaktive Abfälle (LMA) vorgesehen. Im vorliegenden Bericht wird die Auswirkung der Hoch-pH-Fahne auf die Sorptionseigenschaften des Opalinustons bewertet und entsprechende Sorptionsdatenbasen bereitgestellt.

Résumé

L'interaction des eaux souterraines avec de grandes quantités de béton/ciment, utilisées pour la construction et le remplissage des cavernes contenant des déchets de moyenne radioactivité à longue vie, pourrait causer le relâchement d'un fluide hyperalcalin dans la roche d'accueil. Puisque le pH de ce fluide pourrait rester supérieur à 12.5 pendant des dizaines de milliers d'années, la plupart des minéraux présents dans la roche d'accueil sédimentaire seraient instables. Ceci entraînerait la dissolution d'une partie des minéraux primaires, la précipitation de minéraux secondaires et, par conséquent, des modifications de la chimie des eaux souterraines.

La formation d'Argile à Opalinus dans le Weinland Zurichois est considérée par la Nagra comme roche d'accueil potentielle pour un dépôt souterrain en profondeur destiné aux assemblages combustibles usés (AC), aux déchets de haute activité vitrifiés (DHA) issus du retraitement, ainsi qu'aux déchets de moyenne activité à vie longue (DMAL). L'objectif de ce rapport est d'évaluer les conséquences de l'interaction du fluide hyperalcalin et de l'Argile à Opalinus sur les propriétés de sorption ainsi que de délivrer une base de données de sorption appropriée.

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1 Introduction

The main option currently under consideration by Nagra for the disposal of long-lived intermediate level radioactive waste (ILW) is to place such waste in caverns at depth (-650 m) in an Opalinus clay (OPA) formation (NAGRA, 2002). Large quantities of cements and concretes will be used in the conditioning of the waste, waste packaging and construction. After the caverns re-saturate, interactions between the deep groundwater/porewater and the cement/concrete present in the repository will take place. The cementitious materials are unstable under the local conditions and will gradually degrade. The leaching of the hydrated cement could give rise to a pulse of hyperalkaline fluid moving out into the host rock, a so called pH plume, which could last for many thousands of years. Under the high pH conditions predicted (BERNER, 1992; NEALL, 1994; LAGERBLAD & TRÄGARDH, 1994), sheet silicate and quartz minerals in the OPA will be unstable. (See for example SAVAGE et al., 1990, 1991.) While certain minerals would dissolve, others would tend to form further out in the OPA rock where conditions favour the precipitation of secondary minerals. Further, the groundwater/porewater chemistry would be significantly changed, and also possibly the hydrogeological characteristics around the repository. All of these processes would be varying in time and space along migration pathways.

New mineral phases likely to form are notably calcium silicate hydrates (CSH), calcium aluminium silicate hydrates (CASH) including tobermorite, jennite and hydrogarnet; chlorite, brucite ($\text{Mg}(\text{OH})_2$) and zeolites such as mordenite (CRAWFORD & SAVAGE, 1994; BATEMAN et al., 1995; ALEXANDER & MAZUREK, 1996; MILODOWSKI et al., 1998). It is worth noting that many of these secondary minerals are similar to those found in hydrated cements and consequently the sorption properties of the altered OPA could, to a first approximation, be related to those in hardened cement paste (HCP).

In a recent study ADLER et al. (1999) investigated the effect of high-pH solutions on the mineralogy of whole rock OPA under conditions relevant for the disposal of waste in a cementitious repository. The results of these batch investigations showed that the mineralogy of OPA is significantly changed through interaction with high-pH solutions (pH ~13) even at temperatures as low as 20 – 30°C after 4 – 18 months. Secondary mineral precipitates include calcite and illite. C(A)SH and Ca-zeolites were identified after 4-6 months. Reactive primary minerals include kaolinite, quartz and dolomite.

A core infiltration experiment with OPA and a K-Na-Ca-OH solution (pH ~13) at 30°C was carried out by ADLER (2001) at a fixed confining pressure (60 bar) and hydraulic head (30 bar). The results from this experiment showed after 400 days the presence of secondary minerals such as calcite, illitic clay minerals, hydrotactite and a Mg-silicate (sepiolite/talc) and compared well with the results of the experiments on dispersed systems, except for the lack of C(A)SH and zeolite phases.

MÄDER (2003) has recently reviewed the possible effects of high pH fluids in an OPA formation. The single most important factor influencing any potential effects is that the transport is dominated by diffusion. Various aspects such as the hyperalkaline source term as a function of cement degradation, sealing within the cement repository, cementation (see for example PFINGSTEN, 2001), secondary mineral formation, the role of the excavated disturbed zone etc. are discussed. By considering mass balance constraints (source term and the OPA buffer capacity) and reactive diffusive transport, MÄDER (2003) makes the strong concluding statements that the effects due to the hyperalkaline plume are confined to the close vicinity of the repository and the impact on barrier performance is negligible. DE WINDT et al. (2004) have modeled the interactions between cement and a clay rich host rock using the reactive transport

code HYTEC. Though they conclude that the region of intense mineral transformations is localized close to the cement/argillaceous rock interface, the porewater chemistry is disturbed over a dozen meters due to the continuous flux of hydroxyl, potassium and calcium ions. Further, the migration of Cs, Ra, Tc and U was modeled in the strongly coupled system.

However, the mineralogical reaction scheme of cement/OPA interactions and its effect on pH plume buffering is not in general well known, and thus there still remain significant areas of uncertainties in the assessments given. Partly because of this, but also to cover various “what if scenarios”, the aim of this report is to consider the potential effects of a pH plume on the far-field sorption properties of OPA and to construct appropriate sorption data bases. This report is based on some previous work on a similar topic carried out for Palfris marl (BRADBURY & BAEYENS, 1997a).

2 Opalinus clay/pH-plume: Approach for generating sorption data bases

2.1 General

The procedures adopted to generate sorption data bases (SDBs) for OPA reflecting the changes resulting from the interaction of the host rock mineralogy and groundwater chemistry with the hyperalkaline fluid from the cementitious near-field are essentially similar to those described in a previous report for the case of Palfris marl (BRADBURY & BAEYENS, 1997a). Only aspects of these procedures essential for understanding will be given here; for more details, justifications and discussions the reader is referred to the above mentioned work.

In the case of the OPA/pH-plume system, the rock mineralogy and water chemistry are areas of large uncertainty. Normally, such information is a pre-requisite for the construction of SDBs. Nevertheless, and despite all the uncertainties, the procedures outlined below allow reasonable statements concerning the effects of the pH plume to be made and robust sorption values for data bases to be selected. A key question in this respect is whether the influence of the pH plume is likely to lead to better or worse far-field sorption characteristics for the safety relevant radionuclides. (A SDB for an undisturbed OPA system is already available, BRADBURY & BAEYENS, 2003).

Although many consequences of the interaction between OPA and the high pH plume are uncertain, the fluid emerging from the cementitious near-field will tend to increase the pH of the groundwater in the far-field. How great this increase is, depends on many factors such as the starting pH of the emerging cement porewater (NEALL, 1996), dilution by the OPA groundwater, the mineral phases which the fluid "sees" and how rapidly and to what extent reactions can take place etc.

2.2 Clay minerals and pH

The initial premise is that clay minerals are the most important class of minerals in OPA governing the sorption properties of many of the safety relevant radionuclides (BOLT & BRUGGENWERT, 1978; YARIV & CROSS, 1979; SPOSITO, 1984). A second premise is that the pH in the groundwater will increase as a result of the pH plume. These factors lead to the consideration of two cases, depending on whether the clay minerals are in a pH regime where they are stable or whether the pH conditions are such that the clay minerals are unstable and tend to dissolve.

In BRADBURY & BAEYENS (1997a) a pH of ~11 was taken as the limit of stability for illite, the major clay mineral in OPA. However, although this value was based partially on clay stability diagrams (TARDY et al., 1987), the choice was recognised as being somewhat arbitrary because such diagrams mainly apply to neutral pH conditions and are not necessarily valid at high pH. A study by BAUER (1997) and BAUER et al. (1998) into the behaviour of clay minerals (kaolinite and smectite) under alkaline conditions did not directly help in selecting a more defensible upper bound for the pH stability of illite. The stability boundary, as in the previous report, still remains unclear. In order to reflect this uncertainty in the following, the two cases discussed are for pH < 10 and pH > 10.

2.2.1 Terminology

In order to clearly distinguish between the various “states of OPA” existing in the different pH regions, the following terminology is used throughout.

“OPA” will be reserved for the undisturbed host rock in its natural state.

“Disturbed OPA” will be used to refer to the rock in a system where the pH has risen above its ambient level to values less than 10 and where the mineralogy has not changed in any significant way.

At pH values greater than 10, where minerals can dissolve and new secondary minerals form, the term “altered OPA” will be used.

2.2.2 pH < 10

In the first case when the pH is rising from its natural level (pH ~7 - 8, PEARSON, 2002) up to pH values less than 10, the system is viewed as being essentially the same as for OPA but at a higher pH. In general terms, metal aqueous species which are interpreted to sorb predominantly by surface complexation, tend to exhibit an increasing affinity for solid surfaces with increasing pH whereas for anionic species, the reverse is the case. (See for example DAVIS & KENT, 1990; DZOMBAK & MOREL, 1990.) Where cation exchange is the main uptake mechanism, pH does not have a significant effect except possibly through competition from additional species in solution arising from mineral dissolution (see for example POINSSOT et al., 1999). However, increased levels of K/Na will lead to increased competition for the exchange sites.

Hence, in a regime where the mineral surfaces remain stable, a rise in solution pH is likely to have an overall positive (or at least neutral) influence on the uptake of positively charged and neutral species and a negative effect on anionic species. Increased competition from the higher K/Na concentrations will adversely effect uptake by cation exchange. (For examples see Chapter 6 in BRADBURY & BAEYENS, 1997a.) In all cases the effects on sorption with changes in aqueous speciation as a function of pH must be considered on an element by element basis.

2.2.3 pH > 10

At pH values greater than 10 most of the minerals present in OPA, in particular the clay minerals and quartz, are unstable and tend to dissolve (see for example BAUER, 1997, BAUER et al., 1998). The most recent information available indicates that the main sorbing phases are likely to be secondary “hydrated cement like” minerals e.g. ettringite, CSH, CASH; and possibly zeolites (MILODOWSKI et al., 1998; ADLER et al., 1999).

In Chapter 4 of this report it is assumed that the clay minerals are “converted” to CSH phases on a one to one basis. THOENEN (1996, pers. comm.) carried out some simple mass balance calculations on the transformation of clay minerals to the crystalline CSH phase tobermorite and found that to a first approximation 1 gram of “clay mineral” converted to 1 gram of tobermorite.

Estimates of sorption values for altered OPA given later in Table 4.1 were made with the aid of the updated cement SDB from WIELAND & VAN LOON (2003). The CSH phase content of HCP is ~40 - 60 wt. % whereas the maximum CSH phase content of a fully altered OPA would be between ~45 and ~60 wt.%, corresponding to the range of clay mineral contents in OPA. However, all of these clay minerals may not be fully converted to CSH phases. To take this into account HCP sorption values were reduced by a factor of 2 to yield the values given in column 3 in Table 4.1. Some factors might indicate that this may be a conservative assumption: the CSH phases precipitated in OPA are likely to have a lower Ca/Si ratios than in HCP and therefore to have a higher sorption potential for alkaline-earth metals, the quantities of

precipitated CSH phases may be higher than anticipated because the constitutive elements could be provided by other mineral phases (quartz, calcite), potential contributions from zeolites/illitic clays have been neglected. On the other hand, an implicit assumption here is that CSH related phases are the major sorbents in HCP which may not be true for all radioelements considered.

2.3 Redox

The estimated Eh for the OPA reference condition given in PEARSON (2002) is -167 mV at pH 7.24, based on sulphate/pyrite as the controlling redox couple. In the undisturbed OPA the conditions are sufficiently reducing so that the redox states of the most important safety relevant radionuclides are Se(-II), Tc(IV), U(IV), Np(IV) and Pu(III). In the case of disturbed OPA (pH < 10), Chapter 3, where an increase in pH is anticipated, the redox state of the radionuclides is taken to be the same as in the undisturbed OPA. Eh and pH are coupled and the general tendency is for Eh values to become more negative as pH values increase, see for example BROOKINS (1988).

For the altered OPA case, Chapter 4 (pH > 10), where a comparison is made between undisturbed OPA sorption data and sorption data for cement in a Stage II degradation state, section 4.1, "reducing" conditions have been chosen for the latter (WIELAND & VAN LOON (2002). Again the reason is that for an altered OPA at a pH near 12.5, where the controlling redox couple is sulphate/pyrite, the radionuclides will be maintained in the same redox state as in the OPA, with the possible exception of plutonium which will most probably be in the tetravalent rather than the trivalent state (BROOKINS, 1988).

Note that in the solubility assessments for a cementitious near-field (BERNER, 2003), an Eh value of -230 mV is taken at pH ~ 12.5 based on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ as the controlling couple. For some radionuclides this choice implies higher redox states than in altered OPA e.g. Se(IV), Tc(VII), Sb(IV), U(VI) instead of Se(-II), Tc(IV), Sb(III), U(IV).

2.4 Temperature

The temperature considered in this work is 25°C . That is, the sorption values in the SDB and the stability constants in the TDB used in any speciation calculations refer to this temperature. The OPA formation temperature is 38°C . Temperature effects and their potential influence on sorption were not considered in this report. Very little information exists in the open literature on the effects of temperature. Some recent work by BAUER et al. (2004) on Eu on smectite as a function of pH at 25, 60 and 80°C indicated that temperature had no effect.

2.5 Zeolites

Increasing interaction with the OPA minerals tends to buffer the hyperalkaline plume to lower pH values which thereby increases the likelihood of the formation of zeolites. Zeolites are powerful cation exchange materials and there is a considerable amount of data available in the open literature on their sorption characteristics. However, hardly any information could be found on the pH dependency of sorption and on sorption under high pH conditions (VALKE & CREMERS, 1994). In addition, it still remains rather unclear as to which zeolites form where and when and to what extent and under what water chemistry conditions. Because of the general uncertainties concerning zeolites, the relevance of this class of minerals to the sorption characteristics of altered marl is not assessed here.

3 Sorption data for disturbed Opalinus clay (pH < 10)

In the pH range below 10, clay minerals are considered to be stable and provide the dominant sorbents in OPA. Any differences here between the sorption characteristics of disturbed OPA and OPA are primarily due to pH and speciation effects. Only brief explanatory notes to the recommendations will be given here; more details and pertinent references can be found in BRADBURY & BAEYENS (1997a).

3.1 Alkaline, alkaline-earth metals

The dominant sorption mechanism for these elements on clay minerals is cation exchange which exhibits virtually no dependency on pH at the ionic strengths under consideration. Hence, any rise in pH will not significantly influence the sorption behaviour of these weakly hydrolysable cations (BAES & MESMER, 1976).

Cs(I)

General comment

At trace equilibrium concentrations ($< 10^{-8}$ M), Cs sorbs predominantly on the so called frayed edge sites of illite (SAWHNEY, 1970, 1972; EBERL, 1980; BROUWER et al., 1983; CREMERS et al., 1988; DE PRETER, 1990) and the sorption is not significantly influenced by rises in pH up to ~ 10 in moderate to high ionic strength solutions in which Na is the major cation (POINSSOT et al., 1999).

If we assume that the rise in pH from 7.2 to 10 is due to alkali-hydroxides, then the concentration of (K,Na)OH will increase. Since K is the most important competing cation for Cs sorption on the high affinity frayed-edge sites (SAWHNEY, 1970, 1972; BROUWER et al., 1983) and both Na and K will be competitive on the other exchange site types, their concentrations will be important in determining the extent of any reduction in the sorption of Cs. Unfortunately, it is very difficult to estimate the concentration of K and Na. pH buffering reactions will take place; dissolution of quartz and dolomite and precipitation of calcite and brucite. Such hydroxyl ion consuming reactions will result in K and Na concentrations which are higher than those simply required to raise the solution pH to 10. Simultaneously, other processes will be taking place which lead to a decrease in their concentrations e.g. cation exchange. The local K and Na concentrations will thus be dependent on the above reactions and their kinetics.

In order to illustrate the influence of K and Na concentrations on the uptake of Cs on OPA, the Cs sorption model of BRADBURY & BAEYENS (2000) was used to calculate the two sorption curves given in Figure 3.1. The continuous curve was calculated for the OPA groundwater reference conditions ($[K] = 5.65 \times 10^{-3}$ M; $[Na] = 1.69 \times 10^{-1}$ M) and the dashed curve for the extreme case where the K in the modified OPA porewater reaches the same level as in the "fresh" cement porewater ($[K] \sim 3.03 \times 10^{-1}$ M, SCHWYN et al., 2004) equilibrated at pH 10.

Potassium moves into the OPA via diffusion, and thus if the K level in the OPA groundwater reaches the same concentration as in the cement porewater, the movement of K will cease. Hence a K concentration of 3.03×10^{-1} M represents an absolute upper bound value. (Note that the Na concentration in the reference OPA porewater is greater than that in the cement porewater, so the relevant Na concentration in the modified porewater is the same as in the OPA reference porewater.)

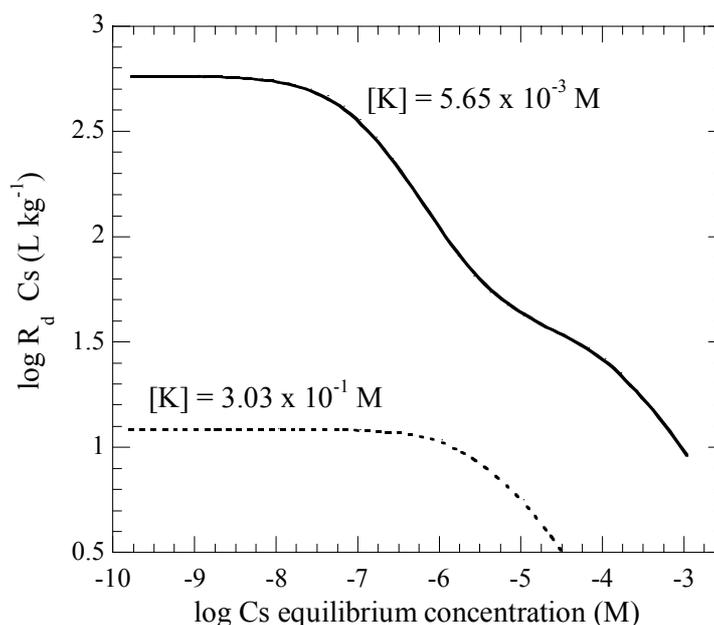


Fig. 3.1: Cesium sorption curves for the reference OPA groundwater composition, $[K] = 5.65 \times 10^{-3} \text{ M}$ (continuous line); and for a disturbed OPA for an upper bound value of $[K] = 3.03 \times 10^{-1} \text{ M}$ (dashed line). The two curves were calculated using the generalised Cs sorption model of BRADBURY & BAEYENS (2000).

Recommendation

From the above argument, a Cs sorption value calculated for K and Na concentration of $3.03 \times 10^{-1} \text{ M}$ and $1.69 \times 10^{-1} \text{ M}$ respectively should yield a lower bound value for the distribution ratio. At equilibrium Cs concentrations below 10^{-6} M the dashed curve in Figure 3.1 indicates a sorption value for Cs of $1.2 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$. This R_d value is selected for disturbed OPA.

Ca(II), Sr(II) and Ra(II)

General comment

Although the main sorption mechanism for alkaline earth metals is cation exchange, there is a tendency for sorption to increase as a function of pH (RAFFERTY et al., 1981; MAHONEY & LANGMUIR, 1991; BAEYENS & BRADBURY, 1995; BRADBURY & BAEYENS, 2004), possibly due to an additional contribution from surface complexation reactions. This is a clear but not particularly strong effect.

In the SDB for OPA (BRADBURY & BAEYENS, 2003), no relevant sorption data for Ra could be found and Sr was taken as a chemical analogue.

Following the arguments given in the previous section for Cs, the sorption of Ca, Sr and Ra were calculated for the same modified porewater composition using the selectivity coefficients given in BRADBURY & BAEYENS (2003).

Recommendation

The calculated sorption values for Ca, Sr and Ra of 3.5×10^{-5} , 3.5×10^{-5} and $2.6 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$ respectively are selected for disturbed OPA. The principle reason for the reduction is the increased occupancy of K on the OPA due to the high K concentration in the modified OPA water considered.

3.2 Transition metals and heavy metals

There is a large body of information in the open literature which indicates clear increases in sorption with increasing pH for transition and heavy metals at trace concentrations on a variety of solid phases; so-called “sorption edges”. (For examples on clay minerals see Chapter 6 in BRADBURY & BAEYENS, 1997a.)

Sorption data can be interpreted by a combination of cation exchange and surface complexation, e.g. BRADBURY & BAEYENS (1997c, 2004). At lower pH values (< ~5) sorption tends to be dominated by cation exchange and is influenced primarily by the water composition. At higher pH values surface complexation becomes the main sorption mechanism. Metal uptake is characterised by a strong dependency on pH and a weak dependency on ionic strength.

Ni(II), Co(II), Pb(II)

General comment

Ni, Co and Pb exhibit clear and strong sorption edges on clay minerals with rapidly increasing R_d values occurring in the pH range from ~5 to ~9. At higher pH values sorption tends to level off. The R_d values at pH 10 will certainly be greater than or equal to those at pH 7.2. Thus, rises in pH up to ~10 are likely to lead to an increase in the uptake of such elements by the solid phase.

Recommendation

Increases in pH up to 10 are likely to promote the uptake of elements such as Co, Ni and Pb by clay minerals. Consequently, the sorption values for OPA probably represent underestimates for disturbed OPA.

Cd(II)

General comment

In general Cd is expected to exhibit similar sorption behaviour to Ni, Co and Pb except in concentrated Cl systems where Cd tends to form strong negatively charged chloro complexes. The formation of such complexes is the reason why the selected sorption value for Cd in the OPA system is a factor of ten less than that of Ni (BRADBURY & BAEYENS, 2003).

As the pH increases, hydrolysis reactions become more important but at pH 10, still more than 90 % of Cd is present as chloro complexes.

Recommendation

The speciation changes as the pH increases would tend to lead to an increased uptake of Cd in the disturbed OPA system. Selecting the same R_d value for disturbed OPA as for OPA is likely to be an underestimate of the true sorption value.

Pd(II)

General comment

No sorption data for Pd could be found in the open literature. $\text{Pd}(\text{OH})_2^0$ remains the dominant aqueous species up to pH 10.

Recommendation

Since there is no significant change in the speciation of Pd between pH 7.24 and 10, it would be expected that the selected sorption value for OPA is also valid for disturbed OPA.

Ag(I)General comment

No sorption data for Ag at high pH could be found in the open literature.

In a NaCl-type groundwater Ag probably does not sorb on OPA because of the formation of Ag-chloro complexes (BRADBURY & BAEYENS, 2003). Any increase in pH will not change this situation.

Recommendation

A sorption value of zero, selected for Ag on OPA, is also taken for the disturbed OPA.

3.3 Lanthanides**Eu(III)**General Comment

Eu exhibits strong sorption edges on clay minerals (e.g. POINSSOT et al. 1999; BRADBURY & BAEYENS, 2004) and increasing sorption as a function of pH on argillaceous rocks e.g. on Boom clay (BAEYENS, 1982) and on OPA (LAUBER et al., 2000). Thus there is reliable experimental evidence indicating that there is a strong tendency for the sorption of trivalent lanthanides to remain high and virtually constant when the pH increases from neutral up to values around 10. Speciation calculations indicate that approximately 80 % of the Eu in aqueous solution exists as positively charged or neutral hydroxy species at pH 10.

Recommendation

The sorption value of Eu for disturbed OPA are taken to be the same as for OPA.

Ce(III), Pm(III), Sm(III) and Ho(III)Recommendation

Because of the chemical similarity of lanthanides, Eu is taken as an analogue for these trivalent rare earth's. The sorption values of Ce, Pm, Sm and Ho for disturbed OPA are taken to be the same as for OPA.

3.4 Actinides**Am(III), Ac(III) and Cm(III)**

ALLARD (1982) studied the pH dependent sorption behaviour of Am on approximately 40 minerals and rocks in a synthetic groundwater. In all cases where measurements were extended to pH values above 9, there were no indications of decreases in Am sorption. GORGEON (1994) measured the sorption of Am as function of pH on three clay minerals (illite, montmorillonite and kaolinite) at equilibrium concentrations between 4×10^{-8} M and 3×10^{-11} M and in all three cases increasing sorption values with increasing pH were measured up to pH ~12. As an example, Figure 3.2 shows the measured Am sorption edges on conditioned Na-illite at 2 different ionic strengths.

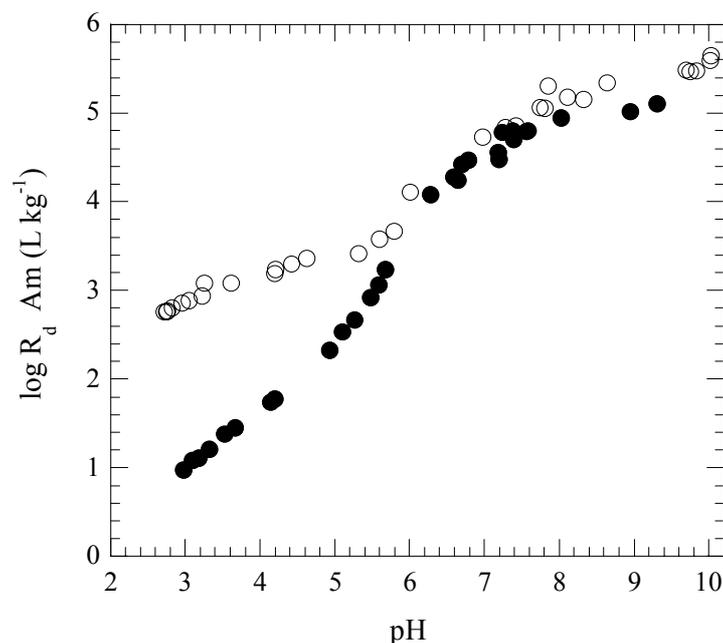


Fig. 3.2: Sorption edges of Am on conditioned Na-illite in 0.1 M (O) and 1 M (●) NaClO₄ (Gorgeon, 1994).

No relevant sorption measurements could be found for Ac and Cm, and Am has been taken as their chemical analogue.

General comment

At pH values above ~5, Am, and by inference the other trivalent actinides Ac and Cm, sorb extremely strongly on almost all mineral surfaces, particularly clay minerals. In general the sorption tends to increase strongly up to pH ~8 where after the rate of increase decreases or plateaus up to pH ~12.

Recommendation

Am, Ac and Cm sorption values tend, if anything, to increase between pH values 7.24 and 10. The sorption values selected for OPA are considered to be conservative for pH values up to and including 10 and can be used for disturbed OPA.

Pu(III)

Under the redox/pH conditions being considered, Pu is predominantly present in the trivalent state. No sorption data could be found for Pu(III) and consequently Am was chosen as a chemical analogue.

Recommendation

Following the discussion above for Am, the sorption of Pu(III) is not expected to decrease as the pH increases from 7.24 to 10. Moreover, Pu(III) speciation shifts towards positive and neutral hydrolysed species which would favour increased sorption. Consequently, it is probably conservative to select the same sorption value for the disturbed OPA as for OPA.

Th(IV), U(IV), Np(IV)

Sorption studies of Th(IV) and U(IV) (and Pu(IV)) on London clay, Caithness flagstones and St. Bees sandstone at pH values between ~8 and ~11 show almost constant sorption (BERRY et al., 1991; BASTON et al., 1992).

Speciation calculations indicate that in the pH range 7.24 to 10, the neutral hydroxy species become increasingly dominant for all three elements.

General comment

Arguments based on chemical analogy and speciation calculations lead to the conclusion that the sorption of Th(IV), U(IV) and Np(IV) should not be adversely affected by a rise in pH up to 10, and this is supported by sorption data reported in the literature.

Recommendation

The selected sorption values for Th(IV), U(IV) and Np(IV) on OPA are essentially valid at higher pH values and can be used for disturbed OPA.

Pa(V)

Following the arguments given in BRADBURY & BAEYENS (2003) Np(V) was no longer seen as an appropriate chemical analogue for Pa(V).

For Pa in the OPA groundwater, PaO_2OH^0 is the dominant aqueous species and since neutral hydroxy species tend to sorb strongly, a relatively high sorption value for Pa was selected. This is in keeping with the few, but somewhat scattered data existing in the open literature (BERRY et al., 1988).

General comment

The neutral hydroxy species remains the major aqueous species up to pH ~10.

Recommendation

The sorption value deduced for Pa(V) for OPA can also be used for the disturbed OPA.

3.5 Other elements

3.5.1 Sb(III), Sn(IV), Zr(IV), Hf(IV) and Nb(V)

General

These elements have been grouped together because of the broad similarities in their hydrolysis behaviour. They all tend to form neutral $\text{X}(\text{OH})_y^0$ species ($y=3$ for Sb, 4 for Sn, Zr, Hf, Tc and 5 for Nb) which then hydrolyse further to negatively charged hydroxy species.

Sb(III)

Sb(III) forms predominantly neutral hydroxy species, $\text{Sb}(\text{OH})_3^0$, in the pH range 4 to 10 and if anything the sorption would be expected to increase with increasing pH in this range. Therefore selecting a sorption value of Sb for disturbed OPA to be the same as that in OPA is considered to be conservative.

Recommendation

It is recommended that the same Sb(III) sorption value of $5.6 \text{ m}^3 \text{ kg}^{-1}$ given for OPA is also selected for disturbed OPA.

Sn(IV)

When the fraction of $\text{X}(\text{OH})_y^0$ species is high, the sorption is generally observed to be extremely high. This has been seen for example in the case of Sn sorption on OPA carried out at pH values of 6.3 and 8.1 (LAUBER et al., 2000). In addition some recent sorption edge measurements of Sn(IV) on conditioned Na-illite (BRADBURY & BAEYENS, unpublished data) have indicated that the sorption remains high and constant up to pH ~ 10 even though speciation calculations predict that the negatively charged hydrolysis species is predominantly present (AMAYA et al., 1997), see Figure 3.3.

Recommendation

Even though the data of AMAYA et al. (1997) predict that the major Sn(IV) aqueous species at pH > 8 is $\text{Sn}(\text{OH})_5^-$, the sorption data show clearly that the uptake of Sn remains constant and very high from pH ~ 3 to ~ 10 . At pH > 10 the sorption decreases rapidly. Either the predictions of the speciation calculations are erroneous or the negatively charged hydroxy species must sorb. In any event the experimental evidence is that the sorption of Sn on illite remains high at pH ~ 10 . The recommendation is therefore that the same Sn sorption value is selected for disturbed OPA as for OPA.

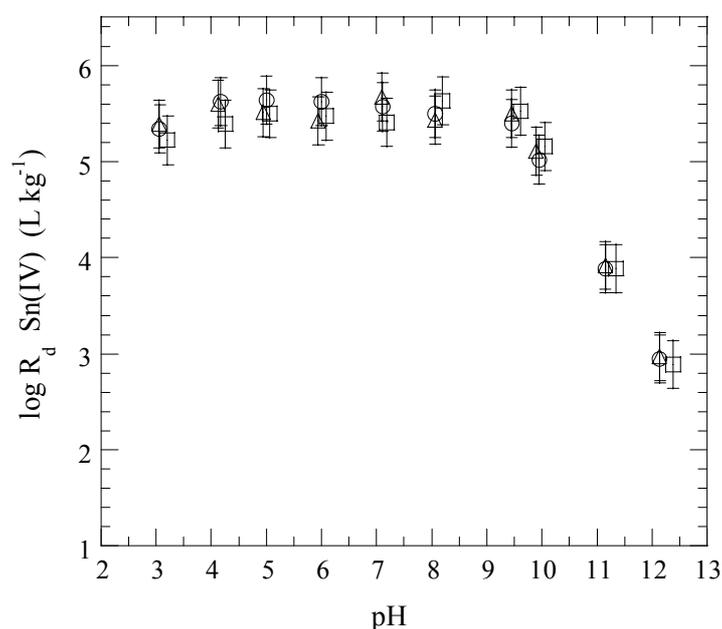


Fig. 3.3: Sorption edge of Sn(IV) on conditioned Na-illite in 0.1 M NaClO₄. (O) 7 days; (Δ) 21 days; (□) 60 days equilibration time. (Initial Sn concentration $\sim 10^{-8}$ M, S:L ratio = 1.1×10^{-3} kg L⁻¹). (BRADBURY & BAEYENS, unpublished data.).

Zr(IV), Hf(IV)

No relevant sorption data for Zr and Hf could be found in the open literature.

Sn is taken as a chemical analogue for both of these elements. However, for Zr and Hf negatively charged hydroxy species begin to form already at pH ~6 (BAES & MESMER, 1976) which is at least two pH units lower than for Sn (AMAYA et al., 1997). This in turn means that the influence of the formation of $Zr(OH)_5^-$ and $Hf(OH)_5^-$ species on their respective sorption values at pH 10 is expected to be significantly greater than in the case of Sn. At pH > 6 the concentration of $X(OH)_5^-$ species increases in direct proportion to the hydroxyl ion activity (BAES & MESMER, 1976), and sorption would be expected to decrease at the same rate. Thus at pH 10, Zr and Hf distribution coefficients would be approximately a factor of 100 lower than at pH 8.

Recommendation

The selected sorption values for Zr and Hf in the OPA reference system (pH 7.24) were both $10.9 \text{ m}^3 \text{ kg}^{-1}$. On the basis of the above discussion values of $0.1 \text{ m}^3 \text{ kg}^{-1}$ for Zr and Hf are selected for disturbed OPA.

Nb(V)

Nb behaves in a chemically similar manner to Sn. The $Nb(OH)_6^-$ species first begin to become significant at pH < 7.5 (BAES & MESMER, 1976). The few sorption measurements available indicate that the uptake of Nb is strong (BERRY et al., 1988) and, in the pH range up to 8, that it is approximately constant (LEGOUX et al., 1992). Following similar arguments to those given for Zr and Hf, it is proposed to reduce the sorption value for Nb by an order of magnitude.

Recommendation

Nb is treated in a similar manner to Zr and Hf, and the Nb sorption value selected for disturbed OPA is a factor of 10 less than that for OPA i.e. $0.4 \text{ m}^3 \text{ kg}^{-1}$

3.5.2 Tc(IV)

No sorption data for Tc(IV) could be found at elevated pH.

General comment

As the pH increases from 7.24 to 10 the redox state of Tc will not change and though speciation calculations indicate the increased formation of a negatively charged hydroxy complex, the neutral hydroxy complex remains dominant.

Recommendation

The sorption value for Tc for the disturbed OPA is taken to be the same as for undisturbed OPA.

3.5.3 Oxyanions

Po(IV)

No sorption data for Po were found in the literature.

General comment

Under the Eh/pH conditions prevailing in the disturbed OPA groundwater, the dominant aqueous species is PoO_3^{2-} . In BRADBURY & BAEYENS (2003) SeO_3^{2-} was taken as chemical analogue. The most likely sorption mechanism is ligand exchange for which the tendency is to weaker sorption with increasing pH.

Recommendation

In view of the above and the lack of any relevant experimental data, the sorption value for Po for the disturbed OPA is taken to be zero.

Mo(VI)

From the little data available, Mo appears to sorb via a ligand exchange mechanism (MOTTA & MIRANDA, 1989).

General comment

Mo is present in solution at pH 7.24 predominantly as MoO_4^{2-} and exhibits correspondingly weak sorption. Since increases in pH tend to decrease the sorption of anionic species, and molybdate remains the dominant aqueous species, then the tendency will be towards decreased uptake of Mo at pH 10.

Recommendation

The sorption value for Mo for the disturbed OPA is taken to be zero.

Ru(III/IV)

Recommendation

In the undisturbed OPA Ru was treated the same as Pd. Consequently, by analogy, the selected Ru sorption value for OPA is taken as being valid for disturbed OPA.

3.6 Anions

Cl(-I) and I(-I)

All measurements reported in the open literature on the sorption of anionic species indicate that the uptake tends to decrease with increasing pH irrespective of the sorbent; see for example DAVIS & KENT (1990), THENG (1971), NEAL et al. (1987a,b).

General comment

For anions sorbing via a ligand exchange mechanism, the universal experience is that the uptake onto mineral surface decreases with increasing pH. The pH at which the sorption becomes effectively zero may vary with element and solid phase but generally for clay minerals the boundary lies around pH 8 to 9.

Recommendation

At elevated pH values the sorption for the elements I and Cl should be set to zero for the disturbed OPA system

Se(-II)

Under the Eh/pH conditions prevailing in situ in the OPA, Se is expected to be present predominantly as HSe^- . (See for example NEAL et al., 1987a,b; BROOKINS, 1988.) No sorption data under relevant conditions were found for HSe^- species. The speciation of Se between pH 7 and 10 does not change significantly.

Recommendation

The sorption for Se (as HSe^-) is taken to be zero for the disturbed OPA.

3.7 ¹⁴Carbon

¹⁴C in organic molecules

General comment

Since no specific information on the types and inventories of "¹⁴C containing organics" in the repository was available, it was assumed conservatively in the undisturbed OPA SDB (BRADBURY & BAEYENS, 2003) that they are non-sorbing.

Recommendation

Due to the lack of specific information and data, the sorption of ¹⁴C containing organic molecules is taken to be zero for the disturbed OPA system.

¹⁴C as ¹⁴CO₃/H¹⁴CO₃

General comment

Following the approach given in BRADBURY & BAEYENS (1997b, 2003), the uptake of ¹⁴C existing in solution as ¹⁴CO₃/H¹⁴CO₃ is considered to take place via an isotope exchange mechanism at the surface of calcite. As the pH increases the tendency will be for the CO₃/HCO₃ concentrations to decrease because the solubility of calcite decreases with rising pH. Also, there may be significant Ca levels in solution arising from the portlandite in the cement which would have the effect of further reducing the CO₃/HCO₃ concentrations via the common ion effect. Any decreases in carbonate concentrations would tend to result in an increased uptake of ¹⁴C existing in solution as ¹⁴CO₃/H¹⁴CO₃.

Recommendation

At pH < 10 the sorption data given for ¹⁴C as ¹⁴CO₃/H¹⁴CO₃ in the OPA data bases are taken as conservative values for disturbed OPA systems.

3.8 Sorption data base for disturbed Opalinus clay, pH < 10

The proposed sorption data base for disturbed OPA in NaCl-type groundwaters at pH < 10 is given in Table 3.1; column 3. Note that the distribution ratios and uncertainty factors given are calculated values (for details see BRADBURY & BAEYENS, 2003) and no attempt has been made to round them for traceability and transparency reasons. The uncertainty factors associated with the sorption values selected for the disturbed OPA are taken as being the same as those for undisturbed OPA.

In column 2, Table 3.1, the sorption values for undisturbed OPA at pH 7.24 are given.

Table 3.1: Sorption values selected for disturbed OPA (pH < 10). All data in m³ kg⁻¹.

Element	OPA SDB: Reference values at pH 7.24	Disturbed OPA: R_d values	Uncertainty factor
C(inorg.)	1.6 x 10 ⁻³	1.6 x 10⁻³	-
C(org.)	0	0	-
Cl(-I)	0	0	-
Ca(II)	1.1 x 10 ⁻³	3.5 x 10⁻⁵	6
Co(II)	4.9 x 10 ⁻¹	4.9 x 10⁻¹	15.1
Ni(II)	9.3 x 10 ⁻¹	9.3 x 10⁻¹	11.6
Se(-II)	0	0	-
Sr(II)	1.1 x 10 ⁻³	3.5 x 10⁻⁵	6
Zr(IV)	10.9	1 x 10⁻¹	19.6
Nb(V)	4	4 x 10⁻¹	18.2
Mo(VI)	1.7 x 10 ⁻²	0	-
Tc(IV)	55.4	55.4	6.3
Ru(III/IV)	5	5	15
Pd(II)	5	5	15
Ag(I)	0	0	-
Cd(II)	1.8 x 10 ⁻¹	1.8 x 10⁻¹	16.4
Sn(IV)	110	110	14
Sb(III)	5.6	5.6	25.5
I(-I)	3.5 x 10 ⁻⁵	0	-
Cs(I)	5.5 x 10 ⁻¹	1.2 x 10⁻²	6
Ce(III)	59.8	59.8	6.3
Pm(III)	59.8	59.8	6.3
Sm(III)	59.8	59.8	6.3
Eu(III)	59.8	59.8	4.5
Ho(III)	59.8	59.8	6.3
Hf(IV)	10.9	1 x 10⁻¹	19.6
Pb(II)	2.7	2.7	47.3
Po(IV)	1.8 x 10 ⁻¹	0	-
Ra(II)	7.6 x 10 ⁻⁴	2.6 x 10⁻⁵	6
Ac(III)	17.0	17.0	8.2
Th(IV)	55.4	55.4	4.5
Pa (V)	5	5	10
U(IV)	20.5	20.5	6.3
Np(IV)	55.4	55.4	6.3
Pu(III)	22.6	22.6	8.2
Am(III)	17.0	17.0	5.8
Cm(III)	17.0	17.0	8.2

4 Sorption data for altered Opalinus clay (pH > 10)

4.1 Sorption data selection procedure

In this pH region it is assumed that clay minerals have dissolved and the main sorbing phases are the precipitated secondary minerals. From the information given in Chapter 2 these are most likely to be similar to those found in hydrated cements i.e. of the CSH-gel type. This is the first general assumption upon which the SDB for altered OPA is constructed. (A more detailed discussion can be found in Chapter 7 in BRADBURY & BAEYENS, 1997a).

The central question in defining a SDB for altered OPA is whether the transformation of the clay minerals at high pH to "hydrated cement paste like minerals" tends to lead to an overall increase or decrease in the sorption of particular elements.

The general assumption is made that CSH-type phases are the principle sorbing solids in both hardened cement paste (HCP) and altered OPA and that the magnitude of sorption is determined by the CSH-type phase content. On this basis, and as discussed in section 2.3.3, a fully altered OPA at high pH (all clay minerals converted to "hydrated cement paste like minerals") is estimated to have sorption values a factor of ~2 less than the corresponding ones selected in a SDB for cement. However, it must be mentioned that the reaction products identified in the interaction between argillaceous rocks and hyperalkaline fluids seem to depend strongly on the conditions and time, see for example SAVAGE et al. (1990), CRAWFORD & SAVAGE (1994), BATEMAN et al. (1995), MILODOWSKI et al. (1998), ADLER et al. (1999). It may well be that CSH phases are somewhat less dominant than indicated above. Clay minerals such as illite and cement type minerals such as hydrotalkite may be important products. From a mineralogical point of view, the formation of illite, for example, can only influence the sorption of argillaceous rocks in a positive sense.

In the compilation of both the OPA and cement SDBs the procedure was to modify the selected laboratory data by applying conversion factors so that the final sorption values corresponded to in situ conditions. These sorption values, Table 7 in BRADBURY & BAEYENS (2003) and Table 5 (Stage II, "reducing conditions") in WIELAND & VAN LOON (2002) are listed in columns 2 and 3 respectively in Table 4.1. A scaling factor of 2 has already been applied to the cement data (section 2.3.3), and for traceability and transparency reasons sorption values have not been rounded. Transport in OPA is diffusive, and as the considerations concerning altered OPA revolve around clay mineral dissolution and CSH formation as well as the substantial formation of secondary hydroxides (e.g. Mg-silicate-hydroxides, Mg-aluminate-hydroxides), the quantities of hydroxy ions required for this cannot be supplied by cement while still in a Stage I condition. Cement degradation must be well into Stage II at least, if not Stage III. In view of this the comparison made to select sorption values representative of altered OPA is made between unaltered OPA data and Stage II HCP data. As indicated in section 2.2 the sorption data for Stage II "reducing" conditions was chosen as being appropriate for the sulphate/pyrite redox couple at pH values around 12.5.

In the first instance such a comparison indicates whether the individual sorption values in altered OPA tend to be higher or lower than in the unaltered system. Robust sorption data are selected for the altered OPA SDB by always taking the lowest distribution ratio in any corresponding pair of values. This procedure is applied to the sorption values given in Table 4.1 to provide the R_d values proposed for an altered OPA SDB, column 5. Some supporting sorption data measured directly on CSH phases (TITS et al., 1998, 2000; EWART et al., 1990) are listed in column four.

WIELAND & VAN LOON (2002) do not give distribution ratios for C(org.), Ca, Co, Ni, Cd and Hf in hardened cement paste.

C(org.) is taken to be non-sorbing, Sr is taken as chemical analogue for Ca, and Zr for Hf.

Ni and Co are considered to be solubility controlled in the cement system. In a HCP the inventories of these transition metals come from the clinker components, and this is clearly not the same for altered OPA, where the CSH phases form in situ. The solubility limits for Co and Ni in the HCP provide the (low) input concentrations to the altered OPA where the main retention process is viewed as being sorption. In order to estimate appropriate sorption values in the absence of distribution ratios from HCP, the sorption value on CSH phases for Ni, Table 4.1, reduced by a factor of 2 (section 2.3.3), was used. Ni is taken as chemical analogues for Co and Cd.

As can be seen from Table 4.1, a comparison between the sorption values for Pu given in the OPA SDB and the cement SDB is not appropriate because of the difference in the redox states. Following the brief discussion given in section 2.3, the sorption value for Pu(IV), cement Stage II, was taken over for the altered OPA SDB.

The uncertainty factor associated with each selected value for altered OPA is that given in the database (unaltered OPA SDB or cement SDB) from which the value was selected.

As the alteration of OPA progresses, the scaled cement sorption values given in the third column in Table 4.1 would tend to become more representative of the real system.

4.2 Sorption data base for altered Opalinus clay, pH > 10

The proposed sorption data base for altered OPA (pH > 10) is given in Table 4.1; column 5. The associated uncertainties are given in column 6. Sorption values for the OPA system (BRADBURY & BAEYENS, 2003), scaled cement sorption values (WIELAND & VAN LOON, 2002) and sorption values for CSH phases are also given for comparison.

Table 4.1: Sorption values selected for altered OPA (pH > 10). All data in m³ kg⁻¹.

Element	OPA SDB: Reference values at pH 7.24	CEMENT SDB: Stage II, reducing. (Scaled values)	Measured data on CSH phases	Selected Values	Uncertainty factor
C(inorg.)	1.6 x 10 ⁻³	4.6 x 10 ^{-3*}		1.6 x 10⁻³	-
C(org.)	0	not in SDB		0	-
Cl(-I)	0	2.5 x 10 ⁻³		0	-
Ca(II)	1.1 x 10 ⁻³	not in SDB		5 x 10⁻⁴	1.4
Co(II)	4.9 x 10 ⁻¹	not in SDB		5 x 10⁻²	no value
Ni(II)	9.3 x 10 ⁻¹	not in SDB	1 x 10 ^{-1**}	5 x 10⁻²	no value
Se(-II)	0	1.5 x 10 ⁻²		0	-
Sr(II)	1.1 x 10 ⁻³	5 x 10 ⁻⁴	6 x 10 ^{-1**}	5 x 10⁻⁴	1.4
Zr(IV)	10.9	5		5	3.3
Nb(V)	4	5 x 10 ⁻¹		5 x 10⁻¹	1.4
Mo(VI)	1.7 x 10 ⁻²	0		0	-
Tc(IV)	55.4	5 x 10 ⁻¹		5 x 10⁻¹	1.4
Ru(III/IV)	5	0		0	-
Pd(II)	5	5 x 10 ⁻²		5 x 10⁻²	1.4
Ag(I)	0	0		0	-
Cd(II)	1.8 x 10 ⁻¹	not in SDB		5 x 10⁻²	no value
Sn(IV)	110	5		5	3.3
Sb(III)	5.6	5 x 10 ⁻²		5 x 10⁻²	1.4
I(-I)	3.5 x 10 ⁻⁵	5 x 10 ⁻⁴		3.5 x 10⁻⁵	14
Cs(I)	5.5 x 10 ⁻¹	2.5 x 10 ⁻³	2 x 10 ^{-3***}	2.5 x 10⁻³	1.4
Ce(III)	59.8	50 ^{*****}		50	3.3
Pm(III)	59.8	50 ^{*****}		50	3.3
Sm(III)	59.8	50 ^{*****}		50	3.3
Eu(III)	59.8	50	>10 ^{***}	50	3.3
Ho(III)	59.8	50 ^{*****}		50	3.3
Hf(IV)	10.9	not in SDB		5	3.3
Pb(II)	2.7	2.5 x 10 ⁻¹		2.5 x 10⁻¹	1.4
Po(IV)	1.8 x 10 ⁻¹	0		0	-
Ra(II)	7.6 x 10 ⁻⁴	2.5 x 10 ⁻²		7.6 x 10⁻⁴	6
Ac(III)	17	50		17	8.2
Th(IV)	55.4	50	>10 ^{***}	50	3.3
Pa (V)	5	5 x 10 ⁻²		5 x 10⁻²	1.4
U(IV)	20.5	50		20.5	6.3
Np(IV)	55.4	50		50	3.3
Pu	22.6 (Pu(III))	50 (Pu(IV))	~20 ^{****}	50	3.3
Am(III)	17	50	>50 ^{****}	17	5.8
Cm(III)	17	50		17	8.2

* Appendix F, Table F2 in BRADBURY & SAROTT (1994), ** TITS et al. (1998), *** TITS et al. (2000)
 **** EWART et al. (1990), ***** Eu taken as a chemical analogue for Ce, Pm, Sm and Ho.

5 Organics in a disturbed/altered Opalinus clay far-field

There are likely to be two major sources of organic ligands in the aqueous phase.

The first is the soluble component of the solid organic matter in the OPA itself which is released into solution during interaction with the hyperalkaline fluid. This process will be most significant during the period of highest pH where the solution chemistry is dominated by the (K,Na)OH concentrations i.e. during the first stage in cement degradation.

LAUBER et al. (1998) performed alkaline and neutral extractions on OPA samples from Mont Terri and showed that no significant difference could be found between the extracts. The effect of sorption reduction of Eu(III) in the presence of these extracts was investigated. Eu was chosen for these experiments because HUMMEL et al. (2000) had previously predicted that trivalent rare earths and actinides would exhibit the greatest tendency of all metals to complex with humic substances, even when these were present at exceedingly low levels ($\mu\text{g L}^{-1}$). The conclusion from this study was that the solid organic matter did not contain humic substances. Reductions in the sorption of Eu of less than one order of magnitude were measured at dissolved organic carbon at the $10 \mu\text{g L}^{-1}$ level and consequently the overall effects on the sorption of altered OPA at high pH are considered to be negligible.

GLAUS et al. (2001) investigated the effect of aqueous extracts from OPA (Mont Terri and Benken) on the sorption and speciation of Ni(II), Eu(III) and Th(IV). The conclusion was that within the range of estimated uncertainties, no difference in sorption was observed in most of the cases as compared to the synthetic waters devoid of organic carbon. In addition, fluorescent spectroscopy experiments with extracts from Mont Terri and Benken OPA using Cm(III) as a fluorescent probe did not show any influence of the extracts on metal ion speciation. The conclusion from this study was that the largest part of the dissolved organic matter in the extracts from OPA are most probably either small-molecular weight molecules or macromolecules with a very low content of complexing ligand sites. Consequently, sorption will not be appreciably affected by the extractable organic matter contained in OPA.

The second source of organic ligands is the degradation products from the organic substances in the radioactive waste and admixtures from the concrete such as isosaccharinic acid and Na-Gluconate (VAN LOON et al., 1997; TITS et al., 1998; GLAUS & VAN LOON, 2003). Of the degradation products, isosaccharinic acid (ISA) from cellulose is by far the most important. (See BRADBURY & VAN LOON, 1998.) These organic ligands could migrate from the near-field and be present in the high pH solutions in contact with the altered OPA. From an extensive study on cellulose degradation (VAN LOON & GLAUS, 1998), and discussions given in Chapter 9 in BRADBURY & BAEYENS (1997a) for an altered marl system, the same conclusions are considered to be valid for altered OPA i.e. all of the information currently available indicates that the concentrations of cement additives and cellulose degradation products are likely to be too low to adversely influence the sorption properties of metals in an altered OPA far-field.

6 Acknowledgements

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