Sorption of Selected Radionuclides on Sedimentary Rocks in Saline Conditions – Updated Sorption Values

NWMO-TR-2018-03 **August 2018**

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ABSTRACT

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Company: Atomic Energy of Canada Limited[1], Nuclear Waste Management Organization[2]
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Abstract

Sedimentary rocks in Canada, including shales and limestone, are being considered as potential host rocks for a deep geologic repository for radioactive waste. Some of these rocks may contain Na-Ca-Cl brine solutions with total dissolved solids (TDS) of up to 350 g/L. The sorption properties of these rocks and the clay-based sealing materials (e.g., bentonite) in the repository must be evaluated if contaminant sorption (in the geosphere and repository) is to be considered in the safety assessment calculation. A database of sorption K_d values for Canadian sedimentary rocks (shale and limestone) and bentonite in highly saline waters was developed following a review of the open literature and international sorption databases to find sorption data that would be relevant to Canadian sedimentary rocks and bentonite, in a setting that would include saline and brine Na-Ca-Cl solutions at near neutral pH.

The original database was first published in a NWMO technical report, NWMO TR-2011-12. The objectives of the present report were to: (1) fill data gaps in the database; (2) provide data for nine new elements (Ni, Cs, Eu, Cl, Ca, Ag, Cd, Hg, I); (3) reduce the need for the use of chemical analog elements; and (4) identify information that may aid with extrapolations to higher ionic strengths.

The main approaches used to achieve these objectives were: (1) a literature review, (2) a revaluation of existing data to aid with extrapolations to higher ionic strengths, (3) an incorporation of "in-house" determined sorption values for Ni, Cu, As, Se, Zr, Tc, Pd, Sn, Cs, Pb, Eu, Th, U, Np and Pu, and (4) sorption modelling to fill data gaps and to extrapolate results obtained from more dilute lab solutions to brine conditions. This report presents the revised sorption database for sedimentary rocks and includes K_d values for C, Cl, Ca, Ni, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Ag, Cd, Sn, I, Cs, Eu, Hg, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am.

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1. INTRODUCTION

The sorption of radionuclides onto mineral surfaces within the geosphere and on the materials making up the engineered barriers of a deep geologic repository is an important mechanism for slowing the transport of some radionuclides to the surface environment. If sorption is to be considered in safety assessment calculations, there must be a process for quantifying sorption for each radionuclide. Presently, the approach is to use sorption coefficient (K_d) values that describe radionuclide attachment to specific rock types in the presence of specific groundwater compositions.

The development of a sorption database for Canadian sedimentary rocks was initiated with a review of the open literature and international sorption databases to find data that would be relevant to Canadian sedimentary rocks (shale and limestone) and bentonite, in a setting that would include Na-Ca-Cl brine solutions at near neutral pH. The review focused on 19 elements: C, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am (Vilks 2011).

The purpose of this report is to document continuing development of the sorption database for Canadian sedimentary rocks and bentonite in highly saline waters. The objectives of this report were to: i) fill data gaps for the 19 elements in the database (Vilks 2011); ii) find sorption data for nine new elements (Ni, Cs, Eu, Cl, Ca, Ag, Cd, Hg, I); iii) reduce the need for the use of chemical analog elements; and iv) identify information that may aid with extrapolations to higher ionic strengths.

The main approaches used to achieve these objectives were to: i) perform a review of published literature to discover new sorption data; ii) revaluate the existing sorption data to identify information that may aid with extrapolations to higher ionic strengths; iii) incorporate the results of “in-house” sorption measurements of Ni, Cu, As, Se, Zr, Tc, Pd, Sn, Cs, Pb, Eu, Th, U, Np and Pu sorption; and iv) make use of sorption modelling to fill data gaps and to extrapolate results obtained from more dilute lab solutions to in-situ brine conditions. In this report, more information is provided regarding experimental parameters such as redox conditions and contact (i.e., sorption reaction) time. The use of chemical analogs was significantly reduced in this revision when compared to the previous report by Vilks (2011).

Where sorption data are not available for limestones and shales, sorption was estimated based on the important mineral components of these rocks, notably calcite and dolomite for limestone, and illite and chlorite for shales. Other clay-rich rocks, including mudstones, could be considered as analogs for shale. Table 1 summarizes the mineralogical compositions of limestone, shale and clay-based engineered barriers (bentonite) considered for the literature review and sorption modelling in this report.

The primary seal material considered in Canada for engineered barriers is Na-rich Wyoming bentonite clay, which may also be mixed with sand (e.g., in backfill materials). MX-80 is a Wyoming bentonite that has passed through an 80 mesh sieve, and is a commonly specified reference bentonite material. The review of sorption values for bentonite considers sorption data for bentonite and for the main component of bentonite, which is either Na-montmorillonite or Ca-montmorillonite. The term smectite applies to weathered volcanic rock that contains high montmorillonite concentrations, and sorption data for smectites was also considered.

Sedimentary rocks in Canada, for example in the Michigan Basin and the Western Canada Sedimentary Basin, have been observed to contain brackish to highly saline fluids. Table 2 summarizes the reference groundwater compositions which are used as a guide to establishing the range of water chemistries for which sorption data must be relevant. The reference groundwaters include Ca-Na-Cl, Na-Ca-Cl, and NaCl brines with TDS concentration of 157-317 g/L, as well as a saline water SR-20 with TDS of 20 g/L that is more oxidizing. The ionic strengths range up to 7.2 mol/kgw (M), based on PHREEQC Version 3.1.2 (Parkhurst and Appelo 1999) calculations using the SIT database that was provided with PHREEQC. It should be noted that the reliability of the SIT database at ionic strengths above 4 M is questionable. As discussed later in the speciation calculations, Pitzer parameters are not available for most of the 29 elements, and thus the SIT database was used in this report for speciation and ionic strength calculations. The brines are all reducing, and the saline water is less reducing. The pH of these waters is expected to be near neutral. In this report, the reference SR-270-PW brine solution was used for sorption modelling purposes and it is also the brine that has been used for "in-house" sorption measurements that have contributed to the database development (Vilks 2011; Vilks and Miller 2014, 2018; Bertetti 2016; Nagasaki et al. 2016, 2017; Nagasaki 2018).

Chapter 2 in this report provides the background information for the criteria and modelling used for identifying and recommending K_d values for saline solutions. The principal differences in this report, when compared to Vilks (2011), are found in Chapter 3 – including the addition of 9 new elements, new data acquired from the literature, new modelling results and changes to the recommended values for 19 elements. Chapter 4 provides a summary of recommended sorption values.

Table 1: Mineralogical Compositions of Reference Rock/Clay

Argillaceous Limestone	**Shale**	**Bentonite Clay Seal**	**Bentonite/Sand Seal**
2% porosity	7% porosity	100% MX-80 clay dry bulk density 1.6 Mg/m^3	70% MX-80 clay with 30% silica sand dry bulk density 1.6 Mg/m^3
calcite 80 wt% dolomite 7 wt% illite 5 wt% chlorite 5 wt% quartz 2 wt% other 1 wt%	clay 60 wt% - illite 60 wt% - chlorite 40 wt% quartz 30 wt% feldspars 3 wt% dolomite 2 wt% other 5 wt%	montmorillonite 82 wt% quartz 3 wt% felds. & mica 8 wt% cristobalite/tridymite 4 wt% pyrite, calcite, illite, gypsum 3 wt%	See previous column for MX-80, diluted by 30 wt% silica sand

Table 2: Reference Sedimentary Groundwater Compositions

Water Name	**SR-300**	**SR-270-PW**	**SR-270-NaCl**	**SR-160**	**SR-20**
Nominal pH	6.0	6.0	6.1	6.5	6.5
Redox State	Reducing	Reducing	Reducing	Reducing	Oxidizing
Nominal Eh (mV)	-200	-200	-200	-200	90
Solutes (mg/L)					
Na	43,100	50,100	101,200	37,000	4,300
K	3,600	12,500	-	1,780	130
Ca	57,300	32,000	3,700	14,700	1,500
Mg	9,900	8,200	1,300	3,900	900
HCO_3	40	110	180	50	330
SO_4	160	440	2,470	420	1,100
Cl	199,500	168,500	165,000	97,600	11,300
Br	2,000	1,700	-	570	80
Sr	900	1200	-	510	30
Li	7	5	-	7	-
F	2	2	-	5	-
I	90	3	-	90	-
B	-	80	-	-	-
Si	5	4	-	10	-
Fe	30	30	-	30	0.1
NO_3	<10	<10	-	<10	-
PO_4	-	-	-	-	-
TDS (mg/L)	317,000	275,000	273,000	157,000	20,000
Ionic Strength (M) *	7.2 (8.1)	6.0 (6.7)	5.3 (5.5)	3.2 (3.4)	0.40
Water type	Ca-Na-Cl	Na-Ca-Cl	Na-Cl	Na-Ca-Cl	Na-Cl

* Ionic strength estimated using PHREEQC Version 3.1.2 (SIT database); the ionic strength in the bracket is estimated with the Pitzer database (pitzer.dat).

- not available

2. CONSIDERATIONS FOR SELECTING SORPTION VALUES

2.1 SORPTION MECHANISMS

This section summarizes the current understanding of sorption processes. This provides important information for selecting those sorption values that are the most relevant for describing radionuclide sorption on sedimentary rocks in contact with solutions with a range of salinities.

Non-specific coulombic sorption: Mineral surfaces may acquire a charge either from a permanent charge imbalance in the structure or from potential determining reactions at surface sites. For example, in clay minerals a negative charge imbalance in the structure can result from the substitution of small quantities of Mg^{+2} for Al^{+3} in the octahedral layer or from the replacement of Si^{+4} by Al^{+3} in the tetrahedral layer. The charge on a clay surface will be determined by the charge in the structure, provided the atoms at the surface do not interact with the solution to produce a different charge. On the other hand, the edges of clay crystals contain broken bonds resulting from the interruption of the gibbsite and silica sheets. Since the exposed metal ions in this surface layer have a reduced coordination number, they will behave as Lewis acids. In the presence of water, the exposed silica or alumina will coordinate with water molecules (Stumm 1992), as described by equation 1, where $\equiv S^+$ represents a metal at the surface. The resulting surface site, $\equiv SOH$, has a neutral charge.

$$\equiv S^+ + H_2O \Leftrightarrow \equiv SOH + H^+ \qquad (1)$$

The acid base properties of the surface site are determined by the reactions described by equations 2 and 3. The values of the protolysis constants associated with reactions 2 and 3 depend upon the mineral and the exposed metal creating the surface site. Depending upon the pH, the charge on the surface site can be either positive ($\equiv SOH_2^+$), neutral ($\equiv SOH$), or negative ($\equiv SO^-$). Therefore, the charge on the surface dominated by these sites will be positive at low pH and become negative above a certain pH value that is specific to the composition of the solid.

$$\equiv SOH + H^+ \Leftrightarrow \equiv SOH_2^+ \qquad (2)$$

$$\equiv SOH \Leftrightarrow \equiv SO^- + H^+ \qquad (3)$$

The cations located near a negatively charged surface are subject to the electrostatic pull of the surface and the kinetic energy of the cations, which tries to pull them in various directions away from the surface. As a consequence of these two opposing tendencies, the ions adjacent to the surface form a diffuse layer, which is known as the electric double layer (Figure 1). Ions that have the opposite sign as the surface and that balance the surface charge are known as counter ions. The counter ion concentration is maximum immediately adjacent to the surface and decreases away from the surface as described by the Boltzmann function (Parks 1967). Stern (1924) proposed the existence of a surface monolayer in which the total amount of adsorbed ions is restricted by their size and available surface area. The Stern layer neutralizes some of the charge on the surface so that the diffuse layer must neutralize a smaller charge than is found at the immediate surface.

In the diffuse layer, ions are able to move freely as in the free solution, so that there is minimal entropy decrease with sorption. Therefore, adsorption of ions in the diffuse layer should not be affected by temperature. In the Stern layer, ion movement is more restricted, causing an entropy decrease during sorption that should result in decreased sorption at a higher temperature. In the Stern layer, cations must compete for space and ions with smaller hydrated radii are preferred. Also, since ions with smaller hydrated radii can approach the surface more closely, Coulomb's law predicts that they will be sorbed more strongly. Gouy-Chapman theory (Stumm 1992) of the diffuse layer does not distinguish between ions by any property other than charge. Non-specific coulombic sorption should be completely reversible because no bonds have to be broken to remove a sorbed ion. Since diffusion is the only rate limiting step, sorption and exchange rates should be very fast. As salt levels are increased, any trace cations will be displaced from the surface by cations in the solution with higher concentration or a higher sorption affinity.

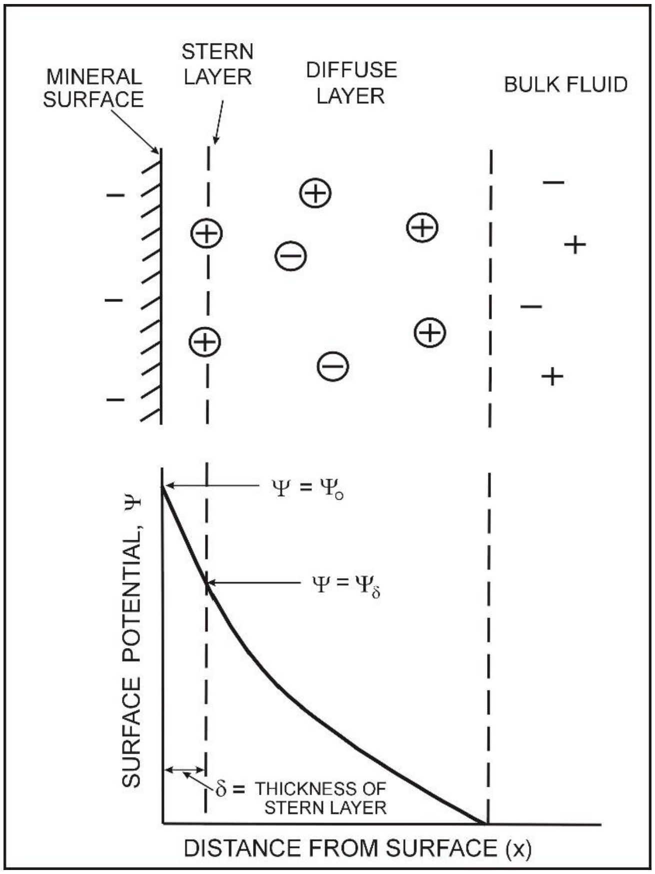


Figure 1: A Schematic Diagram Showing the Distribution of Ions and Electric Potential with Distance from a Charged Surface According to Stern's Model (Stern 1924)

Coulombic sorption can be conceptualized and described as an ion exchange reaction. In the case of cations, the sorbing cation would displace a cation (including H^+) that was present in the diffuse layer or the Stern layer of the negatively charged surfaces of the solid. In this cation exchange process, charge balance would be maintained, such that 2 monovalent cations would interact with 1 divalent cation. Cation exchange reactions and associated selectivity coefficients are described by equations 8 and 9 in Section 2.5. A key parameter in quantifying cation exchange reactions is the cation exchange capacity (CEC). The CEC is defined as the moles of adsorbed cationic charge per unit mass of solid that compensates the negative charge associated with the crystal structure of the solid. The CEC is determined by first saturating the solid with a “standard” cation (Na^+, Cs^+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}) to displace all exchangeable cations. Commonly the next step is to wash out the excess of the “standard” salt. The amount of “standard” salt is then determined by displacing it with another salt and measuring it in solution. Alternatively, the “standard” salt contains a radioisotope that can be determined without having to displace it with another cation. CEC measurements can provide a good measure of the total exchangeable cations provided the standard salt is able to displace all exchangeable cations and provided it is not affected by hydrolysis.

In summary, coulombic sorption has very rapid sorption and desorption kinetics and is very reversible. It is an important sorption mechanism for group 1 and 2 cations, which form weaker bonds with oxygen than transition metals. Higher valence cations are preferred, but cations of the same valence have only a slight relative selectivity determined by their hydrated radii. The temperature dependence of non-specific sorption should be small. In practice it will probably not be feasible to distinguish non-specific sorption in the diffuse layer from that in the Stern layer. Since non-specific coulombic attractions interact with ions as if the ions were point charges without other significant chemical properties, the cations of a salt solution may displace trace cations from surfaces. Thus, radionuclides that are attached to surfaces only by non-specific coulombic attraction may not sorb in brine solutions.

Specific chemical sorption: Due to the ability of metals to be sorbed in sea water, Jenne (1977) operationally defined specific chemical sorption as “that quantity adsorbed from micro concentrations of the trace element in the presence of macro concentrations of alkaline earth or alkali cations, and which is largely desorbable by chemically similar elements”. Specific chemical sorption is also used to explain the sharp increase in sorption with pH produced in the mid pH ranges (Figure 2). If sorption on Fe oxide was only controlled by charge, one would expect the sorption of all cations to increase in a narrow pH range where the positive charge of the oxide became negative as the pH became higher than the pH value at which the oxide has zero charge. Since the pH increases of the different metals do not occur in the same pH range, something other than coulombic attraction must be responsible for their sorption. This phenomenon of a sharp increase in sorption with pH was described for the sorption of transition metals on oxides of Si, Al, Fe, and Mn by Kurbatov et al. (1951), Dugger et al. (1964), Grimme (1968), James and Healy (1972), Schindler et al. (1976), and Hohl and Stumm (1976). The sorption jump for different metals occurs at different pH values. The cations with the strongest hydrolysis constants have their sorption jumps at lower pH values, suggesting the formation of metal oxygen bonds is responsible for specific chemical sorption.

The most common concept used to explain specific chemical sorption is surface complexation, which involves metal complexation with surface oxygen atoms. Surface complexation has been widely proposed to explain metal sorption on oxides (Dugger et al. 1964, Schindler et al. 1976, Hohl and Stumm 1976, and Davis et al. 1978). Oxide surfaces and the edges of clay minerals have broken bonds where unsatisfied oxygen atoms are exposed. These oxygen atoms quickly bond H^+ from the surrounding water. The ability of metal ions to sorb and displace H^+ from these surface oxygens depends upon the pH and the composition of the solution. Therefore, the sorption of metal ions can be treated as a coordination reaction with a surface ligand. Using this approach, Schindler et al. (1976) were able to model Fe, Cu, Cd and Pb sorption on silica, and Hohl and Stumm (1976) were able to model Pb sorption on gamma Al_2O_3.

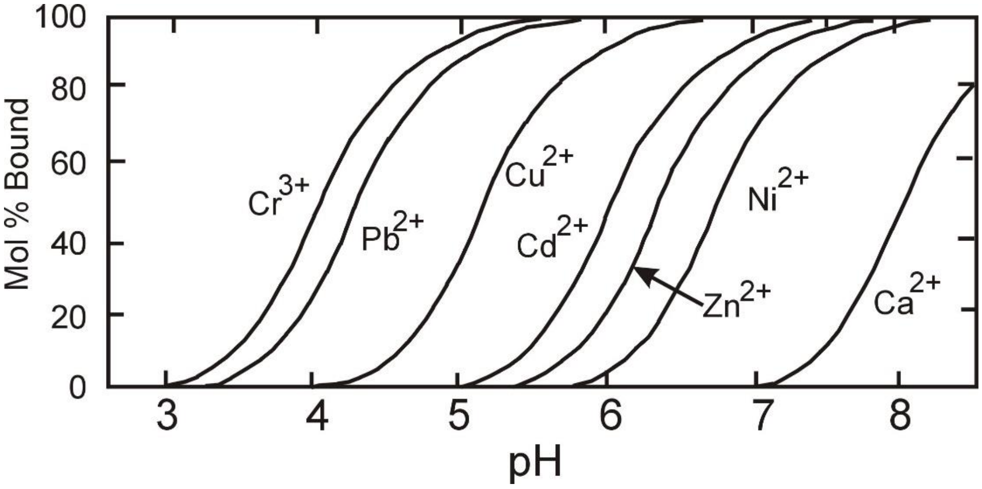


Figure 2: The pH Dependence of Metal Sorption on Fe Oxide (After Stumm 1992)

Discussions of surface complexation often include the terms “inner-sphere complex” and “outer-sphere complex”. An inner-sphere complex refers to a case where a chemical (largely covalent) bond is formed between the metal and the electron donating oxygen ion (Stumm 1992). The inner-sphere complex is located in direct contact with the mineral surface shown in Figure 1. An outer-sphere complex is formed when a cation approaches negatively charged surface groups to within a critical distance, which is the Stern layer shown in Figure 1. This is analogous to solute ion pairs in solution in which the cation and anion are separated by one or more water molecules (Stumm 1992). Outer-sphere complexes can be considered as being held by coulombic attraction within the Stern layer (Figure 1). However, outer sphere complexes are considered distinct from ions held in the diffuse layer, whose movements are less restricted, as previously discussed.

Structural penetration: The penetration of metals into mineral structures has been proposed by some researchers as one possible mechanism to explain metal fixation in clays (Elgabaly 1950, Nelson and Melsted 1955; Tiller and Hodgson 1960). Hodgson (1960) looked at Co sorption on montmorillonite in the presence of 0.1 M $CaCl_2$ solution, which is expected to reduce or eliminate electrostatic adsorption of Co. He found a fast (several hours) and reversible sorption reaction, which was attributed to chemisorption in a surface monolayer, and a slow irreversible sorption thought to represent penetration of Co into the montmorillonite structure.

If cations are to penetrate a mineral structure, they must be dehydrated and their dehydrated radius must fit into the crystal structure. Calvet and Prost (1971) and McBride and Mortland (1974) suggested that as cations are dehydrated, they may penetrate clays by entering into the hexagonal holes of the tetrahedral layer, and if they are small enough, they may pass to vacant octahedral sites. If these cations remain in the hexagonal hole, they may be rehydrated; while if they are in the octahedral layer, they remain fixed when water is added to the clay. McBride and Mortland (1974) have shown that cations as large as Cu could enter the octahedral layer, while Calvet and Prost (1971) have indicated that K, Ca and probably Na are too large to enter. However, should cations enter into fractures, cleavages or other defects, then such size restrictions may no longer be valid.

Chemical substitution is a special case of structural penetration. A dissolved constituent is removed from solution by chemical substitution when it is incorporated into a solid by replacing a chemically similar constituent that makes up the main component of the solid phase. This usually involves the formation of a solid solution, whose solubility may be lower than the original solid before the addition of the dissolved constituent. The dissolved constituent may be either an anion or a cation, and is likely to be a trace element. Chemical substitution may occur by the incorporation of the dissolved constituent into an existing solid, or during a co-precipitation process. Examples of chemical substitution include the replacement of Ca in calcite by Cd (Davis et al. 1978), and the replacement of sulphur by iodide ions in galena and other sulphide minerals (Strickert et al. 1980; Zhuang et al. 1988). In some cases, chemical substitution may be irreversible (Zhuang et al. 1988).

In summary, structural penetration is a very slow process, limited by dehydration and solid-state diffusion. Any cation that has penetrated the structure will be irreversibly sorbed. Structural penetration likely will be limited to cations with a radius not greater than around 0.74 angstroms, if the cation must pass through the tetrahedral layer. Penetration of a cation into a mineral structure may be favoured at higher pH values and higher temperatures.

Isotopic exchange: This is not strictly a sorption process. All radioisotopes that are released from a waste form, with the exception of Pm, Tc and the higher actinides, have corresponding stable isotopes in nature (Vandergraaf and Ticknor 1994). When released to the environment, a radioisotope will exchange with its stable isotopes on solids and in solutions. The isotope will most readily exchange with stable isotopes on solids that are sorbed by coulombic attraction. However, exchange may also occur with inner sphere isotopes, as well as isotopes that are part of the mineral structure. The exchange of a radioisotope in solution with a stable isotope in a solid will reduce the concentration of radioisotope in solution. For example, the concentration of ^{14}C in solution can be reduced by isotopic exchange with stable C in calcite (Mozeto et al. 1984).

Physical sorption: This sorption mechanism (Serne 1992) is caused by non-specific, long-range forces of attraction that involve the entire electron shells of the sorbate and the sorbing surface (such as Van der Waal's forces). This mechanism has been used to conceptualize the sorption of neutral metal hydrolysis complexes on solid surfaces that are also neutral. Physical sorption is believed to be rapid and reversible, and independent of 1) temperature, 2) the chemical composition of the sorbing solid, and 3) the ionic strength of the solution. Physical sorption is affected by pH, which determines whether neutral hydrolysis complexes are present and whether the mineral surfaces are neutral.

Summary: An element may sorb by one or more mechanisms, depending on its chemistry, the chemical composition of the solution, and the properties of the sorbing solid. The element that sorbs only by non-specific coulombic attraction may not sorb to any significant extent in brine solutions due to the competitive sorption behavior of cations in the brine solutions, and in particular the competitive sorption of the Ca^{2+} ion. Its sorption coefficients determined in dilute solutions cannot be used for brine solutions. The sorption of an element that is affected only by specific chemical sorption may not be significantly affected by the salt concentration, but will likely be affected by the pH of the solution, particularly in the vicinity of a sorption edge. Therefore, its sorption coefficients determined in lower ionic strength solutions can probably be used for brine solutions. However, when selecting sorption coefficient K_d values from the literature to apply to the reference brine solutions, one should understand how the element's sorption varies with pH, which helps to identify the element's sorption mechanism(s).

Many elements sorb by a combination of coulombic attraction and specific chemical sorption. In dilute solutions, the coulombic component may dominate or be very important if the pH of solution is in the right range for the sorbing element to exist as a positively charged species and for the surface complexation to be insignificant. In brine solutions, only specific chemical sorption will be a factor. When selecting sorption values for these elements, one should consider their sorption mechanisms, the relationships between sorption and the ionic strength of solution, and the relationship between sorption and the pH of solution. Sorption values from solutions with ionic strengths and pH values close to the reference brine solutions are preferred. If structural penetration is an important sorption mechanism for a given element in brine (such as Cs^+), one should consider that this is a slow process and should select sorption values measured over longer time periods.

2.2 DATA SOURCES

The sorption data compiled in this report were taken from the open literature and from published sorption databases. Sorption databases that were consulted included: (1) the Canadian sorption database for crystalline rock (Vandergraaf and Ticknor 1994; Ticknor and Vandergraaf 1996); (2) the Swedish sorption dat abase for granite (Carbol and Engkvist 1997; Crawford et al. 2006); (3) the Swiss sorption database for Opalinus clay and bentonite (Bradbury and Baeyens 2003a, 2003b); (4) the sorption database for the WIPP site in dolomite (USEPA 1998; Lucero et al. 1998); (5) the existing sorption data for OPG's proposed deep geological repository (DGR) for low and intermediate level nuclear waste in sedimentary rock (Walke et al. 2011); and (6) the Japanese sorption database for a broad range of rocks and minerals (Tachi et al. 2009; Japan SDB https://migrationdb.jaea.go.jp). The Japanese online sorption database is a very useful compilation of data, allowing the user to search a broad variety of sorption coefficients for different minerals, rock types and solution compositions.

Sorption data are most commonly reported in the form of a sorption coefficient. If a contaminant's concentration in solution is low enough, its sorption may be linear with its concentration and a sorption coefficient or distribution coefficient can be used to describe its sorption behaviour. The sorption coefficient is defined as

$$K_d = \frac{S}{C} \qquad \text{or} \qquad R_d = \frac{S}{C} \tag{4}$$

where S is the concentration of sorbed sorbate (mol/kg)
C is the concentration of sorbate in solution (mol/m^3)
K_d and R_d are sorption coefficients (m^3/kg)

The sorption coefficient is a convenient and simple way of expressing sorption. However, it is an empirical parameter and by itself tells us very little about the sorption reaction mechanism. It may change with pH of solution, the solid/liquid ratio and the ionic strength of solution. If Henry's law is not obeyed at high sorbate concentrations, sorption will no longer be a linear function of sorbate concentration. Originally the concept of a sorption coefficient (K_d) assumed that the sorption reaction is reversible and that the measured sorption coefficient represents equilibrium. However, the concept of reversible sorption reactions has been questioned by numerous authors, and often it may be difficult to prove that the sorption data represent a true equilibrium measurement. Since sorption measurements may represent an approximation of an equilibrium K_d, it has become a common practice to present sorption data as an empirical sorption coefficient, designated as R_d (Vandergraaf and Ticknor 1994). The validity of using sorption coefficients has been the subject of much debate. A comparison of K_d values obtained from batch and mass transport tests is one way to address this debate. Despite the debate, the fact remains that all sorption experiments measure a sorption coefficient and, in mass transport calculations, the detailed understanding of particular sorption processes is condensed into sorption coefficient values.

If sorption measurements are being performed on rock coupons in which the sorbate does not significantly penetrate into the mass of the coupon and sorption occurs mainly on the surface, it is better to report sorption in terms of sorbed mass per specific surface area (A_{sp}). The specific surface area has units of area per mass solid (m^2/kg). In this case the sorption coefficient is defined as K_a or R_a where

$$K_a = \frac{S_a}{C} \approx R_a \quad \text{(m)} \qquad (5)$$

and where S_a is the concentraton of the sorbed sorbate (mol/m^2). The value of R_a is related to R_d by the following:

$$R_a = \frac{R_d}{A_{sp}} \qquad (6)$$

In this report the sorption values will be reported as the traditional mass based sorption coefficient, K_d, with units of m^3/kg. Elements that have a K_d value of 0, will not sorb and will be transported with the same velocity as groundwater. Elements with K_d values of 0.0001 m^3/kg and lower are weakly sorbed. As K_d values increase from 0.0001 to 1.0 m^3/kg, sorption becomes progressively stronger and retardation more significant. K_d values that are greater than 1 m^3/kg are extremely high and indicate that the element is essentially immobile (Freeze and Cherry 1979).

The data compiled in this report were obtained mostly from batch sorption experiments. Those values obtained from mass transport studies are identified as being derived from transport tests. Batch sorption methods in various configurations have provided the largest fraction of sorption data because of their relative simplicity, lower cost, and lack of complicating factors associated with mass transport experiments. In batch experiments, the sorbing solid and the solution containing the sorbate (usually dissolved ion) are contained in a vessel. The parameters that should be considered during the batch sorption tests include: (1) the mass, physical form (crushed or solid) and composition of the solid; (2) the composition of the solution (TDS, pH, Eh, sorbate and complexing ligand concentrations); (3) the atmospheric composition (pO_2, pCO_2); (4) solid /liquid ratio; and (5) temperature. After a given sorption reaction time, the solid and liquid are separated by centrifugation or filtration, and the liquid (or solid) are characterized for sorbate concentration (or chemical form). Batch methods have been used for both sorption and desorption reactions.

Many sorption studies have been performed over a wide pH range in order to define the sorption edge, which marks the pH interval where there is a dramatic increase in sorption as a result of surface charge reversal or deprotonation of surface complexation sites. The challenge with performing sorption experiments over an extended time period at a controlled pH value is that the solids tend to buffer solution pH. This buffering action, as well as the addition of acid or base to control the pH, will change the sorbing surfaces with time. As a result, sorption experiments are often focused on a limited pH range (Vandergraaf and Ticknor 1994). The Eh is also very difficult to control if there is a need to work under reducing conditions. It is possible to perform sorption experiments in anaerobic chambers to eliminate atmospheric O_2. However, without redox buffering components in the water, it may not be possible to reproduce in-situ reducing conditions in laboratory experiments (Kumata and Vandergraaf 1998). Therefore, the addition of redox buffers, such as NaHS or hydrazine, has been used to achieve reducing conditions.

Mass transport experiments for sorbing radionuclides have been used extensively to improve understanding of the sorption processes during mass transport and to derive sorption coefficients. Mass transport experiments include diffusion, advection, and diffusion combined with advection methods. The mass transport results are then simulated by mass transport calculations using both measured physical transport parameters (such as porosity and tortuosity) and measured sorption data. For example, Ohlsson and Neretnieks (1997) produced a set of apparent diffusion coefficients for Aspö granite based on diffusion measurements with tritium (physical transport) and sorption data from Carbol and Engkvist (1997). The validity of this approach needs to be demonstrated by mass transport experiments and the understanding of the sorption processes occurring during mass transport. In some cases, where sorption is very weak, mass transport tests may be able to quantify sorption that could not be detected in batch studies.

The application of batch derived sorption values to mass transport experiments often requires the application of scaling factors to account for the difference in the available surface area between the batch and transport tests. It is not the purpose of this report to discuss these scaling factors. However, scaling factors, such as the solid/liquid ratio, sorption time, and the conditioning of the solid phases with the aqueous phase before the sorption test are aspects that may be considered. The solid/liquid ratio may affect the value of a sorption coefficient and is important for determining a sorption value with a reasonable accuracy. Typically, sorption experiments last for 1 to 4 weeks, or longer. These sorption experimental times are virtually instantaneous in comparison to the time scales used in the performance assessment calculations. Sorption values usually increase with the experimental time, but the stability of the solid phase may become an issue for extended sorption reaction periods. The use of conditioned solids is a good practice to help eliminate artefacts associated with grinding and to establish a system with a stable pH over the duration of the experiment.

Different experimental designs and execution will introduce various levels of uncertainty in the sorption values reported in the literature. Measured sorption values that are lower than the actual in-situ values are conservative; while reported sorption values that are higher than the actual in-situ values are non-conservative, i.e., they result in over prediction of radionuclide retardation. The measurement and control of pH may pose difficulties in high ionic strength solutions or if the solids are buffering the pH to a value that is outside the desired experimental range. In some cases, the reported experimental pH value might have drifted over several pH units and the pH was poorly defined. In these cases, the uncertainty in reported sorption values could be moderate to high. Redox control under reducing conditions is difficult. In the case of redox sensitive elements, such as U(IV) or Tc(IV), the uncertainty associated with poor redox control can be high, particularly if the Eh values of the experiments were not reported. Fortunately, in the case of these two elements, poor redox control would result in conservative sorption values. The choice of sorbate concentration could introduce a low to moderate level of uncertainty. If the sorption isotherm is nonlinear, measured K_d values will decrease with higher sorbate concentration. Since radionuclides released to groundwater are likely to be at trace concentrations, the K_d values determined at higher sorbate concentrations are conservative. However, sorption values derived from experiments where the sorbate concentration is high enough (i.e., exceeding its solubility limit) to induce precipitation should not be used because the resulting sorption values may be high and non-conservative. The experimental sorption reaction time lasting for several days to a week may introduce a relatively low uncertainty. Since sorption appears to increase with time, short term sorption tests (hours to several days) will produce conservative sorption values. The steps used for conditioning solids to remove the effects of sample grinding have some effect on sorption values, but the uncertainties introduced by these procedures are relatively low (Vilks et al. 2011).

2.3 SELECTION CRITERIA

The following sections describe some of the factors that are considered in the selection of sorption values for sedimentary rocks (shale and limestone) from the literature and sorption databases. These include: 1) water chemistry used in sorption measurements in comparison to the reference groundwaters; 2) rocks and minerals of interest in the sedimentary environment; and 3) chemical analogs.

2.3.1 Water Chemistry

Water chemistry plays a key role in sorption reactions and is given a high priority in selecting sorption data. The pH of water affects hydrolysis and surface complexation reactions of elements. As illustrated in Figure 2, most elements that have a tendency to hydrolyze display a sharp increase in sorption at a particular pH value, referred to as the sorption edge. The position of the sorption edge varies from element to element. The selection of the sorption value will become simpler if the sorption of a given element has reached a plateau in the pH range of interest for the Canadian sedimentary rocks (i.e., pH of 6 to 7). This will be best determined by plotting sorption data for the given element as a function of pH. In an ideal situation, sorption data can be selected in the pH range of 6 to 7. If not, then a judgement must be made as to whether a given sorption value is applicable, based on the known trend of sorption with respect to pH.

The total salt concentration, as well as the dissolved constituents, influences the sorption of elements in several ways. The ionic strength of solution influences activity coefficients of dissolved and sorbed species. More importantly, the competitive sorption of major ions (Na^+, Ca^{2+}, Mg^{2+}, K^+) reduces sorption of elements, particularly the group 1 and 2 elements. For example, the sorption coefficient for Ra^{2+} measured in a dilute solution with an ionic strength of 0.001 M would not be applicable to sea water or brine with an ionic strength of 2 M. Divalent cations are more effective than monovalent cations at displacing elements sorbed on a solid by coulombic attraction due to their divalent charge. If a trace element sorbs only by coulombic attraction, its sorption in a brine solution is likely to be reduced to 0. However, if a trace element sorbs by surface complexation reactions, then its sorption will not be reduced to the same extent because the major salt ions may not be able to participate in the surface complexation reactions due to their weaker hydrolysis constants. Even though the major cations do not participate strongly in surface complexation reactions they might have some effect on sorption due to their high concentration. For example, the Ca^{2+} ion is weakly sorbed by surface complexation reactions and could affect the sorption of some elements. Vilks et al. (2011) noted that Ca^{2+} reduced the sorption of Ni^{2+} but not U(VI). The presence of anions, such as HCO_3^-, may complex with and reduce sorption of metals. For example, Vilks et al. (2011) observed that U(VI) sorption was reduced in the presence of higher carbonate concentrations.

For the purposes of this report, it was desirable to choose a parameter that could be used to identify the effect of salt concentration on sorption. Ionic strength of solution was chosen because it summarizes the total ion concentration (as molar quantities) and the influence of ion charges. Sorption values of an element as a function of ionic strength may help to determine whether the element will sorb in a brine solution, or whether the sorption data can be extrapolated from a low ionic strength to brine conditions. Therefore, the initial selection process tries to capture sorption values over a range of ionic strengths, including brine if possible.

Some elements have different dominant oxidation states depending upon the redox conditions. For these elements, it is important to report sorption values for both oxidizing and reducing conditions. Although deep groundwater is generally reducing, it is also useful to have sorption data for oxidizing conditions to compare with sorption data for reducing conditions to illustrate the effect of the redox on sorption. The redox condition at which a given element switches between reduced and oxidized form is specific to that element. In this report, these redox conditions are identified for each redox sensitive element in the form of an approximate Eh value. These Eh values were based on the SR-270-PW brine solution with a pH value of 6. Note that these Eh values, which depend on pH, should be used as an approximate guide. For redox sensitive elements, it is important to distinguish between those measurements made in an aerobic atmosphere from those made in solutions where redox has been controlled and reducing conditions maintained.

2.3.2 Mineralogy and Rock Type

In selecting sorption data the first priority was given to bentonite, shale, and limestone. Since the composition of rocks is variable and the sorption of many elements was not measured on every type of sedimentary rock, the initial selection process also focused on key minerals making up the reference bentonite, shale, and limestone (Table 1). Minerals making up bentonite include the swelling clays, montmorillonite, and smectite. The principle components of shale are illite, chlorite, and quartz. Limestone is composed mostly of calcite and dolomite, with approximately 10% illite and chlorite. In this report no distinction is made between calcite and dolomite since they are both carbonates.

If sorption values for bentonite, shale, and limestone are available for solutions with reasonably similar compositions to the reference groundwater (Table 2), they were selected as recommended values. Since bentonite is composed mainly of expanding clays such as montmorillonite or smectite, sorption data from these expanding clays were considered to approximate sorption on bentonite. No adjustments were made to sorption values from montomorillonite or smectite to account for the fact that the fraction of these clays in bentonite is less than 100%.

If sorption data for shale are not available, data for some other clay rich rock, such as mudstone, were used as an approximation. If sorption data for illite and/or chlorite are available, these data were also used to estimate sorption on shale. The assumption made is that the total clay content of shale is 60%, and the remaining minerals (quartz, feldspar and carbonate) do not sorb significantly compared to the clay component. Vilks and Miller (2014) found that, in the case of Ni, Cu, Pb and U, if calculated sorption values for illite were reduced by 40% (i.e. reduced to to 60%), they would match measured sorption values for shale. With this assumption, the sorption value of the clay (e.g., illite) is reduced by 40% of its original value to estimate shale sorption value. If reasonable sorption data for both illite and chlorite are available, a weighted average (60% illite and 40% chlorite) was used to represent sorption on the clay fraction of the shale. However, in most instances sorption values were available only for illite or chlorite. In these cases it was assumed that the entire clay component of shale could be approximated by either illite or chlorite. This suggests that the literature reported sorption values for illite should be reduced by 40% of their given values to represent sorption values for shale.

Sorption values for marl were used to estimate sorption for limestone. Otherwise, sorption on limestone is approximated by sorption values reported for calcite. At this time the sorption properties of the clay minerals that might be present in the limestone were not considered, and the calcite content of limestone was assumed to be 100%.

2.3.3 Use of Analog Elements

Chemical analogs are used for those elements without measured sorption data because they are difficult to study experimentally due to redox control issues, low solubility and detection issues, or challenges with licensing the use of radioisotopes in field-scale experiments.

Lanthanide elements, such as Sm, Eu, and Ho, have been used as chemical analogs for trivalent actinides Ac(III), Pu(III), Am(III) and Cm(III). Since Th(IV) is not redox sensitive it can be used as an analog for tetravalent actinides U(IV), Np(IV), and Pu(IV), which require strictly controlled reducing conditions for study. For example, the USEPA (1998) reported sorption data for Am(III), Pu(III), Pu(IV), U(IV), U(VI), Th(IV), Np(IV) and Np(V) for performance assessment of the WIPP site. The sorption data were based on batch sorption experiments performed at Los Alamos, and on transport experiments using intact dolomite cores. First, K_d ranges were established for Am(III), Th(IV), Np(V) and U(VI). Then, the oxidation-state analogy approach was used to extrapolate the established sorption ranges to represent Pu(III) by Am(III), and Pu(IV), U(IV), Np(IV) by Th(IV).

The use of chemical analogs was significantly reduced in this revised sorption database report compared to the previous report (Vilks 2011). In this report, measurements of Sr(II) sorption in brine solution were used as a chemical analog for Ra(II) sorption on bentonite, shale and limestone. The analog for trivalent elements was Eu(III), which was used for Bi(III) and Am(III) sorbing on limestone. The main attraction for using Eu(III) was that its sorption was measured on limestone in brine solutions. Th(IV) was used as an analog for tetravalent actinides, as in the case of U(IV) and Np(IV) sorbing on limestone.

2.4 ELEMENT SPECIATION PREDICTED BY PHREEQC

Element speciation was predicted using PHREEQC (Parkhurst and Appelo 1999), a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations that can be downloaded from the US Geological Survey website. The version used in these calculations was PHREEQC Interactive 3.1.2.

The best estimate of ion activity coefficients in high ionic strength brines is provided by the Pitzer equations. Unfortunately, most of the elements of interest in this report are not included in the Pitzer thermodynamic database, Pitzer.dat, provided with PHREEQC. However, they are included in the sit.dat thermodynamic database distributed with the PHREEQC package.

The sit.dat database distributed with PHREEQC version 3.1.2 is the ThermoChimie v.8.0 database developed for ANDRA, the French National Radioactive Waste Management Agency. The database includes SIT (Specific Ion Interaction Theory) parameters for calculating single ion activity coefficients, when data are available. If the SIT parameters are not available, e.g., for elements such as Bi and Cu, then the Debye-Hückel approach was used for activity corrections. While SIT theory has proved to be simple and adequate for solutions with ionic strengths up to 3-4 M (Grenthe et al. 1997), the Pitzer theory is much better at reproducing experimental behaviour for solutions with ionic strengths up to 20 M (Elizalde and Aparicio 1995).

The sit.dat database was used for the speciation calculations in this report. The main element species for the SR-270-PW reference porewater (Table 2), as calculated using the SIT database, are presented in Table 3.

Table 3: Element Speciation in Reference Groundwater SR-270-PW Predicted by PHREEQC

Element	Oxidation State	Speciation (at Eh = -200 mV; pH = 6.0)
Cl	-I	Cl^- (93%), $MgCl^+$ (7%)
Ca	II	Ca^{+2} (98%), $Ca(SO_4)$ (1.8%), $Ca(HCO_3)^+$ (0.1%)
Ni	II	$NiCl^+$ (63%), Ni^{+2} (36%)
Cu	I	Cu^+ (100%)
As	III	$H_3(AsO_3)$ (100%)
Se	-II	HSe^- (100%) note: HgSe forms if Hg present
Zr	IV	$Zr(OH)_4$ (100%)
Nb	V	$Nb(OH)_6^-$ (92%), $Nb(OH)_5$ (7%), $Nb(OH)_7^{-2}$ (1%)
Mo	VI	MoO_4^{-2} (100%)
Tc	IV	$TcO(OH)_2$ (94%), $Tc(OH)_2CO_3$ (6%)
Pd	II	$PdCl_4^{-2}$ (99%), $PdCl_3^-$ (1%)
Ag	I	$AgCl_4^{-3}$ (99%), $AgCl_3^{-2}$ (1%)
Cd	II	$CdCl_4^{-2}$ (72%), $CdCl_3^-$ (23%), $CdCl_2$ (5%)
Sn	IV	$Sn(OH)_4$ (92%), $SnCl_6^{-2}$ (6%), $Sn(OH)_5^-$ (2%)
I	-I	I^- (53%), CaI^+ (41%), MgI^+ (3%), NaI (3%)
Cs	I	CsCl (64%), Cs^+ (35%)
Eu	III	$EuCl^{+2}$ (51%), Eu^{+3} (30%), $EuCl_2^+$ (10%), $EuSiO(OH)_3^{+2}$ (7%), $EuBr^{+2}$ (1%)
Hg	I	Hg_2^{+2}, note: If Se is present in equal amounts, the II species, HgSe forms.
Pb	II	$PbCl_4^{-2}$ (91%), $PbCl_3^-$ (7%), $PbCl_2$ (2%)
Bi	III	$BiCl_5^{-2}$ (93%), $BiCl_4^-$ (7%)
Ra	II	$RaCl_2$ (44%), Ra^{+2} (37%), $RaCl^+$ (19%)
Th	IV	ThF_2^{+2} (31%), $Th(OH)_3^+$ (27%), ThF^{+3} (11%), $Th(OH)_4$ (9%), ThF_3^+ (6%), $Th(OH)_2^{+2}$ (6%), $Th(OH)_3(CO_3)^-$ (4%), $Th(OH)_2(CO_3)$ (3%), ThF_4 (3%)
Pa	V	PaO_2^+ (96%), $PaO_2(OH)$ (4%)
U	IV	$U(OH)_4$ (77%), $U(OH)_3^+$ (20%)
	V	UO_2^+ (3%)
Np	IV	$Np(OH)_4$ (70%), $Np(OH)_3^+$ (28%), $Np(CO_3)(OH)_3^-$ (2%)
Pu	III	Pu^{+3} (90%), $Pu(OH)^{+2}$(9%), $Pu(CO_3)^+$ (1%)
Am	III	Am^{+3} (45%), $AmCl^{+2}$ (23%), $AmOSi(OH)_3^{+2}$ (21%), $Am(HCO_3)^{+2}$ (5%), $AmCl_2^+$ (3%), $Am(OH)_2^+$ (2%), $Am(CO_3)^+$ (1%)

Note: JAEA thermodynamic database (version 140331s0.tdb) was used for element Bi.
SIT database (Thermochimie TDB incorporated in PHREEQC) was used for all the other elements. The reliability of the SIT database at ionic strengths above 4 M is questionable.

2.5 SURFACE COMPLEXATION MODELLING

Surface complexation modelling has the potential for estimating sorption values that are applicable for in-situ groundwater compositions based on laboratory measured sorption values or sorption properties reported in the literature. For some elements, it may be possible to derive sorption values based on surface site binding constants that are estimated from Linear Free Energy Relationships (LFER) (Bradbury and Baeyens 2005b, 2009b). LFER assumes that for a given metal, there is a relationship between free energies of aqueous species and corresponding surface metal complex constants. This relationship is established for a given solid using measured sorption values for a number of metals. Using this relationship one can predict surface binding constants for other metals based on their aqueous hydrolysis constants.

PHREEQC can be used to incorporate a 2-site protolysis non-electrostatic surface complexation and cation exchange model (2SPNE SC/CE), as described by Baeyens and Bradbury (1997) and Bradbury and Baeyens (1997, 2005a, 2009a). This model assumes that sorption occurring on oxygen sites associated with broken bonds (located on edge sites in clay minerals) can be described by strong and weak amphoteric surface sites. It is also assumed that different minerals may contain the same basic type of sites, except with different site densities (to determine capacities) and slightly different surface binding constants. Site densities and binding constants are determined from acid-base titrations of mineral surfaces (Baeyens and Bradbury 1997). Examples of acid-base surface reactions and associated protolysis constants determined in 0.1 mol/L $NaClO_4$ solution are given in Table 4. Site binding constants are determined by fitting metal sorption data covering a range of pH values and metal concentrations. Model fitting is time consuming because values of site density, protolysis constants and binding constants must be consistent with acid-base titration and sorption edge data (Bradbury and Baeyens 2005a). The constants for the surface complexes, as well as the activity coeffcients of surface species, are considered to be independent of ionic strength. Only the activities of dissolved species are calculated.

Table 4: Surface Protolysis Reactions and Constants for Na-illite and Montmorillonite

Surface Protolysis Reaction	[a]log $K_{protolysis}$ Na-illite	[b]log $K_{protolysis}$ montmorillonite
$\equiv S^{s}OH + H^{+} \Leftrightarrow \equiv S^{s}OH_2^{+}$	4.0	4.5
$\equiv S^{s}OH \Leftrightarrow \equiv S^{s}O^{-} + H^{+}$	-6.2	-7.9
$\equiv S^{w1}OH + H^{+} \Leftrightarrow \equiv S^{w1}OH_2^{+}$	4.0	4.5
$\equiv S^{w1}OH \Leftrightarrow \equiv S^{w1}O^{-} + H^{+}$	-6.2	-7.9
$\equiv S^{w2}OH + H^{+} \Leftrightarrow \equiv S^{w2}OH_2^{+}$	8.5	6.0
$\equiv S^{w2}OH \Leftrightarrow \equiv S^{w2}O^{-} + H^{+}$	-10.5	-10.5

[a] Bradbury and Baeyens (2009a)
[b] Bradbury and Baeyens (2005a)

If sorption isotherms are not linear over the range of metal concentrations used to derive experimental data, a combination of strong and weak sites is required to explain the sorption data. Although strong surface sites, $\equiv S^{s}OH$, have a small surface density, they sorb strongly and account for sorption at trace metal concentrations. The weaker sites have a much higher capacity, but weaker binding constants. The role of the weak sites, $\equiv S^{w1}OH$ and $\equiv S^{w2}OH$, is to account for non-linear sorption behaviour in the presence of high metal concentrations. If the sorption isotherm is linear, the sorption model could be limited to only one type of site. When elements have very low concentrations due to solubility restrictions, as for Th, the contribution of weak sites to the overall sorption process is not significant. Original model development by Bradbury and Baeyens (1997, 1999) for montmorillonite included both strong and weak sites.

When work continued on illite, the decision was made to use only the strong sites. However, even if sorption can be described by one type of site, three site types are required to explain the acid-base titration data for clays.

Surface complexation reactions for metals are formulated by first considering the dominant aqueous species and determining which species are likely to sorb. The approach taken by Bradbury and Baeyens (1997) is to focus on the types of metal hydrolysis species that are present and then to formulate analogous surface species. For example, if the dominant hydroxyl Ni^{+2} species in solution is $NiOH^+$, the corresponding surface species is $\equiv S^sONi^+$. The surface species $\equiv S^sONi(OH)_2^-$ would be equivalent to $Ni(OH)_3^-$. The surface species has one less hydroxyl than the equivalent solutions species. An example of surface complexation reactions and constants for Ni sorbing on montmorillonite (determined in 0.01 to 0.1 mol/L $NaClO_4$ solutions) are provided in Table 5. The general equation used to formulate surface complexation reactions with a metal, Me, having a charge, z, is as follows:

$$\equiv S^sOH + Me^z + yH_2O \Leftrightarrow \equiv S^sOMe(OH)_y^{z-(y+1)} + (y+1)H^+ \qquad (7)$$

Table 5: Nickel Surface Complexation Reactions and Constants for Montmorillonite

Ni Surface Complexation Reaction	Strong Site log $^sK_{x-1}$ montmorillonite	Weak Site log $^{w1}K_{x-1}$ montmorillonite
$\equiv S^sOH + Ni^{+2} \Leftrightarrow \equiv S^sONi^+ + H^+$	-0.6	
$\equiv S^sOH + Ni^{+2} + H_2O \Leftrightarrow \equiv S^sONiOH^0 + 2H^+$	-10	
$\equiv S^sOH + Ni^{+2} + 2H_2O \Leftrightarrow \equiv S^sONi(OH)_2^- + 2H^+$	-20	
$\equiv S^{w1}OH + Ni^{+2} \Leftrightarrow \equiv S^{w1}ONi^+ + H^+$		-3.3

From Bradbury and Baeyens (2005a)

Sorption by coulombic cation exchange reactions can be described with the following exchange reaction describing the exchange of element B, having a charge of b, with element A on solid, having a charge a.

$$bA^a\text{-solid} + aB^b \Leftrightarrow aB^b\text{-solid} + bA^a \qquad (8)$$

The thermodynamic exchange constant for the reaction can be defined as:

$$^B_AK = \frac{(N_B)^a}{(N_A)^b} \times \frac{(f_B)^a}{(f_A)^b} \times \frac{[A]^b}{[B]^a} \times \frac{(\gamma_A)^b}{(\gamma_B)^a} = {}^B_AK_c \times \frac{(f_B)^a}{(f_A)^b} \qquad (9)$$

The thermodynamic exchange constant is ^B_AK, and $^B_AK_c$ is the selectivity coefficient that is valid when the fraction of B on the exchange sites is very small to avoid issues of nonideal mixing of A and B . The equivalent fractions of A and B located on the exchange sites are N_A and N_B, which are defined as equivalents of A or B sorbed per unit mass, divided by the Cation Exchange Capacity (CEC). The total amount of cations in the exchange sites is determined by the CEC which is given in terms of equivalents per mass of solid (kg). The surface activity coefficients are f_A and f_B, while the aqueous activity coefficients are γ_A and γ_B. Aqueous concentrations are [A] and [B]. The distribution ratio between solid and solution (${}^{B}R_d$) of element B that is attributed to cation exchange is defined as:

$$ {}^{B}R_d = \frac{Amount\ of\ sorbate\ B\ on\ solid\ per\ unit\ mass}{Sorbate\ aqueous\ concentration} \tag{10}$$

The value of ${}^{B}R_d$ can be related to the selectivity coefficient if the CEC and the solution activity coefficients are known (Bradbury and Baeyens 2005b) (The following equation is changed from that in Bradbury and Baeyens (2005b)).

$$ {}^{B}K_c = ({}^{B}R_d)^a \times \frac{b^a}{CEC^a} \times [A]^b \times \frac{(\gamma_A)^b}{(\gamma_B)^a} \tag{11}$$

In practice, it is assumed that the CEC of the sorbing solid is dominated by either Na or Ca. Selectivity coefficients with respect to Na or Ca are available for clay minerals for a number of elements. When cation exchange is included in sorption modelling with a code such as PHREEQC, it is apparent that cation exchange of metals with Na or Ca is most important when the concentrations of Na and Ca in solution are low, and at lower pH values where the aqueous speciation of sorbing species is dominated by positively charged species. Cation exchange is not considered for elements dominated by neutral or anionic species.

PHREEQC was used to simulate Ni sorption on Na-montmorillonite and Ca-montmorillonite using a 2-site protolysis non-electrostatic surface complexation and cation exchange model. Nickel selectivity coefficients for cation exchange reported for Na-montmorillonite and Ca-montmorillonite are 3.1 (determined in 0.01 to 0.1 mol/L $NaClO_4$ solution) and 0.8 (determined in 0.0033 to 0.033 mol/L $Ca(NO_3)_2$ solution), respectively (Bradbury and Baeyens 2005b). The surface complexation constants for Ni sorption on montmorillonite are given in Table 5. The CEC for both types of montmorillonite is 0.87 equivalents/kg. The site capacities are 0.002 mol/kg for the strong site, and 0.04 mol/kg for each of the weak sites. Simulations were performed for a solid to liquid ratio of 0.54 g/L. The solid/liquid ratio determines the total sorption site capacity (CEC and complexation) for the system and what fraction of Ni in the system is associated with the solid. The value for the Ni K_d is calculated by summing the Ni concentrations in all of the solid sites (mol/kg) and dividing by the total Ni concentration in solution. The final K_d is not affected by the solid/liquid ratio.

Table 6 summarizes the calculated Ni sorption values for montmorillonite in different selected solutions at a reference pH of 6.3 using the constants provided in Table 4 and Table 5. The contribution of cation exchange to the simulated K_d value is illustrated by the % CEC values for Na and Ca montmorillonites. At a pH value of 6.3, the cation exchange component can contribute to the overall sorption value, depending upon the concentration of the competing cation in solution. For example, if Ni is sorbing on Na-montmorillonite when the solution has negligible Na, the amount of Ni sorbed by cation exchange can be very high (e.g., in 0.1 mol/L $CaCl_2$ solution, cation exchange represents 98% of the simulated K_d value of Ni sorption onto Na-montmorillonite). The same can be said for sorption on Ca-montmorillonite when there is negligible Ca in solution (e.g., in 0.1 M NaCl solution, cation exchange represents 99.8% of the simulated K_d value of Ni sorption onto Ca-montmorillonite). When the concentrations of Na and Ca are higher than around 0.05 M, sorption due to cation exchange becomes negligible. As expected, at this point, sorption on both types of montmorillonite becomes identical.

At a pH of 6.3, sorption due to surface complexation is controlled by the $\equiv S^sONi^+$ surface species. The other surface species become more important at higher pH. If Ni sorption on the weak site is included, then Ni sorption on montmorillonite depends on the concentration of Ni in solution. This is illustrated by the variation in simulated K_d values for the reference Na-Ca-Cl 300 g/L solution (i.e., TDS = 300 g/L Na-Ca-Cl solution) used in the laboratory sorption measurements (Vilks et al. 2011, see Table 6). Assuming the total Ni concentration in equilibrium with solids in the sorption tests is represented by a $[Ni]_{total}$ value of 5×10^{-5} mol/L, the simulated sorption value of 0.035 m^3/kg is in good agreement with the measured Ni sorption values, ranging from 0.034 to 0.053 m^3/kg (Vilks et al. 2011). Given that the Ni surface complexation constants were derived from data measured in 0.1 mol/L $NaClO_4$ solutions, the ability of these complexation constants coupled with an aqueous speciation program, such as PHREEQC, to predict experimental results in brine solutions is encouraging. The 2SPNE SC/CE methodology has a good potential for estimating sorption values and is in the process of being developed. Present-day sorption studies in brine solutions by AECL and others (Karlsruhe Institute of Technology, Germany) will establish the applicability of the model to brine solutions. So, as of today, the model can be used only as an approximation or guide. In the future, the model should be better constrained for estimating sorption values.

However, one should remember that although surface complexation models can be used to reproduce the results of sorption experiments over a wide range of conditions and to extrapolate the sorption values to different solution conditions, the 2SPNE SC/CE methodology is not a mechanistic method for predicting sorption from a very rigorous understanding of all sorption species. It is just a tool for predicting sorption, from the assumption that sorption occurs by cation exchange and by complexation reactions to surface oxygen sites that are analogous to the formation of hydroxide species in solution. A good fit between model simulations and experimental measurements does not prove the actual existence of the proposed surface reactions. The existence of the proposed surface species needs to be demonstrated by independent experimental methods. Nevertheless, sorption modelling remains a useful tool for furthering the understanding of sorption and extrapolating sorption results to new conditions.

Bradbury and Baeyens (2005a) used laboratory-measured (in $NaClO_4$ solutions) and literature-published sorption data to derive surface complexation constants for a number of elements (Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI)) sorbing on montmorillonite. They used the derived surface-binding constants to find a correlation between the logarithms of the surface binding constants and the logarithms of the formation constants of their corresponding hydrolysis species (${}^{OH}K_x$). The purpose of the correlation was to estimate surface complexation constants for elements whose sorption properties had not been measured. The correlation obtained for strong surface sites was:

$$\log {}^{s}K_{x-1} = (8.1 \pm 0.3) + (0.90 \pm 0.02) \log {}^{OH}K_x \qquad R = 0.99 \tag{12}$$

The correlation for weak surface sites was:

$$\log {}^{w1}K_{x-1} = (6.2 \pm 0.8) + (0.98 \pm 0.09) \log {}^{OH}K_x \qquad R = 0.98 \tag{13}$$

The above correlations were used to estimate values of $\log {}^{s}K_{x-1}$ and $\log {}^{w1}K_{x-1}$ for a number of elements, including Pd(II), Pb(II), Pu(III), Zr(IV), U(IV), Np(IV), Pu(IV) and Pa(V).

Bradbury and Baeyens (2009a) repeated the above exercise for Na-illite using experimental data for Ni(II), Co(II), Eu(III), Sn(IV), Am(III), Th(IV), Pa(V) and U(VI). Sorption on illite was modelled using one strong site, and the resulting constants were correlated with hydrolysis constants. The correlation equation using this LFER approach for illite is given by equation 14. Any information on the sorption properties of illite provides insight into the sorption properties of shale.

$$\log {}^{s}K_{x-1} = 7.9 \pm 0.4 + (0.83 \pm 0.02) \log {}^{OH}K_{x} \qquad R = 0.99 \tag{14}$$

Table 6: Calculated Ni K_d Values on Montmorillonite for Selected Solution Compositions

$[Ni]_{total}$ (mol/L)	$[CO_3]_{total}$ (mol/L)	Solution	K_d (m^3/kg)		% CEC Na-mont contributes to K_d of Na-mont	% CEC Ca-mont contributes to K_d of Ca-mont
			Na-mont	Ca-mont		
1×10^{-5}	1×10^{-5}	0.1 mol/L NaCl	0.16	31.0	59.7	99.8
1×10^{-5}	1×10^{-5}	0.1 mol/L $CaCl_2$	31.0	0.063	99.8	7.5
1×10^{-5}	1×10^{-5}	0.1 mol/L Na-Ca-Cl	61.9	0.26	99.9	75.4
1×10^{-5}	1.8×10^{-3}	*SR-270-PW	0.074	0.074	0.4	1.1
1×10^{-7}	5×10^{-5}	Na-Ca-Cl 300 g/L	0.148	0.148	0.2	0.3
1×10^{-5}	5×10^{-5}	Na-Ca-Cl 300 g/L	0.085	0.085	0.4	0.5
5×10^{-5}	5×10^{-5}	Na-Ca-Cl 300 g/L	0.035	0.035	0.9	1.3
1×10^{-4}	5×10^{-5}	Na-Ca-Cl 300 g/L	0.022	0.022	1.5	2.1

*Chemical compositions of SR-270-PW were slightly modified (Vilks et al. 2011).

3. SORPTION DATA

This chapter presents the results of the literature review in a series of sections, each devoted to a given element. Each section begins with a brief discussion of the element's chemistry. Refer to Table 3 for a description of element speciation in the SR-270-PW reference groundwater.

The reporting of sorption data starts with a collection of sorption data for rocks and minerals most closely representing the sedimentary rocks of interest. As mentioned before, emphasis is placed on collecting data for relevant water compositions that include: 1) a range of ionic strengths that would include sea water and brine solutions, and 2) a pH range that would include the near neutral values (6 to 7) of interest. The collected sorption data is plotted to identify useful trends with respect to ionic strength and pH. Such trends were not always found. Sorption values for shale, limestone, bentonite and minerals of interest (e.g.,montmorillonite, illite, chlorite, calcite) that are measured in solutions that best fit reference groundwater conditions are selected and presented in tables that provide information on water composition, experimental time, redox conditions and literature references. On the basis of these tables and scientific reasoning, a table of "recommended sorption coefficients" is presented for each element. The goal was to provide sorption coefficients for sedimentary rocks in highly saline conditions. The SR-270-PW groundwater composition (ionic strength = 6.0 M) was a target reference, even though some reference groundwaters have lower salinities with ionic strengths as low as 0.4 M. This report attempted to focus on the highest salinities on the assumption that sorption generally increases with lower ionic strength and values determined at highest salinities are more conservative. The tabulated data in the "recommended sorption coefficients" tables include a range of sorption coefficients, and for cases where there are two or more values a geometric mean value along with a geometric standard deviation are presented.

An inspection of the data tables shows that sorption values for a number of elements were not available for saline conditions. For the purposes of this report, conditions are considered saline if the ionic strength of the solution is equal to or greater than 0.7 M (sea water). The sorption of some elements is very sensitive to the ionic strength of the solution, while the sorption of other elements is not affected by the ionic strength. The tables of "recommended sorption coefficients" include the range of ionic strengths used to derive sorption values. In some cases, when experimental data was not available for higher ionic strength solutions, surface complexation modelling was used to estimate sorption in brine solutions based on parameters determined at lower ionic strength. In those cases, where no experimental or modelling results were available for higher ionic strength solutions and there was no scientific basis for extrapolating measured sorption values to saline conditions, the recommended K_d values were assumed to be 0 m^3/kg.

3.1 CARBON

Carbon-14 released to groundwater will isotopically exchange with dissolved inorganic carbon species (CO_3^{-2}, HCO_3^-, CO_2) and CO_3 in carbonate solids such as calcite and dolomite (Mozeto et al. 1984). Microbes in the geosphere could potentially incorporate carbon-14 in organic carbon compounds, taking the form of dissolved species or organic colloids.

Reported sorption coefficient values for inorganic carbon are given in Table 7. The first thing to note is that sorption coefficients for calcite are always higher than for clay minerals. Furthermore it was noted that purified montmorillonite, which is free of carbonate, does not appear to sorb carbon-14 (Sheppard et al. 1998; Andersson et al. 1982). Carbon-14 sorption on illite, chlorite and quartz, which are the main mineral components of shale, was assumed to be 0 m^3/kg (Ticknor and Vandergraaf 1996). However, bentonite that includes montmorillonite and carbonate does sorb carbon-14, with K_d values of 2.8×10^{-3} - 7.8×10^{-3} m^3/kg in ionic strength of 0.005 M solution by batch test (Allard et al. 1982) and 5×10^{-5} - 5.5×10^{-4} m^3/kg in ionic strength of 0.25 M solution by diffusion test (Oscarson and Hume 1994). Stenhouse (1995) considered that the reported sorption values on calcite were a realistic approximation of carbon-14 sorption on marl, but proposed a conservative value of 0 m^3/kg on the assumption that the calcite minerals were not accessible to isotopic exchange with carbon-14.

Bradbury and Baeyens (2003a; 2003b; 2010) derived sorption values for rocks containing carbonate on the assumption that inorganic carbon-14 is distributed between carbonate minerals and dissolved carbonate species in groundwater. It was assumed that carbon-14 can exchange with carbon in calcite to a depth of 30 monolayers, which is equivalent to ~ 10^{-8} m. Given a surface area of ~10^2 m^2/kg for calcite, the volume of calcite available for exchange is ~10^{-6} m^3/kg. Considering the density of calcite is 2700 kg/m^3, the mass of calcite available for exchange is 2.7×10^{-3} kg/kg, or 2.7×10^{-2} mol/kg. This is equivalent to only 0.27% of the calcite being available for sorption. Using the calcite content of MX-80 bentonite (0.7 wt.%) Bradbary and Baeyens (2003a) calculated carbon-14 K_d values for MX-80 in contact with a reference porewater with a total inorganic carbon concentration of 2.83 x 10^{-3} mol/L. The K_d values ranged from 2.7×10^{-5} m^3/kg at pH 6.9 to 3.2×10^{-4} m^3/kg at pH 7.25. In the case of Opalinus Clay, containing 16 wt.% calcite, the amount of exchangeable carbonate would be 4.3×10^{-3} mol/kg. The sorption coefficient is calculated by dividing the concentration of exchangeable calcite by the total concentration of dissolved carbonate. Therefore, for a given carbonate content in a rock, the sorption values will increase with decreasing dissolved carbonate, as will likely occur with increasing pH. Inorganic carbon sorption coefficients for Opalinus clay were calculated to be 1.6×10^{-3} m^3/kg at pH 6.3 and 6.0×10^{-3} m^3/kg at pH 7.8.

The concentration of inorganic carbon in the reference sedimentary groundwaters considered in this report varies from 6.6 x 10^{-4} to 5.4 x 10^{-3} mol/L. Using the approach described by Bradbury and Baeyens (2003b, 2010), the calculated K_d values for carbon-14 exchange with calcite in the reference groundwaters (Table 2) range from 5.0×10^{-3} to 4.1×10^{-2} m^3/kg. Considering that the reference shale in this report contains 2 wt.% carbonate, the calculated K_d values for carbon-14 exchange with shale would range from 1.0×10^{-4} to 8.2×10^{-4} m^3/kg. Since the average carbonate content of Georgian Bay and Blue Mountain shale formations ranges from 5 to 6 wt.%, and that in Queenston shale is 18 wt.%, the estimated K_d values for reference shale are likely conservative. Wyoming bentonite contains about 1.4 wt.% carbonate (Wanner et al. 1994). With this assumption one would estimate K_d values for carbon-14 exchange with bentonite ranging from 7.0×10^{-5} to 5.7×10^{-4} m^3/kg, which are within the range of measured sorption values by Oscarson and Hume (1994) and Bradbury and Baeyens (2003a). Note that the estimates of carbon-14 sorption based on isotope exchange are independent of ionic strength.

Table 7: Reported Inorganic Carbon Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.*	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-Ca-Cl	0.25	7.7	80	air	nr	5.0×10^{-5} - 5.5×10^{-4}	diffu	4
bentonite	Na-Cl-SO_4	0.37	6.9	-	-	nr	2.7×10^{-5}	calc.	5
bentonite	Na-Cl-SO_4	0.37	7.3	-	-	nr	3.2×10^{-4}	calc.	5
bentonite/quartz	Na-Cl-HCO_3	0.005	8.1	3 - 182	air	nr	2.8×10^{-3} - 7.8×10^{-3}	batch	3
montmorillonite	Na-Ca-Cl-SO_4	0.22	7.6	months	air	nr	0	batch	2
montmorillonite	Na-Cl-HCO_3	0.005	8.1	3 - 182	air	nr	0	batch	3
Opalinus Clay	Na-Cl-SO_4	0.24	6.3	-	-	nr	1.6×10^{-3}	calc.	6
Opalinus Clay	Na-Cl-SO_4	0.23	7.8	-	-	nr	6.0×10^{-3}	calc.	6
clay	deionized water	0.0003	7.9	nr	nr	nr	3.0×10^{-3}	batch	7
calcite	Na-Ca-Cl-SO_4	0.22	7.6	months	Air	nr	2.2×10^{-2} - 9.0×10^{-2}	batch	1
calcite	Na-Ca-Cl-SO_4	0.22	7.6	months	Air	nr	2.9×10^{-2} - 8.5×10^{-2}	batch	2
calcite	Na-Cl-HCO_3	0.005	8.1	3 - 182	Air	nr	1.0×10^{-3} - 8.3×10^{-2}	batch	3

1. Ticknor and Vandergraaf (1996)
2. Sheppard et al. (1998)
3. Allard et al. (1981)
4. Oscarson and Hume (1994)
5. Bradbury and Baeyens (2003a) [calculation]
6. Bradbury and Baeyens (2003b) [calculation]
7. Ogawa et al. (1996)

*atmosphere diffu: diffusion nr: not recorded
calc.: calculation

Table 8 summarizes recommended sorption values for carbon-14 for bentonite, shale and limestone. The recommended K_d values for bentonite are based on Bradbury and Baeyens (2003a) and the transport experiments by Oscarson and Hume (1994). The sorption values for shale are recommended based on the calculation of the estimated carbon-14 exchange with calcite in the reference groundwaters and the 2 wt.% carbonate content of reference shale. The recommended values for limestone are based on carbon-14 sorption on calcite, reported by Ticknor and Vandergraaf (1996) (2.2×10^{-2} - 9.0×10^{-2} m^3/kg) and Allard et al. (1981) (1.0×10^{-3} - 8.3×10^{-2} m^3/kg). Since the recommended K_d values for calcite that were derived from Ticknor and Vandergraaf (1996) and Allard et al. (1981) are consistent with the estimated values for calcite in the reference groundwaters (5.0×10^{-3} - 4.1×10^{-2} m^3/kg), they are the recommended values for limestone. Because the sorption of inorganic carbon-14 appears to be controlled by isotopic exchange of inorganic carbon between solids and water, which is independent of ionic strength, it follows that inorganic carbon-14 sorption values are also independent of ionic strength.

Table 8: Recommended Sorption Coefficients for Carbon

CARBON – INORGANIC				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**independent**	**6.9 - 7.7**	**2.7×10^{-5} - 5.5×10^{-4}**	**9.0×10^{-5} (5.5)**
comment	Based on Bradbury and Baeyens (2003a) and diffusion experiments of Oscarson and Hume (1994). Values are valid for saline solutions.			
Shale	**independent**	**7.5 - 9**	**1.0×10^{-4} - 8.2×10^{-4}**	**2.8×10^{-4} (4.4)**
comment	Based on 2 wt.% carbonate content of reference shale and the assumption that 0.27% of this carbonate is available for exchange with carbon-14 in water, using the approach described by Bradbury and Bayens (2003b, 2010).			
Limestone	**0.005 - 0.22**	**7.6 - 8.1**	**1.0×10^{-3} - 9.0×10^{-2}**	**1.8×10^{-2} (9.5)**
comment	Based on carbonate data from Ticknor and Vandergraaf (1996) and Allard et al. (1981). Values are assumed to be valid for saline solutions.			
CARBON – ORGANIC				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**-**	**-**	**0**	**-**
comment	Conservative assumption			
Shale	**-**	**-**	**0**	**-**
comment	Conservative assumption			
Limestone	**-**	**-**	**0**	**-**
comment	Conservative assumption			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

At present, there is no specific information on the types and inventories of organic carbon-14 that may be present in high-level nuclear waste. Since the nature of organic carbon is not known, it is assumed that organic carbon is non-sorbing and the recommended organic carbon K_d values are 0 m^3/kg.

3.2 CHLORINE

Chlorine is one of the halogens in group 17 of the periodic table. Since chlorine has a very high electron affinity, it is a very strong oxidizing agent and is rarely found in its elemental form. The most common form of chlorine is as the chloride anion with an oxidation of -1. In brine solutions the majority of chloride species occur as the free anion Cl^- (93%), followed by $MgCl^+$ (7%).

There is very little information in the literature on the sorption of chloride on geologic materials. Table 9 summarizes the chloride sorption information that has been found to date. Only chloride sorption on clay from very dilute solutions has been reported. These sorption values are very low compared to most cations. In brine solutions, these values are likely to be significantly lower due to the competitive sorption behavior of ions in the brine solutions. Therefore, a value of 0 is recommended for chloride sorption on sedimentary rocks (shale and limestone) and bentonite for saline solutions (Table 10).

Table 9: Measured Chloride Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
clay	gw. (no comp.)	nr	7.1	1	nr	nr	0.0008 - 0.0015	batch	1
clay	cement water	nr	10	1	nr	nr	0.0004	batch	1
clay	Ca-Na-Mg-HCO_3-SO_4-Cl	0.008	10	nr	nr	498	0.0004	batch	1
clay	Ca-Na-Mg-HCO_3-SO_4-Cl	0.008	7	nr	nr	498	0.0015	batch	1
clay	syn. gw. no comp.	nr	8.0	nr	N_2	nr	0.0040	batch	2
clay	syn. gw. no comp.	nr	8.5	nr	N_2	nr	0.0040	batch	2
clay	syn. gw. no comp.	nr	8.8	nr	N_2	nr	0.010	batch	2

1. Kato and Yanase (1993) 2. Berry et al. (1988)
nr: not recorded gw. (no comp.): groundwater with no composition

Table 10: Recommended Sorption Coefficients for Chloride

CHLORIDE(-I)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 can be recommended.			

3.3 CALCIUM

Calcium is a group 2 alkaline earth metal with an oxidation state of +2. Calcium is the fifth most abundant dissolved element in sea water, after sodium, chloride, magnesium and sulphate. (Radioisotopes of Ca could be retarded in transport by isotopic exchange.) In brine solutions, most calcium is present as the free Ca^{+2} cation, along with very small amounts of $Ca(SO_4)$ and $Ca(HCO_3)^+$. The solubility of calcium is limited by calcite and gypsum.

The information of calcium sorption on geologic materials is limited, with the available information being summarized in Table 11. A significant portion of this data was derived from measurements in $NaClO_4$ solution by Baeyens and Bradbury (1995) as part of their efforts to develope a sorption model for montmorillonite. The calcium sorption on Na-montmorillonite in the pH range of 5-9.5 (Baeyens and Bradbury 1995) is summarized in Figure 3, showing the effect of pH at various ionic strengths. Calcium sorption is significantly reduced as the ionic strength is increased from 0.01 to 0.1 mol/L. There appears to be a slight increase in sorption at pH values above 7.5, particularly at the higher ionic strength. None of the sorption measurements were performed with saline water. Given the observed trend in decreasing sorption values with increasing ionic strength, it is probable that in a brine solution, with its molar quantities of calcium, the sorption of calcium will be very close to 0. Therefore, given the lack of sorption data at higher ionic strengths, it is assumed that calcium will not sorb in saline waters.

Table 11: Measured Calcium Sorption Coefficients

Solid	Solution	I (mol/L)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Na-mont.	$NaClO_4$	0.1	6 - 7	1	N_2	nr	0.128 - 0.131	batch	1
Na-mont.	$NaClO_4$	0.1	6 - 7	3	N_2	nr	0.111 - 0.140	batch	1
Na-mont.	$NaClO_4$	0.1	6 - 7	7	N_2	nr	0.116 - 0.130	batch	1
Na-mont.	$NaClO_4$	0.1	6 - 7	21	N_2	nr	0.115 - 0.123	batch	1
Na-mont.	$NaClO_4$	0.03	6 - 7	3	N_2	nr	1.24 - 1.40	batch	1
Na-mont.	$NaClO_4$	0.01	6 - 7	1	N_2	nr	13 - 14	batch	1
bentonite	NaCl	0.1	6.5	14	air	nr	0.18 - 0.19	batch	5
clay	$Sr\text{-}NO_3$	0.25	6.0 - 6.3	nr	nr	nr	0.0013 - 0.0089	batch	2
clay	$Ca\text{-}Na\text{-}Mg\text{-}HCO_3\text{-}SO_4\text{-}Cl$	0.008	7-10	nr	nr	498	0.025 - 0.028	batch	3
illite/smectite	syn. gw.	≈ 0	7.2	60	nr	nr	0.011 ± 0.004	batch	4
clay	syn. gw.	≈ 0	7.2	60	nr	nr	0.003 ± 0.0004	batch	4
clay	syn. gw.	≈ 0	7.2	60	nr	nr	0.005 ± 0.0002	batch	4
clay	groundwater	0.018	8.1 - 8.6	100 - 180	N_2	nr	0.54 - 0.57	batch	5

1. Baeyens and Bradbury (1995)
2. Graham (1979)
3. Kato (1993)
4. Oscarson (1994)
5. Missana and Garcia-Gutierrez (2007)

nr: not recorded
Na-mont.: Na-montmorillonite
syn. Gw: synthetic groundwater

Experimental measures by Baeyens and Bradbury (1995) were conducted in the pH range of 5-9.5, only K_d values measured under pH of 6-7 were selected.

The recommended calcium sorption values are summarized in Table 12.

Table 12: Recommended Sorption Coefficients for Calcium

CALCIUM(II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			

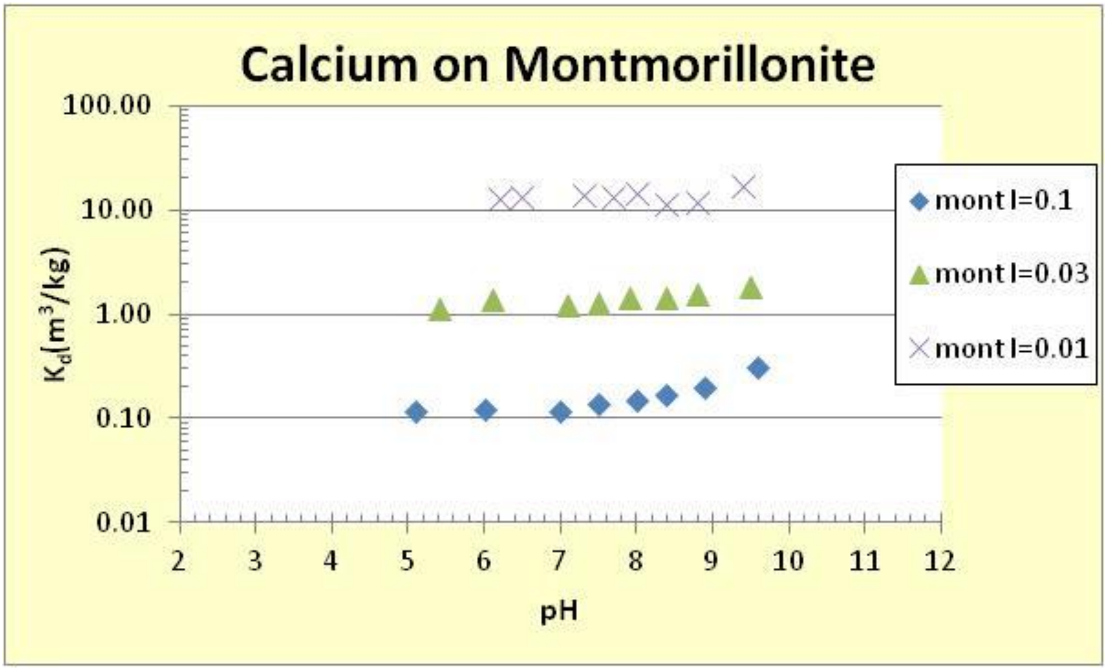


Figure 3: Calcium Sorption on Na-Montmorillonite as a Function of pH and Ionic Strength (Baeyens and Bradbury 1995)

3.4 NICKEL

Nickel is a transition element present most commonly in the +2 oxidation state. PHREEQC (SIT database) predicts that nickel chemistry in the reference groundwaters will be dominated by Ni^{+2} and $NiCl^{+}$ (see Table 3).

Nickel sorption on bentonite, shale and limestone has been measured in a variety of solutions ranging from a dilute solution to the reference SR-270-PW brine (Vilks and Miller 2014; Vilks et al. 2011). Average measured K_d values from these studies are summarized in Table 13. In addition to these values, Table 13 also includes selected Ni sorption values obtained from the literature. The literature values were generally obtained from relatively simple solutions ($NaClO_4$ solution) that were not brines. The data obtained by Vilks et al. (2011) and Vilks and Miller (2014) clearly show that nickel sorption decreases with ionic strength, and sorption on shale and bentonite slightly increase when ionic strength is greater than 6 M (Figure 4). Thermodynamic sorption modelling (Vilks and Miller 2014) was able to simulate measured K_d values for both brine and dilute solutions using surface complexation constants from the literature. The modelling efforts also demonstrated that in dilute water nickel sorption is dominated by cation exchange, while in brine solutions Ni sorption is mainly by surface complexation reactions.

Recommended Ni sorption values for bentonite, shale and limestone are based on measurements in the SR-270-PW brine and are given in Table 14. Following the procedures used for the other elements in this report, recommended sorption values are presented as a range of values and a geometric mean. High and low values were selected from individual measurements (Vilks and Miller 2014) to be more conservative, excluding two outliers for bentonite and one outlier for limestone – which were much higher than other values measured at similar experimental conditions. The geometric mean was calculated considering all of the individual measurements.

Table 13: Measured Nickel Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-Ca-Cl	7.2	6.4	7	air	nr	0.034 ± 0.001	batch	1
bentonite	Na-Ca–Cl	2.4	7.1	7	air	nr	0.022 ± 0.002	batch	1
bentonite	Na-Ca–Cl	0.23	7.5	7	air	nr	0.082 ± 0.006	batch	1
bentonite	Na–Cl	1.9	7.4	7	air	nr	0.050 ± 0.004	batch	1
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	6.5	1-127	air	nr	0 - 0.013	batch	2
bentonite	Na-Ca-Cl	0.012	8.1	7	air	nr	1.58 ± 0.85	batch	2
Na-mont.	$NaClO_4$	0.1	6 - 7	2	N_2	nr	0.14 - 2.7	batch	3
Na-mont.	$Na-ClO_4$	0.5	6 - 7	3	air	nr	0.017 - 0.41	batch	10
Na-mont.	$NaNO_3$	0.1	6.2-6.9	2	air	nr	0.19 - 1.3	batch	11
mont.	$Na-ClO_4$	0.1	6.2	28	Ar	nr	0.122	batch	8
shale	Na-Ca-Cl	7.2	6.2	7	air	nr	0.006 ± 0.0003	batch	1
shale	Na-Ca-Cl	2.4	6.9	7	air	nr	0.0083 ± 0.0005	batch	1
shale	Na-Ca-Cl	0.23	7.4	7	air	nr	0.047 ± 0.004	batch	1
shale	Na-Cl	1.9	7.1	7	air	nr	0.031 ± 0.002	batch	1
shale	Na-Ca-Cl (SR-270-PW)	6.0	6.3	1-127	air	nr	0 - 0.009	batch	2
shale	Na-Ca-Cl	0.012	8.1	7	air	nr	1.62 ± 1.09	batch	2
shale	Na-Ca-Mg-SO_4-Cl	0.095	6.8	nr	N_2	nr	5.4 - 5.9	batch	5
Na-illite	$NaClO_4$	0.5	5.9 - 6.9	3-84	N_2	nr	0.76 - 5.0	batch	4
Na-illite	$Na-ClO_4$	0.1	7	7	N_2	nr	0.083 - 9.1	batch	9
illite	$NaNO_3$	0.1	6.1-7.1	8	N_2		0.040 - 3.0	batch	6
clay	Na-Ca-Mg-SO_4	0.3	6.3	28	CO_2/ N_2	340	0.008 - 0.39	batch	7
clay	Na-Ca-Mg-SO_4	0.39	7.8	28	CO_2/ N_2	340	0.89 - 16	batch	7
limestone	Na-Ca–Cl	7.2	6.0	7	air	nr	0.0004 ± 0.0002	batch	1
limestone	Na-Ca–Cl	2.4	6.8	7	air	nr	0.0011 ± 0.0003	batch	1
limestone	Na-Ca–Cl	0.23	7.4	7	air	nr	0.0061 ± 0.0007	batch	1
limestone	Na-Cl	1.9	7.1	7	air	nr	0.008 ± 0.001	batch	1
limestone	Na-Ca-Cl (SR-270-PW)	6.0	6.3	1-127	air	nr	0 - 0.005	batch	2
limestone	Na-Ca-Cl	0.012	8.1	7	air	nr	0.23 ± 0.16	batch	2
calcite	Na-Ca-Cl-SO_4	0.10	7.3	14	N_2	nr	0.0057	batch	12

1. Vilks et al. (2011)
2. Vilks and Miller (2014)
3. Baeyens and Bradbury (1997)
4. Bradbury and Baeyens (2009a)

nr: not recorded

5. Berry et al. (1990)
6. Elzinga and Sparks (2001)
7. Lauber et al. (2000)
8. Lothenbach et al. (1997)

Na-mont.: Na-montmorillonite

9. Poinssot et al. (1999)
10. Tertre et al. (2005)
11. Xu et al. (2008)
12. Cornell and Aksoyoglu (1992)

mont.: montmorillonite

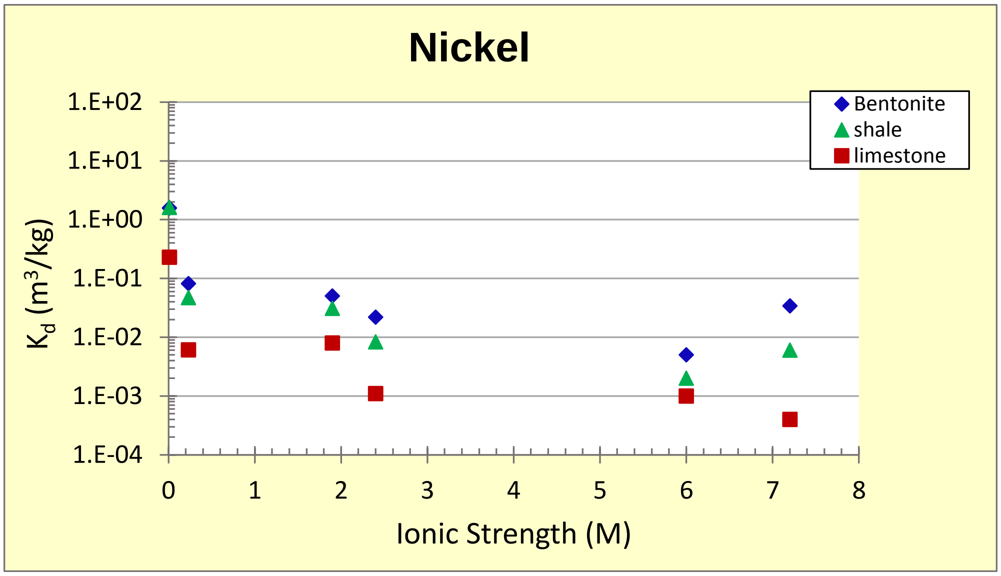


Figure 4: Nickel Sorption as a Function of Ionic Strength (Vilks et al. 2011; Vilks and Miller 2014. Averaged Measured K_d Values)

Table 14: Recommended Sorption Coefficients for Nickel

NICKEL(II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0 - 0.013**	**0.0010 (9.6)**
comment	Measurements in SR-270-PW synthetic brine by Vilks and Miller (2014)			
Shale	**6.0**	**6.3**	**0 - 0.009**	**0.0005 (6.9)**
comment	Measurements in SR-270-PW synthetic brine by Vilks and Miller (2014)			
Limestone	**6.0**	**6.3**	**0 - 0.005**	**0.0004 (4.7)**
comment	Measurements in SR-270-PW synthetic brine by Vilks and Miller (2014)			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

3.5 COPPER

Copper is a transition element with two oxidation states, +1 and +2. Under reducing conditions, copper will likely be present as a monovalent cation, while under more oxidizing conditions both monovalent and divalent copper ions will be present. Simulations with PHREEQC indicate that in the reference SR-270-PW solution, with an Eh of -200 mV, all of the copper is expected to be in the +1 oxidation state, as Cu^+ (Table 3). Under atmospheric conditions all of the copper in the same SR-270-PW brine would be in the +2 oxidation state, as the species $CuCl_2$ (49%), $CuCl^+$ (40%), and Cu^{+2} (10%).

Gu et al. (2010) modelled Cu(II) sorption on montmorillonite in 0.001 to 0.1 M $NaNO_3$ solutions and found that, in the pH range 3 to 6, Cu sorption was very sensitive to ionic strength because sorption was by outer sphere complexes. At pH values higher than ~6, sorption became dominated by inner sphere surface complexation and sorption became independent of ionic strength. Elzinga et al. (2006) studied the mechanisms of metal sorption on calcite and found that Cu(II) sorption was by inner sphere surface complexation that did not change over the 2.5 years of experimental period. Figure 5A illustrates the effect of pH on Cu sorption on montmorillonite in dilute solutions (Akafia et al. 2011), showing a significant increase in sorption at pH values above 6.8. Vilks and Miller (2014) found that in SR-270-PW brine solution copper sorption on bentonite increased at pH values above 6, but sorption on shale and limestone was essentially independent of pH, given experimental uncertainties (Figure 5B). Figure 5C shows data reported by Vilks et al. (2011) and Vilks and Miller (2014) plotted as a function of ionic strength. The data indicate that copper sorption on bentonite, shale and limestone is independent of ionic strength at ionic strength over 0.58 M.

Table 15 presents selected values of Cu(II) sorption on sedimentary rocks and bentonite. Vilks et al. (2011) reported results of Cu(II) sorption on bentonite, shale and limestone in Na-Ca-Cl solutions with ionic strengths varying from 0.2 to 7.2 M, and pH values between 6 and 8. Vilks and Miller (2014) extended the studies of copper sorption to the reference SR-270-PW brine with ionic strength of 6.0 M and a reference dilute solution with ionic strength of 0.012 M. Sorption measurements on montmorillonite by Akafia et al. (2011) demonstrate that copper sorbs significantly more in simple $NaNO_3$ solutions compared to more natural test solutions containing a variety of monovalent and divalent cations, as well as chloride.

Thermodynamic sorption modelling (Vilks and Miller 2014) was able to simulate measured Cu(II) K_d values for both brine and dilute solutions using surface complexation constants from the literature. The modelling efforts demonstrated that, in dilute water, copper sorption is dominated by cation exchange, while in brine solutions, sorption is mainly due to surface complexation reactions. Modelling results also indicated that the Ca in solution is likely to compete with copper for sorption sites.

Measurements of Cu(I) sorption on bentonite, shale and limestone in brine solutions have not been performed. Furthermore, literature searches to date have not found any published data on Cu(I) sorption onto geologic materials. Therefore, only sorption values of 0 m^3/kg can be recommended for the sorption of Cu(I) on these substrates at this time.

Table 15: Selected Copper Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-Ca-Cl	7.2	6.8	7	air	nr	0.0065	batch	1
	Na-Ca–Cl	4.9	7.1	7	air	nr	0.010	batch	1
	Na-Ca–Cl	2.4	7.4	7	air	nr	0.021	batch	1
	Na-Ca–Cl	0.58	7.8	7	air	nr	0.014	batch	1
	Na-Ca–Cl	0.23	8.0	7	air	nr	0.26	batch	1
	Na-Ca-Cl (SR-270-PW)	6.0	6.5	16 - 127	air	nr	0.05 - 0.13	batch	2
	Na-Ca-Cl	0.012	8.1	7	air	nr	1.22 ± 0.0	batch	2
mont.	Na-NO_3	0.001	6.2 - 7.0	1	nr	nr	7.6 - 46	batch	3
	Na-NO_3	0.02	5.9 - 6.7	1	nr	nr	1.9 - 34	batch	3
	Na-NO_3	0.1	5.9 - 7.2	1	nr	nr	0.43 - 223	batch	3
shale	Na-Ca-Cl	7.2	6.4	7	air	nr	0	batch	1
	Na-Ca–Cl	4.9	6.6	7	air	nr	0.0033	batch	1
	Na-Ca–Cl	2.4	7.0	7	air	nr	0.033	batch	1
	Na-Ca–Cl	0.58	7.3	7	air	nr	0.0083	batch	1
	Na-Ca–Cl	0.23	7.5	7	air	nr	0.49	batch	1
	Na-Ca-Cl (SR-270-PW)	6.0	6.3	16 - 127	air	nr	0.017 - 0.15	batch	2
	Na-Ca-Cl	0.012	8.1	7	air	nr	0.61 ± 0	batch	2
limestone	Na-Ca-Cl	7.2	6.2	7	air	nr	0.0002	batch	1
	Na-Ca–Cl	4.9	6.6	7	air	nr	0.0092	batch	1
	Na-Ca–Cl)	2.4	6.9	7	air	nr	0.064	batch	1
	Na-Ca–Cl	0.58	7.3	7	air	nr	0.0075	batch	1
	Na-Ca–Cl	0.23	7.5	7	air	nr	0.12	batch	1
	Na-Ca-Cl (SR-270-PW)	6.0	6.3	16 - 127	air	nr	0.007 - 0.027	batch	2
	Na-Ca-Cl	0.012	8.1	7	air	nr	0.25 ± 0	batch	2

1. Vilks et al. (2011)
2. Vilks and Miller (2014)
3. Akafia et al. (2011) (only include K_d values measured at pH = 5.9-7.2)

nr: not recorded

Table 16 summarizes recommended values for copper sorption on bentonite, shale, and limestone for highly saline solutions. The Cu K_d values determined in the reference SR-270-PW brine provide the best measure of Cu(II) sorption in brine solutions, and are the recommended values for Cu(II) sorption on sedimentary rocks. Due to the absence of data for Cu(I) sorption, only values of 0 m^3/kg can be recommended. Given the likelyhood that conditions will be reducing at the depth of a geologic repository, it is likely that all copper will be in the Cu(I) form in the geological repository.

Table 16: Recommended Sorption Coefficients for Copper

COPPER (II) – Oxidizing Conditions (Eh > ~40 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0.05 - 0.13**	**0.10 (1.3)**
comment	Measured in SR-270-PW reference brine by Vilks and Miller (2014).			
Shale	**6.0**	**6.3**	**0.017 - 0.15**	**0.046 (1.8)**
comment	Measured in SR-270-PW reference brine by Vilks and Miller (2014).			
Limestone	**6.0**	**6.3**	**0.007 - 0.027**	**0.010 (1.5)**
comment	Measured in SR-270-PW reference brine by Vilks and Miller (2014).			
COPPER (I) – Reducing Conditions (Eh < ~40 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 can be recommended.			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

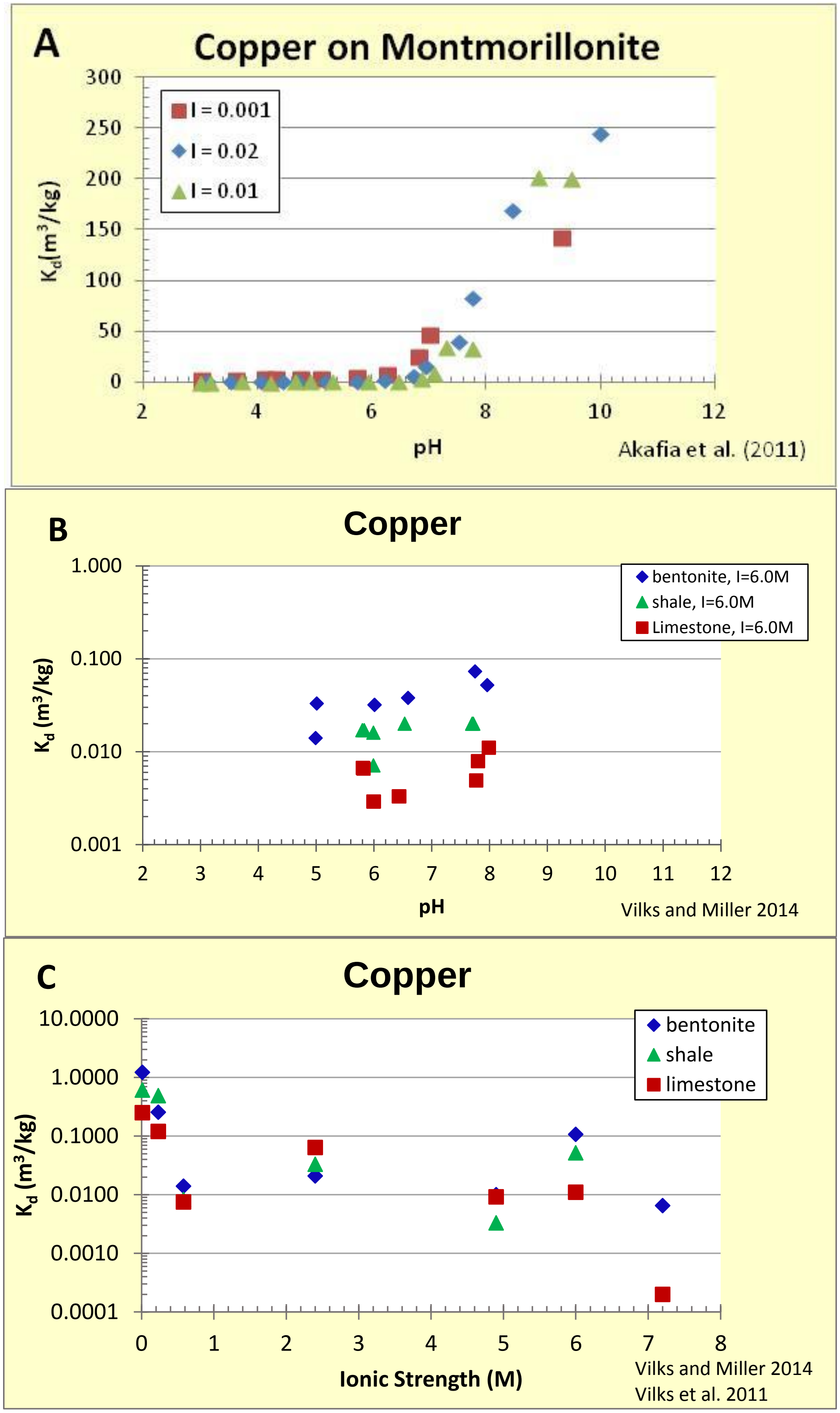


Figure 5: Copper Sorption as a Function of pH and Ionic Strength (Akafia et al. 2011; Vilks et al. 2011; Vilks and Miller 2014)

3.6 ARSENIC

Arsenic is a group 15 non-metal element. PHREEQC (SIT database) predicts that under reducing conditions arsenic is found in the +3 oxidation state (arsenite) as $H_3(AsO_3)$, while under more oxidizing conditions, arsenic is present in both the +3 oxidation state, as $H_3(AsO_3)$, and in the +5 oxidation state (arsenate), mainly as the anionic $H(AsO_4)^{-2}$ and $H_2(AsO_4)^{-}$ species. Arsenite tends to be more mobile than arsenate.

Selected values for arsenic sorption coefficients that were found in the literature are summarized in Table 17. In all cases the starting solutions contained either As(III) or As(V). No additional redox control was described for most cases.

Data for As sorption were not reported by Ticknor and Vandergraaf (1996), and are not present in the Japanese Sorption Database (https://migrationdb.jaea.go.jp). Sorption data for As(V) are only available for low ionic strength solutions. Manning and Goldberg (1996) measured As(V) sorption on kaolinite, illite and montmorillonite at a variable pH and an ionic strength of 0.1 M (0.15 - 0.28 m^3/kg for montmorillonite, and 0.12 - 0.32 m^3/kg for illite). Goldberg and Johnston (2001) studied As(V) sorption on Al and Fe oxides in NaCl solutions with ionic strengths of 0.01, 0.1 and 1.0 M. The results show that As(V) sorbs by inner sphere complexes on amorphous Al and Fe oxides. Sorption of As(V) on Al and Fe oxides did not vary with ionic strength from 0.1 M to 1.0 M. So et al. (2008) reported As(V) sorption on calcite in calcite-equilibrated solution with ionic strength of 0.07 M (0.08 - 0.57 m^3/kg).

Goldberg and Johnston (2001) studied As(III) sorption on Al and Fe oxides in NaCl solutions with ionic strength of 1.0 M and found that As(III) sorbed by both inner and outer sphere complexes on amorphous Fe oxide, but only by outer sphere complexes on amorphous Al oxide. Manning and Goldberg (1997) reported As(III) sorption on kaolinite, montmorillonite and illite in solution with ionic strength of 0.1 M (0.08 - 0.26 m^3/kg for kaolinite, 0.27 - 0.30 m^3/kg for montmorillonite and 0.26 - 1.60 m^3/kg for illite). Paikaray et al. (2005) reported As(III) sorption on Vindhyen shale at pH of 5 and ionic strength of 0.01 M solution (0.03 - 0.09 m^3/kg). So et al. (2008) noted that As(III) did not sorb on calcite in calcite-equilibrated solution.

Bertetti (2016) measured sorption of As(III) on bentonite, shale and limestone in SR-270-PW reference brine (ionic strength of 6.0 M) and in diluted solution (Na-Ca-Cl type with ionic strength of 0.01 M) under reducing conditions. The As(III) K_d values for brine and dilution solutions are similar.

Table 17: Selected Sorption Coefficients for Arsenic

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
As (V)									
Al oxide	NaCl	1.0	5 - 8	0.17	nr	nr	0.92 - 22.48	batch	1
Fe oxide	NaCl	1.0	6 - 8	0.17	nr	nr	0.71 - 8.08	batch	1
calcite	$CaCO_3$	0.07	7 - 9	1.1	N_2 &CO_2	nr	0.08 - 0.57	batch	3
kaolinite	NaCl	0.1	5 - 8	2	nr	nr	0.14 - 2.09	batch	4
mont.	NaCl	0.1	5 - 8	2	nr	nr	0.15 - 0.28	batch	4
illite	NaCl	0.1	5 - 8	2	nr	nr	0.12 - 0.32	batch	4
As (III)									
kaolinite	NaCl	0.1	5 - 8	0.67	nr	nr	0.08 - 0.26	batch	5
mont.	NaCl	0.1	5 - 8	0.67	nr	nr	0.27 - 0.30	batch	5
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	7	43	N_2	-20	0.018	batch	6
bentonite	Na-Ca-Cl	0.01	8.7	43	N_2	-120	0.022	batch	6
shale	$NaNO_3$	0.01	5	nr	nr	nr	0.03 - 0.09	batch	2
shale	Na-Ca-Cl (SR-270-PW)	6.0	7	43	N_2	-20	0.02	batch	6
shale	Na-Ca-Cl	0.01	8.7	43	N_2	-120	0.02	batch	6
illite	NaCl	0.1	5 - 8	0.67	nr	nr	0.26 - 1.60	batch	5
calcite	$CaCO_3$	0.07	7 - 9	1.1	N_2 &CO_2	nr	0	batch	3
limestone	Na-Ca-Cl (SR-270-PW)	6.0	7	43	N_2	-20	0.011	batch	6
limestone	Na-Ca-Cl	0.01	8.7	43	N_2	-120	0.015	batch	6
Al oxide	NaCl	1.0	5 - 8	0.17	nr	nr	0.07 – 0.62	batch	1
Fe oxide	NaCl	1.0	5 - 8	0.17	nr	nr	1.43 – 4.21	batch	1

1. Goldberg and Johnston (2001)
2. Paikaray et al. (2005)
3. So et al. (2008)

nr: not recorded

4. Manning and Goldberg (1996)
5. Manning and Goldberg (1997)
6. Bertetti (2016)

mont.: montmorillonite

Figure 6 illustrates sorption coefficients for As(V) on montmorillonite, illite, and amorphous Fe and Al oxides as a function of pH (Goldberg and Johnston 2001; Manning and Goldberg 1996, 1997). As(V) K_d values on amorphous Al and Fe oxides do not display any significant variation with ionic strength from 0.1 M to 1.0 M. The As(V) sorption on montmorillonite increases with increasing solution pH to an adsorption maximum around pH 4.5 to 6, and decreases with further increase of the solution pH (Manning and Goldberg 1997). The As(V) sorption on illite does not significantly vary with solution pH (sorption is slightly stronger at pH 6 to 7.5). The As(V) sorption on amorphous Al and Fe oxides decreases with higher pH as oxide surfaces become negatively charged (Goldberg and Johnston 2001).

Figure 7 shows the variation in As(III) sorption coefficients on montmorillonite, bentonite, shale, illite, limestone, and amorphous Fe and Al oxides as a function of ionic strength and pH (Goldberg and Johnston 2001; Manning and Goldberg 1997; Bertetti 2016).
The As(III) K_d values for Fe and Al oxides decrease with ionic strength from 0.01 to 1.0 M at solid/solution ratio of 4 g/L. The As(III) K_d values for Fe oxides do not vary with ionic strength

from 0.01 to 1.0 M at solid/solution ratio of 0.5 g/L. The As(III) K_d values for illite and montmorillonite do not vary with ionic strength from 0.05 to 0.1 M (Goldberg and Johnston 2001; Manning and Goldberg 1997). Bertetti (2016) found that As(III) K_d values on bentonite, shale, and limestone are similar in ionic strength of 6.0 M and 0.01 M solutions. The As(III) sorption on Al and Fe oxides increases with increasing solution pH to an adsorption maximum around pH 8 and decreases with further increase in the solution pH (Goldberg and Johnston 2001; Manning and Goldberg 1997). The As(III) shows lower sorption on montmorillonite and illite at low pH and maximum sorption between pH 9 and 10 in 0.1 M ionic strength solutions (Manning and Goldberg 1997).

Table 18 summarizes the recommended arsenic sorption values that are available for bentonite, shale and limestone. As stated before, the As(V) K_d data from the literature are from relatively low ionic strength solutions, and we do not have enough data to establish any trends between sorption values and the ionic strengths. However, it was noted that As(V) sorbed by inner sphere complexes on Al oxide and sorption appeared to be independent of ionic strength. Since Al oxides are the main components of clay minerals, it could be argued that As(V) sorption on bentonite and shale should also be independent of ionic strength. However, it would be conservative to use a K_d value of 0 m^3/kg for sorption of As(V) under saline, oxidizing conditons. As(III) K_d values measured in the SR-270-PW reference brine under reducing conditions are recommended for sorption of As(III).

Table 18: Recommended Sorption Coefficients for Arsenic

ARSENIC (V) – Oxidizing Conditions (Eh > ~90 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
ARSENIC (III) – Reducing Conditions (Eh < ~90 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**7**	**0.018**	**-**
comment	Measured in the SR-270-PW reference brine by Bertetti (2016).			
Shale	**6.0**	**7**	**0.02**	**-**
comment	Measured in the SR-270-PW reference brine by Bertetti (2016).			
Limestone	**6.0**	**7**	**0.011**	**-**
comment	Measured in the SR-270-PW reference brine by Bertetti (2016).			

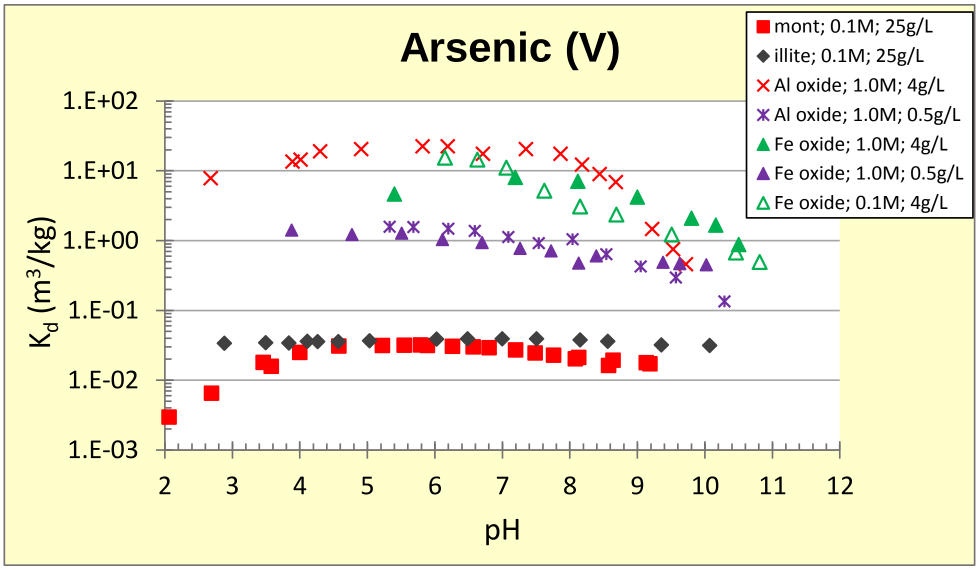


Figure 6: Arsenic (V) Sorption Coefficients on Montmorillonite, Illite, and Amorphous Fe and Al Oxides as a Function of pH (Goldberg and Johnston 2001; Manning and Goldberg 1996, 1997)

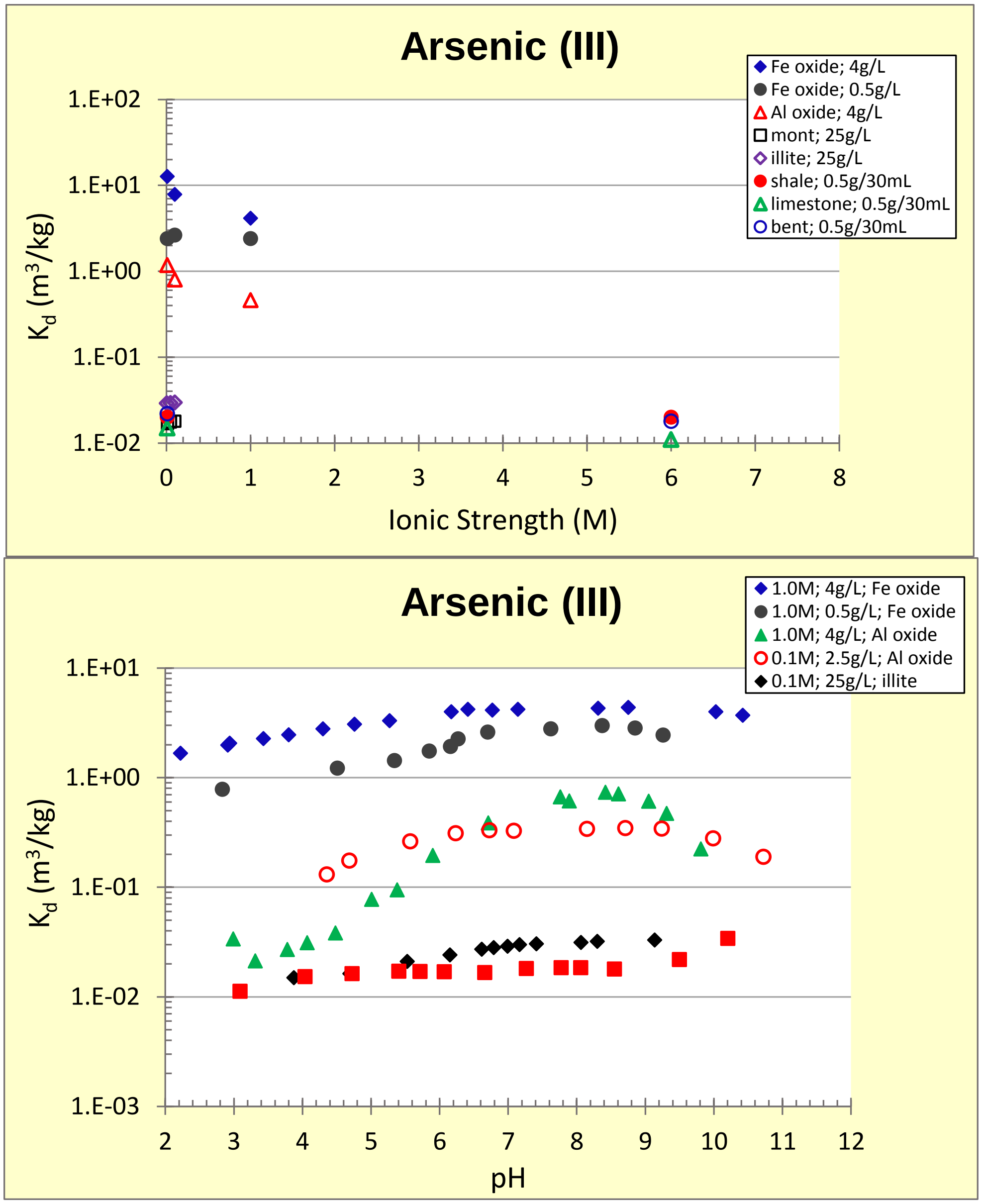


Figure 7: Arsenic (III) Sorption Coefficients on Montmorillonite, Bentonite, Shale, Illite, Limestone, Amorphous Fe and Al Oxides as a Function of Ionic Strength and pH (Goldberg and Johnston 2001; Manning and Goldberg 1997; Bertetti 2016)

3.7 SELENIUM

Selenium is a group 16 non-metal element, with oxidation states of -2, 0, +4 and +6. Under oxidizing conditions open to the atmosphere, the +6 oxidation state dominates, with the SeO_4^{-2} selenate species. Selenate has low sorption, similar to sulphate, and high bioavailability. It sorbs by inner-and outer sphere-complexes, depending upon the solution pH and ionic strength, and mineral surface properties (Charlet et al. 2007). Under mildly reducing conditions, the +4 oxidation state becomes dominant, producing the anionic $HSeO_3^-$ selenite. Selenite is believed to be sorbed by strong inner-sphere complexes, similar to phosphate (Charlet et al. 2007). Therefore, selenite is expected to sorb more strongly than selenate. Under mildly reducing conditions, there is a possibility that Se will also form Se(0), which would precipitate as a solid (Charlet et al. 2007; Breynaert et al. 2010). The precipitation of Se(s) could be triggered by the presence of sulphide minerals, organic matter or microbial action. Under more strongly reducing conditions, the -2 oxidation state dominates, producing the anionic HSe^- selenide species. Selenium speciation in the reference SR-270 brine, with an Eh of -200 mV, is predicted to be dominated by HSe^- (100%).

Selected sorption coefficients for selenium from the literature are presented in Table 19. Sorption measurements on bentonite, shale and limestone in the SR-270-PW reference brine and in a dilute solution (I = 0.01 M) under reducing conditions (Bertetti 2016) are also shown in the table. Selenium sorption on bentonite, smectite and montmorillonite, measured at different ionic strengths as a function of pH in oxidizing conditions (Missana et al. 2009b; Montavon et al. 2009; Goldberg and Glaubig 1988), is illustrated in Figure 8. Sorption on smectite does not appear to decrease with ionic strength (in the range of 0.01 to 0.5 M). Sorption on smectite slightly decreases with increasing pH, up to a pH value of 7, above which there is no longer a variation with pH. Ca-montmorillonite and bentonite show trends of decreasing sorption as pH values increase above 8. Interestingly, sorption measured on bentonite from a low ionic strength solution (0.009 M) is significantly lower than sorption observed with smectite tested using higher ionic strength (0.01 - 0.5 M) solutions. The difference might be attributed to the higher Se concentrations used for the bentonite experiments (1×10^{-3} mol/L versus 4×10^{-10} mol/L).

Figure 9 shows that although Se(-II) sorption on mudstone (Iida et al. 2009) decreases somewhat with increasing ionic strength, up to an ionic strength of 0.5 M, it does not decrease significantly with higher ionic strength values (Iida et al. 2009). Se(-II) sorption on bentontite was not affected by ionic strength over 0.5 M or pH in any significant way (Iida et al. 2011; Tachi et al. 1999a; Bertetti 2016).

Table 20 summarizes recommended sorption values for selenium on bentonite, shale and limestone. Sorption values of interest under oxidizing conditions for bentonite were based on measurements on smectite at ionic strength of 0.5 M and 0.1 M by Missana et al. (2009b), and on bentonite at ionic strength of 0.68 M and 0.24 M by Lee et al. (2012). Because sorption values for bentonite determined at a very low ionic strength (0.009 M) by Shibutani et al. (1994) were lower than for Ca-montmorillonite by Goldberg and Glaubig (1988), smectite by Missana et al. (2009b) and bentonite by Lee et al. (2012), they were considered for the low range of K_d values for bentonite in order to be conservative. Sorption values for shale were based on chlorite data (0.021 to 0.027 m^3/kg) measured in a solution with an ionic strength of 1.5 M and a pH of 8 by Ticknor et al. (1988). It was assumed that the chlorite content of shale was 40 percent. Sorption values for limestone were based on calcite data by Ticknor et al. (1988) (measured in a solution with ionic strength of 1.5 M and pH 7.5).

Bertetti (2016) studied the sorption of Se(-II) on bentonite, shale and limestone in the SR-270-PW reference brine (I = 6.0 M) and in a Ca-Na-Cl diluted solution (I = 0.01 M) under controlled reducing conditions. The observed Se(-II) K_d values are consistent for bentonite, shale and limestone. The Se(-II) K_d values in the 0.01M diluted solution (0.08-0.1 m^3/kg) are similar to that in the SR-270-PW brine (0.1 m^3/kg). The Se(-II) K_d value for bentonite measured in the SR-270-PW brine is very close to the K_d values for montmorillonite determined at an ionic strength of 0.5 M and a pH of 8.6 under reducing conditions (0.1±0.01 m^3/kg) by Iida et al. (2011). Tachi et al. (1999a) also found that the sorption of Se(-II) on bentonite did not appear to be affected by ionic strength. Sorption for shale was estimated considering three sources. The lower range of values was determined from data for chlorite (0.0072 m^3/kg) measured in a solution with an ionic strength of 1.5 M and a pH of 10 by Ticknor et al. (1988), a chlorite content of 40 percent being assumed for shale. Sorption on chlorite in 0.5 M NaCl solution (pH = 8.7) by Iida et al. (2011) (0.065 m^3/kg) was also considered. Considering mudstone to be an analogue to shale, the sorption on mudstone measured by Iida et al. (2009) with an ionic strength of 1.1 M was also considered. The sorption value determined in the SR-270-PW brine by Bertetti (2016) was used to define the upper range of Se (-II) sorption on shale (0.1 m^3/kg). Both data sets of Ticknor et al. (1988) and Iida et al. (2009) were obtained at high pH values of 10.5 and 11, but this should not be a problem since Figure 9 indicates that Se(II) sorption (I = 0.5 M) at pH 11 is low compared to that at pH 8. Therefore, this is a conservative value. The sorption value for limestone was based on values of 0.0037 and 0.0066 m^3/kg measured on calcite in a Ca-Na-Cl solution with an ionic strength of 1.5 M and pH values of 7.5 and 10 by Ticknor et al. (1988), 0.029 m^3/kg measured on calcite in a 0.5 M NaCl solution with pH of 8.6 by Iida et al. (2011), and 0.1 m^3/kg measured in the SR-270-PW reference brine at pH of 8 by Bertetti (2016).

Table 19: Selected Sorption Coefficients for Selenium

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Se (IV, VI)									
Ca-mont	NaCl	0.1	6.3-7.5	0.08	air	nr	0.008 - 0.014	batch	1
smectite	$NaClO_4$	0.1	6.2-6.9	7	air	nr	0.15 - 0.21	batch	3
smectite	$NaClO_4$	0.5	5.2-5.6	7	air	nr	0.30 - 0.31	batch	3
bentonite	sea water	0.68	6-7	14	air	nr	0.01 - 0.014	batch	14
bentonite	Na-Ca-Cl	0.24	7-8	14	air	nr	0.02 - 0.022	batch	14
bentonite	Na-HCO_3-SO_4	0.009	5.1-7.2	30	air	nr	0.004 - 0.0086	batch	5
bentonite	NaCl	0.05	5 - 7	61	N_2	nr	0.01 - 0.03	batch	10
illite	$NaClO_4$	0.2	6 - 7	7	air	nr	0.07 - 0.09	batch	3
chlorite	Ca-Na-Cl	1.5	8	14	N_2	90	0.021	batch	2
chlorite	Ca-Na-Cl	1.5	8	14	air	230	0.027	batch	2
chlorite	Ca-Na-Cl	0.015	7.5	14	N_2	20	0.077	batch	2
chlorite	Ca-Na-Cl	0.015	7.5	14	air	220	0.052	batch	2
shale	syn. gw. (no composition)	0.31-0.41	8	nr	N_2	nr	0.015 - 0.14	batch	6
clay	Na-Ca-K-Mg-SO_4	0.3-0.39	6.3-7.8	28	N_2	340	0.003 - 0.55	batch	7
mudrock	Na-Ca-Cl	0.24	7.5	nr	air	nr	0.138 ± 0.012	diffu	11
argillite	porewater	0.21	7.3	130	N_2	250	0.60 ± 0.03	batch	12
argillite	porewater	0.016	7.8	130	N_2	185 198	0.45 ± 0.05	batch	12
argillite	porewater	0.21	7.9	130	N_2	291	0.90 ± 0.05	batch	12
argillite	porewater	0.21	7.3	60	N_2	nr	0 [Se(VI)]	batch	12
argillite	porewater	0.016	7.8	60	N_2	nr	0 [Se(VI)]	batch	12
calcite	Ca-Na-Cl	1.5	7.5	14	air	370	0.0013	batch	2
calcite	Ca-Na-Cl	1.5	7.5	14	N_2	0	0.0037	batch	2
calcite	Ca-Na-Cl	0.015	7.5	14	air	220	0.0025	batch	2
calcite	Ca-Na-Cl	0.015	8	14	N_2	110	0.0034	batch	2
calcite	Na-Cl	0.1	6.0-7.5	0.08	air	nr	0.13 - 0.41	batch	1
Se (-II)									
bentonite	NaCl	0.1	6.2-7.4	14	$N_2/Na_2S_2O_4$	-310 -251	0.026 - 0.048	batch	4
bentonite	NaCl	0.01	6.3-7.8	14	$N_2/Na_2S_2O_4$	-346 -53	0.013 - 0.11	batch	4
mont.	Na-Cl	0.5	8.6	14	argon/N_2H_4	-370	0.10 ± 0.01	batch	8
mont.	NaCl	0.05	8.8	14	argon/N_2H_4	-340	0.29 ± 0.02	batch	8
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	8	30	N_2/H_2	-210	0.1	batch	13
bentonite	Na-Ca-Cl	0.01	9.2	30	N_2/H_2	-360	0.08 - 0.1	batch	13
shale	Na-Ca-Cl (SR-270-PW)	6.0	8	30	N_2/H_2	-210	0.1	batch	13
shale	Na-Ca-Cl	0.01	9.2	30	N_2/H_2	-360	0.08 - 0.1	batch	13
sandy mudrock	$NaNO_3$	1.1	11	27	argon/hydrazine	-297	0.022	batch	9
chlorite	Ca-Na-Cl	1.5	10.5	14	N_2/hydrazine	-200	0.0072	batch	2
chlorite	NaCl	0.5	8.7	14	argon/N_2H_4	-460	0.065 ± 0.006	batch	8
chlorite	NaCl	0.05	8.8	14	argon/N_2H_4	-490	0.12 ± 0.01	batch	8

Table 19 Continued …

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
calcite	Ca-Na-Cl	1.5	10	14	N_2/hydrazine	-390	0.0066	batch	2
calcite	Ca-Na-Cl	1.5	7.5	14	N_2	0	0.0037	batch	2
calcite	Ca-Na-Cl	0.015	10	14	N_2/hydrazine	-440	0.0066	batch	2
calcite	NaCl	0.5	8.6	14	argon/N_2H_4	-470	0.029 ± 0.006	batch	8
calcite	NaCl	0.05	8.7	14	argon/N_2H_4	-430	0.079 ± 0.006	batch	8
limestone	Na-Ca-Cl (SR-270-PW)	6.0	8	30	N_2/H_2	-210	0.1	batch	13
limestone	Na-Ca-Cl	0.01	9.2	30	N_2/H_2	-360	0.08 - 0.1	batch	13

1. Goldberg and Glaubig (1988)
2. Ticknor et al. (1988)
3. Missana et al. (2009b)
4. Tachi et al. (1999a)
5. Shibutani et al. (1994)
6. Xia et al. (2006a)
7. Lauber et al. (2000)
8. Iida et al. (2011)
9. Iida et al (2009)
10. Montavon et al. (2009)
11. Lee et al. (2009)
12. Frasca et al. (2014)
13. Bertetti (2016)
14. Lee et al. (2012)

nr: not record
Ca-mont: Ca-montmorillonite
syn. gw.: synthetic groundwater

Table 20: Recommended Sorption Coefficients for Selenium

SELENIUM (IV, VI) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.009-0.68**	**5.2 - 7**	**0.004 - 0.31**	**0.039 (5.5)**
comment	The high value based on smectite measured with I = 0.5 M by Missana et al. (2009b). The low value based on bentonite measured at low ionic strength I = 0.009 M by Shibutani et al. (1994).			
Shale	**1.5**	**8**	**0.008 - 0.011**	**0.01 (1.2)**
comment	Estimated using sorption values on chlorite from Ticknor et al. (1988). Likely as Se(IV) (0.021-0.027 m^3/kg), assuming shale contained 40% chlorite.			
Limestone	**1.5**	**7.5**	**0.0013**	**-**
comment	Based on sorption data on calcite from Ticknor et al. (1988). Likely as Se(IV).			
SELENIUM (-II) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.5 - 6.0**	**8 - 8.6**	**0.09 - 0.11**	**0.099 (1.1)**
comment	Based on sorption data measured on montmorillonite at I = 0.5 M by Iida et al. (2011) (0.1±0.01 m^3/kg) and measured on bentonite in SR-270-PW brine by Bertetti (2016) (0.1 m^3/kg).			
Shale	**0.5 - 6.0**	**8 - 11**	**0.003 - 0.1**	**0.02 (4.3)**
comment	Estimated using sorption data on chlorite from Ticknor et al. (1988) (0.0072 m^3/kg) and Iida et al. (2011) (0.065 m^3/kg), assuming shale contains 40% chlorite. Also considered data determined with mudstone at I = 1.1 M by Iida et al. (2009) (0.022 m^3/kg) and sorption data on shale determined in the SR-270-PW reference brine by Bertetti (2016) (0.1 m^3/kg).			
Limestone	**1.5 - 6.0**	**7.5 - 10**	**0.0037 - 0.1**	**0.013 (5.8)**
comment	Based on calcite data from Ticknor et al. (1988) (0.0037-0.0066 m^3/kg) and Iida et al. (2011) (0.029 m^3/kg) and limestone data in the SR-270-PW reference brine by Bertetti (2016) (0.1 m^3/kg).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

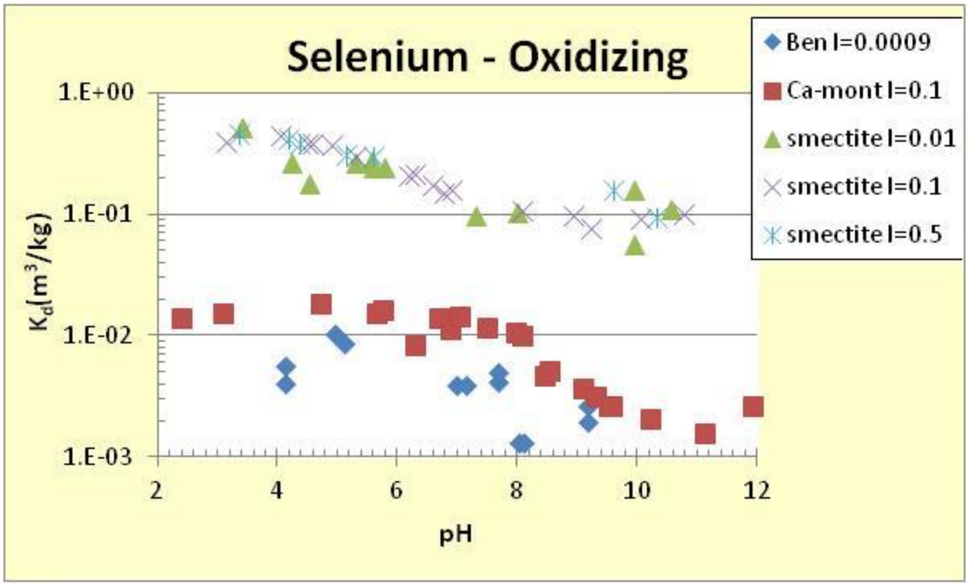


Figure 8: Selenium Sorption Coefficients on Bentonite, Montmorillonite and Smectite Under Oxidizing Conditions as a Function of Ionic Strength and pH (Missana et al. 2009b; Montavon et al. 2009; Goldberg and Glaubig 1988)

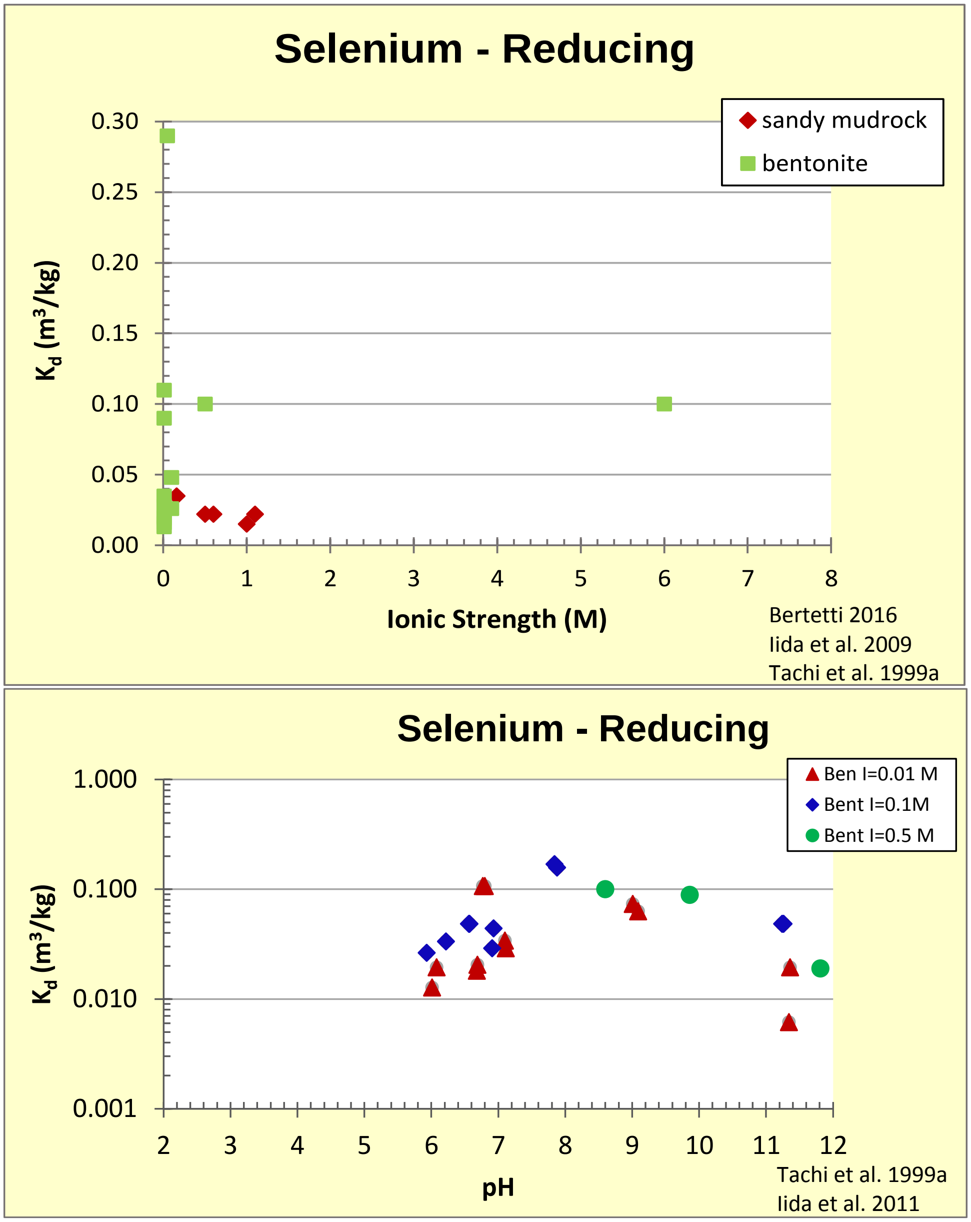


Figure 9: Selenium Sorption Coefficients on Mudrock and Bentonite Measured under Reducing Conditions as a Function of Ionic Strength and pH (Iida et al. 2009; Iida et al. 2011; Tachi et al. 1999a; Bertetti 2016)

3.8 ZIRCONIUM

Zirconium is a transition metal with an oxidation state of +4. PHREEQC (SIT database) predicts that the neutral $Zr(OH)_4$ species will be present in the reference groundwaters. Zirconium has a low solubility and is expected to sorb by surface complexation due to its tendency to form hydrolysis species. Therefore, it is likely to be sorbed in brine solutions.

Selected sorption data for zirconium are presented in Table 21. The data include “in-house” sorption measurements made on bentonite, shale, and limestone in the SR-270-PW brine (Vilks and Miller 2018, 2014), as well as values from the literature. Zirconium sorption measured on bentonite in sea water produced K_d values that were similar to the “in-house” sorption measurements. Sorption on mudstone in sea water was also within the range of values observed with “in-house” sorption measurements. Since the “in-house” sorption measurements were made with brine solutions, they are considered to be the most appropriate for Canadian sedimentary rocks. Zirconium sorption in SR-270-PW brine as a function of pH is illustrated in Figure 10B. Sorption between pH values of 3 to 4 is low, while in the pH range of interest (i.e., 6 to 7) experimental variablility had a more significant impact on Zr sorption values than did pH variation. The Zr K_d values on bentonite, shale and limestone in the SR-270-PW brine were lower by factors of 10 to 20 than in the dilute solution with ionic strength of 0.01 M (Vilks and Miller 2018).

Recommended zirconium K_d values are taken from Vilks and Miller (2014) and Vilks and Miller (2018), and are summarized in Table 22. The ranges in K_d values are based on ranges of measured values and the geometric means were calculated from these measured values.

Table 21: Selected Zirconium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	6.5	14	air	nr	0.45 ± 0.066	batch	1
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	5.9-6.5	14 - 180	N_2	nr	0.49 - 14.8	batch	6
bentonite	Na-Ca-Cl	0.01	6.9-8.3	7 - 184	N_2	nr	9.11 - 112	batch	6
Bent/qtz 10:90	Na-Ca-Cl-HCO_3	0.02	8.2	7 - 180	air	nr	0.63 - 1.58	batch	2
bentonite	sea water	0.72	7.5	1 - 24	air	nr	0.95 - 8.3	batch	3
shale	Na-Ca-Cl (SR-270-PW)	6.0	6.3	14	air	nr	0.49 ± 0.0	batch	1
shale	Na-Ca-Cl (SR-270-PW)	6.0	5.6-6.5	14 - 180	N_2	nr	0.32 - 7.82	batch	6
shale	Na-Ca-Cl	0.01	7.8-8.3	7 - 184	N_2	nr	3.67 - 85	batch	6
illite	Ca-Na-Cl-HCO_3	0.002	8	nr	air	nr	200	batch	4
mudstone	sea water	0.72	7.7	24	air	nr	2.28	batch	3
sediment	sea water	0.72	8	30	air	420	1.0 - 76	batch	5
limestone	Na-Ca-Cl (SR-270-PW)	6.0	6.3	14	air	nr	0.14 ± 0.03	batch	1
limestone	Na-Ca-Cl (SR-270-PW)	6.0	5.7-6.5	14 - 180	N_2	nr	0.13 - 4.68	batch	6
limestone	Na-Ca-Cl	0.01	7.7-8.4	7 - 184	N_2	nr	1.24 - 33.9	batch	6

1. Vilks and Miller (2014)
2. Allard et al. (1979)
3. Taki and Hata (1991)
4. Rochon et al. (1980)
5. Duursma and Eisma (1973)
6. Vilks and Miller (2018)

nr: not recorded

Table 22: Recommended Sorption Coefficients for Zirconium

ZIRCONIUM (IV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**5.9 - 6.5**	**0.49 - 14.8**	**2.15 (3.8)**
comment	Measured in SR-270-PW synthetic brine by Vilks and Miller (2014) and Vilks and Miller (2018)			
Shale	**6.0**	**5.6 - 6.5**	**0.32 - 7.82**	**0.97 (3.0)**
comment	Measured in SR-270-PW synthetic brine by Vilks and Miller (2014) and Vilks and Miller (2018)			
Limestone	**6.0**	**5.7 - 6.5**	**0.13 - 4.68**	**0.50 (4.0)**
comment	Measured in SR-270-PW synthetic brine by Vilks and Miller (2014) and Vilks and Miller (2018)			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

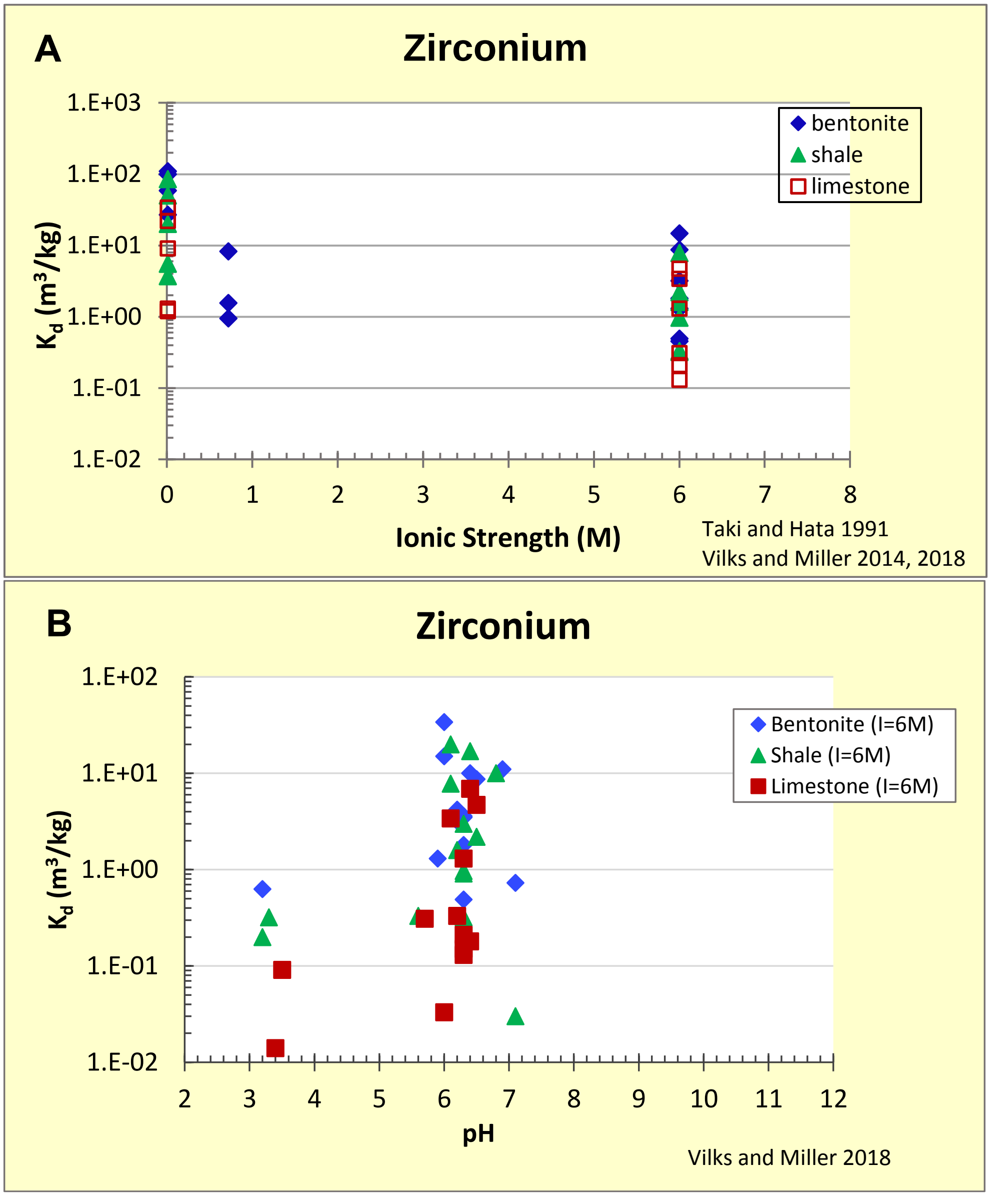


Figure 10: Effect of Ionic Strength and pH on Zirconium Sorption Coefficients in Brine. Effect of pH Based on One-hour Short Sorption Tests (Vilks and Miller 2018, 2014; Taki and Hata 1991)

3.9 NIOBIUM

Niobium is a transition metal element with an oxidation state of +5. The dominant solution species in the reference groundwaters is $Nb(OH)_6^-$, with minor amounts of $Nb(OH)_5$ and $Nb(OH)_7^{-2}$ (predicted with PHREEQC and SIT database). Niobium solid phases include Nb_2O_5 and niobite $[(Fe,Mn)(Nb,Ta)_2O_8]$. Given its tendency to form hydrolysis species, Nb might be expected to sorb by surface complexation.

Selected niobium K_d values are summarized in Table 23. Figure 11 (based on data from Taki and Hata 1991; Erdal et al. 1977; Ikeda and Amaya 1998; Duursma and Bosch 1970) indicates that niobium sorption on bentonite increases with increasing ionic strength, suggesting that measurements on bentonite at low ionic strength would be conservative for higher ionic strengths. Sorption on mudstone does decrease as the ionic strength is increased from approximately 0 M to the ionic strength of sea water. Since niobium sorption measurements were made in a narrow pH range, the dependence of Nb sorption on pH is not clear and a variation with pH was not plotted. Given niobium's oxidation state and affinity for oxygen, niobium is expected to sorb in brine solutions by surface complexation.

Sorption values for bentonite and shale were derived from measurements in sea water. Taki and Hata (1991) found that in sea water Nb sorption on bentonite increased with contact time, going from 1.2 to 6.4 m^3/kg as time increased from 1 to 24 days. The value determined after 24 days is considered to be the most appropriate. The K_d value of 23 m^3/kg, determined by Ikeda and Amaya (1998) for Nb sorption on bentonite in sea water after 26 days, was also considered. Sorption on shale considered K_d values for Nb sorption on mudstone and sediment in sea water, reported by Duursma and Bewers (1986), Duursma and Bosch (1970), Duursma and Eisma (1973), and Taki and Hata (1991). The selected range of values for shale is 1.1 to 6.3 m^3/kg.

The relationship between the logarithm of the sorption coefficient on calcite and the ionic radii of elements indicates that sorption decreases with the ionic radii of the element (Bradbury et al. 2010). Since the ionic radius of Nb (0.64 Å) is less than 0.69 Å, which is the lowest ionic radius in Figure 8.1 of Bradbury et al. (2010), the sorption value of Nb(V) for calcite was assumed to be 0 m^3/kg.

Table 24 summarizes the recommended niobium sorption values for bentonite, shale and limestone.

Table 23: Selected Sorption Coefficients for Niobium

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	sea water	0.72	7.1	1	air	nr	1.2	batch	4
bentonite	sea water	0.72	7.1	3	air	nr	1.8	batch	4
bentonite	sea water	0.72	7.1	24	air	nr	6.4	batch	4
bentonite	distilled water	≈ 0	8	1	air	nr	1.2	batch	4
bentonite	distilled water	≈ 0	8	3	air	nr	1.4	batch	4
bentonite	distilled water	≈ 0	8	24	air	nr	1.4	batch	4
bentonite	groundwater	0.005	8.5	2.8	air	400 - 435	0.18 - 0.94	batch	5
bentonite	groundwater	0.005	8.5	11.6	air	400 - 435	0.51	batch	5
bentonite	groundwater	0.005	8.5	27.6	air	400 - 435	0.47 - 0.84	batch	5
bentonite	groundwater	0.005	8.5	41.8	air	400 - 435	0.47 - 1.7	batch	5
bentonite	sea water	0.67	8.1	26	nr	nr	23	batch	6
illite	$NaClO_4$	0.1	6.2	3	N_2	nr	28	batch	7
illite	$NaClO_4$	0.1	6.6	3	N_2	nr	100	batch	7
illite	$Ca(ClO_4)_2$	0.25	5.7	3	N_2	nr	300	batch	7
illite	$Ca(ClO_4)_2$	0.25	6.6	3	N_2	nr	108	batch	7
sediment	sea water	0.72	8	24	nr	nr	4.74	batch	1
sediment	sea water	0.72	8	2	nr	nr	2.5	batch	2
sediment	sea water	0.72	8	50	nr	nr	3.5	batch	2
sediment	sea water	0.72	8	150	nr	nr	4.5	batch	2
sediment	sea water	0.72	8	nr	nr	nr	2.1 - 6.3	thin lay technique	3
mudstone	sea water	0.72	7.8	1	air	nr	1.4 - 2.8	batch	4
mudstone	sea water	0.72	7.8	3	air	nr	1.1 - 1.9	batch	4
mudstone	sea water	0.72	7.8	24	air	nr	6.3	batch	4
mudstone	distilled water	≈ 0	8	1	air	nr	3.3	batch	4
mudstone	distilled water	≈ 0	8	3	air	nr	5.0	batch	4
mudstone	distilled water	≈ 0	8	24	air	nr	25	batch	4
clay	groundwater	0.018	8.7 - 9	100 - 180	N_2	nr	0.24 - 0.34	batch	8

1. Duursma and Bewers (1986)
2. Duursma and Bosch (1970)
3. Duursma and Eisma (1973)
4. Taki and Hata (1991)
5. Erdal et al. (1977)
6. Ikeda and Amaya (1998)
7. Ervanne et al. (2014)
8. Baston et al. (1992)

nr: not recorded

Table 24: Recommended Sorption Coefficients for Niobium

NIOBIUM (V)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.68 - 0.72**	**7.1 - 8.1**	**6.4 - 23**	**8.5 (4.1)**
comment	Based on measurements on bentonite in sea water by Taki and Hata (1991), and Ikeda and Amaya (1998)			
Shale	**0.72**	**7.8 - 8.0**	**1.1 - 6.3**	**3.3 (1.5)**
comment	Based on measurements on mudstone in sea water by Taki and Hata (1991) and on sediment by Duursma and Bewers (1986), Duursma and Bosch (1970), and Duursma and Eisma (1973).			
Limestone			**0**	**-**
comment	Set to 0 m^3/kg based on the K_d vs ionic radius correlation found in Bradbury et al. (2010) for calcite.			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

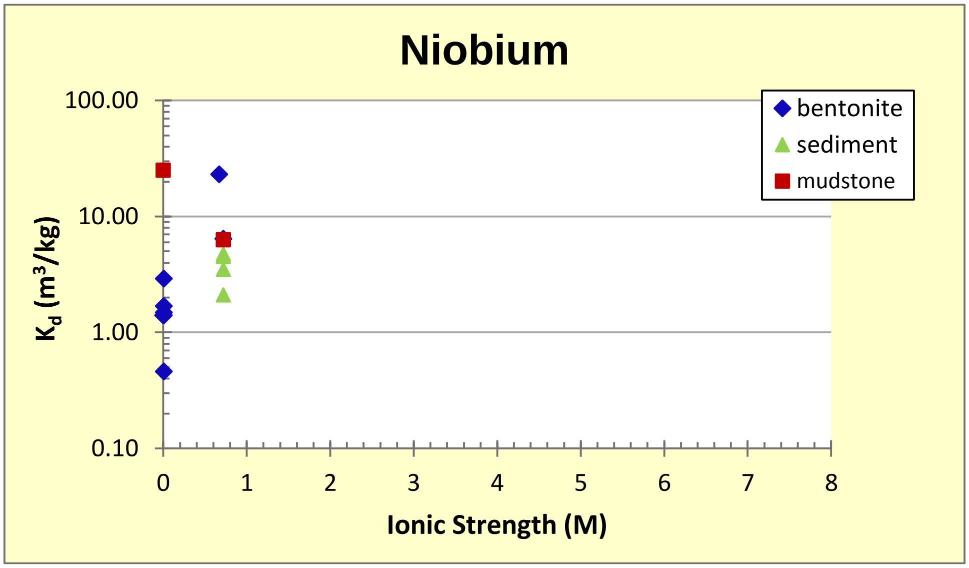


Figure 11: Niobium Sorption Coefficients on Bentonite, Sediment and Mudstone as a Function of Ionic Strength (Taki and Hata 1991; Erdal et al. 1977; Ikeda and Amaya 1995; Duursma and Bosch 1970; Duursma and Eisma 1973; Duursma and Bewers 1986)

3.10 MOLYBDENUM

Molybdenum is a transition metal element with a dominant oxidation state of +6. The expected dissolved species is the anion MoO_4^{-2}, which is not expected to sorb very strongly.

Selected molybdenum sorption coefficients are given in Table 25. The solids for which molybdenum sorption was reported only include clay, alluvium, silt, and soil. However, all measurements were made in very dilute water and are not appropriate for saline solutions. Bradbury et al. (2010) recommended a sorption coefficient of 0 m^3/kg for Mo(VI) for generic Swiss calcareous rocks. Furthermore, Vandergraaf and Ticknor (1994) assigned a sorption coefficient value of 0 m^3/kg for molybdenum sorbing on all minerals found in granitic rocks.

Table 25: Selected Sorption Coefficients for Molybdenum

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
clay	Na-Ca-HCO_3-Cl-SO_4	0.004	7.1	nr	air	nr	0.04 - 0.4	batch	1
clay	Na-Ca-HCO_3-Cl-SO_4	0.004	4.5 - 8.2	nr	air	nr	0.01 - 0.4	batch	1
alluvium	Na-HCO_3	0.005	8.5	2.7	air	400 435	0.016	batch	2
alluvium	Na-HCO_3	0.005	8.5	11.7	air	400 435	0.023	batch	2
alluvium	Na-HCO_3	0.005	8.5	18.7	air	400 435	0.023	batch	2
silt	Na-Ca-HCO_3-Cl-SO_4	0.004	4.5 - 8.2	nr	air	nr	0.27	batch	1
silt	Na-Ca-HCO_3-Cl-SO_4	0.004	7.1	nr	nr	nr	0.27	batch	1
sandy soil	Ca-Na-HCO_3-Cl	0.004	7.4	nr	nr	nr	0.014	batch	3
sandy soil	Ca-Na-K-SO_4-Cl	0.002	6.7	nr	nr	nr	0.008 - 0.052	field	3
sandy soil	Ca-Na-K-SO_4-Cl	0.003	6.7	nr	nr	nr	0.016 - 0.026	field	3
sandy soil	Ca-K-SO_4-Cl	0.016	5.7	nr	nr	nr	0.021 - 0.05	field	3
mont.	NaCl	0.1	5	nr	air	nr	0.0075	batch	4
mont.	NaCl	0.1	6.5	nr	air	nr	0.001	batch	4

1. Inoue and Morisawa (1975)
2. Erdal et al. (1977)
mont.: montmorillonite

3. Sheppard et al. (1987)
4. Goldberg et al. (1996)
nr: not recorded

Table 26 summarizes the recommended sorption values that should be considered for bentonite, shale and limestone under saline conditions.

Table 26: Recommended Sorption Coefficients for Molybdenum

MOLYBDENUM (VI)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			

3.11 TECHNETIUM

Technetium is a transition metal element that may be present in groundwater in several oxidation states (+2 to +7), although the most stable oxidation states are Tc(IV) under reducing conditions and Tc(VII) under oxidizing conditions. Under oxic conditions Tc(VII) forms the anionic TcO_4^- species. Since the TcO_4^- species is anionic, its sorption is expected to be very low on most minerals. Under slightly reducing conditions, TcO_4^- is reduced to $TcO(OH)_2$ by Fe-containing minerals (Vandergraaf et al. 1984; Haines et al. 1987). This induces technetium sorption or surface precipitation on Fe-containing minerals. $TcO(OH)_2$ has a low solubility and is prone to be strongly sorbed. PHREEQC (SIT database) predicts that in the reference groundwater SR-270-PW, Tc will be in the +4 oxidation state (Table 3). In reducing brine solutions, the sorption of $TcO(OH)_2$ is expected to be determined by surface complexation and/or a redox surface-induced precipitation. The technetium sorption database must consist of two data sets, one for oxidizing conditions and one for reducing conditions.

Selected technetium K_d values from the literature are given in Table 27. The criteria for accepting sorption values for Tc(IV) is that the Eh must be reported to confirm that technetium is present in its reduced state. If Eh is not reported, or if Eh values > 100 mV are reported, the reported K_d value is considered valid only for Tc(VII).

For oxidizing conditions, sorption values that are of interest for bentonite were determined by Berry et al. (2007) and Baston et al. (1995) in sea water (0.065 - 0.24 m^3/kg), and by Mucciardi et al. (1978) in a NaCl brine with an ionic strength of 5.1 M (1.7×10^{-4} - 3.9×10^{-4} m^3/kg). The sorption value of 0 m^3/kg reported by JGC Corporation (1991) for sorption on bentonite in sea water was not considered because the total Tc concentration used in the test ($3.4x10^{-3}$ mol/L) was excessively high. Sorption values for shale were based on Tc(VII) measurements on shale measured in 5.1 M NaCl brine (3.5×10^{-3} - 8.45×10^{-2} m^3/kg) by Mucciardi et al. (1978), and in NaCl brine with an ionic strength of 2.0 M (3.5×10^{-4} - 1.1×10^{-3} m^3/kg) by Francis and Bondietti (1979). Measurements on mudstone in sea water (0.048 to 0.051 m^3/kg) reported by JGC Corporation (1991) were also considered. The recommended K_d value for limestone is from measurements in 5.1 M NaCl brine by Mucciardi et al. (1978) (2.4×10^{-3} - 7.3×10^{-3} m^3/kg). In summary, the respective recommended K_d values for Tc(VII) sorption on bentonite, shale and limestone are 1.7×10^{-4} - 0.24 m^3/kg, 3.5×10^{-3} - 8.5×10^{-2} m^3/kg, and 2.4×10^{-3} - 7.3×10^{-3} m^3/kg. Sorption values for bentonite (Jedinakova-Krizova et al. 1998; Shade et al. 1984; Wang and Tao 2004) under oxidizing conditions are given in Figure 12A. Sorption on bentonite is lower at higher ionic strength (from 0 to 0.1 M). However, the effect of pH on Tc(VII) sorption is not clear.

The K_d data that were confirmed to be obtained under reducing conditions are the measurements on bentonite reported for sea water by Baston et al. (1995) and Berry et al. (2007), and for dilute water by Baston et al. (1997). Hallam et al. (2011) reported Tc(IV) sorption values for shale derived from sorption tests using deionized water (pH 5.6 - 7.1). A 6 V electropotential was applied to reduce the pertechnetate to Tc(IV). The reported range of K_d values, with a range of 1.6 - 4.2 m^3/kg and a geometric mean of 2.8 (2.0) m^3/kg, are consistent with the K_d values reported for bentonite in sea water. Bradbury et al. (2010) proposed a sorption coefficient of 0 m^3/kg for Tc(IV) onto calcite (the main component of limestone), considering the ionic radius (0.645 Å) of Tc(IV) is less than 0.69 Å, which is the lowest ionic radius in Figure 8.1 of the paper. Bertetti (2016) measured Tc(IV) sorption on bentonite, shale and limestone in the SR-270-PW reference brine and in a dilute solution (Na-Ca-Cl type, I = 0.01 M) under reducing conditions. The reported K_d values for bentonite in SR-270-PW brine is

5 m^3/kg, within the range of K_d values for sea water by Baston et al. (1995) and Berry et al. (2007). The Tc(IV) sorption has a K_d value of 0.02 m^3/kg for shale and a value of 10 m^3/kg for limestone in SR-270-PW reference brine. Tc(IV) sorption values for bentonite, shale and limestone under reducing conditions are given in Figure 12B. Sorption on bentonite, shale and limestone is lower at higher ionic strength (from ionic strength of 0 (or 0.01) to 6.0 M).

Table 27: Selected Sorption Coefficients for Technetium

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Tc (VII)									
bentonite	sea water	0.73	8	120	N_2	300 310	0.065 - 0.21	batch	1
bentonite	Na-Ca-HCO_3-SO_4	0.007	4 - 9	8	air	nr	$(3.0 - 15)\times10^{-4}$	batch	2
bentonite	Na-Cl-SO_4	0.06	7	36	air	nr	0.0008 - 0.45	batch	3
bentonite	sea water	0.68	8	120	nr	300	0.21 - 0.24	batch	4
bentonite	HCl/NaOH	≈ 0	5.7 - 8	1	air	nr	0.59 - 2.3	batch	11
bentonite	NaCl	5.1	8.2	3	air	473	3.9×10^{-4}	batch	6
bentonite	NaCl	5.1	8.1	29	air	209	1.7×10^{-4}	batch	6
bentonite	Na-ClO_4	0.1	6 - 8	nr	nr	nr	$(7.0 - 20)\times10^{-4}$	diffu.	14
bentontie	sea water	0.68	7.6	30	nr	334 337	0	batch	8
illite	NaCl	5.1	6.2	3	air	573	3.0×10^{-4}	batch	6
illite	NaCl	5.1	6.7	10	air	573	7.3×10^{-4}	batch	6
illite	NaCl	5.1	6.3	29	air	278	4.7×10^{-3}	batch	6
illite	$CaCl_2$	0.015	7	3 - 29	air	270 573	$(0.07 - 6.7)\times10^{-4}$	batch	6
illite	NaCl	0.03	6 - 7	10-29	air	310 570	$(4.1 - 10.2)\times10^{-3}$	batch	6
illite	NaCl	0.4	8.4	21	air	nr	3.0×10^{-3}	batch	9
mudstone	sea water	0.68	8	30	nr	351	0.048 - 0.051	batch	8
shale	NaCl	2.0	nr	5	N_2	nr	3.5×10^{-4}	batch	10
shale	NaCl	2.0	nr	12	N_2	nr	1.1×10^{-3}	batch	10
shale	NaCl	2.0	nr	13	N_2	nr	3.7×10^{-4}	batch	10
shale	NaCl	5.1	7.8	3	air	316	3.5×10^{-3}	batch	6
shale	NaCl	5.1	7.5	30	air	288	8.45×10^{-2}	batch	6
shale	Ca-HCO_3-SO_4	0.005	8	7	air	nr	1.0×10^{-4}	batch	12
shale	Na-NO_3	0.26	7.6	0.83	nr	nr	0.02 ± 0.006	batch	7
argillite	Na-Ca-Mg-K	0.004	8.2 - 8.7	60	air	nr	0.001 - 0.016	batch	13
limestone	NaCl	5.1	8.0	3	air	308	2.37×10^{-3}	batch	6
limestone	NaCl	5.1	7.8	10	air	346	7.3×10^{-3}	batch	6
limestone	NaCl	0.03	8.4 - 8.5	3 - 30	air	386 437	$(1.15 - 77.6)\times10^{-3}$	batch	6

Table 27 continued…

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Tc (IV)									
bentonite	sea water	0.68	8.2	120	N_2/ $Na_2S_2O_4$	-430	9.8 - 10	batch	4
bentonite	deionized water	≈ 0	10	120	N_2	-450 -460	1.4 - 21	batch	5
bentonite	sea water	0.73	8.2	120	N_2/ $Na_2S_2O_4$	-410 -430	4.2 - 8.8	batch	1
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	7	116	N_2+H_2	-20	5	batch	16
bentonite	Na-Ca-Cl	0.01	8.5	116	N_2+H_2	-160	10	batch	16
shale	deionized water	≈ 0	5.6	7	N_2	*	1.6 ± 0.4	batch	15
shale	deionized water	≈ 0	6.4	7	N_2	*	2.5 ± 3.1	batch	15
shale	deionized water	≈ 0	6.5	7	N_2	*	3.7 ± 3.4	batch	15
shale	deionized water	≈ 0	7.1	7	N_2	*	4.2 ± 0.6	batch	15
shale	Na-Ca-Cl (SR-270-PW)	6.0	7	116	N_2	-20	0.02	batch	16
shale	Na-Ca-Cl	0.01	8.5	116	N_2+H_2	-160	0.01	batch	16
limestone	Na-Ca-Cl (SR-270-PW)	6.0	7	116	N_2	-20	10	batch	16
limestone	Na-Ca-Cl	0.01	8.5	116	N_2+H_2	-160	100	batch	16

1. Berry et al. (2007)
2. Jedinakova-Krizova et al. (1998)
3. Hooker et al. (1986)
4. Baston et al. (1995)
5. Baston et al. (1997)
6. Mucciardi et al. (1979)
7. Ito and Kanno (1988)
8. JGC Corporation (1991)
9. Palmer and Meyer (1981)
10. Francis and Bondietti (1979)
11. Shade et al. (1984)
12. MaClean et al. (1978)
13. Erdal et al. (1979)
14. Wang and Tao (2004)
15. Hallam et al. (2011)
16. Bertetti (2016)

*Tc reduced to (IV) oxidation state by applying a 6 V electropotential with a vitreous carbon cathode and a platinum wire anode.

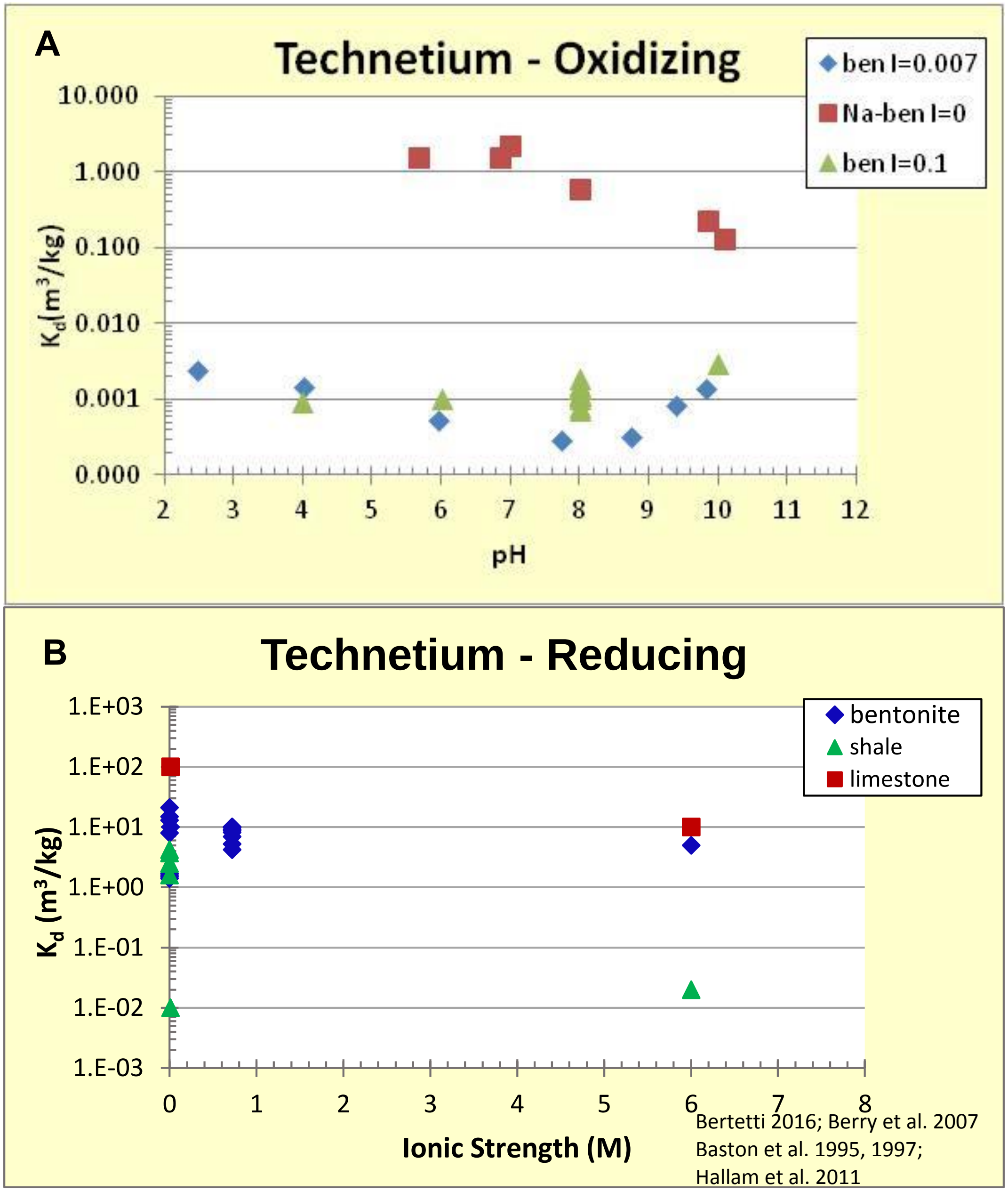
nr: not recorded

Technetium sorption values recommended for bentonite, shale and limestone are summarized in Table 28.

Table 28: Recommended Sorption Coefficients for Technetium

TECHNETIUM (VII) – Oxidizing Conditions (Eh > ~100 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.68 - 5.1**	**8.0 - 8.2**	**1.7×10^{-4} - 0.24**	**0.008 (113)**
comment	Measured sorption value for bentonite by Mucciardi et al. (1979) and Baston et al. (1995).			
Shale	**5.1**	**7.5 - 7.8**	**3.5×10^{-3} - 8.45×10^{-2}**	**0.017 (9)**
comment	Measured sorption data on shale by Mucciardi et al. (1979)			
Limestone	**5.1**	**7.8 - 8.0**	**2.37×10^{-3} - 7.3×10^{-3}**	**0.004 (2)**
comment	Measured sorption data on limestone by Mucciardi et al. (1979)			
TECHNETIUM (IV) – Reducing Conditions (Eh < ~100 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**7**	**5**	
comment	Based on measurements on bentonite in the SR-270-PW reference brine by Bertetti (2016).			
Shale	**6.0**	**7**	**0.02**	
comment	Based on measurements on shale in the SR-270-PW reference brine by Bertetti (2016).			
Limestone	**6.0**	**7**	**10**	
comment	Based on measurements on limestone in the SR-270-PW reference brine by Bertetti (2016).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.



Bertetti 2016; Berry et al. 2007
Baston et al. 1995, 1997;
Hallam et al. 2011

Figure 12: Technetium Sorption Coefficients on Bentonite under Oxidizing and Reducing Conditions (Jedinakova-Krizova et al. 1998; Shade et al. 1984; Wang and Tao 2004; Bertetti 2016; Baston et al. 1995, 1997; Hallam et al. 2011)

3.12 PALLADIUM

Palladium is a transition element with several valence states (e.g., 0, +1, +2, +4 and +6), the +2 oxidation state being dominant in aqueous solutions. Palladium, along with ruthenium, rhodium, osmium, iridium and platinum, make up the platinum group elements. PHREEQC (SIT database) predicts that the reference groundwaters will mainly contain the anionic $PdCl_4^{-2}$ species (e.g., SR-270-PW reference water in Table 3). Vandergraaf and Ticknor (1994) suggested that the chemistry of palladium may be similar to that of Ni. However, speciation calculations indicate that Ni chemistry will be dominated by the cationic species $NiCl^+$ and Ni^{+2} as opposed to palladium’s anionic species. On the other hand, the aqueous chemistry of Pb(II) is dominated by chloride complexes in brine solutions (Table 3), suggesting that Pb could be used as an analog for Pd.

Palladium sorption data are indicated in Table 29. Riddoch (2016) and Riddoch and Nagasaki (2016) investigated the effects of ionic strength (0.1 to 4.0 M) and pH (5 to 9) on sorption of Pd on bentonite, shale and illite, as shown in Figure 13A and 13B, respectively. The K_d values decrease with increasing the ionic strength from 0.1 to 3 M but is independent of the ionic strength at greater than 3.0 M. The relationship between K_d values and pH depends on the ionic strengths. At ionic strength of 4 M, the K_d values have no clear relationship with pH for bentonite and illite. For shale, the K_d values increase with increasing pH from 5 to 7 and then decrease with further increases in pH from 7 to 9. At ionic strength of 4 M and pH of 6-7, measured sorption coefficients values are 0.03 to 1.25 m^3/kg for bentonite and 0.05-3.11 m^3/kg for shale (Riddoch and Nagasaki 2016).

Tachi et al. (1999b) studied sorption on bentonite from 0.01 and 0.1 M NaCl solutions (illustrated in Figure 13C). Sorption decreases with increasing pH, particularly from pH values of 5 to 8, and then decreases to a lesser degree as pH increases to 11. Vilks et al. (2016) performed sorption tests in the reference SR-270-PW brine solution and found significant palladium sorption (Table 29). Palladium sorption coefficients ranged from 0.14 to 14.5 m^3/kg for bentonite, 0.04 to 14.3 m^3/kg for shale and 0.05 to 22 m^3/kg for limestone. The K_d values for bentonite and shale measured in the SR-270-PW brine solution (Vilks and Miller 2018) are close to that measured in ionic strength of 4 M Na-Ca-Cl brine (Riddoch and Nagasaki 2016).

Table 29: Selected Sorption Coefficients for Palladium

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	NaCl	0.01	5	30	air	nr	82	batch	1
bentonite	NaCl	0.01	8	30	air	nr	0.96 - 17	batch	1
bentonite	NaCl	0.01	11	30	air	nr	1.1 - 25	batch	1
bentonite	NaCl	0.1	5	30	air	nr	17 - 62	batch	1
bentonite	NaCl	0.1	8	30	air	nr	0.70 - 28	batch	1
bentonite	NaCl	0.1	11	30	air	nr	0.36 - 16	batch	1
bentonite	nr	nr	nr	nr	nr	nr	0 - 0.01	diffu	2
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	5.7-6.4	8-17	N_2	nr	0.14 - 14.5	batch	5
bentonite	Na-Ca-Cl	0.1	6.8-6.9	14	air	501-506	0.99 - 1.61	batch	6,7
bentonite	Na-Ca-Cl	0.5	6.6-6.7	14	air	473-506	0.5 - 0.59	batch	6,7
bentonite	Na-Ca-Cl	1.0	6.3-6.5	14	air	484-508	0.27 - 0.38	batch	6,7
bentonite	Na-Ca-Cl	2.0	6.2-6.3	14	air	497-514	0.17 - 0.2	batch	6,7
bentonite	Na-Ca-Cl	3.0	6.1-6.3	14	air	503-513	0.02 - 0.08	batch	6,7
bentonite	Na-Ca-Cl	4.0	5	14	air	433-441	0.07 - 0.20	batch	6,7
bentonite	Na-Ca-Cl	4.0	6	14	air	513-519	0.03 - 0.07	batch	6,7
bentonite	Na-Ca-Cl	4.0	7	14	air	353-376	0.06 - 1.25	batch	6,7
shale	Na-Ca-Cl (SR-270-PW)	6.0	5.6-6.4	8-17	N_2	nr	0.04 - 14.3	batch	5
shale	Na-Ca-Cl	0.1	7.4-7.7	14	air	481-498	3.9 - 4.42	batch	6,7
shale	Na-Ca-Cl	0.5	7.2-7.4	14	air	465-476	1.92 - 3.6	batch	6,7
shale	Na-Ca-Cl	1.0	7.1-7.2	14	air	467-470	3.02 - 3.89	batch	6,7
shale	Na-Ca-Cl	2.0	6.8-6.9	14	air	485-493	1.4 - 1.83	batch	6,7
shale	Na-Ca-Cl	3.0	6.7	14	air	498-501	0.68 - 0.83	batch	6,7
shale	Na-Ca-Cl	4.0	5	14	air	404-422	0.01 - 0.09	batch	6,7
shale	Na-Ca-Cl	4.0	6	14	air	417-427	0.05 - 0.27	batch	6,7
shale	Na-Ca-Cl	4.0	7	14	air	405-514	1.29 - 3.11	batch	6,7
illite	Na-Ca-Cl	0.1	5.3-5.8	14	air	528-542	0.33 - 0.6	batch	6,7
illite	Na-Ca-Cl	0.5	5.4	14	air	550-555	0.5 - 0.67	batch	6,7
illite	Na-Ca-Cl	1.0	5.4-5.5	14	air	536-546	0.63 - 0.66	batch	6,7
illite	Na-Ca-Cl	2.0	5.5-5.8	14	air	519-527	0.32 - 0.35	batch	6,7
illite	Na-Ca-Cl	3.0	5.7-5.8	14	air	517-530	0.02 - 0.27	batch	6,7
illite	Na-Ca-Cl	4.0	5.5-5.7	14	air	541-545	0.01 - 0.38	batch	6,7
illite	Na-Ca-Cl	4.0	7	14	air	436-443	0.08 - 0.12	batch	6,7
silica	Na-Cl	0.05	7	nr	air	nr	0.46	batch	3
soil	KCl	0.1	6.4-6.8	0.92	air	nr	0.95	batch	4
limestone	Na-Ca-Cl (SR-270-PW)	6.0	5.7-6.4	8-17	N_2	nr	0.05 - 22	batch	5

1. Tachi et al. (1999b)
2. Yu and Neretnieks (1997)
3. Wang et al. (2001a)
4. Sako et al. (2009)
5. Vilks and Miller (2018)
6. Riddoch (2016)
7. Riddoch and Nagasaki (2016)

nr: not recorded

diffu: diffusion

Table 30 summarizes the recommended sorption values for palladium on bentonite and sedimentary rocks (shale and limestone). The recommended values are based on measurements reported by Vilks and Miller (2018) and Riddoch and Nagasaki (2016).

Table 30: Recommended Sorption Coefficients for Palladium

PALADIUM (II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**4.0 - 6.0**	**5.7 - 7**	**0.03 - 14.5**	**0.30 (10.2)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018) and Riddoch and Nagasaki (2016).			
Shale	**4.0 - 6.0**	**5.6 - 6.5**	**0.04 - 14.3**	**2.61 (6.6)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018) and Riddoch and Nagasaki (2016).			
Limestone	**6.0**	**5.7 - 6.4**	**0.12 - 22**	**2.16 (5.4)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

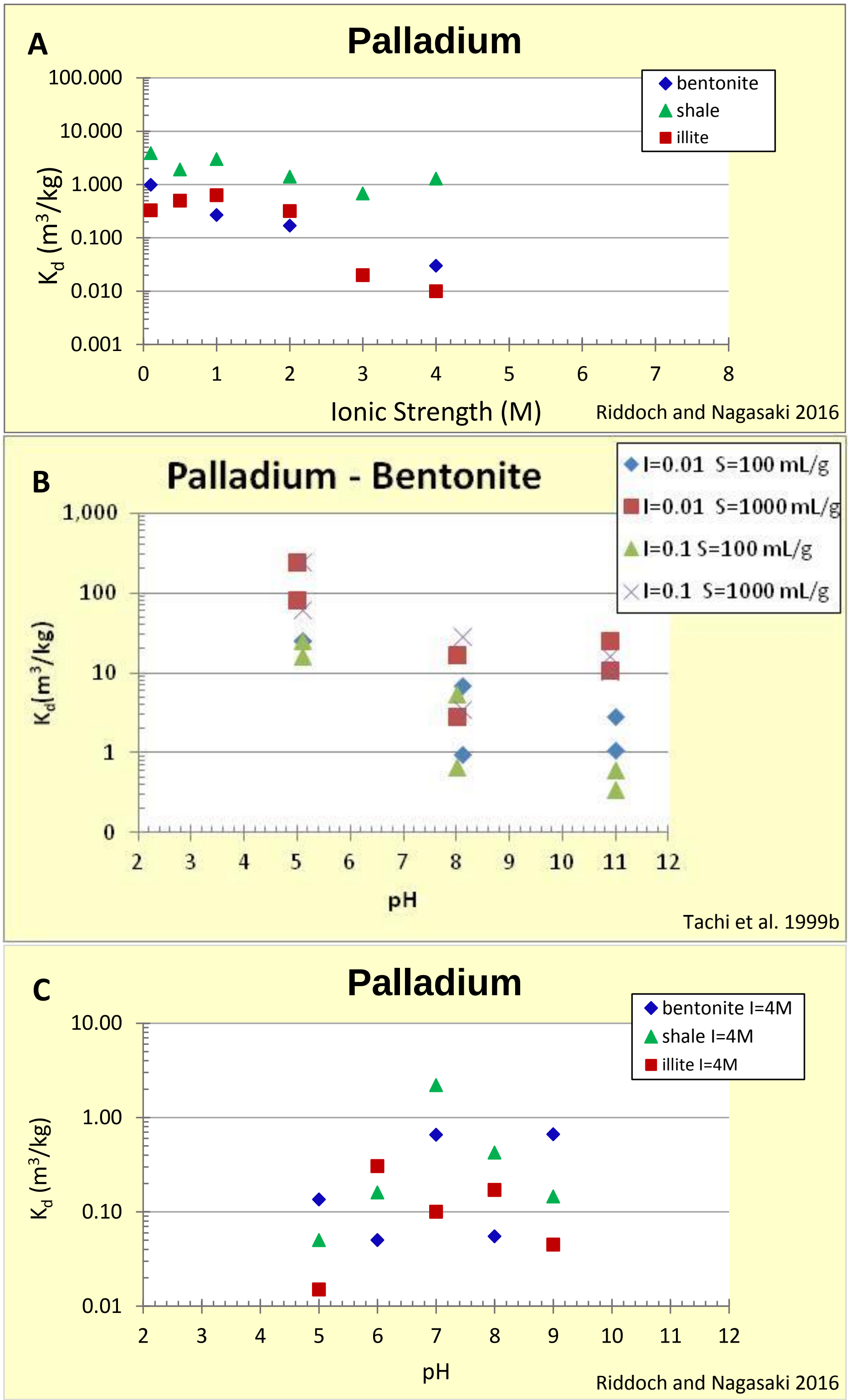


Figure 13: Palladium Sorption Coefficients as a Function of Ionic Strength and pH for Bentonite, Shale and Illite (Riddoch and Nagasaki 2016) and Sorption Coefficients for Bentonite in NaCl Solution at Different Liquid to Solid Ratio (S) as a Function of Ionic Strength (Tachi et al. 1999)

3.13 SILVER

Silver is a group 11 d-block element. Silver can be found in nature in its native form, as an alloy with gold or another metal, or as a component of sulfide minerals or as a silver chloride. The dominant oxidation form is Ag(I), although less commonly higher oxidation states do exist (+2, +3, +4). In brine solutions, its solution chemistry is dominated by chloride complexes ($AgCl_2^-$, $AgCl_3^{-2}$, $AgCl_4^{-3}$).

The amount of data on silver sorption in the literature is limited. Table 31 summarizes K_d values for silver sorption on clay, silt, silica, bentonite and soil from relatively dilute solutions. The sparcity of sorption measurements over a range of ionic strengths and chloride concentrations precludes the development of an understanding of how sorption would be affected by ionic strength. Furthermore, since the solution chemistry of Ag is dominated by chloride complexes, it is likely that Ag K_d values in brine solutions would be extremely low. Therefore, only sorption values of 0 m^3/kg can be recommended for the sorption of silver at this time, as indicated in Table 32.

Table 31: Measured Silver Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
clay	Na-Ca-Cl-HCO_3-SO_4	0.004	7.1	nr	air	nr	0.08 - 0.30	batch	1
silt	Na-Ca-Cl-HCO_3-SO_4	0.004	7.1	nr	air	nr	0.10	batch	1
silica	Na-Cl	0.05	4	nr	air	nr	1.4	batch	2
silica	Na-Cl	0.05	7	nr	air	nr	1.3	batch	2
silica	Na-Cl	0.05	7	nr	air	nr	0.029	batch	2
silica	Na-Cl	0.05	9	nr	air	nr	1.3	batch	2
bentonite	deionized water	≈ 0	6	0.08	ari	nr	0.010	batch	3
bentonite	deionized water	≈ 0	7	0.08	ari	nr	0.012	batch	3
bentonite	deionized water	≈ 0	8	0.08	ari	nr	0.40	batch	3
soil	$Ca(NO_3)_2$	0.0025	5.1	365	air	nr	140	batch	4
soil	$Ca(NO_3)_2$	0.0025	5.3	365	air	nr	4.4	batch	4
soil	$Ca(NO_3)_2$	0.0025	6.6	365	air	nr	140	batch	4
soil	$Ca(NO_3)_2$	0.0025	7.1	365	air	nr	14	batch	4
clay	groundwater	0.018	7.7	100 - 180	N_2	nr	4.3	batch	5
clay	groundwater	0.018	8.2	100 - 180	N_2	nr	6.1	batch	5

1. Inoue and Morisawa (1975)
2. Wang et al. (2001)
3. Khan et al. (1995)
4. Jacobson et al. (2005)
5. Baston et al. (1992)

nr: not recorded

Table 32: Recommended Sorption Coefficients for Silver

SILVER(I)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions under reducing conditions only a value of 0 m^3/kg can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions under reducing conditions only a value of 0 m^3/kg can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions under reducing conditions only a value of 0 m^3/kg can be recommended.			

3.14 CADMIUM

Cadmium is a group 12 d-block element whose dominant oxidation state is +2. Although it has chemicaly similarities to the other group 12 elements, Zn and Hg, the differences between these elements are sufficiently significant that they do not make good chemical analogs for each other. In brine solutions, cadmium chemistry is dominated by choride complexes ($CdCl^+$, $CdCl_2$, $CdCl_3^-$, $CdCl_4^{-2}$).

The available data on cadmium sorption on clays and silica are summarized in Table 33. The variations with pH of cadmium sorption on montmorillonite and smectite (Akafia et al. 2011; Zachara and McKinley 1993) are illustrated in Figure 14. The tests with montmorillonite were performed in $NaNO_3$ solutions with ionic strengths of 0.001 to 0.1 M, and the experiments with smectite were conducted in $NaClO_4$ solutions with ionic strengths of 0.01 and 0.1 M. Sorption on both these expanding clays demonstrated a decrease with increasing ionic strength and an increase with higher pH. Unfortunately, the available data for cadmium sorption did not include tests with chloride solutions. Therefore, not only do the available data fail to include ionic strengths that could represent saline conditions, but they also do not include the complexing effects of the chloride ion. Since cadmium is strongly complexed by chloride, the available data are not appropriate for saline groundwaters. Therefore, only sorption values of 0 m^3/kg can be recommended for the sorption of cadmium at this time, as indicated in Table 34.

Table 33: Measured Cadmium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
mont.	Na-NO_3	0.001	6.1 - 7.3	1	nr	nr	3.6 - 3.9	batch	1
mont.	Na-NO_3	0.02	6.0 - 7.4	1	nr	nr	0.56 - 2.9	batch	1
mont.	Na-NO_3	0.1	6.3 - 7.0	1	nr	nr	0.091 - 1.9	batch	1
smectite	Na-ClO_4	0.01	6.1 - 7.1	0.83	Air	nr	4.8 - 21	batch	2
smectite	Na-ClO_4	0.1	6.0 - 7.2	0.83	Air	nr	0.60 - 11	batch	2
clay	Na-ClO_4	0.01	6	1	nr	nr	4.4 - 3600	batch	3
silica	Na-ClO_4	0.05	7	nr	Air	nr	0.011	batch	4

1. Akafia et al. (2011)
2. Zachara and McKinley (1993)
3. Baker (2009)
4. Wang et al. (2001a)

nr: not recorded

mont.: montmorillonite

Table 34: Recommended Sorption Coefficients for Cadmium

CADMIUM(II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions under reducing conditions, only a value of 0 m^3/kg can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions under reducing conditions, only a value of 0 m^3/kg can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions under reducing conditions, only a value of 0 m^3/kg can be recommended.			

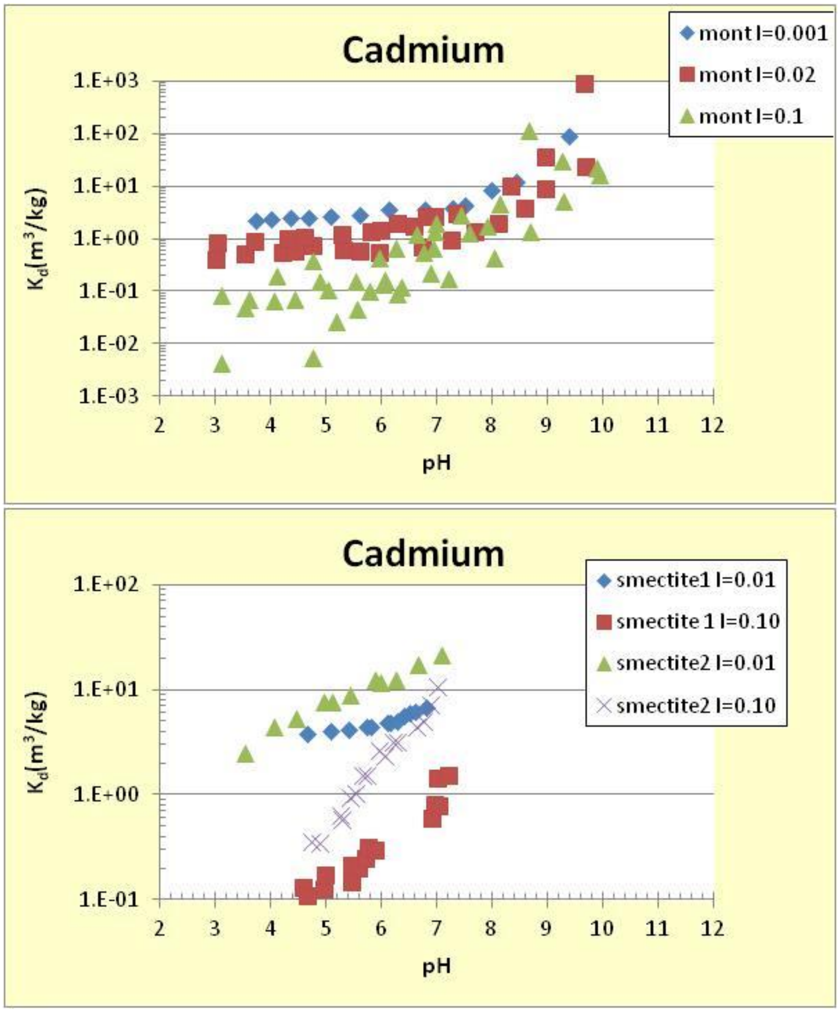


Figure 14: Cadmium Sorption Coefficients on Montmorillonite and Smectite at Different Ionic Strengths as a Function of pH (Akafia et al. 2011; Zachara and McKinley 1993)

3.15 TIN

Tin is a group 14 metal in the +2 and +4 oxidation states in aqueous media. PHREEQC (SIT database) predicts that the +4 oxidation state will dominate in the reference groundwaters with the $Sn(OH)_4$ and $Sn(OH)_5^-$ species being the most important.

Selected K_d values for tin from the literature are summarized in Table 35. Since most tin sorption values reported in the literature were determined at low ionic strength, Vilks and Miller (2018) measured tin sorption on shale, limestone and bentonite in the SR-270-PW brine solution.

Table 35: Selected Sorption Coefficients for Tin

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	NaCl	0.01	6	60	argon	nr	290 - 400	batch	1
bentonite	NaCl	0.01	9	60	argon	nr	110 - 560	batch	1
bentonite	NaCl	0.01	11	60	argon	nr	25 - 30	batch	1
bentonite	NaCl	0.1	5.8-6.4	30	argon	nr	660 - 2700	batch	1
bentonite	NaCl	0.1	9	30	argon	nr	130 - 1000	batch	1
bentonite	NaCl	0.1	11	30	argon	210 220	6.7 - 13	batch	1
bentonite	Ca-K-Na-OH	0.018	11	60-100	argon	nr	2.3 - 110	batch	2
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	5.9-6.4	14-195	N_2	nr	4.2 - 95	batch	8
bentonite	$NaNO_3$	0.05	7-8.5	1	Air	nr	4.57	batch	6
mont.	NaCl	0.01	6	118-297	argon	nr	420 - 7000	batch	3
mont.	NaCl	0.01	7	56	argon	nr	134	batch	3
mont.	NaCl	0.01	9	60	argon	nr	13 - 14	batch	3
mont.	NaCl	0.01	11	60	argon	nr	3.1 - 3.3	batch	3
shale	Na-Ca-Cl (SR-270-PW)	6.0	5.6-6.4	14-195	N_2	nr	1.5 - 44	batch	8
illite	$NaClO_4$	0.1	6 - 7	7	N_2	nr	316 - 398	batch	4
illite	$NaClO_4$	0.1	6 - 7	21	N_2	nr	257 - 433	batch	4
illite	$NaClO_4$	0.1	6 - 7	60	N_2	nr	268 - 293	batch	4
clay	Na-Ca-K-Mg-SO_4	0.3	6.3	7	N_2	340	86 - 132	batch	5
clay	Na-Ca-K-Mg-SO_4	0.3	6.3	21	N_2	340	92 - 140	batch	5
clay	Na-Ca-K-Mg-SO_4	0.3	6.3	50	N_2	340	105 - 129	batch	5
argillite	$NaNO_3$	0.05	7 - 8.5	1	Air	nr	1.29 - 6.46	batch	6
argillite	Na-Ca-K-Cl-HCO_3	0.1	7.2-7.8	7	anoxic	240 270	12.0 - 111	batch	7
limestone	Na-Ca-Cl (SR-270-PW)	6.0	5.7-6.4	14-195	N_2	nr	0.99 - 18	batch	8

1. Oda et al. (1999)
2. Baston et al. (1990)
3. Ikeda et al. (1995)
4. Bradbury and Baeyens (2009a)
5. Lauber et al. (2000)
6. Kedziorek et al. (2007)
7. Latrille et al. (2006)
8. Vilks and Miller (2018)

nr: not recorded

mont.: montmorillonite

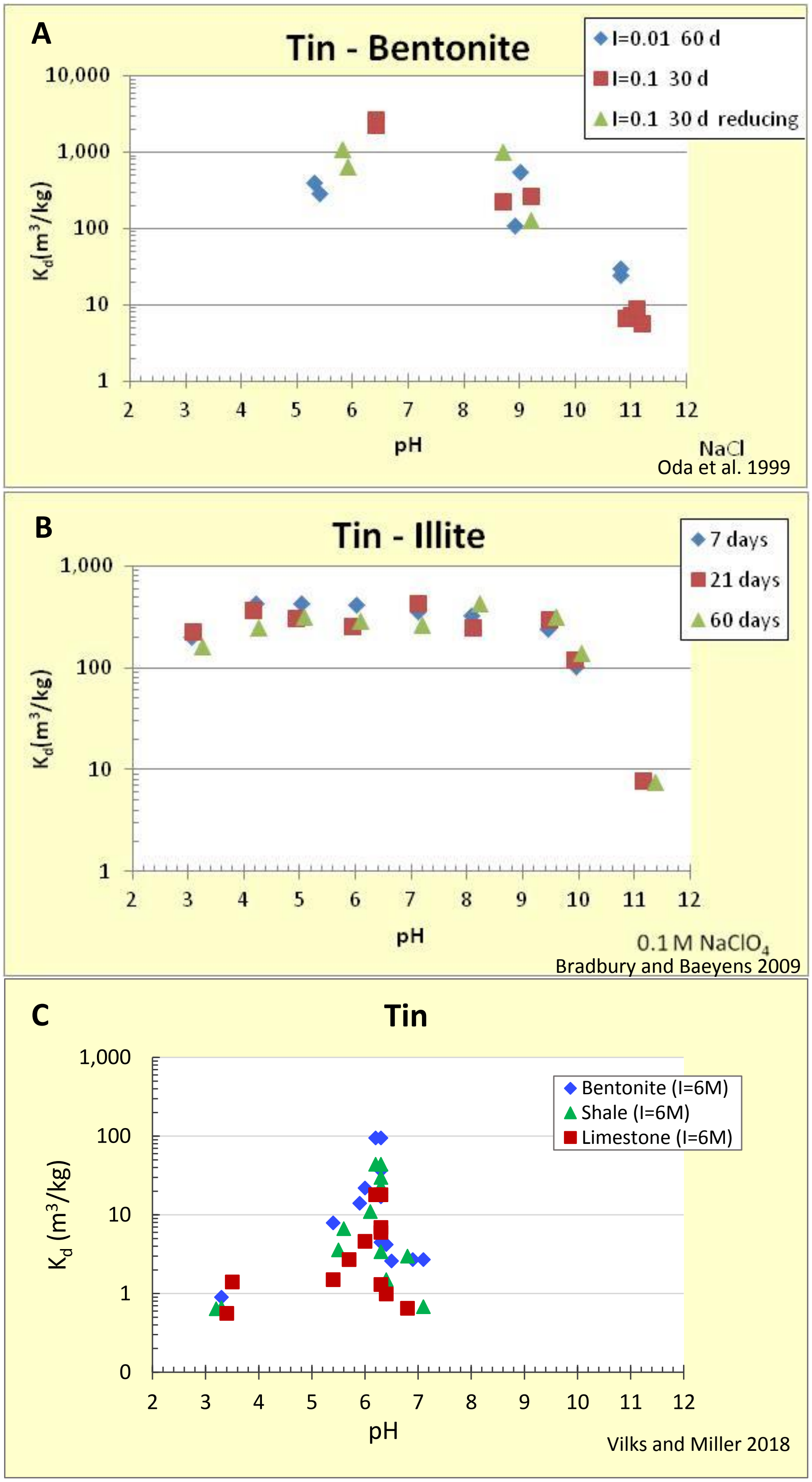
Figure 15A and 15B illustrate the variation of tin sorption on bentonite (Oda et al. 1999) and illite (Bradbury and Baeyens 2009a) in dilute solutions as a function of pH. Tin sorption on bentonite increases with pH up to a pH value of about 6.2, but then decreases at pH values above 8. Sorption on illite does not vary significantly with pH when values are less than 9; however, sorption decreases with increasing pH above a value of 9. Based on the cluster of K_d values around pH 9, it appears that ionic strength did not significantly affect sorption. Figure 15C illustrates tin sorption on bentonite, shale and limestone in the SR-270-PW brine as a function of pH (Vilks and Miller 2018). The scatter in Sn K_d values masks any clear trends with pH. Since tin forms neutral and negatively charged hydroxyl species in solution, it is likely to sorb by inner sphere surface complexation with oxygen groups.

The tin sorption coefficient values determined in the SR-270-PW reference brine are recommended, 1.4 - 95 m^3/kg for bentonite, 0.51 - 44 m^3/kg for shale and 0.33 - 18 m^3/kg for limestone, as indicated in Table 36.

Table 36: Recommended Sorption Coefficients for Tin

TIN (IV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**5.9 - 6.4**	**4.2 - 95**	**19 (3.6)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			
Shale	**6.0**	**5.6 - 6.4**	**1.5 - 44**	**11 (3.6)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			
Limestone	**independent**	**5.7 - 6.4**	**0.99 - 18**	**4.4 (3.2)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.



NaCl
Oda et al. 1999

0.1 M $NaClO_4$
Bradbury and Baeyens 2009

Vilks and Miller 2018

Figure 15: Tin Sorption Coefficients on Bentonite, Shale, Limestone and Illite at Different Ionic Strengths as a Function of pH

3.16 IODINE

Iodine is a group 7 element that has a number of potential oxidation states (-1, +1, +5 and +7). Except for very oxidizing conditions, the most stable oxidation state is I(-I), or iodide. In brine solutions, iodide can occur in its free form as I^-, or associated with major elements as with CaI^+ and MgI^+. Iodide is not expected to sorb strongly due to its negative charge, and therefore has been used as a conservative tracer in migration experiments. However, numerous studies have shown that iodide is weakly sorbed by geologic materials, and sorption is influenced by factors such as the presence of organic matter and Fe oxides, pH and microbial activity (Wittebroodt et al. 2008). Iodide appears to have a low affinity for pure phases of quartz, montmorillonite, dolomite, kaolinite and calcite (Kaplan et al. 2000). The presence of organics and Fe oxides as mineral coatings could enhance iodide sorption by providing positively charged sites for sorption. Illite, a major component of shale, is known to sorb iodide (Bazer-Bachi et al. 2006), possibly due to attachment to positively charged edge sites. Iodide diffusion has been compared to the diffusion of chloride and tritium (Van Loon et al. 2003). Due to anion exclusion the two anions diffused slower than tritium. However, the larger rock capacity factor for iodide compared to chloride suggested that iodide was weakly sorbed, while chloride was not.

Under oxidizing conditions, a fraction of the iodine may be oxidized to I(V), in the form of IO_3^- (iodate). Since iodate is negatively charged, it tends to be sorbed weakly, like iodide.

Table 37 summarizes iodide K_d values obtained from the literature under conditions that range from freshwater to brine solutions. Figure 16 illustrates iodide sorption on argillite as a function of total iodide concentration and sorption reaction time (Wittebrodt et al. 2008; Montavon et al. 2014; Descostes et al. 2008). It is important to note that K_d values are sensitive to the total iodide concentration used in sorption tests. As iodide concentrations increase above $1x10^{-4}$ mol/L, K_d values decrease significantly, dropping to almost 0 m^3/kg at an iodide concentration of $1x10^{-3}$ mol/L. This may help to explain why iodide makes a good conservative tracer at higher iodide concentrations. Figure 16 also shows that iodide sorption may increase with contact time. Figure 17 shows that iodide sorption on montmorillonite is independent of the ionic strength, and sorption on limestone may decrease in brine solutions when compared to very dilute water (Sazarashi et al. 1996).

Table 38 summarizes recommended iodide K_d values for bentonite and sedimentary rocks (shale and limestone) under saline conditions, using data selected from Table 37. Recommended K_d values for bentonite were based on experiments with montmorillonite in brine solutions (NaCl), reported by by Mucciardi et al. (1979), Sazarashi et al. (1996), Miller et al. (2015) and Andersson et al. (1983). Sorption values for shale were based on tests with argillite in Na-Ca-Cl-SO_4 solution, reported by Descostes et al. (2008) and Bazer-Bachi et al. (2006), with Opalinus (OPA) clay in Na-Cl solution, and with illite in 5.1 M NaCl brine by Muciardi et al. (1979), assuming 60% illite in shale. Iodide K_d values for limestone were based on measurements made with limestone and marl in Ca-Mg-Cl brine, that were reported by Sazarashi et al. (1996).

Table 37: Measured Iodine Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	syn. gw.	≈ 0	7.2	60	nr	nr	$(2.5 \pm 0.14)\times10^{-4}$	batch	1
mont.	NaCl	0.03	8.3	17	air	398	$(1.67 \pm 1.7)\times10^{-3}$	batch	2
mont.	$CaCl_2$	0.03	7.5-7.7	3-31	air	357 407	2.6×10^{-4} - 1.39×10^{-3}	batch	2
mont.	NaCl	4	6 - 8	1 - 7	air	nr	5.0×10^{-2}	batch	8
mont.	NaCl	4	6.2	nr	air	nr	1.81×10^{-4}	batch	7
mont.	NaCl	4	6.7	nr	air	nr	1.42×10^{-3}	batch	7
mont.	NaCl	4	7.8	nr	air	nr	4.0×10^{-4}	batch	7
mont.	NaCl	4	8.6	nr	air	nr	2.40×10^{-4}	batch	7
mont.	NaCl	5.1	7.7	3	nr	407	2.8×10^{-3}	batch	2
mont.	NaCl	5.1	7.9	17	nr	407	4.8×10^{-3}	batch	2
mont.	NaCl	1.0	7.7	7	air	nr	6.0×10^{-4}	batch	11
illite	NaCl	1.0	7.9	7	air	nr	2.7×10^{-4}	batch	11
illite	NaCl	5.1	6.9	17	nr	392	3.04×10^{-2}	batch	2
kaolinite	NaCl	5.1	6.9	17	nr	440	3.1×10^{-3}	batch	2
vermiculite	NaCl	5.1	8.4	31	nr	322	2.81×10^{-3}	batch	2
vermiculite	NaCl	5.1	8.2	31	nr	367	5.61×10^{-3}	batch	2
argillite	Na-Ca-Cl-SO_4	0.06	7.5	31	N_2/ CO_2	nr	1.0×10^{-5} -1.4×10^{-4}	col.	3
argillite	Na-Ca-Cl-SO_4	0.06	7.5	31	N_2/ CO_2	nr	5.0×10^{-5} - 3.1×10^{-4}	batch	3
argillite	Na-Ca-Cl-SO_4	0.1	7.3	42	N_2	nr	$(4.2 \pm 0.8)\times10^{-4}$	batch	4
argillite	Na-Ca-Cl-SO_4	0.1	7.3	42	N_2	nr	4.0×10^{-6} - 1.5×10^{-4}	diffu	4
argillite	Na-Cl-HCO_3	0.01	nr	60	N_2	nr	0 - 2.1×10^{-5}	diffu	5
argillite	Na-Ca-Cl-SO_4	0.098	7.1	28	N_2	nr	1.50×10^{-4}	col.	6
argillite	Na-Ca-Cl-SO_4	0.098	7.1	40	N_2	nr	8.70×10^{-5}	diffu	6
argillite	Na-Ca-Cl-SO_4	0.098	7.1	90	N_2	nr	2.65×10^{-2}	batch	6
argillite	Na-Ca-Cl-SO_4	0.098	7.1	28	N_2	nr	3.30×10^{-4}	col.	6
shale	Na-HCO_3	0.005	8.2	nr	nr	nr	0 - 8.2×10^{-5}	batch	10
OPA clay	Na-Cl	0.2	7.9	90-160	air	nr	1.0×10^{-5} - 2.0×10^{-5}	diffu	9
limestone	Na-Ca-Cl-SO_4	0.018	7.5	40	N_2	nr	1.7×10^{-5}	diffu	6
limestone	Na-Ca-Cl-SO_4	0.018	7.5	40	N_2	nr	2.7×10^{-5}	diffu	6
limestone#1	Na-Cl-HCO_3-SO_4	0.009	7.2	6	nr	358	1.0×10^{-4} - 4.0×10^{-4}	batch	7
limestone#4	Na-Cl-HCO_3-SO_4	0.009	7.2	6	nr	358	5.0×10^{-4} - 4.4×10^{-3}	batch	7
limestone#2	Ca-Mg-Cl	2.67	6	6	nr	195	0 - 3.0×10^{-4}	batch	7

Table 37 Continued …

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
marl	Ca-Na-HCO_3-SO_4	0.014	6	6	air	195	3.9×10^{-3} - 6.8×10^{-3}	batch	7
marl	Ca-Mg-Cl	2.67	6	6	air	195	0 - 2.0×10^{-4}	batch	7

1. Oscarson (1994)
2. Muciardi et al. (1979)
3. Montavon et al. (2014)
4. Bazer-Bachi et al. (2006)
5. Wittebroodt et al. (2008)
6. Descostes et al. (2008)
7. Sazarashi et al. (1996)
8. Andersson et al. (1983)
9. Van Loon et al. (2003)
10. Savoye et al. (2006)
11. Miller et al. (2015)

col.: column mass transport test
syn. gw.: synthetic groundwater
nr: not recorded
diffu: diffusion
mont.: montmorillonite

Table 38: Recommended Sorption Coefficients for Iodide

Iodide(-I)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**1.0 - 5.1**	**6 - 8.6**	**1.8×10^{-4} - 5.0×10^{-2}**	**1.3×10^{-3} (6.5)**
comment	Measurements with montmorillonite reported by Muciardi et al. (1979), Sazarashi et al. (1996), and Andersson et al. (1983) and Miller et al. (2015)			
Shale	**0.098 - 5.1**	**6.9 - 7.9**	**4.0×10^{-6} - 2.65×10^{-2}**	**1.3×10^{-4} (12)**
comment	Measurements with argillite reported by Descostes et al. (2008) and Bazer-Bachi et al. (2006), OPA clay reported by Van Loon et al. (2003), and illite reported by Muciardi et al. (1979) at 5.1 M NaCl solution assuming 60% illite in shale.			
Limestone	**2.67**	**6.0**	**0 - 3.0×10^{-4}**	**1.08×10^{-4} (1.8)**
comment	Measurements with limestone and marl at ionic strength of 2.67 M reported by Sazarashi et al. (1996)			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

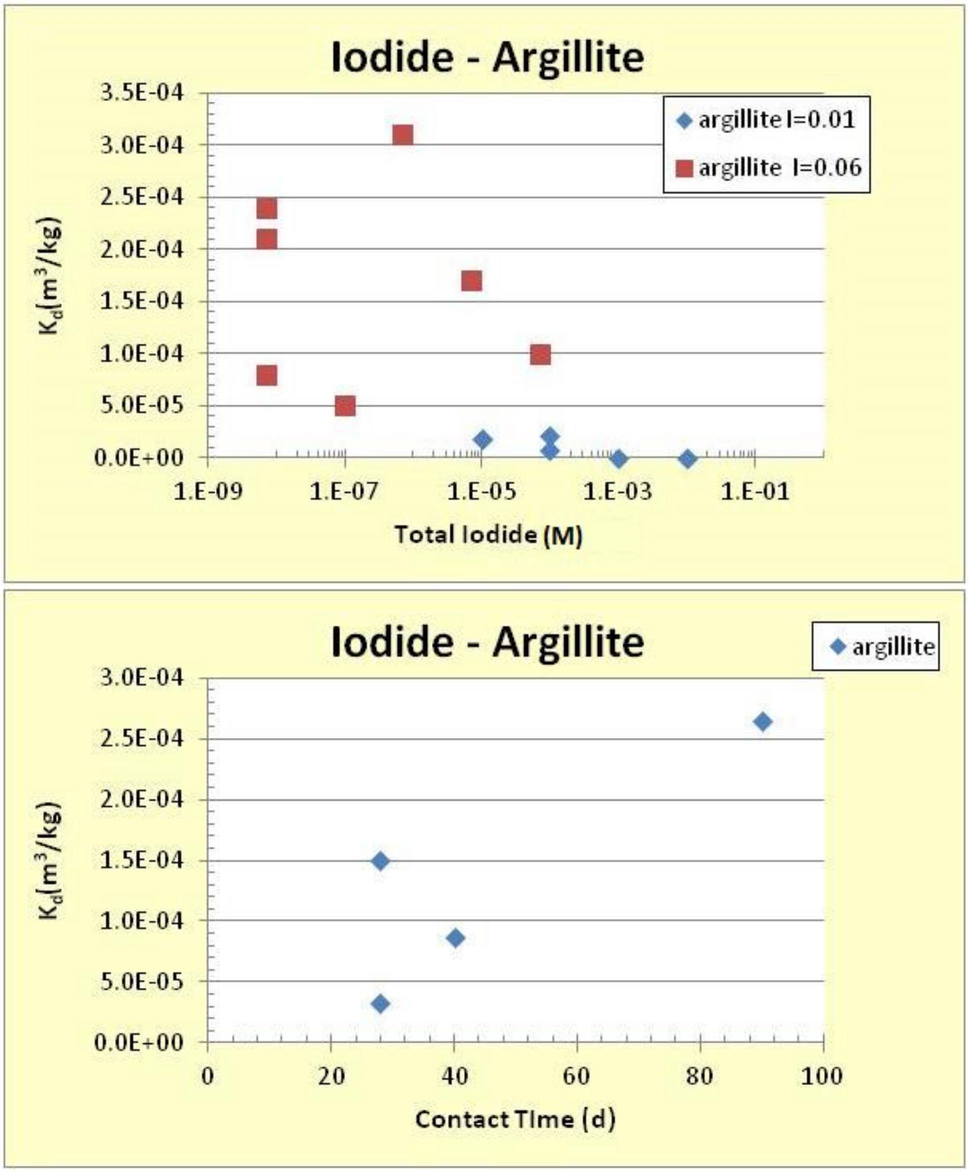


Figure 16: Iodide Sorption Coefficients on Argillite as a Function of Iodide Initial Concentration and Contact Time (Wittebrodt et al. 2008; Montavon et al. 2014; Descostes et al 2008)

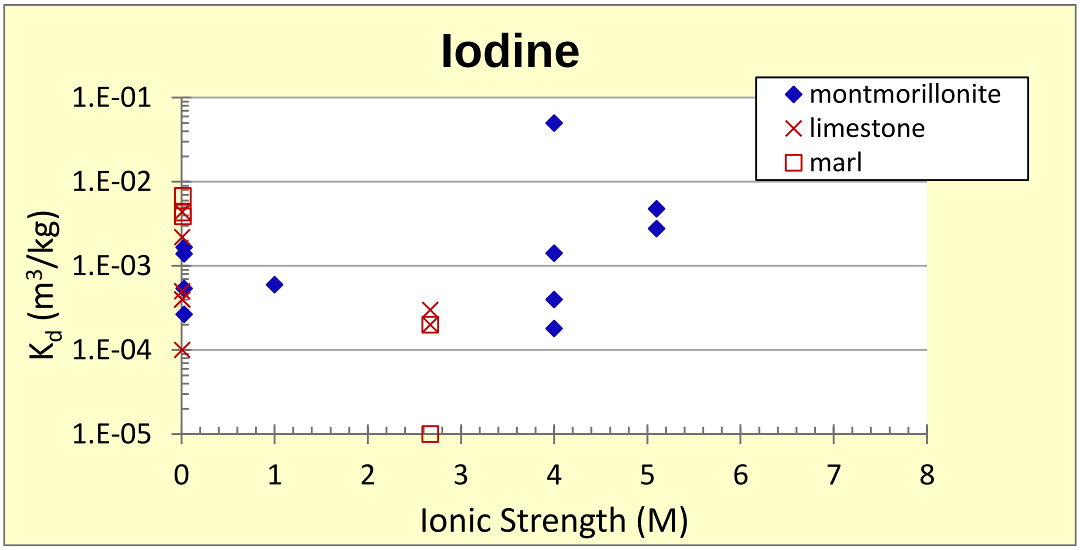


Figure 17: Iodide Sorption Coefficients on Montmorillonite, Limestone and Marl as a Function of Ionic Strength (Sazarashi et al. 1996; Muciardi et al. 1979; Andersson et al. 1983; Miller et al. 2015)

3.17 CESIUM

Cesium is a group 1 element that has an oxidation state of +1. Speciation calculations with PHREEQC (SIT database) predict that in the reference groundwaters the dominant cesium species are CsCl and Cs^+. Cesium is an alkali element and is not expected to be sorbed by complexation reactions to surface sites. In dilute waters, the dominant sorption mechanism is expected to be coulombic attraction. In brine solutions, the competitive sorption of the ions could be expected to reduce cesium sorption to insignificant levels. However, in most clays, the cation with the larger hydrated radius will be displaced with a cation of a smaller hydrated radius (Stumm and Morgan 1981). Therefore, for monovalent cations, the relative affinities for clays would be as follows:

$$Cs^+ > K^+ > Na^+ > Li^+$$

Although cesium has a relatively large ionic radius, its hydrated radius is small. This allows it to compete with other cations in the Stern layer, and to displace Na^+ from the interlayer of clay minerals in a similar way that K^+ replaces Na^+ in illite. Since this cation exchange involves diffusion into the clay structure, this reaction is expected to be slow. Despite the overwhelming concentration of salts in brine solutions, cesium sorption values reported in the literature support this theory (Table 39). The clay contents of bentonite, shale and limestone are the main control of cesium sorption in these solids.

Table 39 summarizes cesium sorption coefficients reported in the literature, as well as the results of more recent measurements of cesium sorption on shale, limestone and bentonite in brine solutions, as reported by Vilks and Miller (2018). Cesium sorption values are sensitive to the initial concentration of total cesium used in the sorption tests, particularly when total cesium is above $1x10^{-5}$ mol/L. Lee et al. (2013) noted that Cs sorption decreased with increasing temperature (20 to 80 ^{o}C) and salinity. Figure 18A and Figure 19A show that the cesium K_d values for bentonite and shale show no clear variation with ionic strength. The reason for variability of sorption values at any given ionic strength is not always clear. One reason could be due to the differences in experimental times. Sorption values determined over 60 days are significantly larger than values obtained from 1 hour (0.042 d) experiments (Vilks and Miller 2018). Vilks and Miller (2018) found that Cs sorption on bentonite, shale and limestone in the SR-270-PW reference brine (I = 6.0 M) was a factor of 3 to 7 lower than in the reference dilute solution (I = 0.01 M). Wanner et al. (1994) observed that Cs sorption on bentonite was lower at higher ionic strength solutions (from 0.025 to 1 M). Mucciardi et al. (1979) found that Cs sorption on bentonite and shale in brine (I = 5.1 M) was lower than in dilute solution (I = 0.03 M). Xia et al. (2006b) found that cesium K_d values of shale dropped as the ionic strength increased from 0.003 to 0.3 M, but then did not change significantly as the ionic strength increased to 0.4 M. Cesium sorption on bentonite in ionic strength of 0.1 M solutions increases with pH up to values of about 5, and then is independent of pH above 5, as shown in Figure 18B. Sorption on illite shows a clear trend of increasing with increasing pH, as shown in Figure 19B. However, the increase in pH from 4 to 11.8 only results in an increase in K_d values by about a factor of 2. Therefore, in the pH range of interest (say 6 to 8), the effect of pH variability is minor. Vilks and Miller (2018) noted that in the SR-270-PW reference brine Cs sorption on bentonite and shale in brine appeared to be independent of pH in the range of 5-7 (Figures 18C and 19C). The data in Table 39 indicate that some of the highest K_d values were reported from $CaCl_2$ brine solutions, lacking Na^+, which might compete with Cs^+. Therefore, measurements without Na^+ or K^+ were excluded when considering recommended values.

The “in-house” measured Cs K_d values for bentonite, shale and limestone in the SR-270-PW reference brine were recommended as summarized in Table 40. The K_d values measured for smectite in 1 M Na-HCO_3-Cl-SO_4 solution by Ames et al. (1981) and for bentonite in 1.0 M NaCl solution by Kasar et al. (2014) fall in the range of the “in house” measured K_d values for bentonite in brine with an ionic strength of 6 M.

Table 39: Selected Sorption Coefficients for Cesium

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-K-Ca-Cl	0.25	6 - 8	nr	air	nr	0.021 - 0.11	batch	1
bentonite	Ca-Mg-Na –Cl	0.6	8.4	nr	air	nr	0.11 - 0.12	batch	1
bentonite	Ca-Mg-Na-Cl	1.0	8.4	nr	air	nr	0.087 - 0.11	batch	1
bentonite	KCl	1	8	nr	air	nr	0.015	batch	4
bentonite	KCl	0.5	8	nr	air	nr	0.036	batch	4
bentonite	$MgCl_2$	1	7	nr	air	nr	0.036	batch	4
bentonite	$MgCl_2$	0.5	7	nr	air	nr	0.045	batch	4
bentonite	$MgCl_2$	0.05	7.7	nr	air	nr	0.117	batch	4
bentonite	NaCl	1	7.4	nr	air	nr	0.034	batch	4
bentonite	NaCl	0.5	7.4	nr	nr	nr	0.056	batch	4
bentonite	$CaCl_2$	0.25	7.2	nr	air	nr	0.053	batch	4
bentonite	$CaCl_2$	0.025	7.4	nr	air	nr	0.18	batch	4
bentonite	Na-K-Mg-Ca-Cl-SO_4	7.7	6.5	7	air	nr	0.004	batch	5
bentonite	Na-Cl-SO_4	5.6	7.0-7.2	7	air	nr	0.004	batch	5
bentonite	Na-Ca-Cl	0.6	7.7-8.5	28	N_2	nr	0.066 - 0.093	batch	11
bentonite	$NaClO_4$	1.0	nr	nr	air	nr	$1x10^{-6}$	diffu	12
bentonite	$NaClO_4$	0.1	6.6	nr	nr	nr	0.18	diffu	14
bentonite	NaCl	1.0	5.6	nr	air	nr	0.50	batch	15
bentonite	NaCl	1.0	7.8	nr	air	nr	0.59	batch	15
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	5.9-6.4	14-195	N_2	nr	0.14 - 1.43	batch	17
bentonite	Ca-Na-Cl	0.01	6.9-8.3	7-187	N_2	nr	0.57 - 2.82	batch	17
smectite	$CaCl_2$	0.01	7.7	60	air	nr	43	batch	2
smectite	$CaCl_2$	0.11	7.5	60	air	nr	8.67	batch	2
smectite	NaCl	0.01	7.8	60	air	nr	2.62	batch	2
smectite	Na-HCO_3-Cl-SO_4	0.1	7.6	60	air	nr	6.86	batch	2
smectite	Na-HCO_3-Cl-SO_4	1	8.1	60	air	nr	1.16	batch	2
smectite	NaCl	1	6-7	0.042	air	nr	0.066 - 0.068	batch	3
mont.	NaCl	5.1	6-8	3-29	air	209 473	0.031 - 0.041	batch	6
mont.	$NaClO_4$	0.5	7	3	air	nr	0.0066 - 0.469	batch	13
shale	NaCl	5.1	7-7.5	3-30	air	288 317	0.12 - 1.26	batch	6
shale	Na-K-Ca-Mg-Cl-HCO_3	0.41	7.5	nr	low O_2	-250	0.005 - 0.55	batch	7

Table 39 continued...

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
shale	no composition	0.31	8	nr	N_2	nr	0.009 - 0.42	batch	8
shale	no composition	0.41	8	nr	N_2	nr	0.014 - 0.37	batch	8
shale	Na-Ca-Cl (SR-270-PW)	6.0	5.6 - 6.4	14 -195	N_2	nr	0.069 - 0.63	batch	17
shale	Ca-Na-Cl	0.01	7.1 - 8.4	7 - 187	N_2	nr	0.65 - 2.65	batch	17
shale	deionized water	0.003	8	28	N_2	nr	0.73 - 8.3	batch	8
mudstone	NaCl	0.7	8	28	N_2	nr	0.18	batch	11
illite	NaCl	1	5 - 8	0.042	Air	nr	2.5 - 3.1	batch	3
illite	NaCl	5.1	6 - 7	3 - 29	Air	157 557	0.164 - 0.748	batch	6
illite	$NaClO_4$	1.0	7	7	Air	nr	0.16 - 2.0	batch	16
limestone	Na-Ca-Cl	5.1	6.5	7	Air	nr	5.7×10^{-4}	batch	9
limestone	Na-Ca-Cl	5.1	6.5 - 7.4	7	Air	nr	4×10^{-5} - 3.3×10^{-3}	batch	10
limestone	NaCl	5.1	7 - 8	3 - 30	Air	300 346	0.002 - 0.0106	batch	6
limestone	Na-Ca-Cl (SR-270-PW)	6.0	5.7 - 6.4	14 -195	N_2	nr	0.032 - 0.69	batch	17
limestone	Ca-Na-Cl	0.01	7.4 - 8.4	7 - 187	N_2	nr	0.094 - 1.05	batch	17

1. Murali and Mathur (2002)
2. Ames et al. (1981)
3. Gorgeon (1994)
4. Wanner et al. (1994)
5. Nowak (1980)
6. Mucciardi et al (1979)
7. Doi et al. (2007)
8. Xia et al. (2006b)
9. MaClean et al. (1978)
10. Relyea and Serne (1979)
11. Kitamura et al. (2008)
12. Molera and Eriksen (2002)
13. Tertre et al. (2005)
14. Wang et al. (2005)
15. Kasar et al. (2014)
16. Benedicto et al. (2014)
17. Vilks and Miller (2018)

nr: not recorded
mont.: montmorillonite
diffu: diffusion

Table 40: Recommended Sorption Coefficients for Cesium

CESIUM (I)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6**	**5.9 - 6.4**	**0.14 - 1.43**	**0.43 (3.3)**
comment	Measured by Vilks and Miller (2018) in the SR-270-PW reference brine.			
Shale	**6**	**5.6 - 6.4**	**0.069 - 0.63**	**0.20 (2.8)**
comment	Measured by Vilks and Miller (2018) in the SR-270-PW reference brine.			
Limestone	**6**	**5.7 - 6.4**	**0.032 - 0.69**	**0.14 (4.0)**
comment	Measured by Vilks and Miller (2018) in the SR-270-PW reference brine.			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

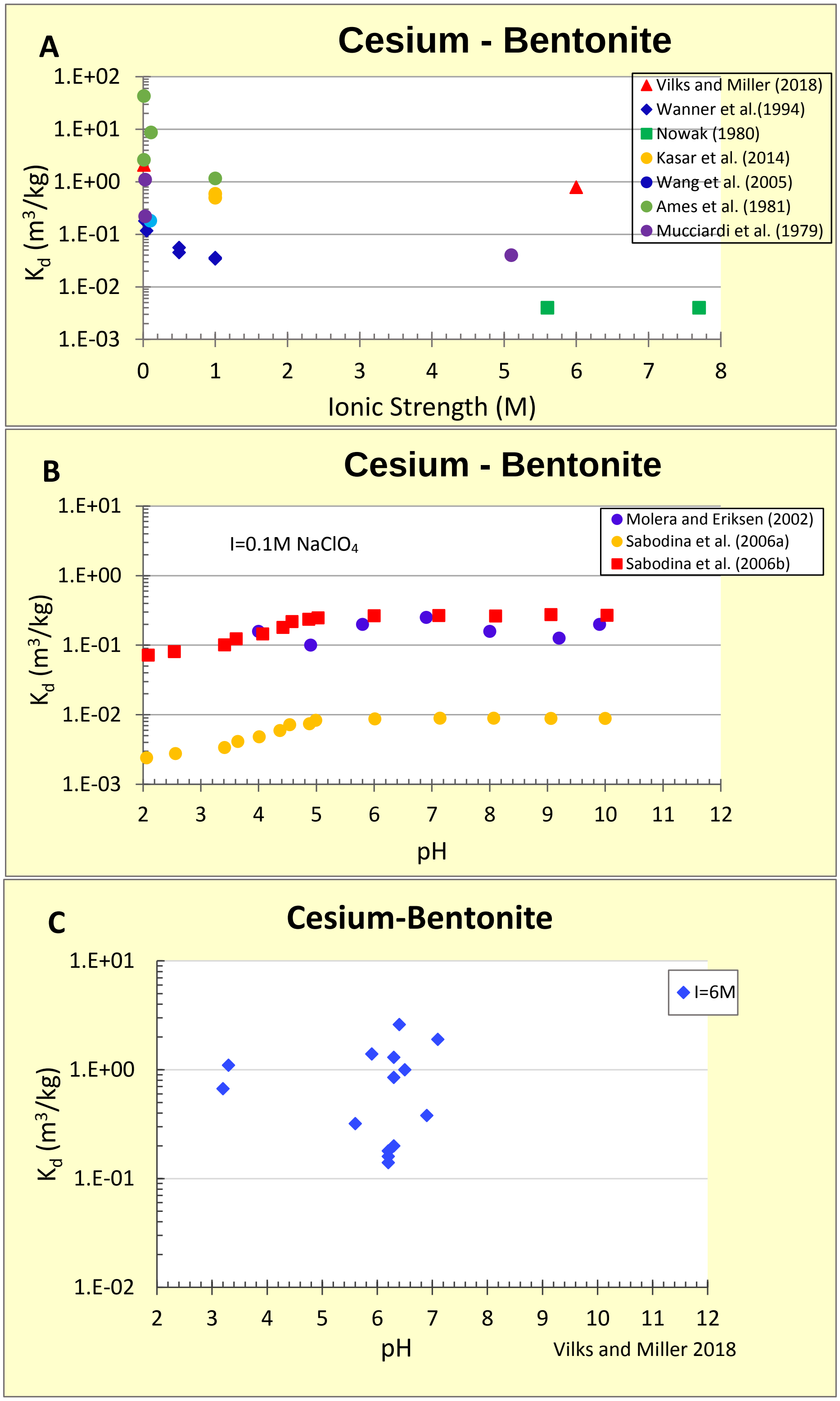


Figure 18: Cesium Sorption Coefficients on Bentonite as a Function of Ionic Strength and pH (Wanner et al. 1994; Wang et al. 2005; Vilks and Miller 2018; Sabodina et al. 2006a, 2006b; Molera and Eriksen 2002; Mucciardi et al. 1979; Kasar et al. 2014; Nowak 1980; Ames et al. 1981)

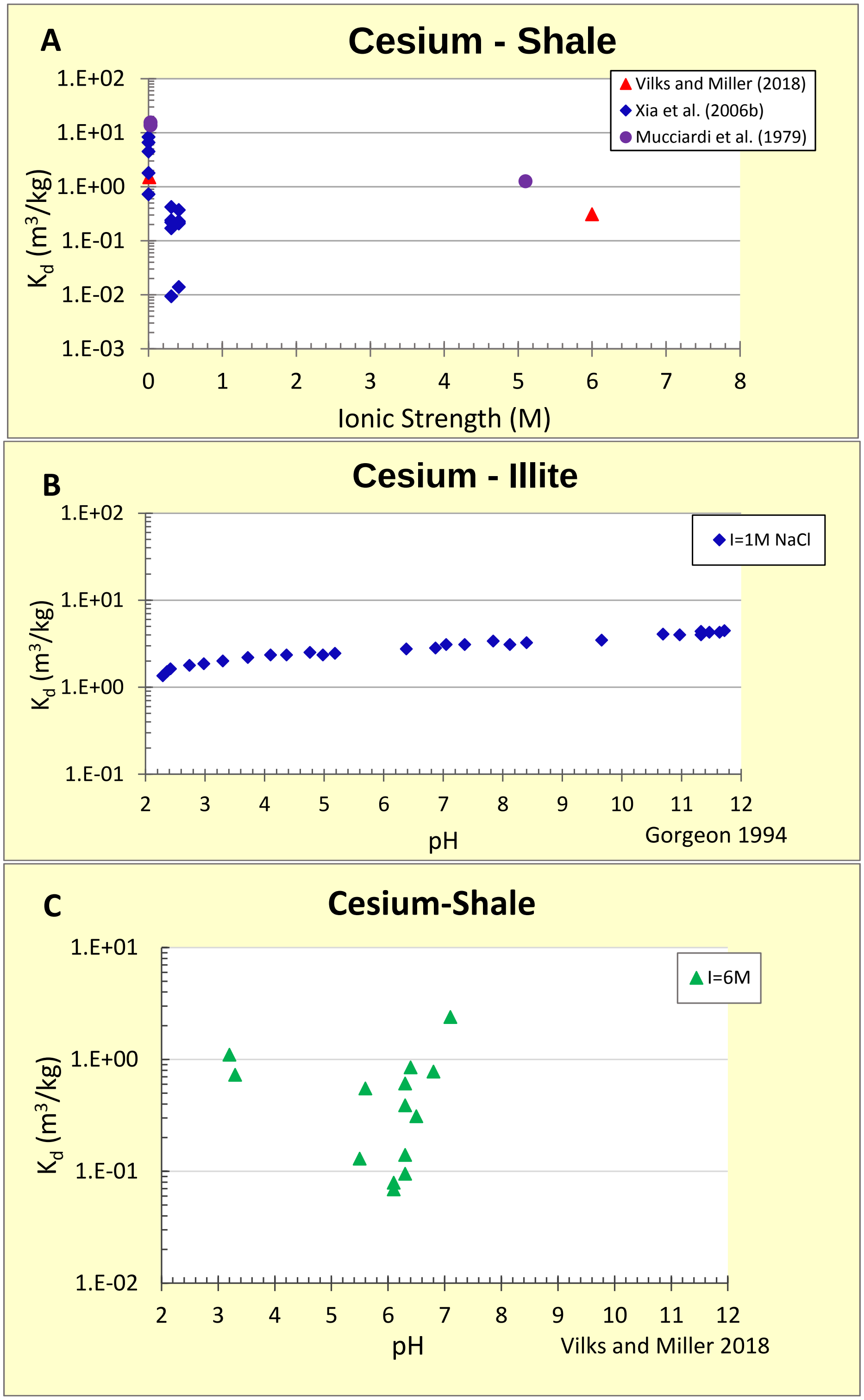


Figure 19: Cesium Sorption Coefficients on Shale and Illite as a Function of Ionic Strength and pH (Xia et al. 2006b; Gorgeon 1994; Vilks and Miller 2018; Mucciardi et al 1979)

3.18 EUROPIUM

Europium is a member of the lanthanide series with oxidation states of +2 and +3. PHREEQC (SIT database) predicts that in the reference groundwater SR-270-PW the +3 oxidation state dominates and the main aqueous species would be $EuCl^{+2}$, Eu^{+3}, $EuCl_2^{+}$ and $EuSiO(OH)_3^{+2}$. Europium has been used as a chemical analog for elements with a trivalent oxidation state, such as Pu(III).

Selected europium K_d values are presented in Table 41. Data reported by Vilks et al. (2011) represent “in-house” sorption measurements of europium on bentonite, shale and limestone using Na-Ca-Cl brine solutions. The data from the literature were selected to represent sorption values obtained from various solutions with ionic strengths ranging from 0.1 to 7.7 M. Figure 20A illustrates the variation of europium K_d values measured on montmorillonite in $NaClO_4$ solutions with ionic strengths of 0.05, 0.1 and 0.5 M (Kowal-Fouchard et al. 2004). Sorption increases with pH up to values of about 7.5. At pH values below 7, sorption decreases in the higher ionic strength solutions. Europium sorption on illite in $NaClO_4$ solutions with ionic strengths of 0.02, 0.1, 0.5 and 1 M, reported by Wang et al. (1998) also show increased sorption with higher pH, up to a value of 7.2 (Figure 20B). At pH values below 6, sorption decreases in the higher ionic strength solutions, but the difference between ionic strengths of 0.5 and 1 M was not significant. Figure 21 shows europium sorption on bentonite, shale and limestone as a function of ionic strength. The europium K_d values for bentonite, shale, and limestone show no clear variation with ionic strength. Vilks et al. (2011) noted that europium sorption on bentonite is affected by the concentration of carbonate in solution. The Na-Ca-Cl brine with ionic strength of 7.2 M has lower carbonate concentration in equilibrium with calcite than the ionic strength of 2.4 M and 0.23 M solutions. The decreasing carbonate concentration in the higher ionic strength solutions led to increased sorption on bentonite (Vilks et al. 2011).

Recommended Eu K_d values on bentonite, shale and limestone in brine solutions are presented in Table 42. Values for Eu sorption on bentonite were selected from K_d values measured using bentonite in brine solutions with ionic strengths of 2.4 to 7.7 M (Vilks et al. 2011; Nowak 1980; Wang et al. 2001b). Recommended K_d values for shale and limestone were based on “in-house” measurements by Vilks et al. (2011), using ionic strengths of 0.23, 2.4 and 7.2 M.

Table 41: Measured Europium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref.
bentonite	Na-Ca-Cl	7.2	6.4	7	air	nr	5.7 ± 0.0	batch	1
	Na-Ca-Cl	2.4	6.9	7	air	nr	0.76 ± 0.072	batch	1
	Na-Ca-Cl	0.23	7.3	7	air	nr	0.097 ± 0.055	batch	1
bentonite	Na-K-Mg-Cl-SO_4-HCO_3	7.75	6.5	7	air	nr	0.355	batch	2
bentonite	Na-K-Mg-Cl-SO_4-HCO_3	7.75	5.5 - 6.5	14	air	nr	0.10 - 1.1	batch	2
bentonite	Na-Cl-SO_4	5.6	7.1	7	air	nr	1.4 - 1.7	batch	2
bentonite	Na-Cl-SO_4	5.6	5.5 - 6.5	14	air	nr	0.3 - 6.7	batch	2
bentonite	NaCl	2.5	5.5 - 6.5	0.28	air	nr	3.16	batch	8
Na-mont	Na-ClO_4	0.5	6.0 - 7.4	8	nr	nr	0.09 - 500	batch	3
Na-mont	Na-ClO_4	0.5	6.6 - 7.2	3	air	nr	2.1 - 4.7	batch	4
Na-mont	Na-ClO_4	0.1	6.0 - 7.5	7	N_2	nr	6.2 - 586	batch	5
Na-mont	Na-ClO_4	0.1	6.0 - 7.5	7	air	nr	18 - 299	batch	5
shale	Na-Ca-Cl	7.2	6.1	7	air	nr	0.11 ± 0.01	batch	1
shale	Na-Ca-Cl	2.4	6.9	7	air	nr	0.22 ± 0.003	batch	1
shale	Na-Ca-Cl	0.23	7.3	7	air	nr	0.18 ± 0.048	batch	1
clay	Opalinus porewater	0.4	7.6	7	nr	nr	32 - 59	batch	6
Na-illite	Na-ClO_4	0.5	6.0 - 6.6	2	nr	nr	9.1 - 91	batch	7
Na-illite	Na-ClO_4	1.0	6.0 - 7.3	2	nr	nr	6.3 - 146	batch	7
limestone	Na-Ca-Cl	7.2	6.0	7	air	nr	0.15 ± 0.01	batch	1
limestone	Na-Ca-Cl	2.4	6.9	7	air	nr	0.29 ± 0.026	batch	1
limestone	Na-Ca-Cl	0.23	7.5	7	air	nr	0.093 ± 0.058	batch	1

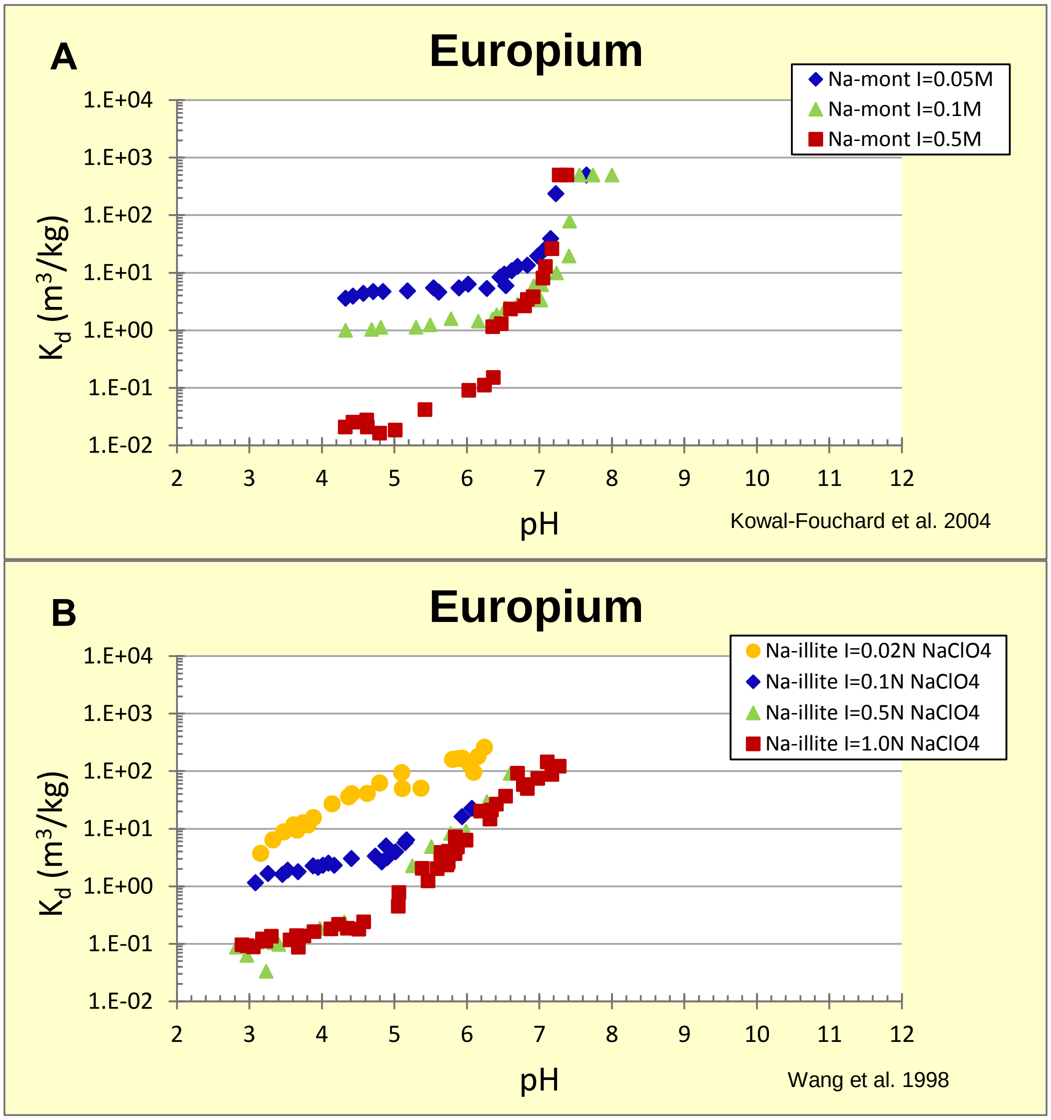
1. Vilks et al. (2011)
2. Nowak (1980)
3. Kowal-Fouchard et al. (2004)
4. Tertre et al. (2005)
5. Marques Fernandes et al. (2008)
6. Schott et al. (2012)
7. Wang et al. (1998)
8. Wang et al. (2001b)

nr: not recorded

Table 42: Recommended Sorption Coefficients for Europium

EUROPIUM (II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**2.4 - 7.7**	**5.5 - 7.0**	**0.1 - 6.7**	**1.3 (4.6)**
comment	Measured in brine solutions by Vilks et al. (2011), Wang et al. (2001) and Nowak (1980).			
Shale	**0.23 - 7.2**	**6.1 - 7.3**	**0.11 - 0.22**	**0.16 (1.6)**
comment	Measured in Na-Ca-Cl brine by Vilks et al. (2011).			
Limestone	**0.23 - 7.2**	**6.0 - 7.5**	**0.09 - 0.29**	**0.16 (1.6)**
comment	Measured in Na-Ca-Cl brine by Vilks et al. (2011).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.



Kowal-Fouchard et al. 2004

Wang et al. 1998

Figure 20: Europium Sorption Coefficients on Montmorillonite and Illite at Different Ionic Strengths as a Function of pH (Kowal-Fouchard et al. 2004; Wang et al. 1998)

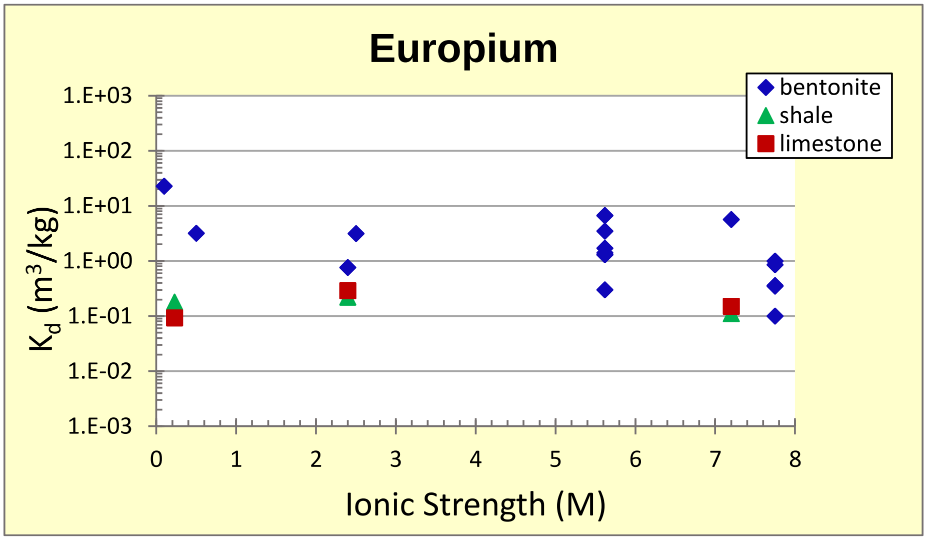


Figure 21: Europium Sorption Coefficients on Bentonite, Shale and Limestone as a Function of Ionic Strength (Vilks et al. 2011; Nowak 1979; Wang et al. 2001b; Tertre et al. 2005)

3.19 MERCURY

Mercury is a group 12, d-block element. The two main oxidation states of mercury are +1 and +2. Higher oxidation states have been detected, but are unimportant. In the reference brine solutions, under reducing conditions, the +1 oxidation state is stable with the species Hg_2^{+2}. The +2 oxidation state becomes important at atmospheric redox conditions, with the species Hg^{+2}. With slightly more reducing condition (Eh < 590 mV) the +1 oxidation state becomes dominant. Ideally, sorption tests with Hg are conducted in a glove box with reduced oxygen levels. Under reducing conditions, the presence of Se^{-2} could stabilize the Hg(II) species as $HgSe^0$.

Sorption data for Hg are very sparse. Table 43 provides several examples of Hg(II) sorption on quartz, montmorillonite, clay, sediments, alluvium and basalt. The K_d value for Hg(II) sorption on quartz was determined under very poorly described conditions. The measurements on sediment, alluvium and basalt were done in dilute Ca-Mg-HCO_3 solutions under oxidizing conditions. Although not recorded, the mercury was probably present as Hg(II). Sorption of Hg(II) onto montmorillonite in 0.6 M NaCl solutions was reported by Green-Ruiz (2009). Sorption values of Hg(II) onto sediment in 0.5 M solutions were described by Parkpoin et al. (2001). Although it is tempting to consider the K_d values for Hg(II) sorption on montmorillonite and sediment for the ionic strength of 0.5 to 0.6 M NaCl solutions, these values might not be appropriate for brine solutions under reducing conditions, where Hg(I) species will dominate. Due to the lack of relevant data for mercury sorption, only a K_d value of 0 m^3/kg can be recommended for mercury sorption on sedimentary rocks (shale and limestone) and bentonite under any conditions (Table 44).

Table 43: Measured Mercury Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
montmorillonite	NaCl	0.6	6	0.083	air	nr	0.138	batch	4
montmorillonite	NaCl	0.6	7.6	nr	air	nr	0.25	batch	4
clay	distilled water	≈ 0	5	0.2	air	nr	0.212	batch	5
clay	distilled water	≈ 0	5.4	0.2	air	nr	0.137	batch	5
clay	distilled water	≈ 0	6.4	0.2	air	nr	0.13	batch	5
clay	distilled water	≈ 0	8	0.2	air	nr	0.124	batch	5
sediment	Ca-Mg-HCO_3	0.006	8	6	oxic	nr	0.081 - 0.998	batch	2
sediment	NaCl	0.5	7.6	1	air	nr	0.32	batch	3
sediment	NaCl	0.5	7.8	1	air	nr	0.15	batch	3
sediment	NaCl	0.5	7.3	1	air	nr	8.3	batch	3
sediment	NaCl	0.5	7.7	1	air	nr	0.27	batch	3
sediment	NaCl	0.5	6.8	1	air	nr	0.58	batch	3
quartz sand	nr	nr	nr	nr	air	nr	0.061	batch	1
alluvium	Ca-Mg-HCO_3	0.006	8	6	oxic	nr	0.236 - 1.91	batch	2
basalt	Ca-Mg-HCO_3	0.006	8	6	oxic	nr	0.00954 - 0.171	batch	2

1. Fukui (2000)
2. Del Debbio (1991)
3. Parkpoin et al. (2001)
4. Green-Ruiz (2009)
5. Eloussaief et al. (2013)

nr: not recorded

Table 44: Recommended Sorption Coefficients for Mercury

Mercury(I)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Shale	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			
Limestone	**6.0**	**6.5**	**0**	**-**
comment	Due to insufficient data for saline conditions only a value of 0 m^3/kg can be recommended.			

3.20 LEAD

Lead is a group 14 metal, which is expected to be in the +2 oxidation state in aqueous solutions. Vandergraaf and Ticknor (1994) suggest that lead will have similar properties to group 2 elements, such as Sr and Ra. However, in chloride brine solutions, lead will form anionic chloride complexes that may not be sorbed as strongly as a simple divalent cation. Speciation calculations with PHREEQC (SIT database) predict that in the concentrated reference SR-270-PW brine, lead aqueous chemistry will be dominated by $PbCl_4^{-2}$ (91%) and $PbCl_3^-$ (7%).

Selected measured lead K_d values are summarized in Table 45. Vilks and Miller (2014) performed "in-house" measurements of lead sorption in SR-270-PW Na-Ca-Cl reference brine, with ionic strength of 6.0 M, for bentonite, shale, and limestone. The other published Pb K_d values for bentonite, montmorillonite, shale, illite, mudstone, limestone, dolomite, and marl were selected to provide a comparison to the "in-house" sorption measurements. Figure 22 illustrates lead sorption on montmorillonite and illite measured in $NaClO_4$ solutions (ionic strength of 0.01 M, Schulthess and Huang 1990), $NaNO_3$ solutions (ionic strength of 0.1 M, Akafia et al. 2011, Tripathi et al. 1993), and NaCl solutions (ionic strength of 0.25 M, Wold and Pickering 1981). The variation of K_d values with pH illustrated lead sorption increased from a pH value around 4 to a pH value of about 8. Varying the ionic strength from 0.01 to 0.25 M did not have a significant effect on measured K_d values. However, Vilks and Miller (2014) noted that lead sorption in brine solution with an ionic strength of 6.0 M was about a factor of 100 lower compared to sorption in water with an ionic strength of 0.01 M. The "in-house" sorption measurements in Na-Ca-Cl brine are significantly lower than other literature values, suggesting that complexation with chloride and competition with Ca in brines may significantly reduce lead sorption.

Recommended lead K_d values for sedimentary rocks (shale and limestone) and bentonite in brine solutions are summarized in Table 46. Lead K_d values measured in the SR-270-PW reference brine for bentonite, shale and limestone, as reported by Vilks and Miller (2014), are used for recommended values. High and low values were selected from individual measurements (Vilks and Miller 2014). Following the procedure used for the other elements in this report, recommended sorption values are presented as a range of values and a geometric mean. High and low values were selected from individual measurements (Vilks and Miller 2014), excluding several outliers, and the geometric mean was calculated considering all of the individual measurements. Average sorption values (in brackets) for comparison are presented in Table 45 for the SR-270-PW groundwater composition.

Table 45: Selected Lead Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	6.5	16-127	air	nr	0 - 0.011 (0.005 ± 0.004)	batch	1
bentonite	Na-Ca-Cl-HCO_3	0.01	8.1	7	air	nr	0.523 ± 0.293	batch	1
bentonite	sea water	0.68	8	30	air	nr	8 - 30	batch	2
bentonite	NaCl	0.1	8.7	30	low O_2	nr	62	batch	3
mont	NaCl	0.25	6 - 7	1	nr	nr	1.5 - 22	batch	6
mont	$NaNO_3$	0.1	6 - 7	1	nr	nr	0.47 - 60	batch	11
Ca-mont	$Ca(ClO_4)_2$	0.23	5	>1	nr	nr	0.01 - 0.017	batch	4
Ca-mont	$NaNO_3$	0.1	5.5 - 6.8	0.83	nr	nr	0.20 - 3.0	batch	5
Na-mont	$NaClO_4$	0.1	5.8 - 7.4	28-420	Ar	nr	0.33 - 24.5	batch	7
Na-mont	$NaClO_4$	0.01	6.3	0.75	nr	nr	10.8	batch	8
Na-mont	$NaClO_4$	0.2	5 - 7	1	nr	nr	4 - 50	batch	9
shale	Na-Ca-Cl (SR-270-PW)	6.0	6.3	16-127	air	nr	0 - 0.009 (0.003 ± 0.003)	batch	1
shale	Na-Ca-Cl-HCO_3	0.012	8.1	7	air	nr	0.293 ± 0.013	batch	1
Ca-illite	$Ca(NO_3)_2$	0.002	5.5	0.25	nr	nr	0.17 - 0.29	batch	10
illite	NaCl	0.25	5 - 6.5	1	nr	nr	0.45 - 5.6	batch	6
mudstone	NaCl	0.1	8.2 - 9.2	1	low O_2	nr	800	batch	3
limestone	Ca-Na-Cl-SO_4	0.48	nr	nr	air	nr	0.05 - 0.08	batch	12
limestone	Na-Ca-Cl (SR-270-PW)	6.0	6.3	16-127	air	nr	0 - 0.004 (0.001 ± 0.001)	batch	1
limestone	Na-Ca-Cl-HCO_3	0.012	8.1	7	air	nr	0.106 ± 0.017	batch	1
dolomite	Ca-Na-Cl-SO_4	0.44	nr	nr	air	nr	0.13 - 0.19	batch	12
marl	Ca-Na-Cl-SO_4	0.56	nr	nr	air	nr	0.09 - 0.12	batch	12

1. Vilks and Miller (2014)
2. Ikeda and Amaya (1998)
3. Ashida et al. (1999)
4. Griffin and Au (1977)
5. Tripathi et al. (1993)
6. Wold and Pickering (1981)
7. Lothenbach et al. (1997)
8. Schulthess and Huang (1990)
9. Ulrich and Degueldre (1993)
10. Khan and Khan (1985)
11. Akafia et al. (2011)
12. Bode (1986)

nr: not recorded
mont: montmorillonite
Na-mont: sodium montmorillonite
Ca-mont: calcium montmorillonite

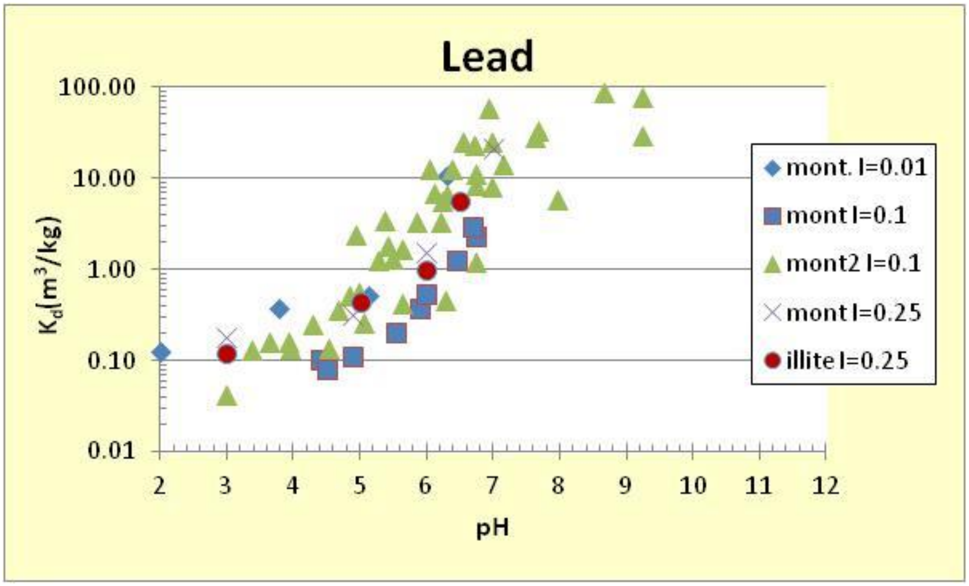


Figure 22: Lead Sorption Coefficients on Montmorillonite and Illite at Different Ionic Strengths as a Function of pH in $NaClO_4$ (I = 0.01 M), $NaNO_3$ (I = 0.1 M) and NaCl (I = 0.25 M) Solutions (Schulthess and Huang 1990; Akafia et al. 2011; Tripathi et al. 1993; Wold and Pickering 1981)

Table 46: Recommended Sorption Coefficients for Lead

LEAD (II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0 - 0.011**	**0.003 (5)**
comment	Measured in SR-270-PW synthetic brine by Vilks and Miller (2014)			
Shale	**6.0**	**6.3**	**0 - 0.009**	**0.0016 (10)**
comment	Measured in SR-270-PW synthetic brine by Vilks and Miller (2014)			
Limestone	**6.0**	**6.3**	**0 - 0.004**	**0.0004 (14)**
comment	Measured in SR-270-PW synthetic brine by Vilks and Miller (2014)			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

3.21 BISMUTH

Bismuth is a group 15 element with a dominant +3 oxidation state, although bismuth(V) species are also formed under oxidizing conditions. Given that conditions are not expected to be oxidizing in the reference groundwaters, the focus of this chapter is only on the dominant +3 oxidation state. Speciation calculations with PHREEQC (Japanese thermodynamic database, version 140331s0, 2014 March 31) predict that the main aqueous species for bismuth in the SR-270 reference brine solution are $BiCl_5^{-2}$ and $BiCl_4^-$. Lower salinity waters, such as the SR-20 reference groundwater, would contain Bi as the hydroxyl species $Bi(OH)^{+2}$ and $Bi(OH)_3^0$. The existence of these hydroxyl species suggests that Bi is likely to sorb by surface complexation to oxygen sites coordinated to metals. The speciation results also indicate that the formation of chloride species in more saline waters will likely reduce Bi sorption.

Selected bismuth K_d values are presented in Table 47. Figure 23 illustrates the sorption of Bi onto bentonite from $NaClO_4$ solutions, and onto clay from sea water (Ulrich and Degueldre 1993; Santshi et al. 1984). Bismuth sorption on bentonite appears to increase with pH. The K_d values do not show any variation with ionic strength. However, the data for bismuth sorption on bentonite did not include brine conditions with molar concentrations of chloride. PHREEQC simulations indicate that under the experimental conditions, with low NaCl concentrations, bismuth solution chemistry will be dominated by hydroxyl species, whereas in brine solutions negatively charged chloride species would dominate. This suggests that the effects of chloride complex formation with Bi need to be evaluated before the values presented in Table 47 can be considered in the context of recommended values.

Table 47: Selected Bismuth Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Ref
red clay particles	sea water	0.67	8.2	25	nr	nr	1000	1
bentonite	$NaClO_4$	0.01 - 0.2	5	1	nr	nr	3	2
bentonite	$NaClO_4$	0.01 - 0.02	6	1	nr	nr	13	2
bentonite	$NaClO_4$	0.05 - 0.2	6	1	nr	nr	20 - 25	2
bentonite	$NaClO_4$	0.01	7	1	nr	nr	32	2
bentonite	$NaClO_4$	0.02 - 0.2	7	1	nr	nr	50	2

1. Santschi et al. (1984); 2. Ulrich and Degueldre (1993) nr: not recorded

Europium (III) could be considered as a chemical analog for Bi(III), although their solution chemistry is slightly different. In the SR-300 reference groundwater (Na-Ca-Cl type, I = 7.2 M, Table 2), the dominant Eu(III) species are $EuCl^{+2}$, $EuSiO(OH)_3^{+2}$, Eu^{+3} and $EuCl_2^+$. In the SR-20 reference groundwater (Na-Cl type with HCO_3 and SO_4 concentration, I = 0.4 M, Table 2), the important species are $Eu(CO_3)^+$, Eu^{+3}, $EuSO_4^+$ and $EuCl^{+2}$. Vilks et al. (2011) found that in a Na-Ca-Cl brine (I = 7.2 M), Eu sorption values were 5.7 m^3/kg for bentonite, 0.103 - 0.117 m^3/kg for shale, and 0.146 - 0.160 m^3/kg for limestone. Based on comparing the above mentioned Eu sorption on bentonite with Bi sorption reported in Table 47, if Eu was used as an analog element then Bi sorption on bentonite would be underestimated by a factor 0.5 to 8.8. As a conservative approximation, Eu sorption could be used to approximate Bi sorption on shale and limestone, if required.

Given the lack of bismuth sorption data for brine solutions, a modelling effort was used to simulate bismuth sorption on montmorillonite and illite in the SR-270-PW reference groundwater. The modelling approach, described in Chapter 2.5, uses a 2-site protolysis non-electrostatic surface complexation and cation exchange model (2SPNE SC/CE) to simulate sorption on montmorillonite (to approximate bentonite) and illite (a major component of shale). Surface complexation constants were estimated using the linear free energy relationships (LFER) developed for montmorillonite and illite by Bradbury and Baeyens (2005b, 2009b). Hydrolysis constants for bismuth that were used for the LFER approach were taken from the JAEA thermodynamic database. The bismuth surface species and their associated binding constants on montmorillonite and illite are given in Table 48. The selectivity coefficients to account for bismuth cation exchange were based on Am^{+3} selectivity coefficients measured in 1 mol/L $NaClO_4$ (Bradbury and Baeyens 2005b, 2009b; Gorgeon 1994). The respective selectivity coefficients for montmorillonite and illite, as log K_c values, were 2.4 and 2.9.

Table 48: Bismuth Surface Complexation Reactions and Surface Complexation Constants for Montmorillonite and Illite

Bi Surface Complexation Reaction	**Strong Site log $^sK_{x-1}$ montmorillonite**	**Strong Site log $^sK_{x-1}$ illite**
$\equiv S^sOH + Bi^{+3} \Leftrightarrow \equiv S^sObi^{+2} + H^+$	7.27	7.14
$\equiv S^sOH + Bi^{+3} + H_2O \Leftrightarrow \equiv S^sObi(OH)^+ + 2H^+$	5.80	5.78
$\equiv S^sOH + Bi^{+3} + 2H_2O \Leftrightarrow \equiv S^sObi(OH)_2^0 + 3H^+$	0.054	0.480
$\equiv S^sOH + Bi^{+3} + 3H_2O \Leftrightarrow \equiv S^sObi(OH)_3^- + 4H^+$	-11.39	-10.08

Simulated Bi sorption values for montmorillonite and illite in SR-270-PW brine are illustrated in Figure 24. Simulated K_d values increase with increasing pH, up to value of about 7, in a similar way as did the Bi K_d values for bentonite in relatively dilute NaCl solutions (Figure 23). However, the simulated K_d values in brine are significantly lower than the measured values in dilute $NaClO_4$ solutions at lower pH values because, in the brine solution, bismuth is totally associated with chloride. Simulated Bi sorption values on montmorillonite in brine for pH values of 6 to 7 ranged from 1.1 to 18 m^3/kg. These values are factors of 2 to 19 lower than measured for bentonite in dilute $NaClO_4$ solutions. Simulated sorption values for illite ranged from 1.40 to 16.7 m^3/kg in the pH range of 6 to 7. The corresponding K_d values for shale, assuming a 60% illite content, would be 0.84 to 10 m^3/kg.

Recommended K_d values for bismuth are summarized in Table 49. The K_d values for bentonite and shale are based on simulated values for SR-270-PW brine solution. The K_d values for limestone are based on using Eu (III) as a chemical analog for Bi(III). These latter values are expected to be conservative given that Bi sorption values for bentonite and shale are higher than the corresponding sorption values for Eu.

Table 49: Recommended Sorption Coefficients for Bismuth

Bismuth (III)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6 - 7**	**1.1 - 18**	**4.4 (7.1)**
comment	Based on simulated sorption values on montmorillonite for SR-270-PW reference brine.			
Shale	**6.0**	**6 - 7**	**0.84 - 10**	**2.9 (5.8)**
comment	Based on simulated sorption values of 1.40-16.7 m^3/kg on illite for SR-270-PW reference brine. Final values for shale adjusted considering shale contains 60% illite.			
Limestone	**0.23 - 7.2**	**6 - 6.9**	**0.09 - 0.29**	**0.16 (1.6)**
comment	Eu sorption on limestone used as chemical analog, Vilks et al. (2011)			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

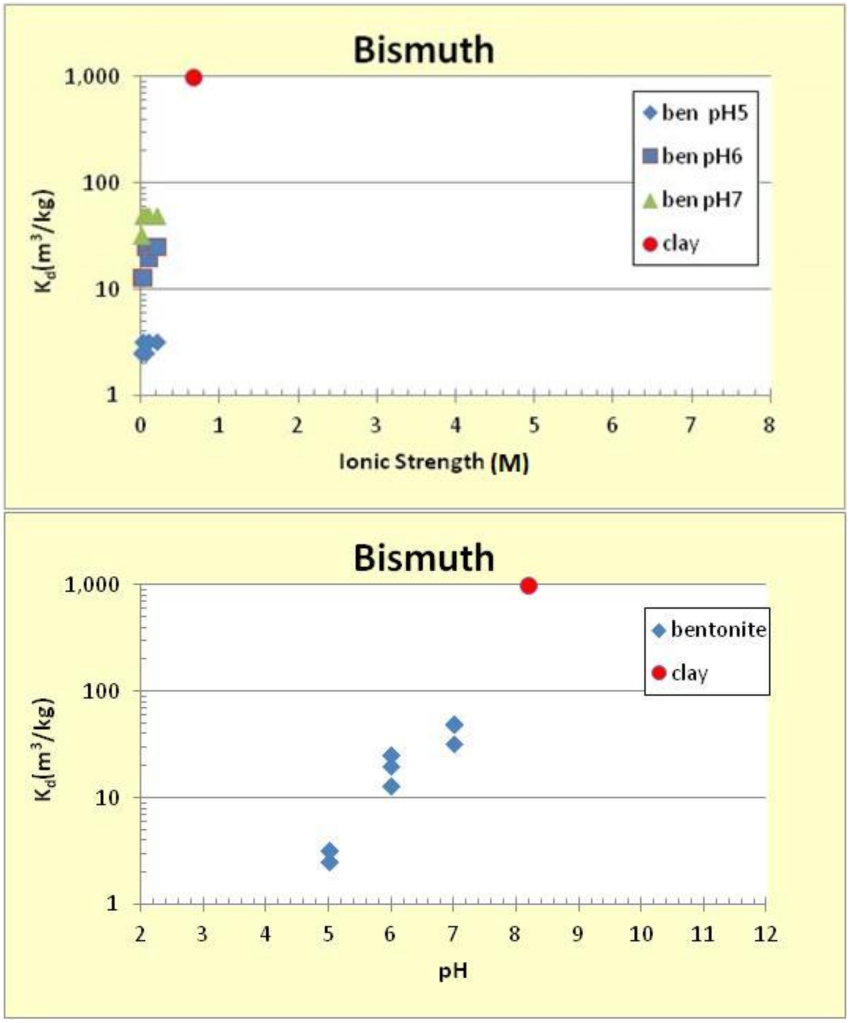


Figure 23: Bismuth Sorption Coefficients on Bentonite and Clay as a Function of Ionic Strength and pH (Ulrich and Degueldre 1993; Santschi et al. 1984)

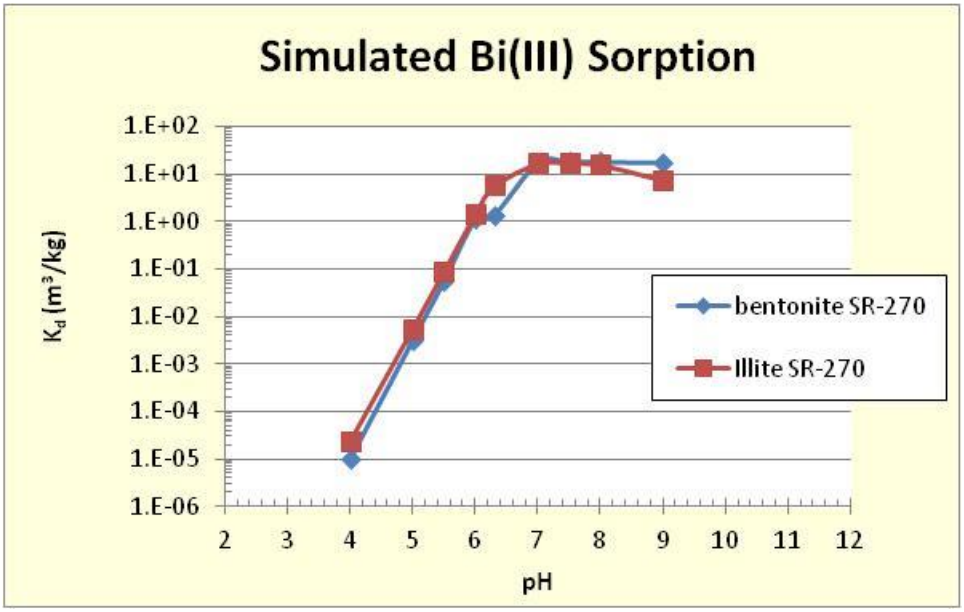


Figure 24: Simulated Bismuth Sorption Coefficients on Bentonite and Illite in the SR-270-PW Brine Solution

3.22 RADIUM

Radium is a group 2 element with a +2 oxidation state. The aqueous chemistry of radium is expected to be similar to that of Sr. It should be remembered that the actual concentration of radium will be orders of magnitude lower than that of Sr and the other group 2 elements (e.g., Ca) in groundwater. Since the group 2 elements sorb mainly by cation exchange, the high Ca concentrations in brine solutions are expected to significantly reduce radium sorption. In the reference SR-270-PW brine, the dominant radium species are predicted to be $RaCl_2$, Ra^{+2}, and $RaCl^{+}$.

Selected K_d values for radium from the literature are given in Table 50. Figure 25 illustrates the effect of pH on radium sorption on bentonite in 0.1 M NaCl solutions (Tachi et al. 2001). Sorption values were not significantly affected by pH or by the solution/solid ratios used in the sorption tests. There might be a minor increase in sorption with increasing pH for sorption with a solution/solid ratio of 50 mL/g. Sorption values were not significantly affected by pH measured with a solution/solid ratio of 500 mL/g. Figure 26 shows that increasing the contact time in the sorption tests for bentonite from 20 days to 40 days did not change the amount of sorption (Tachi and Shibutani 1999). Figure 26B shows that radium sorption on mudstone (Taki and Hata 1991) reached equilibrium after a contact time of 10 days and did not change the amount of sorption after 10 days. Figure 27 compares sorption on mudstone (Taki and Hata 1991) measured in distilled water with that determined in sea water. The K_d values determined in sea water were about a factor of 10 lower than determined in distilled water.

The Ra sorption values that could be considered for bentonite are 0.00484 to 0.0156 m^3/kg, measured in NaCl solution with ionic strength of 1.0 M (Tamamura et al. 2014). The only concern is that the experimental solution did not contain Ca^{+2}, which could compete with Ra^{+2} in natural brines. The Ra sorption coefficients for illite, measured at an ionic strength 0.01 M were also not considered. Instead, the sorption values measured with mudstone in sea water by Taki and Hata (1991) may be a reasonable approximation of sorption on shale. The radium K_d values for mudstone ranged from 0.007 to 0.032 m^3/kg.

In the absence of reasonable sorption data for limestone, one could consider using Sr(II) as a chemical analog. Vilks et al. (2011) measured Sr sorption onto bentonite, shale and limestone in a 300 g/L Na-Ca-Cl brine solution, with an ionic strength of 7.2 M. After 7 days, no Sr sorption was observed on any of the solids, likely due to the competitive sorption of the high concentration Ca^{+2}. Therefore, as a conservative assumption, a Ra sorption value of 0 m^3/kg is recommended for bentonite, shale and limestone. The Ra sorption values for mudstone were rejected because sea water contains about 80 times less Ca than the SR-270-PW brine. Sr sorption on shale was not detected and the use of a Sr analog is consistent with the other solids. Recommended radium sorption values for bentonite, shale and limestone are summarized in Table 51.

Table 50: Selected Radium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	NaCl	0.1	7	20	O_2<1ppm	nr	0.21 - 0.66	batch	1
bentonite	NaCl	0.1	7	40	O_2<1ppm	nr	0.18 - 0.83	batch	1
bentonite	NaCl	0.1	8	20	O_2<1ppm	nr	0.32 - 0.75	batch	1
bentonite	NaCl	0.1	8	40	O_2<1ppm	nr	0.36 - 0.69	batch	1
bentonite	Na-Ca-Cl-HCO_3	0.006 - 0.02	8.2	7	air	nr	0.04 - 0.05	batch	2
bentonite	Na-Ca-Cl-HCO_3	0.006 - 0.02	8.2	180	air	nr	0.16 - 0.25	batch	2
bentonite	NaCl	0.1	7	20	Ar	120 140	0.19 - 0.36	batch	4
bentonite	NaCl	0.1	7	40	Ar	123 144	0.18 - 0.92	batch	4
bentonite	NaCl	0.1	8	20	Ar	105	0.30 - 0.82	batch	4
bentonite	NaCl	0.1	8	40	Ar	89 100	0.27 - 0.60	batch	4
bentonite	NaCl	1.0	5-5.5	2	air	nr	0.00484 - 0.0156	batch	10
smectite	Na-Cl-HCO_3-SO_4	0.01	8.8	30	air	650	0.089	batch	5
mont.	NaCl	0.0013	7.5	0.7	nr	nr	0.66 - 8.1	batch	6
London clay	Ca-K-Na-OH	0.018	7 - 8	60-100	nr	nr	0.14 - 1.2	batch	3
illite	NaCl	0.01	6.5	30	air	nr	4.3 - 8.2	batch	7
mudstone	sea water	0.71	7.8	1	air	nr	0.0125	batch	8
mudstone	sea water	0.71	7.8	3	air	nr	0.007 - 0.0128	batch	8
mudstone	sea water	0.71	7.8	7-10	air	nr	0.022 - 0.028	batch	8
mudstone	sea water	0.71	7.8	14 - 24	air	nr	0.027 - 0.032	batch	8
mudstone	distilled water	≈ 0	7.7	17 - 24	air	nr	0.47 - 0.54	batch	8
marl	Ca-Na-SO_4-Cl	0.094	7	56	nr	nr	0.23 - 2.5	batch	9

1. Tachi et al. (2001)
2. Allard et al. (1979)
3. Baston et al. (1990)
4. Tachi and Shibutani (1999)

nr: not recorded

5. Ames et al. (1981)
6. Benes et al. (1985)
7. Ames et al. (1983)
8. Taki and Hata (1991)

mont.: montmorillonite

9. Baraniak et al. (1999)
10. Tamamura et al. (2014)

Table 51: Recommended Sorption Coefficients for Radium

RADIUM (II)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**7.2**	**6**	**0**	**-**
comment	Using Sr as a chemical analog and measurements of Sr sorption on bentonite in brine solutions (Vilks et al. 2011).			
Shale	**7.2**	**6**	**0**	**-**
comment	Using Sr as a chemical analog and measurements of Sr sorption on Ordovician shale (Vilks et al. 2011).			
Limestone	**7.2**	**6**	**0**	**-**
comment	Using Sr as a chemical analog and measurements of Sr sorption on Ordovician limestone (Vilks et al. 2011).			

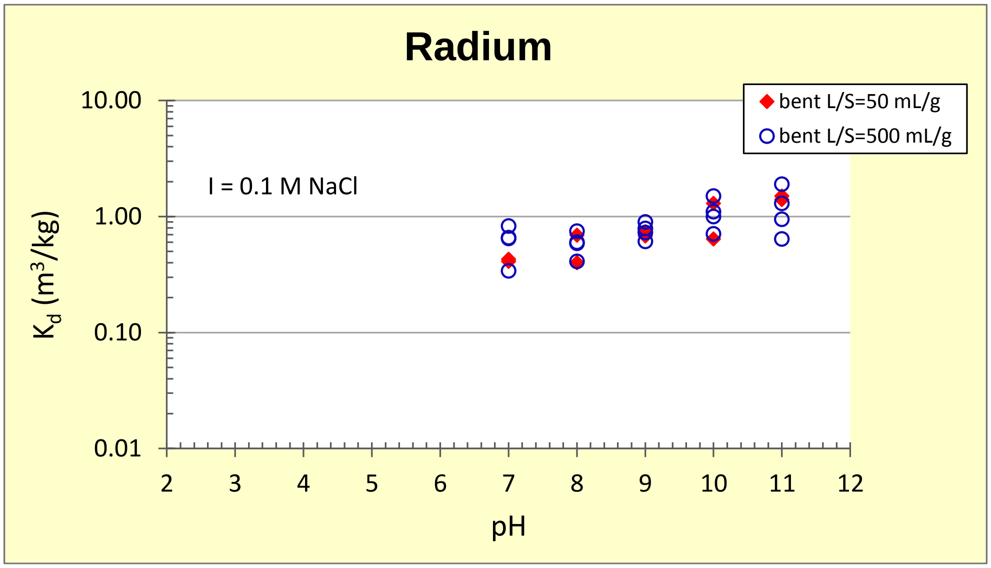


Figure 25: Radium Sorption Coefficients on Bentonite at Different Liquid to Solid Ratios as a Function of pH (Tachi et al. 2001)

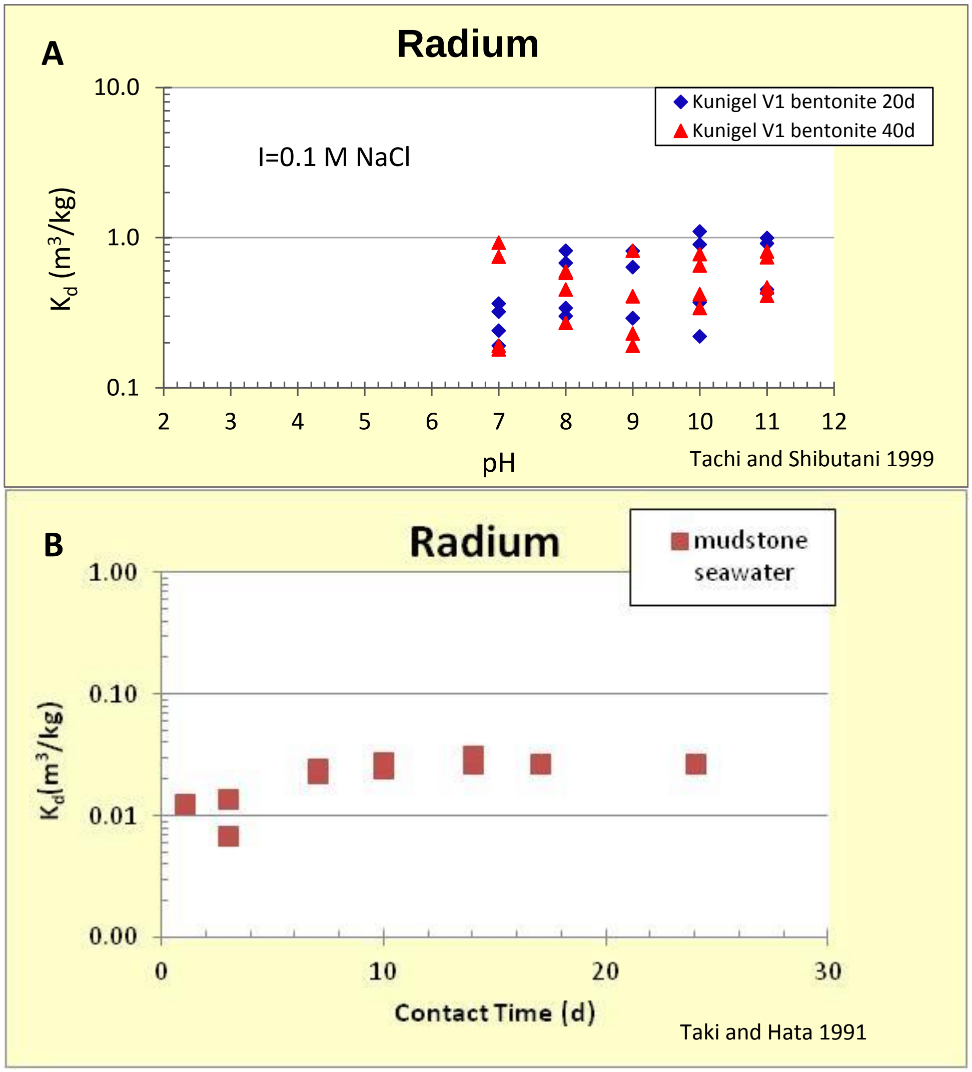


Figure 26: Effect of Contact Time on Radium Sorption on Bentonite and Mudstone (Tachi and Shibutani 1999; Taki and Hata 1991)

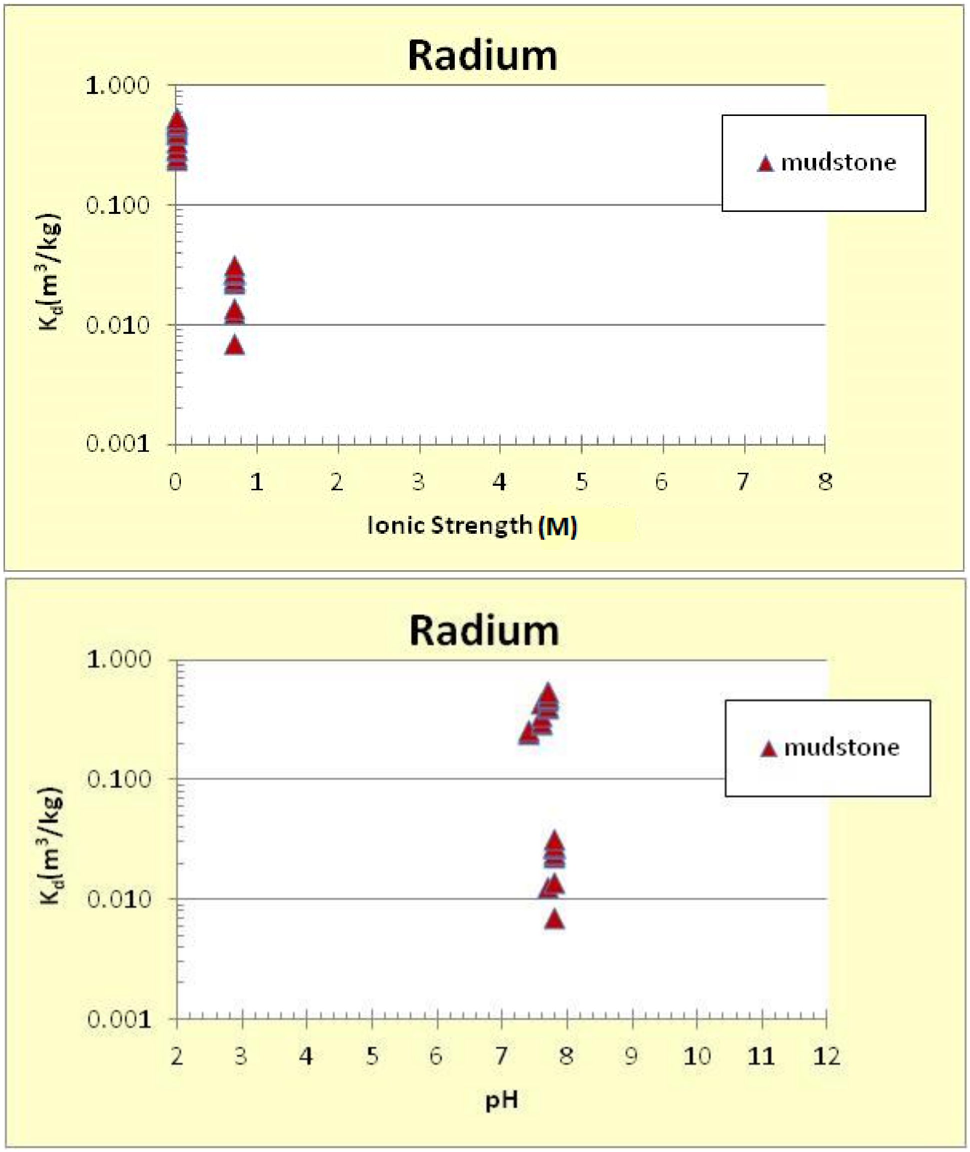


Figure 27: Radium Sorption Coefficients on Mudstone as a Function of Ionic Strength and pH (Taki and Hata 1991)

3.23 THORIUM

Thorium is an actinide element with a +4 oxidation state. Thorium has a very low solubility, making it very difficult to perform sorption measurements without the risk of precipitation. The main thorium aqueous species predicted by PHREEQC (SIT database) in the reference SR-270-PW brine solution are ThF_2^{+2} (31%), $Th(OH)_3^+$ (27%), ThF^{+3} (11%), $Th(OH)_4$ (9%), ThF_3^+ (6%), $Th(OH)_2^{+2}$ (6%), $Th(OH)_3(CO_3)^-$ (4%), $Th(OH)_2(CO_3)$ (3%) and ThF_4 (3%). Note that the small amount of fluoride (2 mg/L) in the SR-270 brine can have a significant impact on thorium chemistry. In the absence of fluoride, all of the thorium aqueous species would be either hydroxides or hydroxide-carbonate species. The solubility of Th is limited by ThO_2.

Selected thorium sorption coefficients are summarized in Table 52. Figure 28 illustrates K_d values of thorium measured on montmorillonite in $NaClO_4$ solutions with an ionic strength of 0.1 M and 1 M (Bradbury and Baeyens 2003a), and on illite in a $NaClO_4$ solution with an ionic strength of 0.1 M (Bradbury and Baeyens 2009b). Thorium sorption on montmorillonite and illite increased with pH, reaching a plateau in the pH range of about 5 to 8. Sorption on montmorillonite did not decrease when the ionic strength increased from 0.1 to 1 M. Thermodynamic sorption modelling efforts by Bradbury and Baeyans (2005b, 2009b) provide good evidence that thorium will likely sorb by surface complexation to oxygen sites on the solid surface.

Thorium sorption values for a bentonite/quartz mixture with 10% bentonite measured in a solution with an ionic strength of 0.02 M and pH of 8.2 ranged from 0.25 to 6.3 m^3/kg (Allard et al. 1979). Bradbury and Baeyens (2003a) reported that the thorium K_d value on bentonite is 63 m^3/kg, which was measured in bentonite porewater (Na-Cl-SO_4) with an ionic strength of 0.31 to 0.34 M and in the pH range of 6.9 to 7.7. The same authors noted that the Th K_d value on a purified montmorillonite, in a $NaClO_4$ solution with an ionic strength of 0.1 M, was 200 – 234 m^3/kg, and 398 - 631 m^3/kg in 1.0 M $NaClO_4$ solution. SKB (2006) reported Th K_d values for bentonite that range from 4 to 700 m^3/kg, with recommended values of 63 and 40 m^3/kg for saline (ionic strength of 0.2 M) and highly saline (ionic strength of 0.7 M) groundwater, respectively. These values were derived using data from Bradbury and Baeyens (2003a) (Ochs and Talerico 2004). More recently, Bradbury and Baeyens (2005b) reported thorium sorption values for montmorillonite measured in 0.1 and 1.0 M $NaClO_4$ solutions. For pH values of 6 and 7 the sorption coefficients were 360 and 410 m^3/kg, respectively.

The measured data were used to produce a 2-site protolysis non-electrostatic surface complexation model to describe thorium sorption on montmorillonite (Bradbury and Baeyens 2005b). The surface reactions and constants for this model are summarized in Table 53. The thorium sorption model for montmorillonite was incorporated into PHREEQC (SIT database), assuming that the sorption constants in the SR-270 Na-Ca-Cl brine are the same as those derived from 0.1 and 1.0 mol/L $NaClO_4$ solutions. The simulated sorption values for the SR-270-PW reference brine were 265 and 279 m^3/kg at pH values of 6 and 7, respectively. These values fall within the range of thorium K_d values for montmorillonite measured in 0.1 M and 1.0 M $NaClO_4$ solutions by Bradbury and Baeyens (2003a, 2005b), as shown in Figure 28A.

Table 52: Selected Thorium Sorption Coefficients from Literature

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bent/quartz (10:90)	Na-Ca-Cl-HCO_3	0.02	8.2	7	air	nr	0.25 - 0.32	batch	1
bent/quartz (10:90)	Na-Ca-Cl-HCO_3	0.02	8.2	180	air	nr	0.63 - 6.3	batch	1
bentonite	Na-Cl-SO_4	0.31-0.34	6.9 - 7.7	120	N_2	nr	63	batch	4
bentonite	Na-Ca-Cl (SR-270)	6.0	5.9 - 6.4	8-195	N_2	nr	3.38 - 15.9	batch	8
mont	Na-ClO_4	0.1	6 - 7	7	N_2	nr	200 - 234	batch	4
mont	Na-ClO_4	1.0	6.4 - 7.4	7	N_2	nr	398 - 631	batch	4
mont	Na-ClO_4	0.1 - 1	6	3	N_2	nr	360	batch	5
mont	Na-ClO_4	0.1 - 1	7	3	N_2	nr	410	batch	5
mont	Na-Ca-Cl (SR-270-PW)	6	6	nr	nr	nr	265	sim	7
mont	Na-Ca-Cl (SR-270-PW)	6	7	nr	nr	nr	279	sim	7
London clay	Ca-K-Na-OH	0.018	8.1	60-100	N_2	-540	1.10	batch	2
shale	Na-Ca-Cl (SR-270-PW)	6.0	5.6 - 6.4	8-195	N_2	nr	1.66 - 6.81	batch	8
London clay	Ca-K-Na-OH	0.018	8.5	60-100	N_2	-540	1.1 - 3.0	batch	2
Opalinus clay	Na-Ca-Mg-SO_4	0.3	6.3	25	CO_2/ N_2	340	17 - 26	batch	3
Opalinus clay	Na-Ca-Mg-SO_4	0.39	8	25	CO_2/ N_2	340	43 - 95	batch	3
ilite	Na-ClO_4	0.1	6	7	N_2	nr	480	batch	6
illite	Na-ClO_4	0.1	7	7	N_2	nr	96 - 794	batch	6
illite	Na-Ca-Cl (SR-270-PW)	6.0	6	Nr	nr	nr	232	sim	7
illite	Na-Ca-Cl (SR-270-PW)	6.0	7	Nr	nr	nr	228	sim	7
limestone	Na-Ca-Cl (SR-270-PW)	6.0	5.7 - 6.4	8-195	N_2	nr	0.6 - 2.71	batch	8

1. Allard et al. (1979)
2. Baston et al. (1991)
3. Lauber et al. (2000)
4. Bradbury and Baeyens (2003a)
5. Bradbury and Baeyens (2005b)
6. Bradbury and Baeyens (2009b)
7. this work
8. Vilks and Miller (2018)

nr: not recorded
mont: montmorillonite
sim: simulation

Bradbury and Baeyens (2009b) measured thorium sorption on illite in a 0.1 M $NaClO_4$ solution. The measured sorption data were used to construct a thorium sorption model for illite, with sorption constants given in Table 53. This sorption model was incorporated into PHREEQC (SIT database) to simulate thorium sorption on illite in the SR-270-PW reference brine solution. Calculated sorption coefficients at pH values of 6 and 7 were 232 and 228 m^3/kg, respectively. These simulated values (see Figure 28B) are a factor of 1.8 lower compared to the experimental sorption values measured in $NaClO_4$ solution with ionic strength of 0.1 M by Bradbury and Baeyens (2009b). The simulated values of thorium sorption on illite were used to derive sorption values for shale that ranged from 139 to 137 m^3/kg, taking into account that shale contains 60 percent illite.

The USEPA (1998) recommended Th sorption values of 0.7 to 10 m^3/kg for dolomite. These values were based on measurements made at near-neutral pH values in Na-Cl brine solutions with an ionic strength of about 5 M. Stenhouse (1995) used mineral sorption values to estimate sorption on marl and recommended a realistic Th K_d value of 1 m^3/kg and a conservative value of 0.1 m^3/kg.

Table 53: Thorium Surface Complexation Reactions and Constants for Montmorillonite and Illite

Th Surface Complexation Reaction	Mont. Strong Site log $^sK_{x-1}$	Illite Strong Site log $^sK_{x-1}$
$\equiv S^sOH + Th^{+4} \Leftrightarrow \equiv S^sOTh^{+3} + H^+$	7.2	7.4
$\equiv S^sOH + Th^{+4} + H_2O \Leftrightarrow \equiv S^sOTh(OH)^{+2} + 2H^+$	2.7	2.3
$\equiv S^sOH + Th^{+4} + 2H_2O \Leftrightarrow \equiv S^sOTh(OH)_2^+ + 3H^+$	-2.6	-2.4
$\equiv S^sOH + Th^{+4} + 3H_2O \Leftrightarrow \equiv S^sOTh(OH)_3^0 + 4H^+$	-9.1	-8.8
$\equiv S^sOH + Th^{+4} + 4H_2O \Leftrightarrow \equiv S^sOTh(OH)_4^- + 5H^+$	-16.9	-15.3

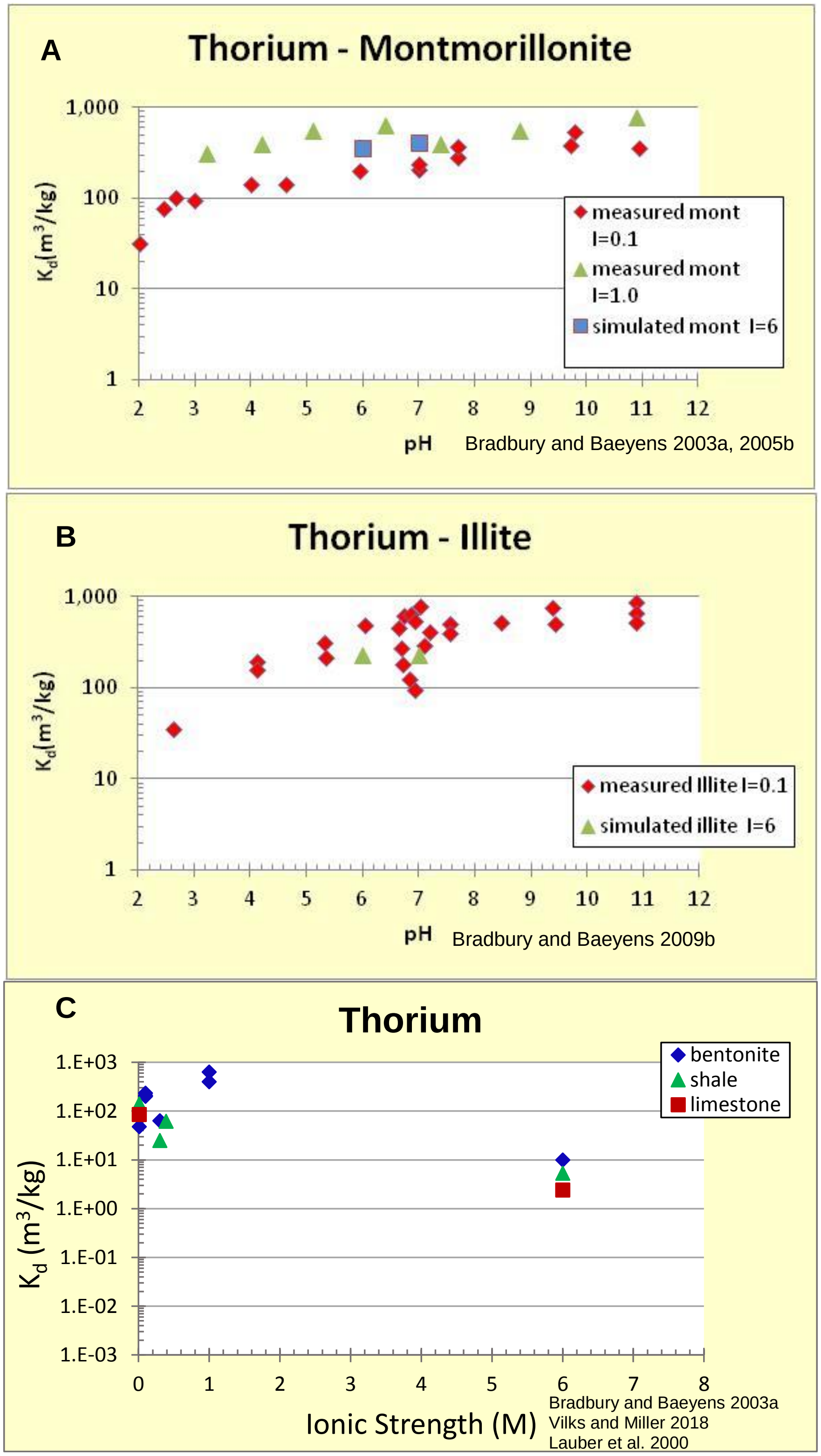
Thorium sorption K_d values measured on sedimentary rocks and bentonite in the SR-27-PW reference brine by Vilks and Miller (2018) are also reported in Table 52. The “in-house” measured values for bentonite and shale are about 2 orders of magnitude lower than Th K_d values measured on purified montmorillonite and illite in simple $NaClO_4$ solutions, as well as the simulated values based on these latter measurements. The “in-house” measurements may be lower because the bentonite and shale were not subjected to the purification processes used to obtain pure montmorillonite and illite samples, and possibly because the SR-270-PW brine has a more complex composition. For example, the fluoride in the SR-270-PW could have complexed with Th and reduced its sorption. Figure 28C shows the ionic strength dependency of Th sorption on bentonite, shale and limestone (Vilks and Miller 2018; Bradbury and Baeyens 2003a; Lauber et al. 2000).

Table 54 summarizes recommended thorium sorption values for sedimentary rocks (shale and limestone) and bentontie. The recommended K_d values for bentonite, shale and limestone were all based on the “in-house” sorption measurements reported by Vilks and Miller (2018).

Table 54: Recommended Sorption Coefficients for Thorium

THORIUM (IV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**5.9 - 6.4**	**3.38 - 15.9**	**8.9 (1.8)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			
Shale	**6.0**	**5.6 - 6.4**	**1.66 - 6.81**	**4.6 (1.8)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			
Limestone	**6.0**	**5.7 - 6.4**	**0.6 - 2.71**	**2.1 (1.9)**
comment	Based on measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.



Thorium - Montmorillonite

Bradbury and Baeyens 2003a, 2005b

Thorium - Illite

Bradbury and Baeyens 2009b

Thorium

Bradbury and Baeyens 2003a
Vilks and Miller 2018
Lauber et al. 2000

Figure 28: Measured (Bradbury and Baeyens 2003a, 2009b) and Simulated Thorium Sorption Coefficients on Montmorillonite (A) and Illite (B) as a Function of pH; Thorium Sorption Coefficients on Bentonite, Shale and Limestone as a Function of Ionic Strength (C)

3.24 PROTACTINIUM

Protactinium (Pa) is an actinide element with oxidation states of +4 and +5. Pa(IV) is only stable under very acidic and very reducing conditions. PHREEQC (SIT database) predicts that the +5 oxidation state will dominate in the reference groundwaters, with PaO_2^+ being the dominant soluble species. The solubility of Pa is controlled by the Pa_2O_5 oxide, which has a very low solubility. Protactininium is prone to form colloids (Cotton and Wilkinson 1980), which is likely to pose an experimental challenge by reducing Pa concentrations that can be used in sorption tests. Given its affinity for oxygen, Pa is likely to sorb by surface complexation to oxygen sites on the solid surface.

Selected protactinium K_d values are presented in Table 55. Torstenfelt et al. (1981) measured a sorption value of 5.0 m^3/kg on bentonite in a very dilute solution (with an ionic strength of 0.004 M and pH of 8.2) using the diffusion method. The K_d value obtained from diffusion tests in bentonite was identical to the sorption value on montmorillonite measured by batch sorption tests in very dilute solution by Allard et al. (1982). Not giving the pH conditions for sorption on claystone and marl, Bode (1989) reported sorption values of 3.5 to 9.4 m^3/kg on claystone and of 4.8 to 24 m^3/kg on marl measured in very dilute solution (with an ionic strength of 0.004 M). Bradbury and Baeyens (2009b) reported Pa(V) sorption values on illite in $NaClO_4$ solution over a pH range of about 2 to 11 (with an ionic strength of 0.1 M), as illustrated in Figure 29. Protactinium K_d values of interest in this data set, for pH values of 5.9 to 7.7 ranged from 27 to 154 m^3/kg. Geibert and Usbeck (2003) reported natural Pa(V) sorption values (derived from natural distribution ratios) for particles in sea water (ionic strength = 0.62 M, pH = 8.2) that were between 1220 and 1840 m^3/kg for smectite and 130 to 340 m^3/kg for calcite. These natural distribution ratios for suspended sea water particles were not considered for sedimentary rocks since these ratios might not represent equilibrium.

Except for the measurement of protactinium distribution ratios between sea water and suspended solids (smectite and calcite), there are virtually no sorption measurements to show the effect of high salinity on protactinium sorption. Bradbury and Baeyens (2009b) used their data for protactinium sorption on illite in 0.1 mol/L $NaClO_4$ solutions to develop a 2-site protolysis non-electrostatic surface complexation and cation exchange model (2SPNE SC/CE) to simulate sorption on illite (a major component of shale). The reactions and surface complexation constants for this model are summarized in Table 56. Cation exchange was not considered for protactinium because the monovalent PaO_2^+ would not be able to compete with Na^+ in brine solutions. Protactinium sorption on illite was simulated for the reference SR-270-PW brine composition using the 2SPNE SC/CE method. The modelling results for SR-270-PW brine are compared with measured K_d values for illite (in ionic strength of 0.1 M $NaClO_4$ solution) in Figure 30. The simulated K_d value for illite is 41 m^3/kg and 59 m^3/kg for pH = 6 and pH = 7, respectively. The model simulations are very close to the measured values indicating: (1) the usefulness of the sorption model, and (2) that the SR-270-PW brine solution has had a minimal effect on protactinium sorption.

Bradbury et al. (2010) filled data gaps for sorption on calcite by finding an empirical relationship between log K_d values for sorption on calcite and the ionic radii of sorbing elements. Based on this correlation, the estimated sorption value for Pa(V) (ionic radius 0.78 Å) on calcite is 0.091 m^3/kg, which is assumed valid over the pH range of 6 to 9.

Table 55: Selected Protactinium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Pa(V)									
mont.	syn. gw. (no composition)	0.008	8.2	6	air	nr	5.01	batch	1
bentonite	syn. gw. (no composition)	0.004	8.2	76	air	nr	5.0	diffu	3
smectite	sea water	0.62	8.2	90-119	air	nr	1220 - 1840	batch	5
claystone	groundwater (no composition)	0.001	nr	nr	air	nr	3.5 - 9.4	batch	2
illite	$NaClO_4$	0.1	5.9-7.7	7	N_2	nr	27 - 154	batch	4
marl	groundwater (no composition)	0.004	nr	nr	air	nr	4.8 - 24	batch	2
sea water particles (calcite)	sea water	0.62	8.2	90-119	air	nr	130-340	batch	5
Pa(IV)									
bentonite	$Na\text{-}HCO_3\text{-}SO_4$	0.003	10	30	N_2/ $Na_2S_2O_4$	-330	>190 - >350	batch	6

1. Allard et al. (1982)
2. Bode (1989)

nr: not recorded
diffu: diffusion test

3. Torstenfelt et al. (1981)
4. Bradbury and Baeyens (2009b)

mont.: montimorillonite
syn. gw.: synthetic groundwater

5. Geibert and Usbeck (2003)
6. Berry et al. (2007)

Table 56: Protactinium Surface Complexation Reactions and Constants for Illite

Pa Surface Complexation Reaction	Illite log $^sK_{x\text{-}1}$
$\equiv S^sOH + PaO(OH)^{+2} \Leftrightarrow \equiv S^sOPaO(OH)^{+} + H^{+}$	6.4
$\equiv S^sOH + PaO(OH)^{+2} \Leftrightarrow \equiv S^sOPaO_2^{0} + 2H^{+}$	0.4
$\equiv S^sOH + PaO(OH)^{+2} + 2H_2O \Leftrightarrow \equiv S^sOPaO_2(OH)^{-} + 3H^{+}$	-6.7

Recommended Pa sorption values for sedimentary rocks are summarized in Table 57. The Pa(IV) K_d value for bentonite reported by Berry et al. (2007) was not considered because it is expected that only Pa(V) is stable in the reference groundwaters. Note that although the Pa sorption data were not derived using data for brine solutions, they are likely to be applicable to brines since protactinium sorbs by surface complexation (Bradbury and Baeyens 2009b). This assumption is supported by the simulated protactinium sorption on illite, which indicated that protactinium sorption was not reduced in brine solutions. Sorption values for shale were based on simulated K_d values for illite in SR-270-PW brine. Simulated K_d values for pH 6 and pH 7 were 41 and 59 m^3/kg, respectively. Assuming a 60% illite content in shale, these values correspond to 25 and 35 m^3/kg for shale at pH 6 and pH 7, respectively. Sorption on limestone was based on the LFER approach suggested by Bradbury et al. (2010).

Table 57: Recommended Sorption Coefficients for Protactinium

PROTACTINIUM (V)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.004**	**8.2**	**5.0**	**-**
comment	Torstenfelt et al. (1982). Likely applicaple to saline conditions.			
Shale	**6**	**6 - 7**	**25 - 35**	**30 (1.3)**
comment	Based on simulated sorption data for illite (SR-270-PW brine) with values of 41 (pH 6) to 59 (pH 7) m^3/kg, assuming shale contains 60% illite.			
Limestone	**-**	**6 - 9**	**0.091**	**-**
comment	Based on LFER approach suggested by Bradbury at al. (2010).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

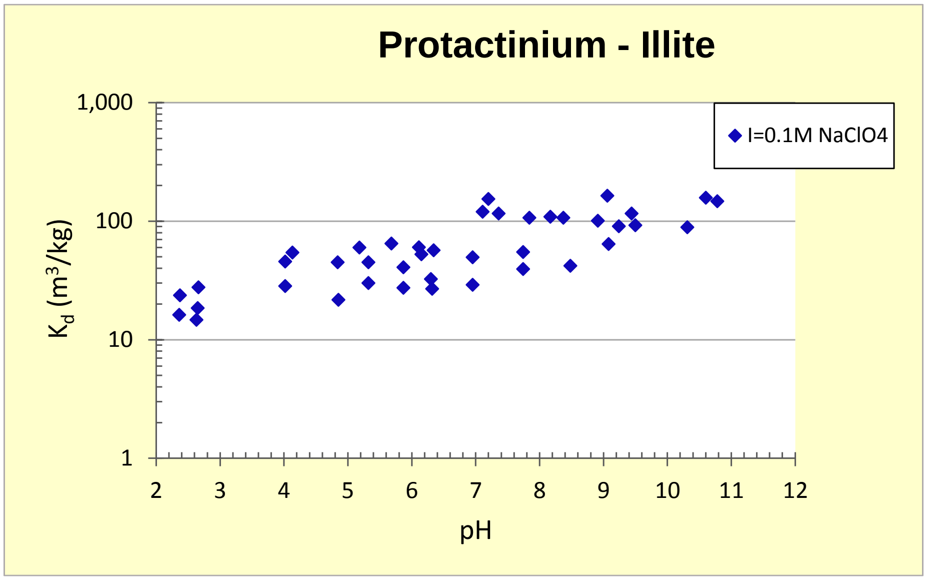


Figure 29: Protactinium Sorption Coefficients on Illite (Bradbury and Baeyens 2009b)

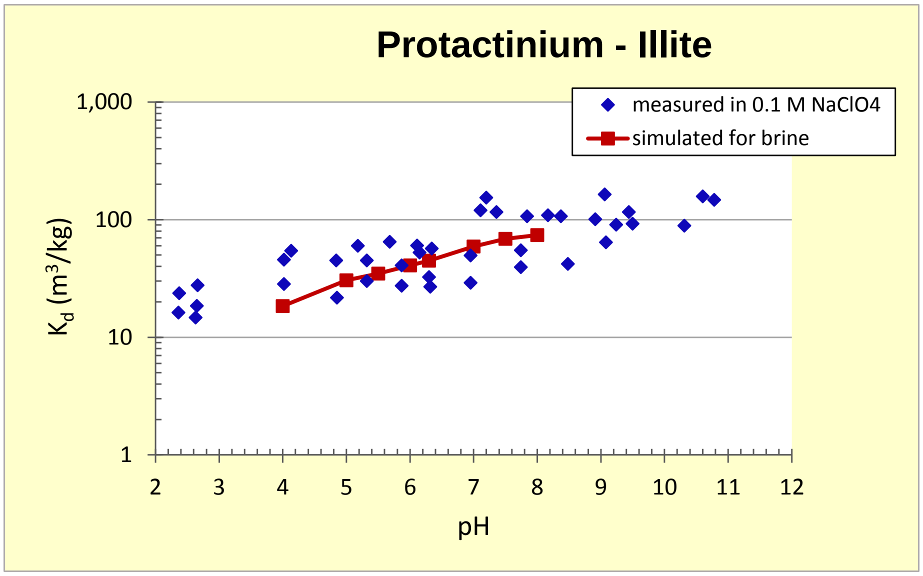


Figure 30: Simulated Protactinium Sorption Coefficients on Illite for SR-270-PW Brine Compared with Sorption Coefficients Measured in Dilute Solution (by Bradbury and Baeyens 2009b)

3.25 URANIUM

Since uranium may occur in the +3, +4, +5, and +6 oxidation states, its chemistry in groundwater is very sensitive to the redox conditions of groundwater. Speciation calculations with PHREEQC (SIT database), see Table 3, predict that in the SR-270-PW reference groundwater (Eh = -200 mV), uranium will be mainly in the +4 oxidation state with $U(OH)_4$ and $U(OH)_3^+$ being the main aqeous species. A small fraction of the uranium is present as the U(V) aqueous species UO_2^+. In the SR-20 reference groundwater (Eh = 90 mV), uranium would be in the +6 oxidation state as $UO_2(CO_3)_3^{-4}$ (84%) and $UO_2(CO_3)_2^{-2}$ (14%). Under reducing conditions, uranium solubility is very low, but under oxidizing conditions its solubility is much higher. In addition to pH, carbonate would also influence the solution chemistry of uranium. In brine solutions, uranium sorption would likely occur by surface complexation to oxygen sites on oxides, aluminosilicates and carbonates. The sorption database for uranium needs to distinguish between oxidizing and reducing conditions.

Table 58 summarizes selected K_d values for U(VI) and U(IV) for a number of solids that include bentonite, shale, limestone, montmorillonite, smectite, illite, chlorite, and calcite in a variety of solutions ranging from freshwater to brine solution. Vilks et al. (2011) and Vilks and Miller (2014) performed “in-house” measurements of U(VI) sorption on bentonite, shale and limestone. Bertetti (2016) performed “in-house” measurements of U(IV) sorption on bentonite, shale and limestone in the SR-270-PW reference brine and in a dilute solution (with an ionic strength of 0.01 M). Data from the literature are provided for comparison.

Uranium(VI) sorption data for oxidizing conditions are summarized in Figure 31 and Figure 32. Figure 31 compares “in-house” measured K_d values on bentonite (Vilks et al. 2011; Vilks and Miller 2014) with values from the literature measured in sea water (Berry et al. 2007; Baston et al. 1995) and $NaClO_4$ solutions with ionic strengths of 0.01 and 0.1 M without carbonate (Bradbury and Baeyens 2005b) and of 0.5 M (Sabodina et al. 2006b). The “in-house” determined K_d values are similar to the values from sea water, and did not display any correlation with ionic strength. The K_d values determined in 0.01 and 0.1 M $NaClO_4$ solutions are several orders of magnitude higher, most likely because the $NaClO_4$ solutions were free of carbonate. The K_d values on montmorillonite determined in 0.01 and 0.1 M $NaClO_4$ solution also displayed an increase with increasing pH, reaching a peak around a pH value of 6, and then decreasing with any further increase in pH.

Figure 32 shows the variation of “in-house” measured K_d values for shale and limestone (Vilks et al. 2011, Vilks and Miller 2014) as a function of ionic strength, as well as K_d values for illite plotted as a function of pH. The K_d values for illite measured with a 1 hour contact time were reported by Gorgeon (1994), while the K_d values determined with a contact time of 7 days were reported by Bradbury and Baeyens (2009b). The tests with illite were performed in $NaClO_4$ solutions without carbonate present. Sorption on shale and limestone was not affected by ionic strength for ionic strengths of 0.2 M and higher (Vilks et al. 2011; Vilks and Miller 2014). Sorption values on shale were over two orders of magnitude lower than measured values on illite, most likely because the tests with illite were performed without carbonate. Ionic strength did not have a significant effect on K_d values for illite measured with 1 hour contact times (compare results between ionic strengths of 0.1 and 1 M). Increasing the contact time from 1 hour to 7 days significantly increased sorption on illite.

Table 58: Selected Measured Uranium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Uranium (VI)									
bentonite	Na-Ca-Cl	7.2	6.5	7	air	nr	0.57 ± 0.05	batch	1
bentonite	Na-Ca-Cl	2.4	7.0	7	air	nr	0.18 ± 0.01	batch	1
bentonite	Na-Ca-Cl	0.23	7.5	7	air	nr	0.19 ± 0.01	batch	1
bentonite	NaCl	1.9	7.3	7	air	nr	0.014	batch	1
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	6.5	14-127	air	nr	0.023 - 0.049	batch	2
bentonite	Na-Ca-Cl	0.012	8.1	14 - 63	air	nr	0.057 ± 0.012	batch	2
bentonite	dilute no comp	≈ 0	9	28	air	330	0.33	batch	3
bentonite	Na-Ca-HCO_3-Cl-SO_4	0.003	8.4	30	air	nr	0.20	batch	4
bentonite	sea water	0.725	8.2	120	N_2	310	0.035 - 0.20	batch	8
mont.	$NaClO_4$	0.01	6 - 7	7	CO_2 free	nr	287 - 428	batch	15
mont.	$NaClO_4$	0.1	6 - 7	7	CO_2 free	nr	172 - 275	batch	15
bentonite	sea water	0.68	8.2	120	N_2	300	0.15 - 0.20	batch	10
mont.	NaCl	0.01	7	30	air	nr	0.38 - 0.62	batch	7
mont.	$NaNO_3$	0.1	6 - 7	10	air	nr	4.2 - 36	batch	18
smectite	$NaClO_4$	0.1	6.1 - 7.2	0.83	N_2	nr	16 - 200	batch	6
smectite	$NaClO_4$	1.0	5.2 - 8.0	0.042	air	nr	0.079 - 0.63	batch	9
bentonite	$NaClO_4$	0.5	5.8 - 7.3	3	N_2	nr	0.0917 - 0.481	batch	22
smectite	NaCl	0.1	6 - 7	0.83	CO_2 free	nr	2.4 - 9.3	batch	7
smectite	$NaNO_3$	0.1	6 - 7	1	Air	nr	0.64 - 4.9	batch	19
smectite	$NaClO_4$	0.1	7.5	7	N_2	nr	0.007 - 22	batch	20
shale	Na-Ca-Cl	7.2	6.2	7	Air	nr	0.051 ± 0.002	batch	1
shale	Na-Ca-Cl	2.4	7.0	7	Air	nr	0.006 ± 0.005	batch	1
shale	Na-Ca-Cl	0.23	7.5	7	Air	nr	0.020 ± 0.003	batch	1
shale	NaCl	1.9	7.2	6	Air	nr	0.039 ± 0.003	batch	1
shale	Na-Ca-Cl (SR-270-PW)	6.0	6.3	56 - 127	Air	nr	0.016 - 0.044	batch	2
shale	Na-Ca-Cl	0.012	8.1	14 - 63	Air	nr	0.14 ± 0.01	batch	2
shale	Na-Ca-SO_4-Cl-HCO_3	0.004	7.3 - 7.8	nr	Air	nr	0.010 - 0.012	batch	11
illite	NaCl	0.01	7	30	Air	nr	0.43 - 0.55	batch	7
illite	$NaClO_4$	1.0	6 - 7	0.042	Air	nr	3.0 - 4.3	batch	9
illite	Na-Ca-Cl-SO_4	0.27	8	30	Air	nr	0.039	batch	12
illite	Na-ClO_4	0.1	6 - 7	7	N_2	nr	41 - 107	batch	17

Table 58 continued...

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Londen clay	Ca-K-Na-OH	0.018	8	60-100	N_2	nr	0.001 - 0.55	batch	5
clay	Na-ClO_4	1.0	5.4-7.6	1	Air	nr	0.32 - 16	batch	16
limestone	Na-Ca-Cl	7.2	6.1	7	Air	nr	0.017	batch	1
limestone	Na-Ca-Cl	2.4	7.0	7	Air	nr	0.002 ± 0.001	batch	1
limestone	Na-Ca-Cl	0.23	7.5	7	Air	nr	0.009 ± 0.001	batch	1
limestone	Na-Cl	1.9	7.2	6	Air	nr	0.003 ± 0.001	batch	1
limestone	Na-Ca-Cl (SR-270-PW)	6.0	6.3	64-127	Air	nr	0.008 - 0.015	batch	2
limestone	Na-Ca-Cl	0.012	8.1	14-63	Air	nr	0.088 ± 0.005	batch	2
calcite	Na-Ca-Cl-SO_4	0.27	8	30	Air	nr	0.0069	batch	12
Uranium (IV)									
bentonite	sea water	0.68	8.2	120	N_2/ $Na_2S_2O_4$	-400	150 - 180	batch	10
bentonite	deionized water	≈ 0	10	120	N_2/ $Na_2S_2O_4$	-440	520 - 670	batch	13
bentonite	sea water	0.72	8	120	N_2/ $Na_2S_2O_4$	-410 -400	7.9 - 230	batch	8
bentonite	Na-Ca-Cl (SR-270-PW)	6	6-8.4	17-37	N_2+H_2	-290 -40	0.42 - 2.2	batch	21
bentonite	Na-Ca-Cl	0.01	9.7	17	N_2+H_2	-420	1.5 - 20	batch	21
shale	Na-Ca-Cl (SR-270-PW)	6	6-8.4	17-37	N_2+H_2	-290 -40	0.42 - 2.2	batch	21
shale	Na-Ca-Cl	0.01	9.7	17	N_2+H_2	-420	1.5 - 20	batch	21
London clay	Ca-K-Na-OH	0.018	8	60-100	N_2	-540	4.3 - 9.0	batch	14
illite	Na-Ca-Cl-SO_4	0.27	9	30	low O_2	nr	0.18	batch	12
calcite	Na-Ca-Cl-SO_4	0.27	9	30	low O_2	nr	0.035	batch	12
limestone	Na-Ca-Cl (SR-270-PW)	6	6-8.4	17-37	N_2+H_2	-290 -40	0.42 - 2.2	batch	21
limestone	Na-Ca-Cl	0.01	9.7	17	N_2+H_2	-420	1.5 - 20	batch	21
chlorite	Na-Ca-Cl-SO_4	0.27	9	30	low O_2	nr	0.069	batch	12

1. Vilks et al. (2011)
2. Vilks and Miller (2014)
3. Erdal et al. (1977)
4. Torstenfelt et al. (1988)
5. Berry et al. (1989)
6. Zachara and McKinley (1993)
7. Ames et al. (1983)

nr: not recorded

8. Berry et al. (2007)
9. Gorgeon (1994)
10. Baston et al. (1995)
11. Berry et al. (1990)
12. Ticknor (1993)
13. Baston et al. (1997)
14. Baston et al. (1991)

mont.: montmorillonite

15. Bradbury and Baeyens (2003a)
16. Stammose et al. (1992)
17. Bradbury and Baeyens (2009b)
18. Pabalan and Turner (1997)
19. Korichi and Bensmaili (2009)
20. Missana et al. (2009a)
21. Bertetti (2016)
22. Sabodina et al. (2006b)

Vilks et al. (2011) measured U(VI) sorption on bentonite, Ordovician shales and limestone, in brine solutions with ionic strengths between 0.24 and 7.2 M, and pH values from 6.0 to 7.5. Uranium(VI) sorption coefficients were 0.014 to 0.57 m^3/kg for bentonite, 0.006 to 0.051 m^3/kg for shale, and 0.002 to 0.017 m^3/kg for limestone. More recent measurements (Vilks and Miller 2014) focused on determining U(VI) sorption in the SR-270-PW reference brine solution, producing average sorption coefficients of 0.034 ± 0.009 m^3/kg (i.e. 0.023 - 0.049 m^3/kg) for bentonite, 0.028 ± 0.009 m^3/kg (i.e. 0.016 - 0.044 m^3/kg) for shale and 0.010 ± 0.004 m^3/kg (i.e. 0.008 - 0.015 m^3/kg) for limestone. These latter sorption values for U(VI) are recommended over those in the literature because they were determined with sedimentary rocks and the reference brine solutions. Furthermore, they are lower than the values selected from the literature, and are considered to be more conservative.

The K_d values for U(IV) sorption on bentonite that are the most relevant to saline solutions were measured in sea water and reported by Baston et al. (1995), with values ranging from 150 to 180 m^3/kg, and by Berry et al. (2007) with values ranging from 22 to 230 m^3/kg. Uranium(IV) sorption values for London Clay measured in cement water at pH of 8 and an ionic strength of 0.018 M ranged from 4.3 to 9.0 m^3/kg (Baston et al. 1991). The reported U(IV) sorption values on calcite and illite measured at ionic strength of 0.27 M by Ticknor (1993) were significantly lower than those on bentonite measured in sea water by Baston et al. (1995) and Berry et al. (2007). The experimental redox conditions may account for the differences in the measured U(IV) sorption coefficients. Experiments with bentonite by Baston et al. (1995, 1997) and Berry et al. (2007) reported Eh values as low as -400 mV, while the tests with calcite, illite and chlorite by Ticknor (1993) only reported low O_2 conditions. Bertetti (2016) measured sorption of U(IV) on bentonite, shale and limestone in the SR-270-PW reference brine and in a dilute solution with ionic strength of 0.01 M under controlled reducing conditions. Bertetti (2016) observed similar K_d values of 0.42 - 2.2 m^3/kg for bentonite, shale and limestone in the brine ($I = 6.0$ M) and 1.5 - 20 m^3/kg in the dilute solution ($I = 0.01$ M).

Sorption values for U(IV) on London clay under reducing conditions (Baston et al. 1991) are illustrated in Figure 33A, showing no effect of pH on sorption. The range of ionic strengths in this figure is too low to say anything about sorption variation with ionic strength. The K_d values for bentonite do not appear to be affected by ionic strength (Figure 33B).

Bradbury and Baeyens (2005b, 2009b) estimated surface complexation constants for U(IV) sorbing on montmorillonite and illite (Table 59) using Linear Free Energy Relationships (LFER) determined from sorption measurements on other elements (Ni(II), Co(II), Eu(III), Sn(IV), Th(IV), Pa(V), U(VI), Am(III), and Np(V)). When these constants are incorporated into a 2-site protolysis non-electrostatic surface complexation model and used to simulate sorption coefficients for the SR-270-PW reference brine (pH 6 to 7), the resulting sorption values for bentonite and illite are 249 to 360 m^3/kg and 153 to 562 m^3/kg, respectively. The simulated sorption values for bentonite are slightly higher than those measured on bentonite in sea water. The recommended values for U(IV) sorption on bentonite considered both the measurements on bentonite in the sea water (Berry et al. 2007; Baston et al. 1995) and in the SR-270-PW reference brine (Bertetti 2016), as well as the simulated sorption values. The recommended values for U(IV) sorption on shale considered both the measurements on shale in the SR-270-PW reference brine (Bertetti 2016) and the simulated sorption values for illite, taking account of the 60% clay content of shale.

The USEPA (1998) recommended U(IV) sorption values of 0.7 to 10 m^3/kg for dolomite that were based on measured Th(IV) values. Sorption experiments with Th(IV) are not affected by difficulties in maintaining low redox, and the Th(IV) sorption data are probably a very reasonable approximation of U(IV) sorption. Bradbury et al. (2010) filled data gaps for U(IV) sorption on calcite by finding an empirical relationship between log K_d values for sorption on calcite and the ionic radii of sorbing elements. Based on this correlation the estimated sorption value for U(IV) (ionic radius 0.89 Å) on calcite is 1.9 m^3/kg, which is assumed valid over the pH range of 6 to 9.

Table 59: Uranium(IV) Surface Complexation Reactions and Constants for Montmorillonite and Illite Estimated Using LFER

U Surface Complexation Reaction	Mont. Strong Site log $^{s}K_{x-1}$	Mont. Weak Site log $^{w1}K_{x-1}$	Illite Strong Site log $^{s}K_{x-1}$
$\equiv S^sOH + U^{+4} \Leftrightarrow \equiv S^sOU^{+3} + H^+$	7.7	5.8	7.6
$\equiv S^sOH + U^{+4} + H_2O \Leftrightarrow \equiv S^sOU(OH)^{+2} + 2H^+$	7.1		7.0
$\equiv S^sOH + U^{+4} + 2H_2O \Leftrightarrow \equiv S^sOU(OH)_2^{+} + 3H^+$	3.8		4.0
$\equiv S^sOH + U^{+4} + 3H_2O \Leftrightarrow \equiv S^sOU(OH)_3^{0} + 4H^+$	-2.1		-1.5

The recommended K_d values for U(VI) and U(IV) sorption on bentonite and sedimentary rocks are summarized in Table 60. The recommended K_d values are presented as a range of values and a geometric mean. The high and low range K_d values for U(VI) were selected from individual measurements deemed to have reached equilibrium in SR-270-PW reference brine (Vilks and Miller 2014), and the geometric mean was calculated considering all of the individual measurements. The K_d values for U(IV) sorption on bentonite were based on measurements performed in sea water reported by Baston et al. (1995) and Berry et al. (2007) and in the SR-270-PW brine reported by Bertetti (2016). The modelling results using LFER were also included to give the high range for U(IV) sorption on bentonite. Sorption values for shale were based on measurements in the SR-270-PW brine reported by Bertetti (2016), and considering the results of sorption modelling on illite in SR-270 brine solution, assuming the shale contains 60% illite. The K_d values for sorption on limestone were based on Th(IV) sorption on limestone in SR-270-PW brine reported by Vilks et al. (2018), which is consistent with the measured K_d values for limestone in the SR-270-PW brine reported by Bertetti (2016).

Table 60: Recommended Sorption Coefficients for Uranium

URANIUM (VI) – Oxidizing Conditions (Eh > ~ -90 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.5**	**0.023 - 0.049**	**0.033 (1.7)**
comment	Experimental data for SR-270 reference brine (Vilks and Miller 2014)			
Shale	**6.0**	**6.3**	**0.016 - 0.044**	**0.027 (2.0)**
comment	Experimental data for Ordovician shale in SR-270 reference brine (Vilks and Miller 2014)			
Limestone	**6.0**	**6.3**	**0.008 - 0.015**	**0.011 (1.6)**
comment	Experimental data for Ordovician limestone in SR-270 reference brine (Vilks and Miller 2014)			
URANIUM (IV) – Reducing Conditions (Eh < ~ -90 mV)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.7 - 6**	**6.9 - 8**	**0.42 - 360**	**53.7 (12.2)**
comment	Based on measurements with bentonite in sea water reported by Baston et al. (1995) and Berry et al. (2007) and in the SR-270-PW brine by Bertetti (2016). The low range value is from measurements by Bertetti (2016). The high range value is from simulated U(IV) sorption value on bentonite of 249 - 360 m^3/kg using LFER.			
Shale	**6.0**	**6 - 8**	**0.42 - 337**	**16.8 (36.8)**
comment	The low range value is from U(IV) sorption on shale measured in the SR-270-PW brine by Bertetti (2016) (0.42-2.2 m^3/kg). The high range value is from simulated U(IV) sorption value on illite of 153 - 562 m^3/kg using LFER, assuming shale contains 60% illite.			
Limestone	**6.0**	**5.7 - 6.4**	**0.42 - 2.71**	**1.8 (1.5)**
comment	Based on Th(IV) measurements on limestone in SR-270-PW brine solution reported by Vilks and Miller (2018) (0.6 - 2.7 m^3/kg) and U(IV) sorption measurements on limestone in SR-270-PW brine by Bertetti (2016) (0.42 - 2.2 m^3/kg).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

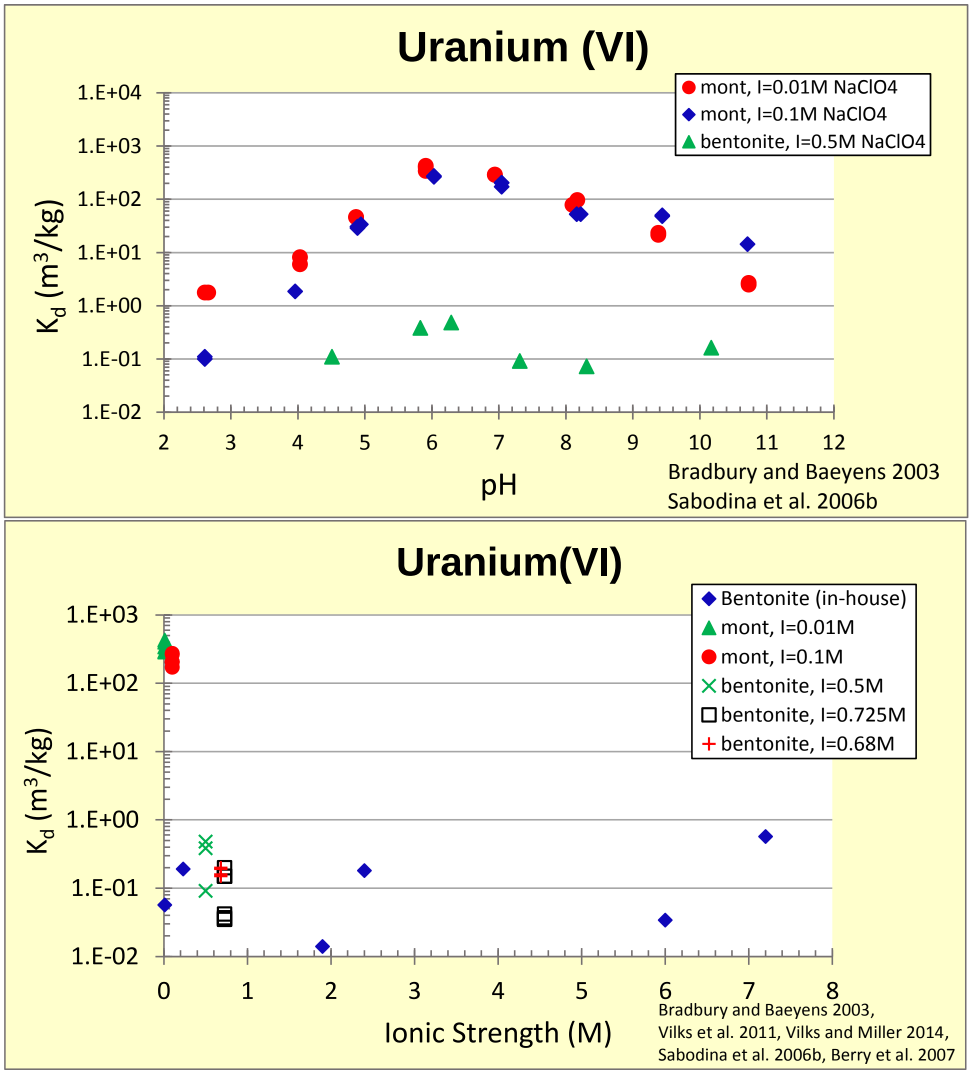


Figure 31: Uranium (VI) Sorption Coefficients on Bentonite and Montmorillonite under Oxidizing Conditions as a Function of pH and Ionic Strength (Vilks et al. 2011; Vilks and Miller 2014; Bradbury and Baeyens 2005b (Montmorillonite); Sabodina et al. 2006b; Berry et al. 2007 and Baston et al. 1995 (Bentonite in Red Square))

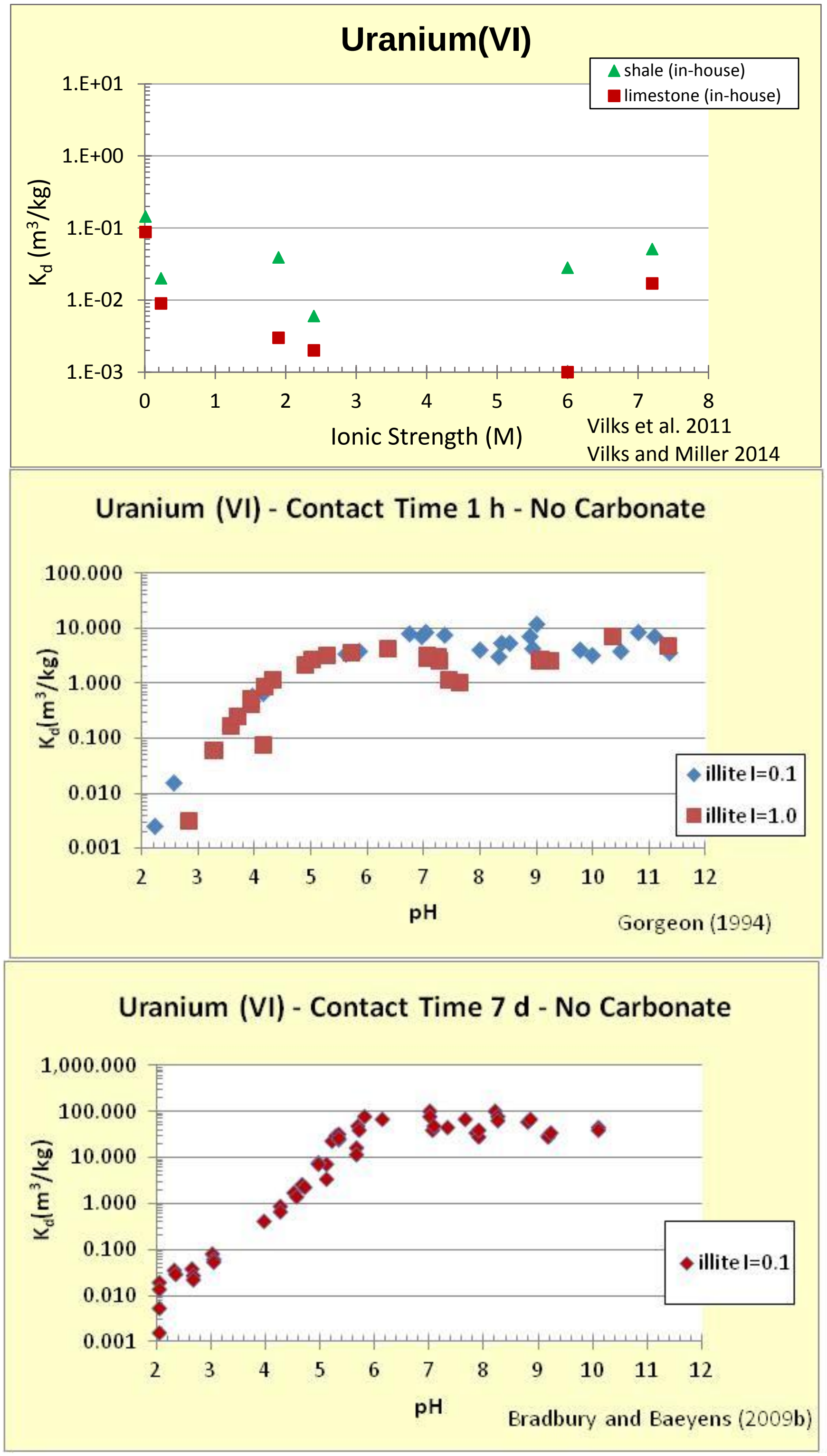


Figure 32: Uranium (VI) Sorption on Shale, Limestone and Illite under Oxidizing Conditions at Different Ionic Strength as a Function of pH (Vilks et al. 2011; Vilks and Miller 2014; Gorgeon 1994; Bradbury and Baeyens 2009b)

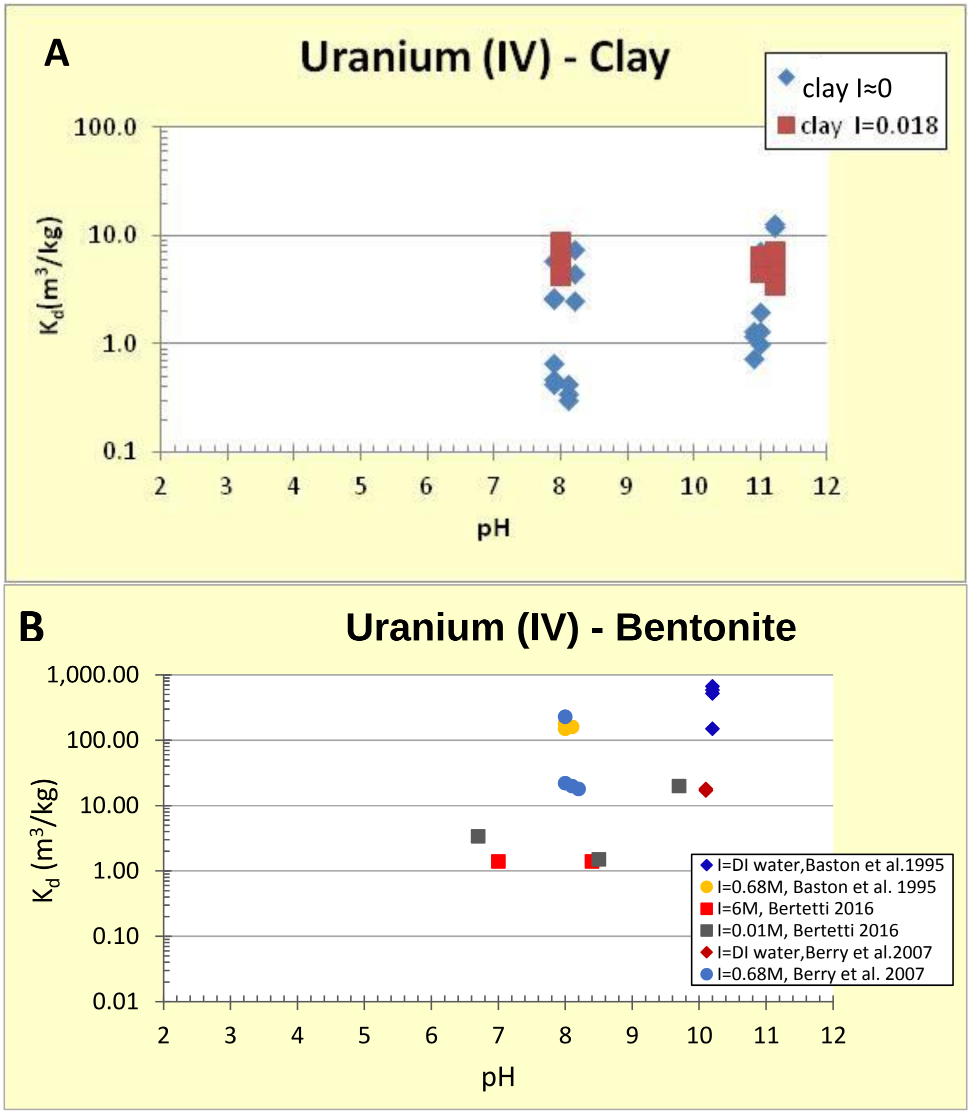


Figure 33: Uranium (IV) Sorption Coefficients on Clay (Baston et al. 1991) and Bentonite (Baston et al. 1995; Berry et al. 2007; Bertetti 2016) under Reducing Conditions

3.26 NEPTUNIUM

Although neptunium has a number of oxidation states (+3, +4, +5, +6), the +4 and +5 states are more common in groundwater. Speciation calculations with PHREEQC (SIT database) predict (see Table 3) that the +4 oxidation state of neptunium will dominate in the SR-270-PW reference water with species $Np(OH)_4$ and $Np(OH)_3^+$. The SR-20 groundwater would likely contain species of both the +4 oxidation state (e.g., $Np(OH)_4$) and the +5 oxidation state (e.g., NpO_2^+). In experiments open to the atmosphere, Np(V) will dominate. Given the tendency of neptunium to form hydrolysis and mixed carbonate-hydrolysis aqueous species, neptunium will likely sorb by surface complexation to surface oxygen sites associated with alumino-silicate minerals and carbonate.

Selected K_d values for Np(V) and Np(IV) sorption are presented in Table 61. Sorption values were classified as oxidizing and reducing based on a description of the experimental atmosphere and reported Eh values. Under oxidizing conditions, Mucciardi et al. (1979) reported neptunium sorption values on montmorillonite in NaCl solution with an ionic strength of 5.1 M and a pH of 7-8 (0.016 - 0.024 m^3/kg). Gorgeon (1994) reported sorption values on smectite in 1 M $NaClO_4$ solution at pH of 6-7 (0.025 - 0.13 m^3/kg). Kitamura and Tomura (2003) reported K_d values for smectite in 1 M NaCl solution at pH of 8-9 (0.002 - 0.021 m^3/kg). Kasar et al. (2014) reported K_d values on bentonite in 1.0 M NaCl solution at pH of 5.3 - 9.1 (0.025 - 0.037 m^3/kg). Nagasaki et al. (2016) and Nagasaki (2018) reported K_d values for bentonite in the SR-270-PW brine (I = 6.0 M) at pH of 8 (0.142-0.161 m^3/kg) and in a NaCl-$CaCl_2$ brine (I = 4.6 M) at pH of 9 (0.16-0.176 m^3/kg).

Mucciardi et al. (1979) measured Np(V) sorption on illite in 5.1 M NaCl solution at pH of 6.5-7 (0.01 - 0.139 m^3/kg). Gorgeon (1994) reported K_d values for illite in 1.0 M $NaClO_4$ solution at pH 6-7 (0.06 - 0.195 m^3/kg). Nagasaki et al. (2016) and Nagasaki (2018) measured Np(V) sorption in the SR-270-PW brine for illite at pH 7.6 (0.065 m^3/kg) and for shale at pH 7.4 (0.051 - 0.057 m^3/kg), as well as in a NaCl-$CaCl_2$ brine (I = 4.6 M) for illite at pH 7.7 to 7.8 (0.05 - 0.056 m^3/kg) and for shale at pH 7.9 to 8.0 (0.039 - 0.04 m^3/kg). USEPA (1998) proposed Np(V) sorption values for dolomite based on experiments performed at neutral pH and an ionic strength of 5 M Na-Ca-Cl solution (0.001 - 0.20 m^3/kg). Ticknor (1993) reported a K_d value of 0.065 m^3/kg for Np(V) sorption on calcite in 0.273 M Na-Ca-Cl solution at pH 8. This is within the range of values recommended by the USEPA (1998).

Under oxidizing conditions (Figure 34), K_d values for Np(V) measured on smectite (Gorgeon 1994) and clay (Stammose et al. 1992) in $NaClO_4$ solutions increased with increasing pH until pH values reached 8 to 11, displaying no plateau. Inreasing the ionic strength from 0.01 to 1 M did not have a significant impact on sorption. Figure 35 illustrates that the K_d values of Np(V) on illite, Queenston shale and bentonite in NaCl-$CaCl_2$ brine solution (I = 4.6 M) increased with pH (Nagasaki et al. 2016; Nagasaki 2018). The K_d values of Np(V) on illite and shale were independent of the ionic strength of 0.1 to 4.6 M being investigated. Sorption of Np(V) on bentonite decreased with increasing ionic strength from 0.10 to 1.0 M, and was independent of the ionic strength above 1.0 M (Figure 35).

Table 61: Selected Neptunium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Neptunium (V)									
bentonite	Na-Cl	0.13	6.4 - 7.4	23	reductive	nr	16 - 25	batch	1
bentonite	Na-Ca-HCO_3-SO_4	0.003	8.7	30	air	nr	0.07 - 0.10	batch	2
bent/qtz 10:90	Na-Ca-Cl-HCO_3	0.02	8.2	180	air	nr	0.020	batch	3
bentonite	deionized water	≈ 0	nr	10	air	nr	0.11 - 4.00	batch	19
bentonite	deionized water	≈ 0	7.8	nr	air	nr	0.078	batch	20
bentonite	NaCl	0.01	8	14	N_2	nr	0.019 - 0.038	batch	8
bentonite	NaCl	1.0	5.3	nr	air	nr	0.037	batch	25
bentonite	NaCl	1.0	9.1	nr	air	nr	0.025	batch	25
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	8 - 8.1	>3	N_2	354 356	0.142 - 0.161	batch	26,28
bentonite	Na-Ca-Cl	4.6	8.1 - 9	>3	N_2	310	0.16 - 0.176	batch	26,28
bentonite	NaCl	4.6	8.7	>3	N_2	314	0.512	batch	28
bentonite	$CaCl_2$	4.6	10.2	>3	N_2	233	0.032	batch	28
mont.	$NaClO_4$	0.01	5.5 - 8.5	7	air	nr	0.015 - 0.044	batch	9
Na-mont.	Na-NO_3	0.1	6 - 7.4	14	atm	nr	0.014 - 0.052	batch	15
mont.	NaCl	5.1	7 - 8	3 - 40	air	320 425	0.016 - 0.024	batch	5
mont.	$CaCl_2$	0.03	7.4 - 8	3 - 40	air	320 425	0.08 - 0.163	batch	5
mont.	NaCl	0.5	8.5 - 9.5	47 - 109	argon	nr	0.059 - 0.22	diffu	24
smectite	$NaClO_4$	1.0	6 - 7	0.042	air	nr	0.025 - 0.13	batch	6
smectite	NaCl	1.0	8.4 - 9.0	30	N_2	62 153	0.00004 - 0.021	batch	13
smectite	sea water	0.67	8	7 - 105	air	300	1.1 - 12.4	batch	12
smectite	Na-Ca-HCO_3-Cl-SO_4	0.02	8	60	air	nr	0.037 - 0.075	batch	10
smectite	Na-Cl-HCO_3-SO_4	0.01	8	30	air	35	1.3	batch	11
shale	Na-Ca-Cl (SR-270-PW)	6.0	7.4	>3	N_2	354	0.051 - 0.057	batch	26,28
shale	Na-Ca-Cl	4.6	7.9	>3	N_2	362 364	0.039 - 0.04	batch	26,28
shale	NaCl	4.6	8.6	>3	N_2	326	0.122	batch	28
shale	$CaCl_2$	4.6	9.2	>3	N_2	313	0.009	batch	28
clay	$NaClO_4$	1.0	6 - 7	1	air	nr	0.028 - 0.40	batch	4
argillite	Na-Ca-Mg	0.015	8.8	4 - 218	air	nr	0.017 - 1.12	batch	14
clay	OPA gw	0.2	7.6	nr	nr	350	0.025 ± 0.005	batch	16
clay	OPA gw	0.2	7.6	nr	nr	350	0.1 ± 0.01	diffu	16
illite	Na-Ca-HCO_3-SO_4	0.004	8.5	30	air	nr	0.080 - 0.090	batch	2

Table 61 continued...

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
illite	$NaHCO_3$	0.025	8 - 9	3 - 40	air	360 377	0.15 - 0.46	batch	5
illite	$CaCl_2$	0.03	6 - 7	3 - 40	air	315 445	0.013 - 0.044	batch	5
illite	NaCl	5.1	6.5 - 7	3 - 40	air	248 385	0.01 - 0.139	batch	5
illite	$NaClO_4$	1.0	6 - 7	0.042	air	nr	0.06 - 0.195	batch	6
illite	Na-Ca-Cl-SO_4	0.27	8	30	air	nr	0.0078	batch	7
illite	Na-Ca-Cl (SR-270-PW)	6.0	7.6	>3	N_2	347	0.065 ± 0.008	batch	26,28
illite	Na-Ca-Cl	4.6	7.7	>3	N_2	349	0.056 ± 0.003	batch	26,28
illite	NaCl	4.6	8.0	>3	N_2	351	0.189	batch	28
illite	$CaCl_2$	4.6	8.6	>3	N_2	339	0.0099	batch	28
calcite	sea water	0.68	8.2	7-105	atm	300	1.2 - 8.6	batch	12
calcite	Na-Ca-Cl	0.273	8	nr	atm	nr	0.065	batch	7
dolomite	Na-Ca-Cl	5	neutral	nr	nr	nr	0.001 - 0.20	batch	22
Neptunium (IV)									
bentonite	Na-Ca-SO_4	0.01-0.02	11	14	hydrazine	-800	0.044 - 0.10	batch	1
bentonite	deionized water	≈ 0	10.4	120	N_2	-440	4.5 - 5.7	batch	21
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	8.1	7	N_2+H_2	-80	130 ± 31	batch	27,28
bentonite	NaCl-$CaCl_2$-$NaClO_4$	6.0	6 - 8	7	N_2+H_2	-100	170 - 220	batch	27,28
bentonite	NaCl-$CaCl_2$	4.0	6 - 9	7	N_2+H_2	-110 -160	130 - 200	batch	27,28
smectite	NaCl	1.0	9	32	N_2/ $Na_2S_2O_4$	-558 -504	0.39 - 0.74	batch	17
smectite	NaCl	1.0	7.4 - 8.0	15	N_2	-540 -441	0.73 - 23	batch	13
bentonite	$NaClO_4$	0.01	6.3	14	N_2	nr	17	batch	23
bentonite	$NaClO_4$	0.01	6.6	14	N_2	nr	18.5	batch	23
bentonite	$NaClO_4$	0.01	7.5	14	N_2	nr	25	batch	23
bentonite	$NaClO_4$	0.01	8.2	14	N_2	nr	27	batch	23
mont.	SR-270-PW	6.0	6 - 7	-	-	-	17.8	sim	27
illite	SR-270-PW	6.0	6	-	-	-	17.9	sim	27
illite	SR-270-PW	6.0	7	-	-	-	17.2	sim	27
mudstone	distilled water	≈ 0	9	7	Ar	-311	1.96 - 2.27	batch	18
shale	Na-Ca-Cl (SR-270-PW)	6.0	7.6	7	N_2+H_2	-80	98 ± 9.3	batch	27,28
shale	NaCl-$CaCl_2$-$NaClO_4$	6.0	6 - 8	7	N_2+H_2	-100 -160	130 - 180	batch	27,28
shale	NaCl-$CaCl_2$	4.0	6 - 8	7	N_2+H_2	-110 -160	120 - 160	batch	27,28

Table 61 continued...

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
illite	Na-Ca-Cl (SR-270-PW)	6.0	7.8	7	N_2+H_2	-80	92 ± 15	batch	27,28
illite	$NaCl-CaCl_2-NaClO_4$	6.0	6 - 8	7	N_2+H_2	-110 -160	120 - 160	batch	27,28
illite	$NaCl-CaCl_2$	4.0	6 - 8	7	N_2+H_2	-110 -160	110 - 160	batch	27,28
mudstone	distilled water	≈ 0	9.3	7	Ar	-311	1.96 - 2.27	batch	18
mont.	Na-Ca-Cl (SR-270-PW)	6.0	6 - 7	-	-	-	17.8	sim	29
illite	Na-Ca-Cl (SR-270-PW)	6.0	6	-	-	-	17.9	sim	29
illite	Na-Ca-Cl (SR-270-PW)	6.0	7	-	-	-	17.2	sim	29

1. Tanaka et al. (1998)
2. Torstenfelt et al. (1988)
3. Allard et al. (1979)
4. Stammose et al. (1992)
5. Mucciardi et al. (1979)
6. Gorgeon (1994)
7. Ticknor (1993)
8. Ohe et al. (1993)
9. Sakamoto (1990)
10. Salter et al. (1981)
11. Ames et al. (1981)
12. Higgo et al. (1983)
13. Kitamura and Tomura (2003)
14. Barney and Brown (1979)
15. Turner et al. (1998)
16. Wu et al. (2009)
17. Ashida et al. (1999)
18. Tachi et al. (1999c)
19. Morgan et al. (1988)
20. Meijer et al. (1990)
21. Baston et al. (1997)
22. USEPA (1998)
23. Nagasaki et al. (1999)
24. Tachi et al. (2010)
25. Kasar et al. (2014)
26. Nagasaki et al. (2016)
27. Nagasaki et al. (2017)
28. Nagasaki (2018)
29. This work

nr: not recorded
Na-mont: Na-montmorillonite
mont: montmorillonite
diffu: diffusion test
sim: simulation

PHREEQC simulations indicate that at Eh values below 0 mV, neptunium chemistry is dominated by Np(IV) species. Experiments performed under reducing conditions were identified using reported Eh values that were negative. Ashida et al. (1999) reported sorption K_d values of Np(IV) on smectite in 1.0 M NaCl solution as 0.39 - 0.74 m^3/kg at pH 9. Kitamura and Tomura (2003) reported Np(IV) sorption on smectite in 1.0 M NaCl solution including 0.06 M to 0.8 M HCO_3^- as 0.73 - 23 m^3/kg at pH 7.4 to 8.0. Sorption values of 1.96 - 2.27 m^3/kg were obtained by Tachi et al. (1999c) for mudstone in very dilute water (with the ionic strength close to 0 M) at a pH of 9.3. Sorption K_d values of Np(IV) on bentonite in 0.01 M $NaClO_4$ solution at pH 6.3 to 8.2 were 17 - 27 m^3/kg, reported by Nagasaki et al. (1999). Np(IV) sorption on bentonite, Queenston shale and illite (Silver Hill) was measured in SR-270-PW brine, $NaCl-CaCl_2-NaClO_4$ brine (I = 6.0 M) and $NaCl-CaCl_2$ brines (I = 0.1-4 M) (Nagasaki 2018; Nagasaki et al. 2017). The Np(IV) sorption values on bentonite, shale and illite in the SR-270-PW reference brine were 130 ± 31 m^3/kg, 98 ± 9.3 m^3/kg, and 92 ± 15 m^3/kg, respectively, and 170 - 220 m^3/kg, 130 - 180 m^3/kg and 120 - 160 m^3/kg, respectively, in the $NaCl-CaCl_2-NaClO_4$ brine (I = 6.0 M).

Figure 36 illustrates K_d values for Np(IV) sorption on smectite under reducing conditions, measured in NaCl solution with ionic strength of 1.0 M by Kitamura and Tomura (2003) and Ashida et al. (1999). Sorption decreased with increasing pH values (7.5 to 10), and contact time of 24 days was required to achieve equilibrium. Figure 37 illustrates the ionic strength dependence of the K_d values of Np(IV) sorption on bentonite, Queenston shale and illite (Silver Hill) in $NaCl-CaCl_2$ solutions (I = 0.1 - 4 M) and $NaCl-CaCl_2-NaClO_4$ solution (I = 6 M) reported by Nagasaki (2018) and Nagasaki et al. (2017). Sorption of Np(IV) on bentonite, shale and illite decreased from ionic strength of 0.1 M to 0.5 M and was independent of the ionic strength in the range of 0.5 - 6 M. Figure 38 illustrates the pH dependences of K_d values of Np(IV) sorption on bentonite, shale and illite in NaCl-$CaCl_2$ solution (I = 4 M) and in NaCl- $CaCl_2$-$NaClO_4$ solution (I = 6.0 M) (Nagasaki 2018 and Nagasaki et al. 2017). Np(IV) sorption on bentonite, shale and illite in ionic strength of 4 M and 6 M was independent of pH between 5-10 (except that Np(IV) sorption on shale in I = 6.0 M brine at pH = 9 - 10 was slightly smaller than those at pH = 5-8).

Bradbury and Baeyens (2005b, 2009b) estimated surface complexation constants for Np(IV) sorbing on montmorillonite and illite (Table 62) using Linear Free Energy Relationships (LFER) determined from sorption measurements on other elements (Ni(II), Co(II), Eu(III), Sn(IV), Th(IV), Pa(V), U(VI), Am(III), Np(V)). When these constants are incorporated into a 2-site protolysis non-electrostatic surface complexation model and used to simulate sorption coefficients for the SR-270-PW reference brine (pH 6 to 7), the resulting values for montmorillonite and illite are 17.8 m^3/kg and 17.2 to 17.9 m^3/kg, respectively. It was assumed that the sorption constants determined in 0.1 to 1 mol/L $NaClO_4$ solutions were applicable to the SR-270-PW reference water. The simulated sorption values for Np(IV) are a factor 13 to 16 lower than simulated values for Th(IV), which were derived from actual measured values in $NaClO_4$ solutions.

Table 62: Neptunium(IV) Surface Complexation Reactions and Surface Complexation Constants for Montmorillonite and Illite Estimated Using LFER

Np Surface Complexation Reaction	Mont. Strong Site log $^sK_{x-1}$	Mont. Weak Site log $^{w1}K_{x-1}$	Illite Strong Site log $^sK_{x-1}$
$\equiv S^sOH + Np^{+4} \Leftrightarrow \equiv S^sONp^{+3} + H^+$	8.5	6.7	8.3
$\equiv S^sOH + Np^{+4} + H_2O \Leftrightarrow \equiv S^sONp(OH)^{+2} + 2H^+$	8.3		8.1
$\equiv S^sOH + Np^{+4} + 2H_2O \Leftrightarrow \equiv S^sONp(OH)_2^+ + 3H^+$	5.5		5.6
$\equiv S^sOH + Np^{+4} + 3H_2O \Leftrightarrow \equiv S^sONp(OH)_3^0 + 4H^+$	0.1		0.5

USEPA (1998) recommended sorption values for Np(IV) on dolomite that ranged from 0.7 to 10 m^3/kg. These values were based on using Th(IV) as a chemical analog. Bradbury et al. (2010) filled data gaps for sorption on calcite by finding an empirical relationship between log K_d values for sorption on calcite and the ionic radii of sorbing elements. Based on this correlation the estimated sorption value for Np(IV) (ionic radius 0.87 Å) on calcite is 1.1 m^3/kg, which is assumed valid over the pH range of 6 to 9. This is within the recommended value from the USEPA (1998).

Recommended neptunium K_d values for bentonite, shale and limestone are summarized in Table 63. As with uranium, the redox potential is an important factor in selecting sorption values for neptunium. In the reference groundwater, with an Eh of -200 mV, Np(IV) clearly will dominate and the higher sorption values for Np(IV) can be used. However, if there is reason to suspect that the geochemical condition will become more oxidizing, with Eh values above 110 mV, one should be conservative and select the sorption values for Np(V) even for repository materials.

Recommended K_d values for Np(V) sorbing on bentonite were based on measured Np sorption on bentonite, montmorillonite and smectite in NaCl, Na-Ca-Cl and $NaClO_4$ brine solutions, reported by Mucciardi et al. (1979) (0.016-0.024 m^3/kg at I = 5.1 M), Gorgeon (1994) (0.025-0.13 m^3/kg at I = 1.0 M), Kitamura and Tomura (2003) (0.002-0.021 m^3/kg at I = 1.0 M), Kasar et al. (2014) (0.025-0.037 m^3/kg at I = 1.0 M) and Nagasaki et al. (2016) (0.142-0.176 m^3/kg at I = 4.6-6.0 M). Np(V) sorption on shale was based on Np(V) sorption measured on shale in Na-Ca-Cl brines by Nagasaki et al. (2016) (0.039-0.057 m^3/kg at I = 4.6-6.0 M), as well as on illite reported by Mucciardi et al. (1979) (0.01-0.139 m^3/kg at I = 5.1 M), Gorgeon (1994) (0.06-0.195 m^3/kg at I = 1.0 M), and Nagasaki et al. (2016) (0.05-0.065 m^3/kg at I = 4.6-6.0 M), assuming 60% illite in shale. Sorption on limestone used values recommended for dolomite by the USEPA (1998). The Np(IV) K_d values for bentonite were based on measured Np(IV) sorption on bentonite in the SR-270-PW reference brine (130±31 m^3/kg by Nagasaki 2018) and the sorption simulations on montmorillonite in SR-270-PW brine. The Np(IV) K_d values for shale were based on measured Np(IV) sorption on shale in the SR-270-PW reference brine (98±9.3 m^3/kg) and simulated sorption data for illite (17.9 m^3/kg at pH = 6 and 17.2 m^3/kg at pH = 7 in SR-270-PW brine), assuming shale contains 60% illite. Given the lack of Np(IV) sorption measurements for limestones, the recommended K_d values for limestone are based on using Th(IV) as a chemical analog. Th(IV) sorption on limestone in SR-270-PW brine was reported by Vilks and Miller (2018).

Table 63: Recommended Sorption Coefficients for Neptunium

NEPTUNIUM (V) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**1.0 - 6.0**	**5.3 - 9**	**0.00004 - 0.176**	**0.065 (3)**
comment	Based on measured Np sorption on bentonite, montmorillonite and smectite in $CaCl_2$, $NaClO_4$, Na-Ca-Cl and NaCl brine solutions, reported by Mucciardi et al. (1979), Gorgeon (1994), Kitamura and Tomura (2003), Kasar et al.(2014) and Nagasaki (2018).			
Shale	**1.0 - 6.0**	**6.1 - 8.0**	**0.006 - 0.12**	**0.042 (1.3)**
comment	Based on sorption on shale (0.039-0.057 m^3/kg) measured in Na-Ca-Cl brine solutions (I = 4.6 - 6.0 M) by Nagasaki (2018). Also considered Np sorption on illite (0.01 - 0.139 m^3/kg) by Mucciardi et al. (1979) at I = 5.1 M, 0.05 - 0.065 m^3/kg by Nagasaki et al. (2016) at I = 4.6 - 6.0 M and 0.06 - 0.195 m^3/kg by Gorgeon (1994) at I = 1.0 M, assuming 60% illite in shale.			
Limestone	**5**	**7.0**	**0.001 - 0.2**	**0.014 (42)**
comment	Based on values recommended for dolomite by USEPA (1998).			
NEPTUNIUM (IV) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6 - 8.5**	**17.8 - 130**	**48.1 (4.1)**
comment	The low range value is based on simulated sorption data for montmorillonite in SR-270-PW brine. The high range value is based on measurements on bentonite in SR-270-PW by Nagasaki (2018).			
Shale	**6.0**	**6 - 7**	**11 - 98**	**32.8 (4.6)**
comment	The low range value is based on simulated sorption data for illite (SR-270-PW brine) with values of 17.2 m^3/kg (pH = 7) and 17.9 m^3/kg (pH = 6), assuming shale contains 60% illite. The high range value is based on measurements on shale in SR-270-PW by Nagasaki (2018).			
Limestone	**6.0**	**5.7 - 7.1**	**0.6 - 2.71**	**2.1 (1.9)**
comment	Based on Th(IV) measurements in SR-270-PW reference brine solution reported by Vilks and Miller (2018).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

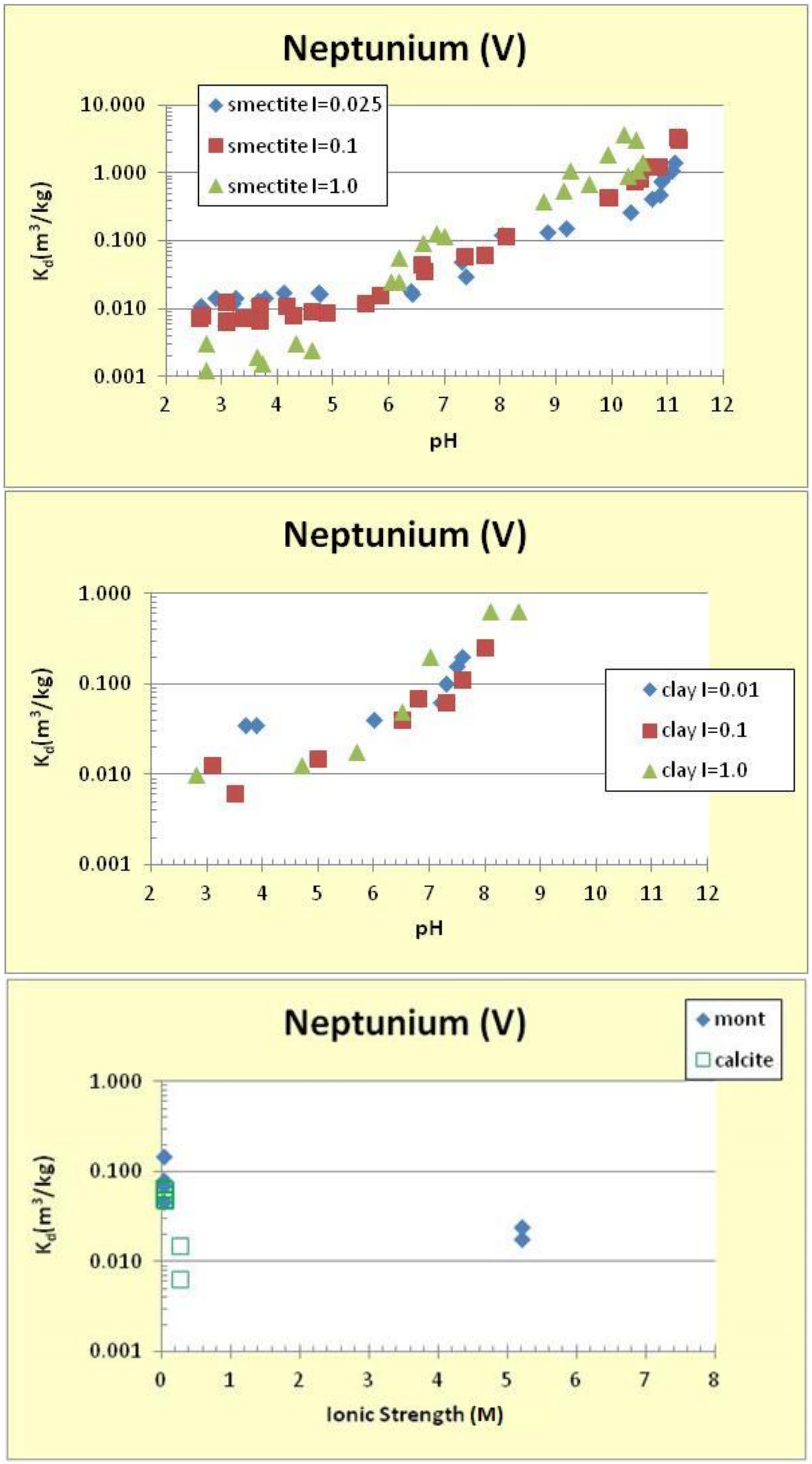


Figure 34: Neptunium Sorption Coefficients on Smectite, Clay, Montmorillonite and Calcite under Oxidizing Conditions as a Function of pH and Ionic Strength (Gorgeon 1994; Stammose et al. 1992; Mucciardi et al. 1979; Ticknor 1993)

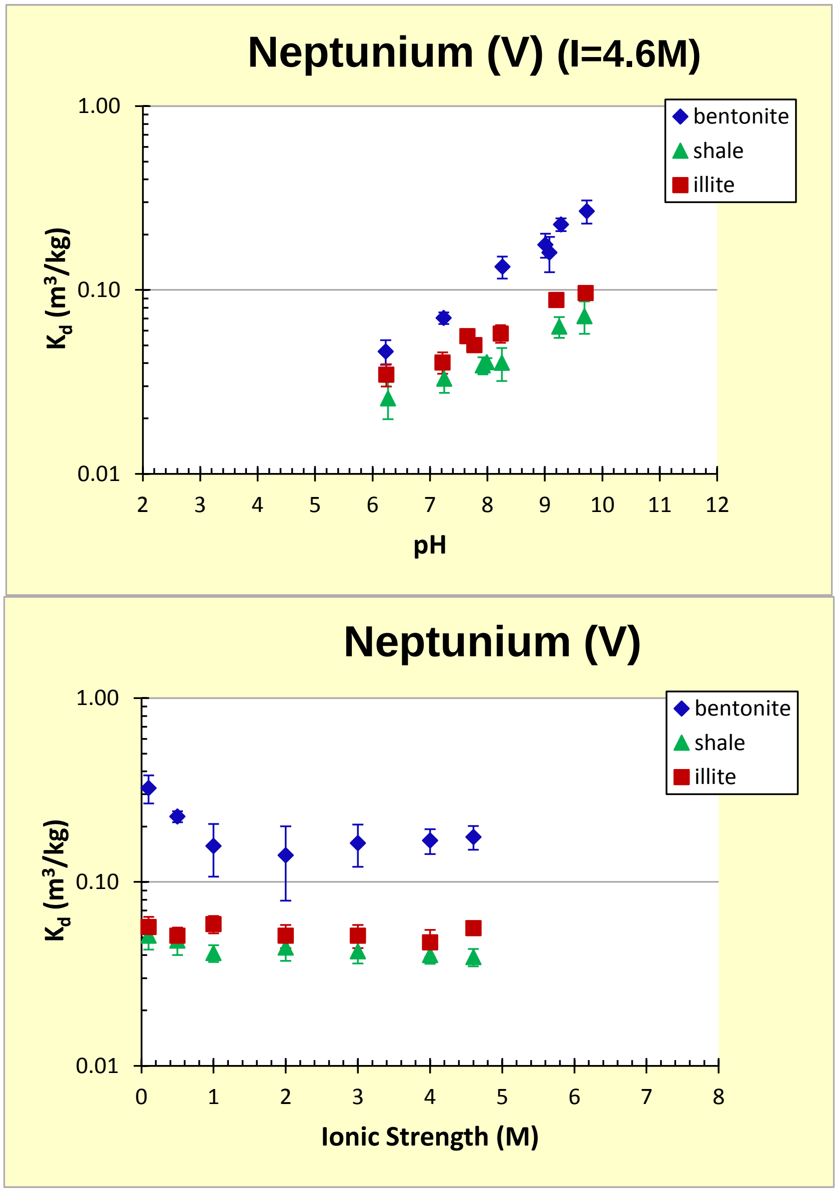


Figure 35: Np(V) Sorption on Illite, Shale and Bentonite in NaCl-$CaCl_2$ Brines under Oxidizing Conditions as a Function of pH and Ionic Strength (Nagasaki 2018)

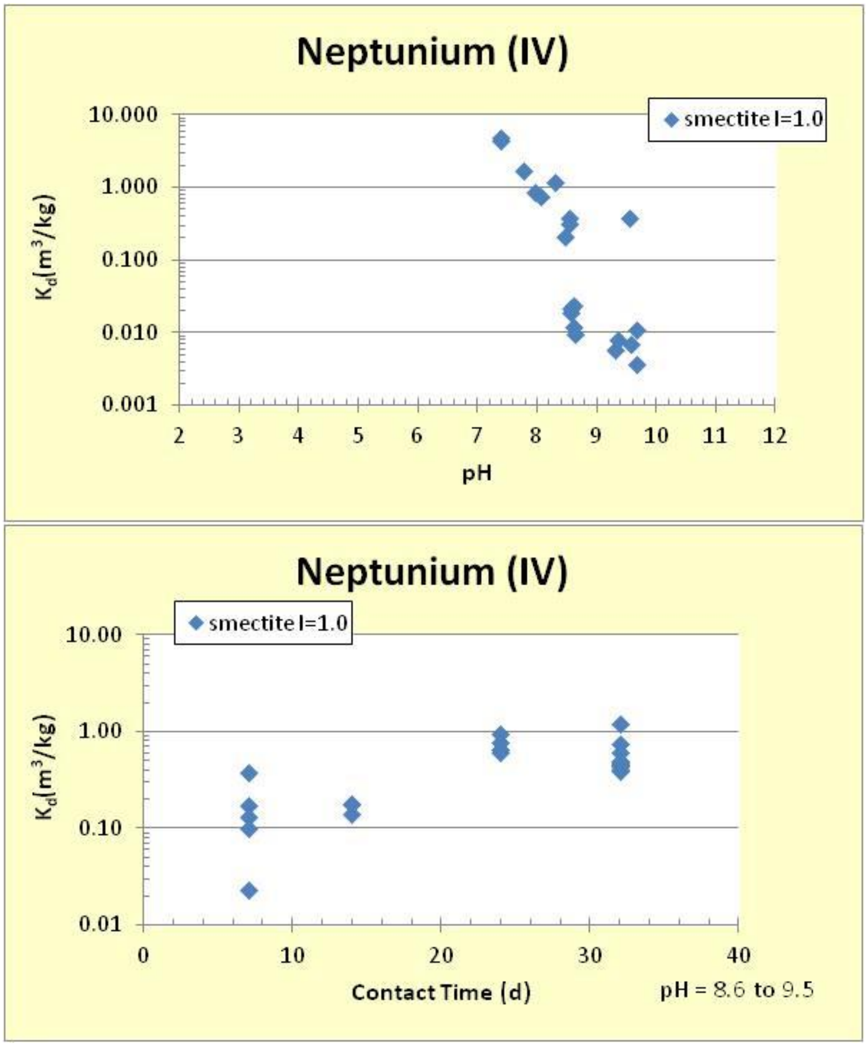


Figure 36: Neptunium Sorption Coefficients on Smectite in NaCl Solutions (with Ionic Strength of 1.0 M) under Reducing Conditions (Ashida et al. 1999; Kitamura and Tomura 2003)

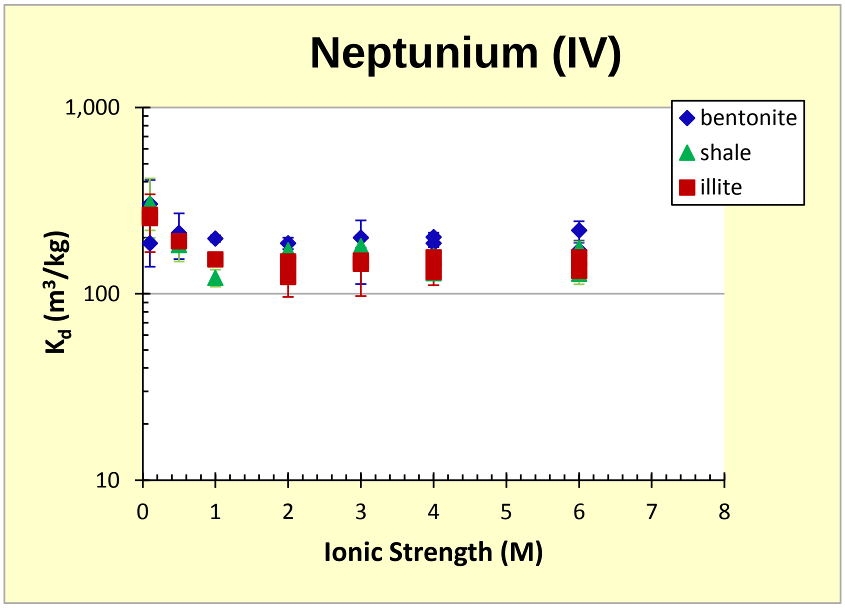


Figure 37: Np(IV) Sorption Coefficients on Bentonite, Shale and Illite as a Function of Ionic Strength in NaCl-CaCl$_2$ Solutions (I = 0.1 - 4 M) and in NaCl-CaCl$_2$-NaClO$_4$ Solution (I = 6 M) under Reducing Conditions (Nagasaki 2018)

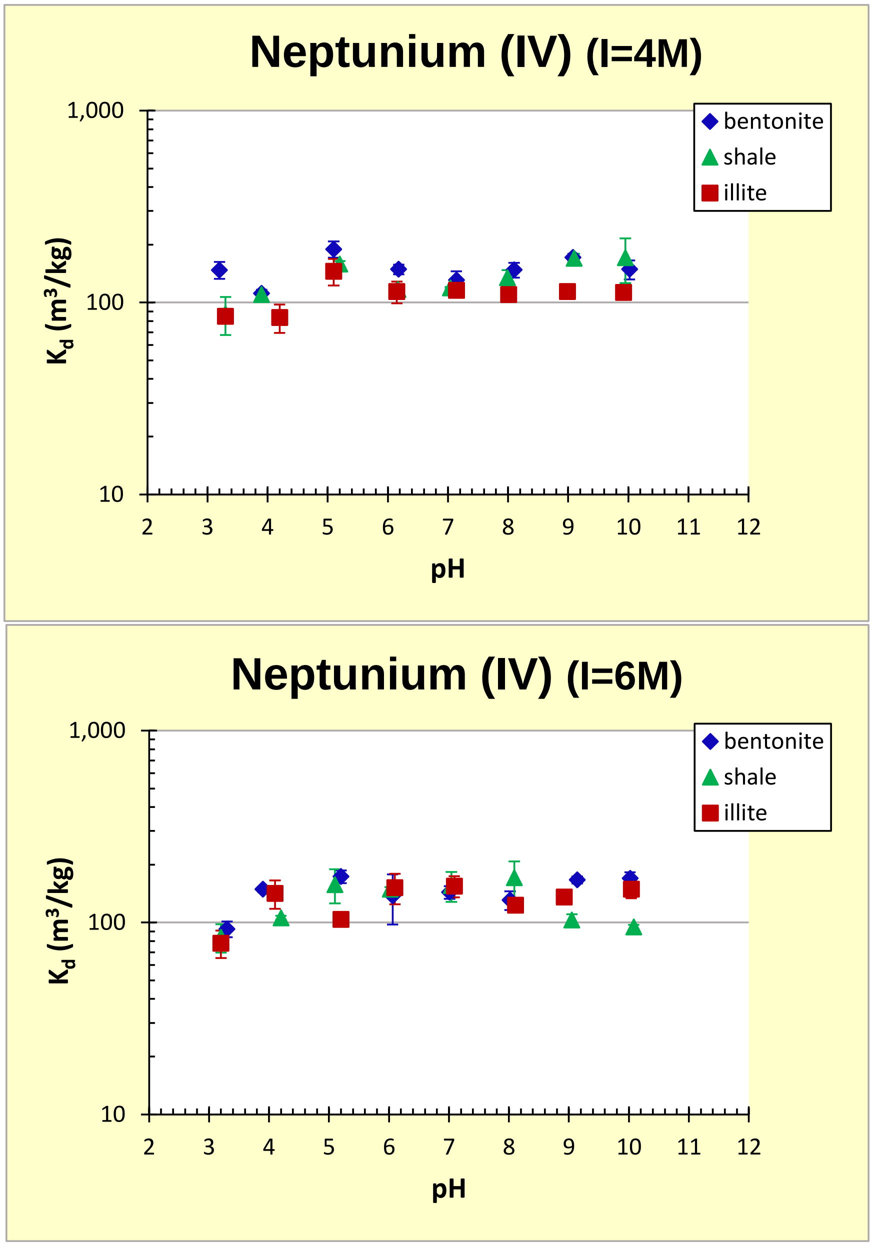


Figure 38: Np(IV) Sorption Coefficients on Bentonite, Shale and Illite in NaCl-$CaCl_2$ Solution (I = 4 M) and NaCl-$CaCl_2$-$NaClO_4$ Solution (I = 6 M) under Reducing Conditions as a Function of pH (Nagasaki 2018; Nagasaki et al. 2017)

3.27 PLUTONIUM

Plutonium has multiple oxidation states (+3, +4, +5, +6) and a complex chemistry. Speciation calculations with PHREEQC (SIT database) predict that under reducing conditions the +3 oxidation state will dominate, while under oxidizing conditions the +4 and +5 states will dominate (see Table 3). The dominant aqueous plutonium species in the SR-270-PW reference groundwater are Pu^{+3} and $Pu(OH)^{+2}$, while a more oxidizing water, such as SR-20, would contain both Pu(III) species (e.g., Pu^{+3}, $Pu(SO_4)^{+}$) and Pu(IV) species (e.g., $Pu(CO_3)_2(OH)_2^{-2}$ and $Pu(OH)_4$). In reducing dilute waters, sorption could include cation exchange with the Pu^{+3} cation. However, in brine solutions, such as SR-270-PW, cation exchange will likely be suppressed by the salt, leaving sorption to occur by surface complexation to oxides, aluminosilicates, carbonate and sulphate minerals. The plutonium sorption data for use in the reference groundwaters under reducing conditions should focus on measurements made with plutonium in the +3 oxidation state. In the absence of reasonable Pu(III) data, one could consider using sorption results for Am(III) and Eu(III) as chemical analogs, although the aqueous speciation of these elements is different from that of Pu(III).

Selected plutonium K_d values are presented in Table 64. Under oxidizing conditions, sorption values of interest for bentonite include 0.44 - 0.51 m^3/kg (measured in I = 6.96 M brine at pH = 6.6) and 1.1 - 3.6 m^3/kg (measured in I = 5.09 M brine at pH = 7.2) reported by Nowak (1980); and 0.52 - 4.04 m^3/kg (measured on montmorillonite in I = 5.1 M NaCl brine at pH = 7 - 8) reported by Mucciardi et al. (1979). Sorption values of interest for illite include 2.2 - 4.6 m^3/kg reported by Mucciardi et al. (1979) (measured in I = 5.1 M NaCl brine at pH = 6 - 7) and 5.4 m^3/kg by Ticknor (1993) (measured in I = 0.247 M solution at pH = 8). The sorption values for illite were selected to represent shale (assuming shale contains 60% illite). Sorption data on sediment in sea water, which ranged from 0.13 to 107 m^3/kg, as measured by Higgo et al. (1987), were not considered because of the very large spread in K_d values and because the K_d values appear excessively high in relation to other reported values. Sorption values for limestone in brine include 0.45 m^3/kg (measured at I = 5.09 M and pH = 6.5) reported by MaClean e al. (1978), and 0.069 - 3.7 m^3/kg (measured at I = 5.1 M and pH = 6.5 to 7.5) by Reylea and Serne (1979). Sorption on calcite at ionic strength of 0.247 M and pH of 8 - 9.5 solution produced a K_d value of 0.02 m^3/kg (Ticknor 1993). The lower sorption on calcite compared to limestone suggests that the limestone may have contained another minerals, such as clay, leading to an increase in its plutonium sorption. The USEPA (1998) reported Pu(V) sorption results for dolomite, which ranged from 0.02 to 0.5 m^3/kg for a brine with an ionic strength of 5 M and neutral pH. The K_d values selected to represent Pu sorption on limestone in saline conditions were based on the measurements reported by MaClean et al. (1978) and Reylea and Serne (1979).

Figure 39 illustrates the variation of Pu(IV,V) K_d values with ionic strength. The K_d values for montmorillonite determined by Mucciardi et al. (1979) did not display a correlation with ionic strength, as shown in Figure 39. Considering sorption on chlorite and calcite measured by Ticknor (1993), and sorption on limestone determined by Reylea and Serne (1979), it appears that Pu(IV,V) sorption is independent of ionic strength (Figure 39). The effect of pH on sorption is shown in Figure 40. The K_d values measured on bentonite (Shibutani et al. 1994), illite (Torstenfelt 1988), limestone (Relyea and Serne 1979) and clay (Berry et al. 1991) do not display any correlation with pH.

Table 64: Selected Plutonium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
Plutonium (IV,V)									
bent/quartz 10:90	Na-Ca-Cl-HCO_3	0.02	8.2	180	Air	nr	0.16	batch	1
bentonite	Na-Ca-HCO_3-SO_4	0.0009	5 - 9	30	Air	nr	0.79 - 31	batch	2
bentonite	Na-K-Mg-Cl-SO_4	6.96	6.6	7	Air	nr	0.44 - 0.51	batch	5
bentonite	Na-Ca-Cl-SO_4	5.09	7.2	7	Air	nr	1.1 - 3.6	batch	5
benonite	Na-Ca-HCO_3-SO_4	0.0035	8.9	30	Air	nr	0.17 - 0.19	batch	6
mont	NaCl	5.1	7 - 8	3 - 30	Air	200 277	0.52 - 4.04	batch	3
mont	$NaHCO_3$	0.03	9	3 - 30	Air	295 330	1.5 - 8.0	batch	3
mont	$CaCl_2$	0.03	7.5 - 7.7	3-30	Air	348 369	1.7 - 5.3	batch	3
mont	NaCl	0.03	7.6 - 8.8	3 - 30	Air	328 383	0.67 - 6.76	batch	3
smectite	Na-Cl-HCO_3-SO_4	0.01	8	60	Air	nr	1.1 - 14	batch	8
smectite	Na-Ca-HCO_3-Cl	0.002	8 - 9	60	Air	nr	2.6 - 3.3	batch	4
clay	Ca-K-Na-OH	0.018	8 - 9	100	N_2	nr	0.50 - 10	batch	7
illite	NaCl	5.1	6 - 7	3 - 30	Air	290 380	2.2 - 4.6	batch	3
illite	Na-Ca-Cl-SO_4	0.247	8	30	air	nr	5.4	batch	9
illite	Na-Ca-HCO_3-SO_4	0.0035	7.3	30	air	nr	0.17 - 0.18	batch	6
chlorite	Na-Ca-Cl-SO_4	0.247	8	30	air	nr	0.57	batch	9
chlorite	Na-Ca-Cl	0.003	8.0 - 9.5	30	air	nr	0.15 - 0.35	batch	9
chlorite	Na-Ca-Cl	0.025	8.0 - 9.5	30	air	nr	0.28 - 0.40	batch	9
chlorite	Na-Ca-Cl	0.247	8.0 - 9.5	30	air	nr	0.15 - 0.57	batch	9
argillite	Na-Ca-K-Cl-HCO_3	0.1	7.2 - 7.8	7	anoxic	240 270	27 - 46	batch	18
sediment	sea water	0.68	8.2	24 - 128	air	nr	0.13 - 107	batch	10
dolomite	deionized water	≈ 0	8.6	3 - 9	air	nr	0.065 - 0.15	batch	11
dolomite	groundwater (no compos.)	≈ 0	7.7	7	air	nr	0.62	batch	12
dolomite	Na-Ca-Cl	5	neutral	nr	nr	nr	0.02 - 0.50	batch	17
limestone	Na-Ca-Cl-SO_4	5.09	6.5	7	air	nr	0.45	batch	12
limestone	Ca-HCO_3-SO_4	0.0045	8.2	7	air	nr	0.77	batch	12
limestone	Na-Ca-Cl-SO_4	5.1	6.5 - 7.5	nr	nr	nr	0.069 - 3.7	batch	13
calcite	Na-Ca-Cl-SO_4	0.247	8	30	air	nr	0.02	batch	9

Table 64 continued...

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
calcite	Na-Ca-Cl	0.003	8.0 - 9.5	30	air	nr	0.39 - 0.48	batch	9
calcite	Na-Ca-Cl	0.025	8.0 - 9.5	30	air	nr	0.09 - 0.20	batch	9
calcite	Na-Ca-Cl	0.247	8.0 - 9.5	30	air	nr	0.019 - 0.02	batch	9
Plutonium (III)									
bentonite	Na-Ca-Cl (SR-270-PW)	6.0	7 - 8	33-37	N_2+H_2/ hydrazine	-35 -230	1.5 - 10	batch	20
bentonite	Na-Ca-Cl	0.01	6 - 8.7	17-37	N_2+H_2/ hydrazine	-340 -380	8 - 78	batch	20
bentonite	Na-HCO_3-SO_4	0.0029	9.4	120	N_2/ $Na_2S_2O_4$	-410	11 - 87	batch	14
bentonite	$NaClO_4$	0.10	7.4 - 8.1	104	$Na_2S_2O_4$	-300	28 - 405	batch	15
bentonite	$NaClO_4$	0.10	5.4	104	$Na_2S_2O_4$	-105	0.0879	batch	15
bentonite	$NaClO_4$	0.01	5.7 - 8	104	$Na_2S_2O_4$	-309 -101	1.56 - 97	batch	15
shale	Na-Ca-Cl (SR-270-PW)	6.0	7 - 8	17-37	N_2+H_2/ hydrazine	-35 -230	1.5-4.0	batch	20
shale	Na-Ca-Cl	0.01	6 - 8.7	17-37	N_2+H_2/ hydrazine	-340 -380	8	batch	20
mudstone	deionized water	≈ 0	6.4	nr	N_2/ 2%CO_2	-360	0.58 - 47	batch	16
mudstone	deionized water	≈ 0	7.2	nr	N_2/ 0.4%CO_2	-370	1.6 - 40	batch	16
mudstone	sea water	0.68	7.5	nr	N_2/ 2%CO_2	-400 -390	6.6 - 1200	batch	16
limestone	Na-Ca-Cl (SR-270-PW)	6.0	7 - 8	33-37	N_2+H_2/ hydrazine	-35 -230	1.5 - 4.0	batch	20
limestone	Na-Ca-Cl	0.01	6 - 8.7	17-37	N_2+H_2/ hydrazine	-340 -380	16	batch	20
mont.	Na-Ca-Cl (SR-270-PW)	6.0	6	-	-	-	1.02	sim	19
mont.	Na-Ca-Cl (SR-270-PW)	6.0	7	-	-	-	12.2	sim	19
illite	Na-Ca-Cl (SR-270-PW)	6.0	6	-	-	-	2.28	sim	19
illite	Na-Ca-Cl (SR-270-PW)	6.0	7	-	-	-	9.03	sim	19

1. Allard et al. (1979)
2. Shibutani et al. (1994)
3. Mucciardi et al. (1979)
4. Salter et al. (1981)
5. Nowak (1980)
6. Torstenfelt et al. (1988)
7. Berry et al. (1991)

nr: not recorded

8. Ames et al. (1981)
9. Ticknor (1993)
10. Higgo et al. (1987)
11. Francis and Bondietti (1979)
12. MaClean et al. (1978)
13. Reylea and Serne (1979)
14. Berry et al. (2007)

sim: simulated

15. Shibutani et al. (1998)
16. Baston et al. (2000)
17. USEPA (1998)
18. Latrille et al. (2006)
19. this study
20. Bertetti (2016)

mont: montmorillonite

Selected values of Pu(III) sorption are also summarized in Table 64. It should be noted that a number of studies have claimed that Pu(III) was present, but since sorption tests were not performed in a reducing atmosphere, it was assumed that the Pu(III) was likely oxidized to Pu (IV, V). Bertetti (2016) measured Pu(III) sorption on bentonite, shale and limestone in SR-270-PW brine (I = 6.0 M) and in a Na-Ca-Cl type dilute solution (I = 0.01 M) under controlled reducing conditions. The measured K_d values of Pu(III) sorption on bentonite, shale and limestone in SR-270-PW brine were 1.5 - 10, 1.5 - 4.0 and 1.5 - 4.0 m^3/kg, respectively. Sorption in brine (I = 6.0 M) was lower than in dilute solution (I = 0.01 M). Sorption on bentonite reported by Shibutani et al. (1998) for $NaClO_4$ solutions increased with pH, reaching a maximum around pH 8 and then decreasing at higher pH values (Figure 41). Sorption on bentonite in 0.1 M and 0.01 M ionic strength solutions was similar. Under reducing conditions, plutonium sorption values for bentonite in 0.1 M ionic strength $NaClO_4$ solution at pH of 7.4 - 8 are 28 to 405 m^3/kg (Shibutani et al. 1998). Pu(III) sorption on bentonite in 6.0 M ionic strength brine is lower than in 0.1 M and 0.01 M ionic strength dilute solutions (Figure 41). Plutonium sorption on mudstone did not decrease with an increase in ionic strength from 0 to 0.68 M, as reported by Baston et al. (2000) (Figure 41). The K_d values for mudstone in sea water reported by Baston et al. (2000) ranged from 6.6 to 1200 m^3/kg. The variability in these values can be attributed to the method of phase separation used to remove solids and colloids from sample solutions.

Bradbury et al. (2010) filled data gaps for sorption on calcite by finding an empirical relationship between log K_d values for sorption on calcite and the ionic radii of sorbing elements. Based on this correlation, the estimated sorption value for Pu(III) (ionic radius 1.00 Å) on calcite was 40 m^3/kg, which is assumed valid over the pH range of 6 to 9.

Sorption models for Pu(III) on montmorillonite and illite were constructed on the assumption that the important Pu(III) species in solution (Bradbury and Baeyens 2005) are $PuOH^{+2}$ ($\log^{OH}K_1 = -7.3$), $Pu(OH)_2^+$ ($\log^{OH}K_2 = -15.2$) and $Pu(OH)_3^0$ ($\log^{OH}K_3 = -25.7$). The surface Pu(III) species based on these hydrolysis species are summarized in Table 65. The surface complexation constants for these reactions were estimated using the Linear Free Energy Relationships (LFER) developed by Bradbury and Baeyens (2005b, 2009b).

The surface complexation constants given in Table 65 were incorporated into a 2-site protolysis non-electrostatic surface complexation model and used to simulate sorption coefficients for the SR-270-PW reference brine. The cation exchange component of the model used to account for the sorption of Pu^{+3} in solution was approximated by assuming that Pu^{+3} would be sorbed to the same degree as Am^{+3}. The resulting exchange coefficients, given as log K_c values, were 2.6 for montmorillonite and 1.9 for illite. Cation exchange for Pu^{+3} in the pH range of interest is actually negligible since most Pu is present as a hydrolysis species.

The simulated sorption values for SR-270-PW brine solution at pH values of 6 and 7 were 1.02 and 12.2 m^3/kg for montmorillonite and 2.28 to 9.03 m^3/kg for illite. When extended over a broader pH range (Figure 42), the simulated K_d values for bentonite followed a similar pattern with pH, as displayed for bentonite in Figure 41. The simulated K_d values for montmorillonite are consistent with those measured on bentonite in SR-270-PW brine solution (1.5 - 10 m^3/kg). If the simulated K_d values for illite were used to approximate sorption on shale, assuming a 60% illite content, the resulting K_d values would range from 1.37 to 5.42 m^3/kg which are similar to those measured on shale in SR-270-PW brine solution (1.5 - 4.0 m^3/kg).

Table 65: Plutonium(III) Surface Complexation Reactions and Constants for Montmorillonite and Illite Estimated Using LFER

Pu Surface Complexation Reaction	Mont. Strong Site log $^{s}K_{x-1}$	Mont. Weak Site log $^{w1}K_{x-1}$	Illite Strong Site log $^{s}K_{x-1}$
$\equiv S^{s}OH + Pu^{+3} \Leftrightarrow \equiv S^{s}OPu^{+2} + H^{+}$	1.5	-0.9	1.8
$\equiv S^{s}OH + Pu^{+3} + H_2O \Leftrightarrow \equiv S^{s}OPu(OH)^{+} + 2H^{+}$	-5.6		-4.7
$\equiv S^{s}OH + Pu^{+3} + 2H_2O \Leftrightarrow \equiv S^{s}OPu(OH)_2^{0} + 3H^{+}$	-15.1		-13.4

Plutonium sorption values recommended for sedimentary rocks (shale and limestone) and bentonite are summarized in Table 66. Under more oxidizing conditions, the K_d values for bentonite were based on measurements with montmorillonite by Muccardi et al. (1979) and on bentonite by Nowak (1980). Plutonium sorption data on illite reported by Ticknor (1993) (5.4 m^3/kg) and Muccardi et al. (1979) (2.2 - 4.6 m^3/kg) were used to recommend K_d values for shale, assuming 60% illite content. Recommended K_d values for limestone were based on Pu(V) sorption on limestone reported by MaClean et al. (1978) and Reylea and Serne (1979). Under reducing conditions, the K_d values for bentonite, shale and limestone measured in SR-270-PW by Bertetti (2016) were recommended.

Table 66: Recommended Sorption Values for Plutonium

PLUTONIUM (IV, V) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**5 - 7**	**6.6 - 8**	**0.44 - 4.04**	**1.37 (2.5)**
comment	Based on measurements on montmorillite by Mucciardi et al. (1979) (0.52 - 4.04 m^3/kg) and on bentonite by Nowak (1980) (0.44 - 3.6 m^3/kg).			
Shale	**0.2 - 5**	**6.2 - 8.3**	**1.3 - 3.2**	**2.57 (1.4)**
comment	Based on Pu sorption data on illite reported by Mucciardi et al. (1979) (2.2 - 4.6 m^3/kg) and Ticknor (1993) (5.4 m^3/kg) assuming 60% illite in shale.			
Limestone	**5.1**	**6.5 – 7.5**	**0.069 - 3.7**	**0.92 (2.8)**
comment	Based on Pu(V) sorption on limestone reported by MaClean et al. (1978) (0.45 m^3/kg) and Reylea and Serne (1979) (0.069 - 3.7 m^3/kg).			
PLUTONIUM (III) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**6.0**	**6.6 - 8.2**	**1.5 – 10**	**3.91 (2.6)**
comment	Based on measurements for bentonite in SR-270-PW brine by Bertetti (2016). These measured K_d values are consistent with the simulation results for montmorillonite in SR-270 brine (1.02 - 12.2 m^3/kg).			
Shale	**6.0**	**6.6 - 8.2**	**1.5 - 4.0**	**2.45 (2.0)**
comment	Based on measurements for shale in SR-270-PW brine by Bertetti (2016). These measured K_d values are consistent with the simulation results for illite in SR-270 brine (2.28 - 9.03 m^3/kg), assuming shale consists of 60% illite (i.e. 1.37 - 5.42 m^3/kg for shale).			
Limestone	**6.0**	**6.6 - 8.2**	**1.5 - 4.0**	**2.45 (2.0)**
comment	Based on measurements for limestone in SR-270-PW brine by Bertetti (2016).			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

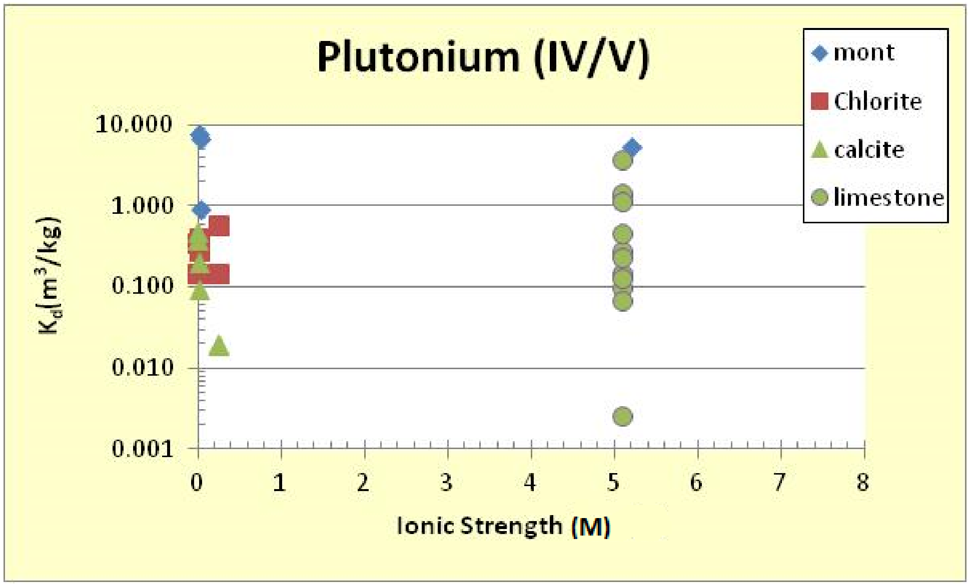


Figure 39: Plutonium Sorption Coefficients on Montmorillonite, Chlorite, Limestone and Calcite under Oxidizing Conditions as a Function of Ionic Strength (Mucciardi et al. 1979; Ticknor 1993; Reylea and Serne 1979)

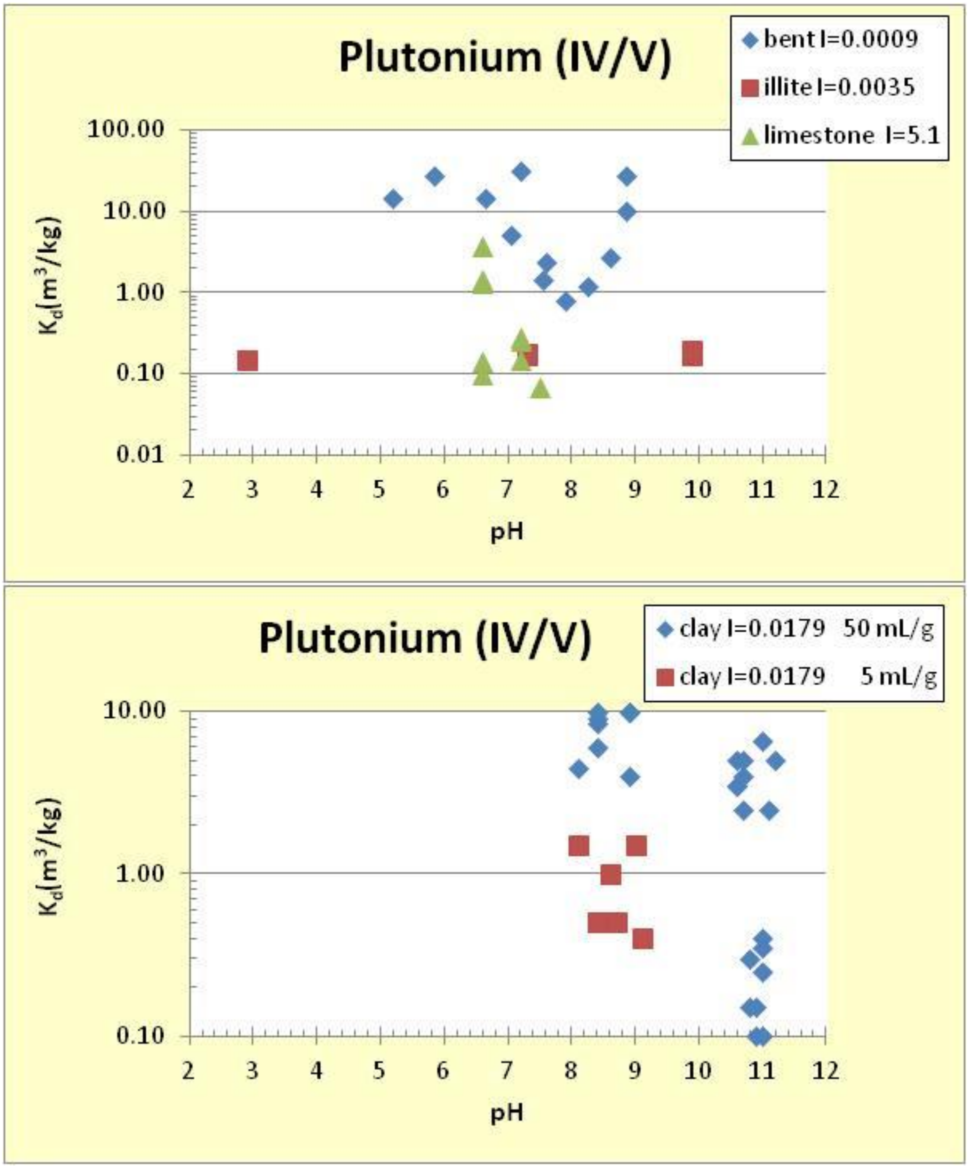
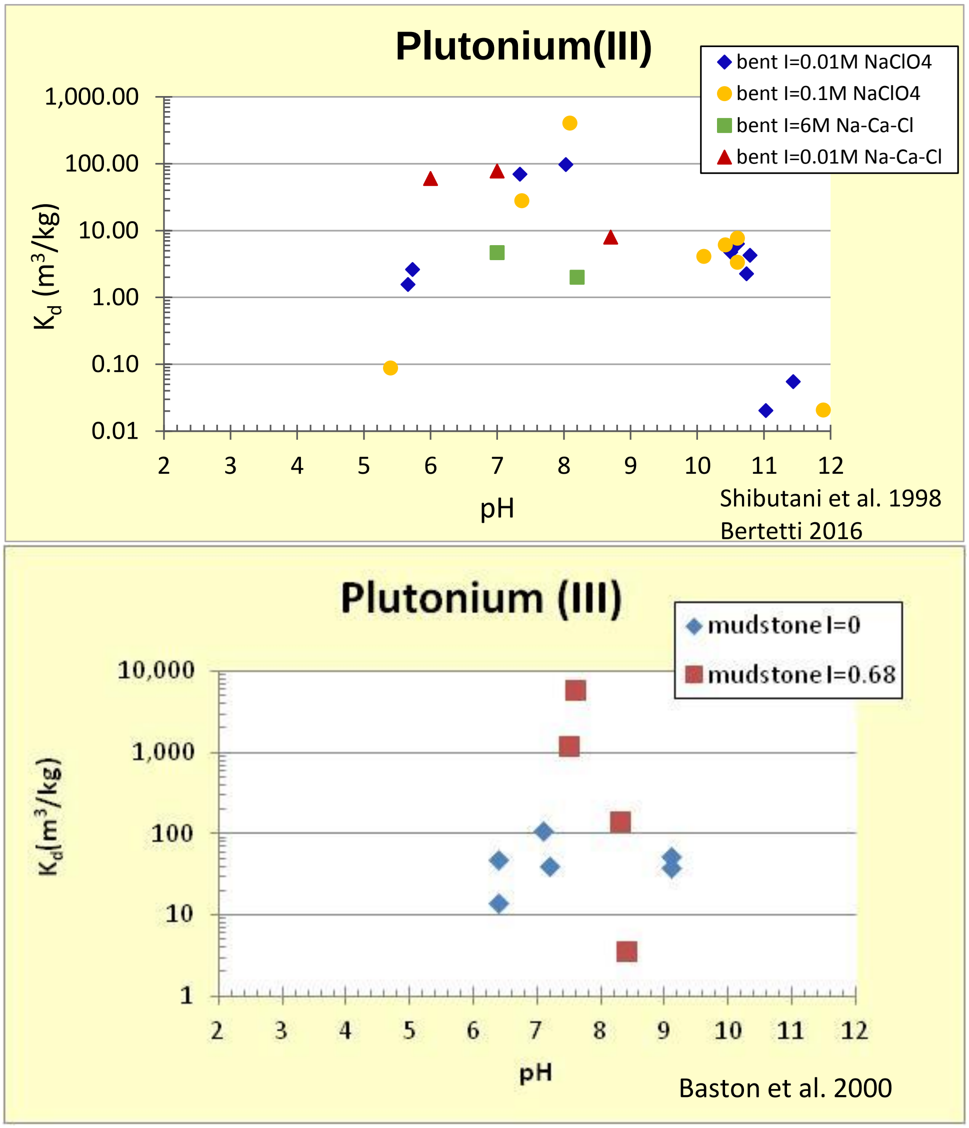


Figure 40: Plutonium Sorption Coefficients on Bentonite, Illite, Limestone and Clay under Oxidizing Conditions as a Function of pH (Shibutani et al. 1994; Torstenfelt 1988; Relyea and Serne 1979; Berry et al. 1991)



Shibutani et al. 1998
Bertetti 2016

Baston et al. 2000

Figure 41: Plutonium Sorption Coefficients on Bentonite and Mudstone under Reducing Conditions (Shibutani et al. 1998; Baston et al. 2000; Bertetti 2016)

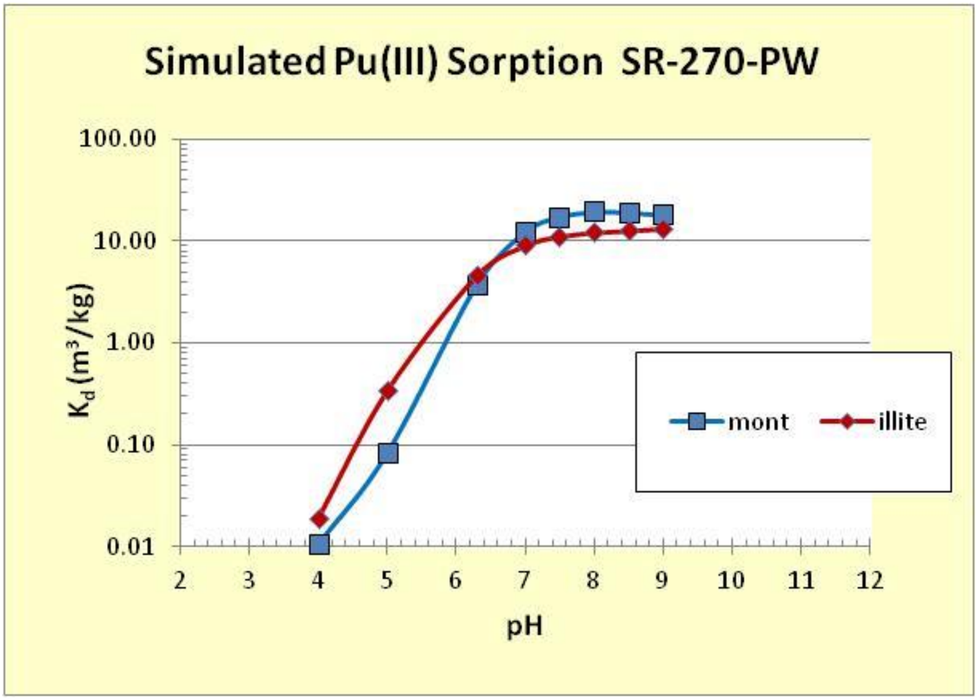


Figure 42: Simulated Plutonium (III) Sorption Coefficients on Montmorillonite and Illite

3.28 AMERICIUM

Americium is an actinide element with a dominant oxidation state of +3. Speciation calculations with PHREEQC (SIT database) predict that in the reference brine SR-270-PW, the main americium aqueous species are Am^{+3}, $AmCl^{+2}$, $AmOSi(OH)_3^{+2}$, and $Am(HCO_3)^{+2}$ (see Table 3). In a solution with a lower chloride concentration such as the reference solution SR-20, the main aqueous species would be Am^{+3}, $Am(CO_3)^{+1}$, and $Am(HCO_3)^{+2}$. Solids that control solubility include $Am(CO_3)OH$ and $Am(OH)_3$. The formation of the $AmCl^{+2}$ complex in chloride brine solutions could reduce sorption compared to more dilute groundwater. Potential chemical analogs are Eu(III) and Pu(III). The USEPA (1998) have also used Pu(V) as a chemical analog to estimate Am(III) sorption on dolomite.

Selected Am sorption values are presented in Table 67. A large fraction of the entries in this table provide K_d values for americium sorption on bentonite or one of the swelling clays (montmorillonite or smectite) that constitute the main component of bentonite. The Am K_d values of interest for bentonite were selected from data reported by Mucciardi et al. (1979), Gorgeon (1994), Ikeda and Amaya (1998), Nowak (1980), Stammose and Dolo (1990), and Stammose et al. (1992). These data represent results of Am sorption on bentonite, montmorillonite and smectite in solutions with an ionic strength range of 1.0 to 5.1 M and pH values of 5 to 8. The sorption coefficient values range from 0.21 to 78 m^3/kg. In the selected data, there is a slight decrease in sorption with increasing ionic strength.

Figure 43 illustrates the variation of K_d values for bentonite and smectite as a function of pH for solutions of various ionic strengths. Data for smectite were reported in $NaClO_4$ solution by Gorgeon (1994), while the data for bentonite were presented by Shibutani et al. (1994), Ikeda and Amaya (1998), Nowak (1980) and Mucciardi et al. (1979). The K_d values for smectite increase with increasing pH. The K_d values measured in the 1 M $NaClO_4$ solution are significantly lower than the K_d values measured in the 0.1 M solution, up to a pH value of about 7. At higher pH the ionic strength does not affect Am sorption. This suggests that in these $NaClO_4$ solutions cation exchange may be important at pH values below 7, but at higher pH surface complexation dominates. The K_d values for bentonite slightly decrease with ionic strength. The K_d values for montmorillonite obtained in 5.1 M NaCl solution at pH of 7.7 to 8.3 (Mucciardi et al. 1979) are much lower than the K_d values for bentonite measured at similar conditions (5.1 M NaCl solution at pH = 7.3 by Nowak 1980).

Figure 44A illustrates Am sorption on illite in 0.1 and 1.0 M $NaClO_4$ solutions (Gorgeon 1994) and on Na-illite in 0.1 M $NaClO_4$ solutions (Bradbury and Baeyens 2009b) as a function of pH. The pattern of K_d value variation with pH is similar to that observed for smectite (Figure 43). As with smectite, the K_d values measured in the 1 M solution are lower than that in the more dilute solution at pH less than 6, and become identical at higher pH values. Figure 44B displays a similar pattern of K_d value variation with pH, as determined by Stammose et al. (1992) for Am sorption on clay in $NaClO_4$ solutions with ionic strengths of 0.1, 1.0 and 3.0 M. Once an ionic strength of 1.0 M is reached, further increases in ionic strength do not appear to affect sorption.

Americium sorption on sediment was measured in sea water (ionic strength = 0.68 M and pH = 8.2) using a large range of solid to liquid ratios, which accounts for the wide range of sorption values (8.6 to 1810 m^3/kg) (Higgo et al. 1983). Sorption values for illite were 0.33 to 2.84 m^3/kg in an ionic strength of 5.1 M NaCl solution (pH = 7) (Mucciardi et al. 1979), and 12 to 89 m^3/kg in a $NaClO_4$ solution with an ionic strength of 1.0 M (pH = 6 - 8) (Gorgeon 1994).

Table 67: Selected Americium Sorption Coefficients

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
bentonite	Na-Cl-SO_4	0.02	10	14	air	200	1.13 - 3.8	batch	1
bentonite	Na-Cl-SO_4	0.02	10	14	hydrazine	-800	0.73	batch	1
bentonite	$Ca(OH)_2$	≈ 0	11	30	air	nr	0.19 - 0.21	batch	12
bentonite	distilled water	≈ 0	8.2	14	N_2	-100 -200	0.3 - 10	batch	16
bentonite	sea water	0.68	6	26	$Na_2S_2O_4$	-180 -190	11 - 21	batch	2
bentonite	NaCl	5.09	7.3	21	air	-190	4.1 - 14	batch	3
bentonite	NaCl	0.1	6.4	2	N_2	nr	38	batch	18
bentonite	NaCl	0.1	7.0	2	N_2	nr	230	batch	18
bent/quartz 10:90	Na-Ca-Cl-HCO_3	0.02	8.2	7	air	nr	1.6 - 4.0	batch	4
bent/quartz 10:90	Na-Ca-Cl-HCO_3	0.02	8.2	180	air	nr	7.9	batch	4
bentonite	NaCl	0.1	5 - 8	30	air	nr	22 - 128	batch	7
mont.	NaCl	5.1	7.7 - 8.3	3 - 38	air	313 407	0.21 - 0.54	batch	8
mont.	NaCl	0.03	6-9	3 - 38	air	323 459	2.19 - 5.82	batch	8
mont.	$CaCl_2$	0.03	7.5 - 7.8	3 - 38	air	348 447	0.23 - 2.52	batch	8
mont.	$NaHCO_3$	0.03	9.1 - 9.5	3 - 38	air	374 392	2.7 - 53	batch	8
mont.	CO_3/Tris*	0.005	8	>5	nr	nr	27 - 139	batch	13
mont.	NaCl	0.1 - 0.64	4	14	air	nr	3.4×10^{-4} - 4.1×10^{-3}	batch	15
smectite	sea water	0.68	8	7 - 56	air	300	136 - 411	batch	9
smectite	$NaClO_4$	1.0	6 - 8	0.042	air	nr	1.6 - 77.6	batch	10
smectite	Na-Ca-HCO_3-Cl	0.002	8	60	air	nr	1.4	batch	11
smectite	Na-Ca-HCO_3-Cl-SO_4	0.0023	7.2 - 7.4	8 - 45	nr	nr	0.13 - 0.15	batch	14
illite	$NaClO_4$	0.1	5.9 - 7.2	7	N_2	nr	203 - 845	batch	17
illite	NaCl	0.03	7	3 - 17	air	332 525	0.92 - 2.88	batch	8
illite	$NaClO_4$	1.0	6 - 8	0.042	air	nr	12 - 89.1	batch	10
Illite	NaCl	5.1	7	3 - 38	air	332 392	0.33 - 2.84	batch	8
clay	$NaClO_4$	1.0	6 - 7	1	air	nr	5.1 - 38.5	batch	5,6
clay	$NaClO_4$	3.0	6	1	air	nr	20.8	batch	5,6
clay	$NaClO_4$	0.1	6 - 7.4	1	air	nr	24.8 - 52.7	batch	5,6
clay	$NaClO_4$	0.1	6.2 - 7.5	1	air	nr	25 - 50	batch	6
clay	$NaClO_4$	1.0	6.0 - 6.7	1	air	nr	5.0 - 32	batch	6
clay	$NaClO_4$	3.0	6.2 - 7.0	1	air	nr	20	batch	6
illite/ kaolinite	sea water	0.68	8	7 - 28	air	nr	142 - 162	batch	9

Table 67 continued…

Solid	Solution	I (M)	pH	Time (d)	Atm.	Eh (mV)	K_d (m^3/kg)	Exp Type	Ref
sediment	sea water	0.68	8.2	23 - 74	air	300	8.6 - 1810	batch	9
calcite	sea water	0.68	7.7	7 - 56	air	300	29 - 312	batch	9

1. Barney (1981)
2. Ikeda and Amaya (1998)
3. Nowak (1980)
4. Allard et al. (1979)
5. Stammose and Dolo (1990)
6. Stammose et al. (1992)
nr: not recorded
*: Tris(hydroxymethl)-aminomethane
7. Shibutani et al. (1994)
8. Mucciardi et al. (1979)
9. Higgo et al. (1983)
10. Gorgeon (1994)
11. Salter et al. (1981)
12. Fukumoto et al. (2000)
mont.: montmorillonite
13. Degueldre et al. (1994)
14. Ames et al. (1981)
15. Nagasaki et al. (1997)
16. Nagasaki et al. (1994)
17. Bradbury and Baeyens (2009b)
18. Kumar et al. (2013)

Recommended americium K_d values are presented in Table 68. Recommended sorption values for bentonite were based on a range of measurements made on bentonite, montmorillonite and smectite for ionic strengths of 1.0 to 5.1 M by Mucciardi et al. (1979), Gorgeon (1994), Ikeda and Amaya (1998), Nowak (1980), Stammose and Dolo (1990) and Stammose et al. (1992). Recommended Am sorption values for shale were based on measurements for illite by Mucciardi et al. (1979) and Gorgeon (1994), as opposed to using sediment, because the K_d values reported by Higgo et al. (1983) seemed excessively high. It was assumed that shale contained 60% illite. Americium sorption on calcite measured in sea water at a pH of 7.7 by Higgo et al. (1983) also seemed to be excessively high, ranging from 29 to 312 m^3/kg. The USEPA (1998) recommended Am sorption values for dolomite that range from 0.02 to 0.50 m^3/kg. These values were based on using Pu(V) measurements as a chemical analog because actual tests with Am failed to produce values that could be used with confidence. Given the uncertainties in americium sorption values for calcite and dolomite, the recommended value for americium sorption on limestone is based on “in-house” sorption measurement of Eu on limestone.

Table 68: Recommended Sorption Values for Americium

AMERICIUM (III)				
			K_d Values (m^3/kg)	
	I (M)	pH	Range	Geometric Mean
Bentonite	**0.68 - 5.1**	**6 - 8**	**0.21 - 77.6**	**5.75 (6.8)**
comment	Based on measurements for bentonite, montmorillonite and smectite for ionic strengths of 0.68 to 5.1 M by Mucciardi et al. (1979); Gorgeon (1994); Ikeda and Amaya (1998); and Nowak (1980).			
Shale	**1 - 5.1**	**6 - 8**	**0.22 - 53.5**	**4.33 (12.4)**
comment	Based on Am sorption on illite reported by Mucciardi et al. (1979) (0.33 - 2.84 m^3/kg) and Gorgeon (1994) (12 - 89.1 m^3/kg), assuming shale contains 60% illite.			
Limestone	**0.23 - 7.2**	**6 - 6.9**	**0.09 - 0.29**	**0.16 (1.6)**
comment	Based on Eu(III) sorption on Ordovician limestone (Vilks et al. 2011) (see Table 42)			

Note: The geometric standard deviation is in parentheses beside the geometric mean.

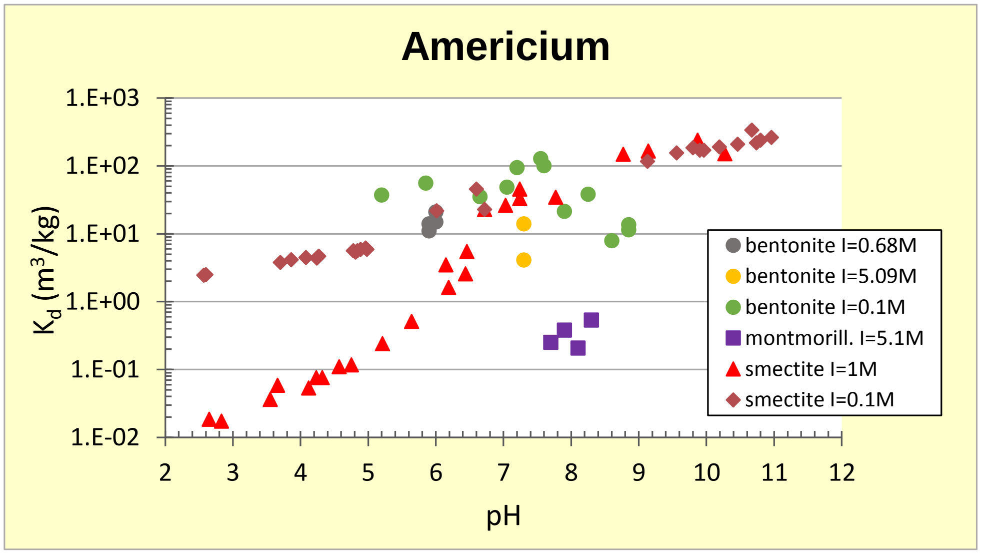
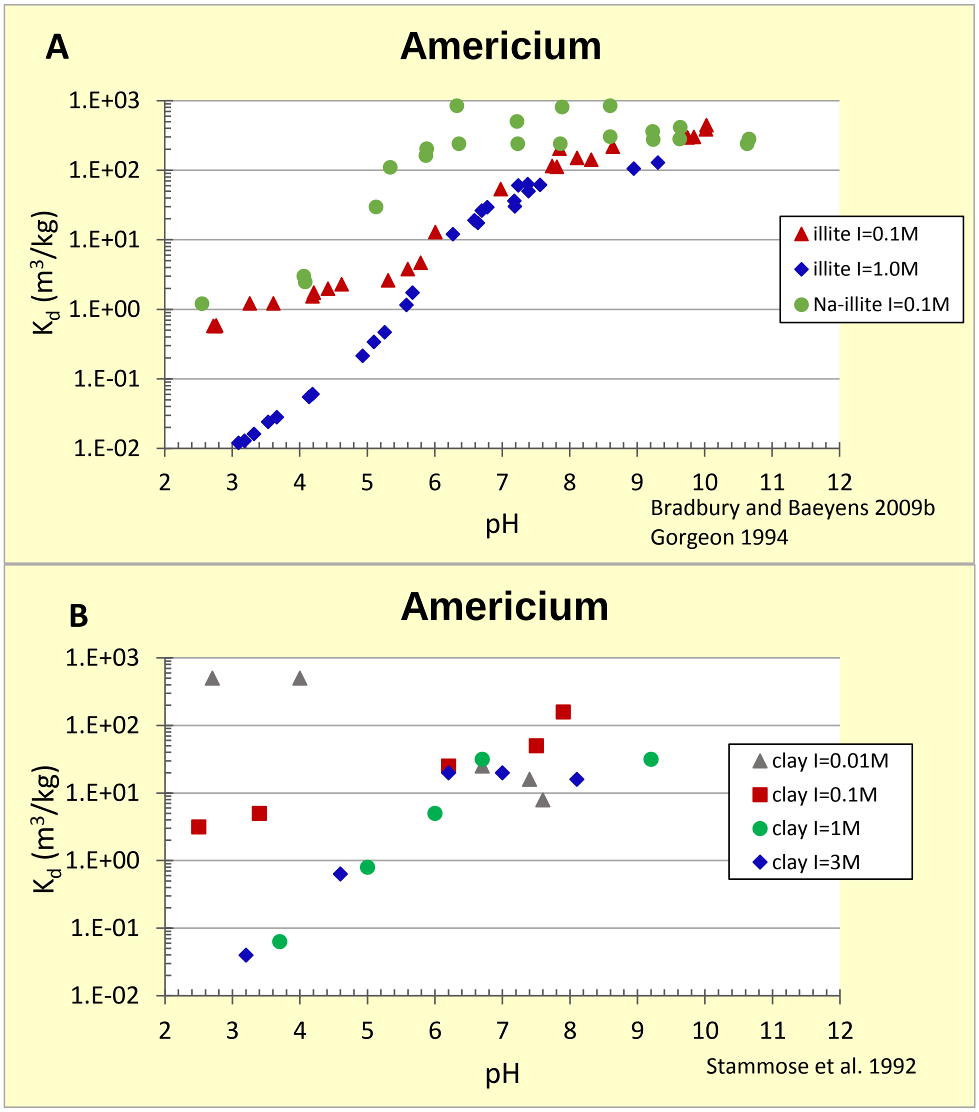


Figure 43: Americium Sorption Coefficients on Smectite and Bentonite as a Function of pH in Different Ionic Strength Solutions (Sato and Shibutani 1994; Ikeda and Amaya 1998; Nowak 1980; Mucciardi et al. 1979; Gorgeon 1994)



Bradbury and Baeyens 2009b
Gorgeon 1994

Stammose et al. 1992

Figure 44: Americium Sorption Coefficients on Illite (Bradbury and Baeyens 2009b; Gorgeon 1994) and Clay (Stammose et al. 1992) as a Function of pH at Different Ionic Strengths

4. SUMMARY

A database of sorption K_d values that would be relevant to Canadian sedimentary rocks (shale and limestone) and bentonite, in a setting that would include Na-Ca-Cl brine solutions at near neutral pH was initiated by Vilks (2011). The 19 elements that were included in the database were C, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. The current work continued the development of the sorption database for Canadian sedimentary rocks and bentonite in highly saline waters by updating sorption values for the 19 elements and developing new sorption data for 9 additional elements (Ni, Cs, Eu, Cl, Ca, Ag, Cd, Hg, I).

This report has: i) filled data gaps for 19 elements in the database (Vilks 2011); ii) found data for nine additional elements (Ni, Cs, Eu, Cl, Ca, Ag, Cd, Hg, I); iii) reduced the need for the use of chemical analog elements; and iv) identified information that may aid with extrapolations to higher ionic strengths. The main approaches used in this report were to: i) perform a review of published literature to discover new sorption data; ii) revaluate the existing data to identify information that may aid with extrapolations to higher ionic strengths; iii) incorporate the results of “in-house” sorption measurements for Ni, Cu, As, Se, Zr, Tc, Pd, Sn, Cs, Pb, Eu, Th, U, Np and Pu; and iv) make use of sorption modelling to fill data gaps and to extrapolate results obtained from more dilute lab solutions to brine conditions. Also, in this report, more information was provided regarding experimental parameters such as redox conditions and contact time. The use of chemical analogs was significantly reduced.

Table 69 summarizes the sorption coefficients for sedimentary rocks (shale and limestone) and bentonite in saline solutions recommended in this report. One should refer to the appropriate sections in Chapter 3 for more information (such as geometric mean, if calculated) on any particular element. The last column in Table 69 provides some information on how recommended K_d values were derived for bentonite (ben), shale (sh) and limestone (lim). Those elements with data from saline conditions were designated with an “S”. In some cases, the recommended K_d value was extrapolated to saline conditions using scientific reasoning (marked with “Ex”). Some elements did not have any data for saline conditions and there were no scientific bases for extrapolating the reported K_d values to brine conditions. The recommended K_d values for these elements, marked with “NR”, were set to 0 m^3/kg. In the current database of 28 elements, there are 10 elements with NR K_d values for some or all of the sorbing solids. Analog elements were used in 7 cases to derive recommended K_d values for some elements. In Table 69, the use of analog elements is identified with the symbol for the analog element given in *italics*. Those cases in which recommended K_d values for bentonite or shale were based on surface complexation modelling to simulate sorption on montmorillonite and illite were marked with “SC”.

Compared to Vilks (2011) the sorption database summarized in Table 69 includes revisions to most of the elements. An entry for Cu(I) was added because the monovalent oxidation state is the dominant form of copper under the assumed repository redox conditions. Due to a lack of data, only a K_d value of 0 m^3/kg can be recommended for Cu(I). The recommended K_d values for Ni(II), Cu(II), Pb(II), Cs(I), Pd(II), Eu(III), Zr(IV), Sn(IV), Th(IV), U(VI), U(IV), As(III), Np(V), Np(IV), Pu(III), Se(-II) and Tc(IV) incorporated the results of “in-house” sorption measurements in SR-270-PW brine solution.

Table 69: Recommended Sorption Values for Sedimentary Rock in Saline Water

	Range in K_d Values			Data Source		
Element	**Bentonite (m^3/kg)**	**Shale (m^3/kg)**	**Limestone (m^3/kg)**	**ben**	**Sh**	**lim**
C inorganic	2.7×10^{-5} - 5.5×10^{-4}	1×10^{-4} - 8.2×10^{-4}	1×10^{-3} - 9×10^{-2}	Ex	Ex	Ex
C organic	0	0	0	NR	NR	NR
Cl(-I)	0	0	0	NR	NR	NR
Ca(II)	0	0	0	NR	NR	NR
Ni(II)	0 - 0.013	0 - 0.009	0 - 0.005	S	S	S
Cu(II)	0.05 - 0.13	0.017 - 0.15	0.007 - 0.027	S	S	S
Cu(I)	0	0	0	NR	NR	NR
As(V)	0	0	0	NR	NR	NR
As(III)	0.018	0.02	0.011	S	S	S
Se(IV)	0.004 - 0.31	0.008 - 0.011	0.0013	Ex	S	S
Se(-II)	0.09 - 0.11	0.003 - 0.1	0.0037 - 0.1	S	S	S
Zr(IV)	0.49 - 14.8	0.32 - 7.82	0.13 - 4.68	S	S	S
Nb(V)	6.4 - 23	1.1 - 6.3	0	S	S	NR
Mo(VI)	0	0	0	NR	NR	NR
Tc(VII)	1.7×10^{-4} - 0.24	3.5×10^{-5} - 8.45×10^{-2}	2.37×10^{-3} - 7.3×10^{-3}	S	S	S
Tc(IV)	5	0.02	10	S	S	S
Pd(II)	0.03 - 14.5	0.04 - 14.3	0.12 - 22	S	S	S
Ag(I)	0	0	0	NR	NR	NR
Cd(II)	0	0	0	NR	NR	NR
Sn(IV)	4.2 - 95	1.5 - 44	0.99 - 18	S	S	S
I(-I)	1.8×10^{-4} - 5×10^{-2}	4.0×10^{-6} - 2.65×10^{-2}	0 - 3.0×10^{-4}	S	S	S
Cs(I)	0.14 - 1.43	0.069 - 0.63	0.032 - 0.69	S	S	S
Eu(III)	0.1 - 6.7	0.11 - 0.22	0.09 - 0.29	S	S	S
Hg(I)	0	0	0	NR	NR	NR
Pb(II)	0 - 0.011	0 - 0.009	0 - 0.004	S	S	S
Bi(III)	1.1 - 18	0.84 - 10	0.09 - 0.29	SC	SC	*Eu*
Ra(II)	0	0	0	*Sr*	*Sr*	*Sr*
Th(IV)	3.38 - 15.9	1.66 - 6.81	0.6 - 2.71	S	S	S
Pa(V)	5.0	25 - 35	0.091	Ex	SC	Ex
U(VI)	0.023 - 0.049	0.016 - 0.044	0.008 - 0.015	S	S	S
U(IV)	0.42 - 360	0.42 - 337	0.42 - 2.71	S	S	*Th*
Np(V)	0.00004 - 0.176	0.006 - 0.12	0.001 - 0.2	S	S	S
Np(IV)	17.8 - 130	11 - 98	0.6 - 2.71	S	S	S,*Th*

Table 69 continued...

	Range in K_d Values			Data Source		
Element	**Bentonite (m^3/kg)**	**Shale (m^3/kg)**	**Limestone (m^3/kg)**	**ben**	**Sh**	**lim**
Pu(IV, V)	0.44 - 4.04	1.3 - 3.2	0.069 - 3.7	S	S	S
Pu(III)	1.5 - 10	1.5 - 4.0	1.5 - 4.0	S	S	S
Am (III)	0.21 - 77.6	0.22 - 53.5	0.09 - 0.29	S	S	*Eu*

S: Data from saline conditions.
Ex: Value extrapolated to saline conditions using scientific reasoning.
SC: Value estimated to saline conditions using surface complexation modelling.
Sr Th Eu: Analog elements used obtain to obtain K_d value.
NR: No suitable data for saline. Assume K_d = 0.

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