Sorption of Selected Radionuclides on Sedimentary Rocks in Saline Conditions – Literature Review

NWMO TR-2011-12 **December 2011**

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ABSTRACT

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Abstract

Sedimentary rocks in Canada, including shales and limestone, are considered as potentially suitable host rock types to host a deep geologic repository. Some of these rocks are known to contain Na-Ca-Cl brine solutions with total dissolved solids (TDS) of up to 375 g/L. The sorption properties of these rocks and the clay based sealing materials (eg.bentonite) in the repository need to be evaluated if contaminant sorption (in the geosphere and repository) is to be included in the safety assessment calculations for the repository. The international literature and sorption databases were searched to find sorption 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. Redox conditions were factored for those elements that are redox sensitive. The elements of interest included C, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. Sorption data relevant to brine solutions were found for bentonite, shale, limestone, illite, chlorite and calcite for some, but not all, elements. Where possible, chemical analog considerations were used to fill data gaps. From these data a set of recommended sorption values was identified for bentonite, shale and limestone. These values are intended as a starting point for the development of a Canadian sorption database for sedimentary rocks.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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 a potential mechanism for slowing the transport of radionuclides to the surface environment.

The purpose of this report is to review and summarize sorption data for sedimentary rocks and for sealing materials, with brackish to saline groundwater conditions. Sedimentary rock types that are of interest in Canada include argillaceous limestone and shale. The materials of interest in the engineered barriers are bentonite and bentonite/sand mixtures. Table 1 summarizes the mineralogical compositions of the rocks and clay-based engineered barriers being considered in this report. The mineral composition of the argillaceous limestone is similar to that reported in by NWMO (2011), while the mineralogy of the shale is similar to the average shale composition for Georgian Bay and Blue Mountain formations (Cavé et al., 2010). Where sorption data is not available for limestones and shales, sorption will be estimated based on the major mineral components, notably calcite and dolomite for limestone, and illite and chlorite for shales. Although clay minerals only account for only 60 wt% of shale mineralogy, they determine the sorption capacity of shale. Other clay rich rocks, including mudstones could be considered as analogs for shale.

The primary seal material considered in Canada for engineered barriers is Na-rich Wyoming bentonite clay, possibly mixed with sand. MX-80 is a Wyoming bentonite that has passed through a 80 mesh sieve, and is a commonly specified reference bentonite material. The review will focus on data for bentonite and 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. Smectites will also be considered.

Sedimentary rocks in Canada, for example in the Michigan Basin and Western Canada Sedimentary Basin, have been observed to contain brackish to highly saline fluids. Therefore, there is a need to establish an understanding of how brine solutions affect sorption. To further the understanding of sorption in a sedimentary brine environment, the review has considered the sorption of key elements on various sedimentary rocks with groundwaters with a range of ionic strengths, pH values and redox conditions. This data will help identify sorption trends, possible mechanisms, and data gaps.

The list of elements of potential interest that are included in this report are C, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. These elements are of interest either because (1) radionuclides of the elements are potentially important dose contributors in the safety assessment calculations (C, Se, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am); or (2) the elements are potentially important chemical toxins or carcinogens (As, Mo); or (3) the mass of the element in a used fuel container is large (Cu, Zr and Nb) (Garisto et al., 2005a, 2005b).

Table 2 summarizes the reference groundwater compositions provided by the NWMO which are being used as a guide to eventually develop a sorption database. The reference groundwaters include brines with compositions of Ca-Na-Cl, Na-Ca-Cl, and NaCl, as well as a saline water that is more oxidizing. The ionic strengths range up to 4.5 mol/L, based on PHREEQC (Parkhurst and Appelo, 1999) calculation using the SIT database. The brines are all reducing, and the saline water is less reducing. The pH of these waters is expected to be around neutral.

Table 1: Reference Rock/clay Compositions

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% - Chlorite 40% 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	5.8	6.1	6.5	6.5
Redox State	Reducing	Reducing	Reducing	Reducing	Less Reducing
Eh (mV)	-200	-200	-200	-200	90
Solutes					
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 (mol/L)**	4.5	3.8	3.3	2.5	0.32
Water Type	Ca-Na-Cl	Na-Ca-Cl	Na-Cl	Na-Ca-Cl	Na-Cl

* Ionic strength estimated using PHREEQC (SIT database)

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, which 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 if 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 becoming 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 forces acting on cations near a negatively charged surface include the electrostatic pull of the surface and the kinetic energy of the cations, which tries to pull them away from the surface. As a consequence of these two opposing forces 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, which 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 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 higher temperature. In the Stern layer cations must compete for space so that 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 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 the mass action of the salt.

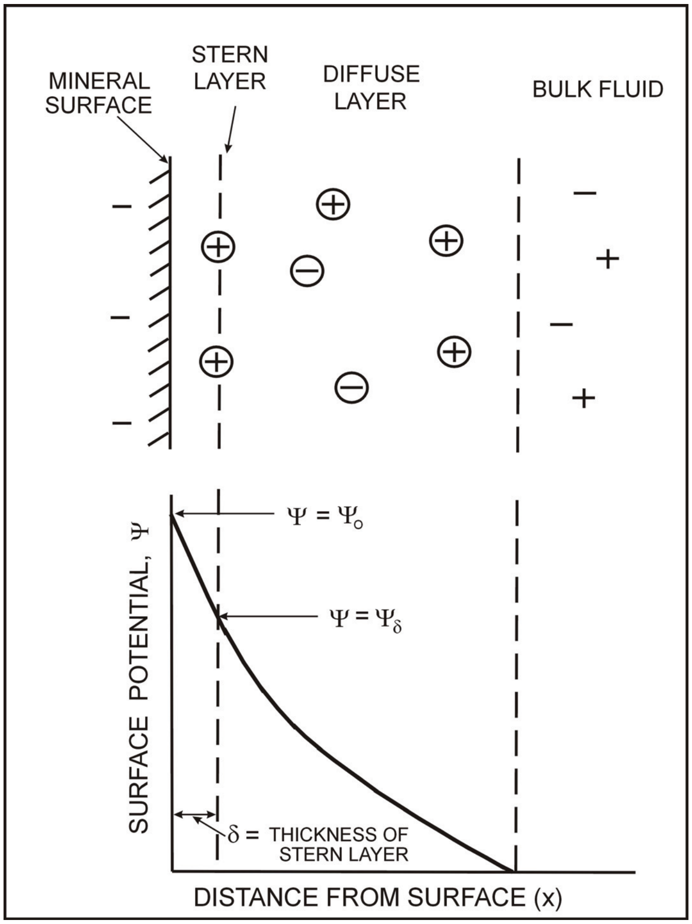


Figure 1: The Distribution of Ions and Electric Potential with Distance from a Charged Surface According to Stern's Model

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 do not form as strong bonds with oxygen as transition metals do. 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 should displace trace cations from surfaces by mass action. Radionuclides that are attached to surfaces only by non-specific coulombic attraction will not sorb in brine solutions.

Specific chemical sorption: Due to the ability of metals to be sorbed in seawater, 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). This phenomenon was described for transition metal sorption 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.

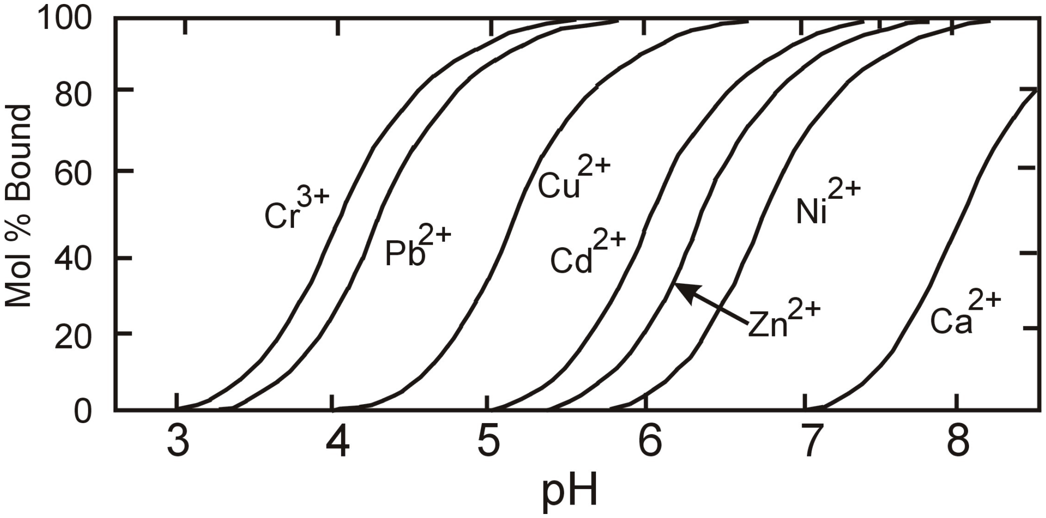


Figure 2: The pH Dependence of Metal Sorption on Fe Oxide (After Stumm, 1992)

The most common concept used to explain specific chemical sorption is surface complexation, which involves metal complexation with surface oxygens. 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.

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). An outer-sphere complex is formed when a cation approaches negatively charged surface groups to within a critical distance, as with solute ion pairs in which the cation and ion are separated by one or more water molecules (Stumm, 1992). Inner-sphere metal ions have different chemical properties from those held as outer-sphere complexes in that they have a higher electron density, different redox properties and their equatorial water is expected to exchange faster. Outer-sphere complexes can be considered as being held by coulombic attraction within the Stern layer, and are distinct from ions held in the diffuse layer.

Chemical substitution: 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, and Zhuang et al., 1988). In some cases chemical substitution may be irreversible (Zhuang et al., 1988).

Structural penetration: Although a number of metals may not form solid solutions within the structures of rock forming minerals, such as clays, the penetration of mineral structure has been proposed by some researchers as one possible mechanism to explain metal fixation in clays (Elgabaly, 1950, Nelson and Melsted, 1955, and Tiller and Hodgson, 1960). Hodgson (1960) looked at Co sorption on montmorillonite in the presence of 0.1 mol/L $CaCl_2$, which is expected to reduce or eliminate electrostatic adsorption of Co. He found a fast (several hours) and reversible reaction, which was attributed to chemisorption in a surface monolayer, and a slow irreversible sorption thought to represent Co penetration of 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 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. However, should cations enter into fractures, cleavages or other defects than these size restrictions may no longer be valid.

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 mineral structure may be favoured by higher pH and by higher temperature.

Isotopic exchange: 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 exchange of a radioisotope with a stable isotope in a solid will reduce the concentration of the radioisotope in solution. For example, the concentrations 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 surfaces that are also neutral. Physical sorption is believed to be rapid and reversible, and independent of temperature, the chemical composition of the sorbing solid, and the ionic strength of the solution. Physical sorption is affected by pH, which determines whether neutral hydrolysis complexes are present and whether the surface charges are neutral.

Summary: Elements may sorb by one or more mechanisms, depending on their chemistry, the water composition and the properties of the sorbing solid. Elements that sorb only by non-specific coulombic attraction will not sorb in brine solutions due to the mass action of the salt, and in particular the Ca^{2+} ion. The sorption of an element that is affected only by specific chemical sorption will not be affected by salt concentration, but will likely be affected by pH, particularly in the vicinity of a sorption edge. An element that sorbs by both coulombic attraction and specific chemical sorption will have its sorption reduced in brine solutions, but it will still sorb. Although structural penetration, isotopic exchange, and physical sorption may contribute to sorption in brine solutions, these processes will not be considered in the selection of sorption values for sedimentary rocks in brine solutions.

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 the Canadian database for crystalline rock (Vandergraaf and Ticknor, 1994, and Ticknor and Vandergraaf, 1996), the Swedish database for granite (Carbol and Engkvist, 1997, and Crawford et al., 2006), the Swiss database for Opalinus clay and bentonite (Bradbury and Baeyens, 2003a, 2003b), the database for the WIPP site in dolomite (USEPA, 1998, and Lucero et al., 1998), existing data for OPG's proposed DGR in sedimentary rock (Walke et al., 2011), and the Japanese sorption database for a broad range of rocks and minerals (Tachi et al., 2009; Japan SDB http://migrationdb.jaea.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. The open literature was consulted for data gaps not present in the databases.

Walke et al. (2011) also recently reviewed the literature to select sorption values for sedimentary rocks for the postclosure safety assessment of OPG's low and intermediate level waste deep geologic repository. The rock types considered included argillaceous lithologies and limestone lithologies, as well as bentonite. The selection of sorption values considered that sorption reactions would take place in Na-Ca-Cl solutions with mid range pH values and TDS values ranging from 27 to 375 g/L. Walke et al. (2011) took a very conservative approach, assigning sorption values of 0 for anions, elements that sorb by coulombic attraction, elements with suspect sorption data and elements for which sorption mechanisms were poorly understood. Where a range of data values were available, normally the lowest sorption values were selected to account for possible complex formation, mass action effects of Ca and because the properties of the Ordovician rocks are not an absolute match to solids used in sorption measurements. In most cases the values adopted by Walke et al. (2011) are less than or equal to the minimum values given in this report. In the other cases, the values adopted by Walke et al. (2011) are within the ranges recommended in this report.

Sorption data are most commonly reported in the form of a sorption coefficient. If a contaminant's concentration is low enough its sorption may be linear with concentration and a sorption coefficient or distribution coefficient can be used to describe its sorption behaviour. Sorption coefficients are 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 reaction mechanism. It may change with pH, solid/liquid ratio and ionic strength, and if Henry's law is not obeyed at high sorbate concentrations, it becomes a function of concentration. Originally the concept of a sorption coefficient (K_d) assumed that the reaction is reversible and that the measured 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 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 in the use of sorption coefficients has been the subject of much debate. Despite the debate, the fact remains that all sorption experiments measure a sorption coefficient and in mass transport calculations the understanding of particular sorption processes is distilled into values of sorption coefficients before being used.

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

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

The value of R_a is related to R_d by the following

$$R_a = \frac{R_d}{A_{sp}} \tag{6}$$

In this report the sorption values will be reported as the traditional mass based sorption coefficient, K_d, with units of m^3/kg. Note that some databases report sorption coefficients with units of cm^3/g, which give values that are 1000 times higher. 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 0.001 to 1.0 m^3/kg sorption becomes progressively stronger and retardation being more significant. Values in the range of 1 to greater than 500 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 for the most part obtained from batch sorption experiments or from transport studies. 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 dynamic experiments that involve diffusion or advective transport. In batch experiments the sorbing solid and the solution containing the sorbate (usually dissolved) are contained in a vessel. The parameters that may be controlled 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 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). The addition of redox buffers, such as Fe^{2+}, in sufficient concentrations to be useful could produce by-products that affect the sorption reaction.

Mass transport experiments involving sorbing radionuclides have been used extensively to demonstrate the role of sorption in mass transport, improve understanding of how sorption works during mass transport and to derive sorption coefficients. Different approaches for measuring the interactions between contaminants and rock are needed to test the compatibility of experimental retardation parameters and transport models used in safety assessments. Mass transport experiments include diffusion, advection and diffusion combined with advection. Mass transport calculations often involve the combination of a measured physical transport process with measured sorption data to produce an estimate of mass transport. For example, Ohlsson and Neretnieks (1997) produced a set of apparent diffusion coefficients for Aspö granite based on diffusion measurements with tritium (physical transport), combined with sorption data from Carbol and Engkvist (1997). The validity of this approach needs to be demonstrated by experiments and an improved understanding of sorption processes 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 dynamic transport experiments often requires the application of scaling factors to account for differences 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 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 may be important for determining a sorption value with a reasonable accuracy. Typically sorption experiments last 1 week to 4 weeks or longer. These times are virtually instantaneous in comparison to the time scales used in performance assessment calculations. Sorption values usually increase with time, but the stability of the solid phase may become an issue for extended 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.

Experimental design and execution will introduce various levels of uncertainty in the sorption values reported in the literature. Errors that produce sorption values that are lower than actual in-situ values are conservative, while reported sorption values that are higher than actual values are non-conservative and result in over prediction of radionuclide retardation. The measurement and control of pH may pose difficulties in high ionic strength solution 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 has drifted over several pH units or else 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 experimental Eh values are 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. Sorption values derived from experiments where the sorbate concentration is high enough to induce precipitation should not be used because the resulting values may be high and non-conservative. The effect of the experimental solid/liquid ratio has been open to debate, but will probably introduce a low level of uncertainty. Experimental sorption times lasting several days to a week may introduce a relatively low uncertainty. Since sorption appears to increase with time, short term tests will produce conservative sorption values. The steps used for conditioning solids to remove the effects of sample grinding have some effect, but the uncertainty introduced by these procedures are relatively low.

2.3 SELECTION CRITERIA

The following sections describe some of the factors that are considered in the selection of sorption values from databases, and in compiling sorption databases for use with sedimentary rocks. These include a consideration of water chemistry used in sorption measurements in comparison to the reference groundwaters, and a discussion of the rocks and minerals of interest in the initiation of a sorption database. The use of chemical analogs is also described.

2.3.1 Water Chemistry

Water chemistry plays a key role in sorption reactions and is given a high priority in the selection process for sorption data. The pH affects hydrolysis and surface complexation reactions. As illustrated in Figure 2, most elements that have any tendency to hydrolyze display a sharp increase in sorption, referred to as the sorption edge. The position of the sorption edge varies from element to element. The selection process is made simpler if the sorption of a given element has reached a plateau in the pH range of interest for sedimentary rocks (6 to 7). This is 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 6 to 7. If not, then a judgement must be made as to whether a given sorption value is applicable, based on a known trend with respect to pH.

The total salt concentration, as well as the dissolved constituents influences sorption in several ways. The ionic strength influences activity coefficients. More importantly, the mass action of the major ions reduces sorption, particularly for 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 mol/L would not be applicable to seawater or a brine with an ionic strength of 2 mol/L. The Na^+/Ca^{2+} ratio will make a difference depending upon the salt concentration and whether Ca^{2+} competes with the element in surface complexation reactions. The Ca^{2+} is more effective than Na^+ at displacing elements sorbed by coulombic attraction due to its divalent charge. In brine solutions this is less important compared to dilute solutions. Many surface complexation reactions may not be affected by the total salt concentration and the Ca^{2+} concentration, but some could be. For example, Vilks et al. (2011) noted that Ca^{2+} reduced the sorption of Ni^{2+} but not U(VI). However, 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 is usually reported with sorption data that could be used to identify the effect of salt concentration on sorption. Ionic strength was chosen because it summarizes the total ion concentration (as molar quantities) and the influence of ion charges. One of the selection processes involves a comparison of sorption values as a function of ionic strength. This may help to determine whether an element will sorb in a brine solution, and whether the data for some elements 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 dominant oxidation states that vary depending upon 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 useful to have data for oxidizing conditions to compare with data from reducing waters to illustrate the effect of redox. In this case, reducing was defined as waters with Eh lower than +100 mV. Although the reference water SR-20 is considered as being relatively oxidizing, it is significantly more reducing than waters used in a laboratory. For redox sensitive elements, it is important to distinguish between those measurements made in an aerobic atmosphere from those determined in solutions where redox has been controlled and maintained as reducing.

2.3.2 Mineralogy and Rock Type

In selecting sorption data the first priority was given for shale, limestone and bentonite. 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. 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 or chlorite.

If sorption values for bentonite, shale and limestone are available for reasonable solution compositions, they were reported as recommended values. If sorption data is not available for shale, data from some other clay rich rock, such as mudstone, was used as an approximation. If data are available for illite and/or chlorite, these data were used to estimate sorption on clay. The assumption was made that the total clay content is 70%, and the remaining 30% quartz does not sorb significantly compared to clay. With this assumption, the sorption value of the clay is reduced to 70% of its original value. If reasonable data for both illite and chlorite are available, a weighted average (60% illite and 40% chlorite) was calculated to represent sorption on the clay fraction. 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.

2.3.3 Use of Analog Elements

Some elements are used as chemical analogs for elements that are difficult to study experimentally due to redox control, low solubility and detection issues, or problems with licensing the use of radioisotopes in field-scale experiments.

Lanthanide elements, such as Sm, Eu, and Ho, have been used as analogs for trivalent actinides, including Ac(III), Pu(III), Am(III) and Cm(III). Since Th(IV) is not redox sensitive, it can be used as an analog for U(IV), Np(IV) and Pu(IV), which require strictly controlled reducing conditions to 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), U(VI), Th(IV) and Np(V). Then the oxidation-state analogy approach was used to extrapolate the established sorption ranges to represent Pu(III), Pu(IV), U(IV) and Np(IV).

In this review, chemical analogs were used to obtain sorption values for a number of elements where data gaps existed. These elements included Zr(IV), Mo(VI), Pd(II), Pb(II), Bi(III), Ra(II), Pa(V), Np(IV) and Pu(III). The chemical analog elements included Nb(V), Np(V), and Th(IV), for which published sorption coefficients were used. In addition, sorption data for Sr(II), Ni(II), Eu(III) and U(VI) measured on bentonite and Ordovician shales and limestone in the presence of brine solutions were used as chemical analogs. Specific details on the use of analog elements are given in the sections where they are used.

2.4 AQUEOUS CHEMISTRY PREDICTED BY PHREEQC

Aqueous chemistry for radionuclides was estimated 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 of this program used in these calculations was PHREEQC Interactive 2.17.4137. The difficulty for chemical speciation calculations for high ionic strength solutions is the determination of ion activity corrections.

The best estimate of ion activities in high ionic strength brines is provided by the Pitzer equations. The Pitzer database “data0.ypf.R2” produced by the Yucca Mountain Project (USDOE, 2007) includes Pitzer ion interaction coefficients. This database, which was converted from EQ3/6 format to PHREEQC format by Benbow et al. (2008), contains thermodynamic data for a number of elements that are of interest to radionuclide transport, including Am, Cm, Cs, Co, Cu, Ni, Nd, Np, Pu, Sr, Tc, Th and U. Unfortunately most of the elements of interest to this report are not included in this database. However, they are included in the sit.dat database that is included with the PHREEQC package.

The sit.dat database is the PHREEQC version of the ThermoChimie v.7.b 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 As, Bi, Nb, Tc, then the Debye-Hückel approach was used for activity corrections. While SIT theory has proved to be simple and adequate for ionic strengths from 0.5 to 3 mol/L, and the Pitzer theory is much better at reproducing experimental behaviour for solutions with ionic strengths up to 20 mol/L (Elizalde and Aparicio, 1995).

Due to the availability of chemical speciation data, the sit.dat data base was used for all speciation calculations in this report for consistency. Differences in the two databases become large with increasing ionic strength. This is apparent when calculating ionic strengths. The ionic strength values quoted in Table 2 were calculated with the sit.dat database. For comparison, use of the Pitzer database would give an ionic strength of 8.39 (factor of 1.9 higher) for SR-300 groundwater, and an ionic strength of 0.357 (factor of 1.1 higher) for SR-20 groundwater. The main element species for two reference groundwaters (Table 2), as calculated using the SIT database, are presented in Table 3.

Table 3: Element Speciation in Reference Groundwaters Predicted by PHREEQC/SIT

Element	SR-300: Ca-Na-Cl, reducing	SR-20: Na-Cl, less reducing
Cu	Cu^+	Cu^+, Cu^{+2}
As	$H_3(AsO_3)$	$H(AsO_4)^{-2}$, $H_2(AsO_4)^-$, *$H_3(AsO_3)$*
Se	HSe^-	$HSeO_3^-$
Zr	$Zr(OH)_4$	$Zr(OH)_4$
Nb	$Nb(OH)_6^-$, *$Nb(OH)_5$*	$Nb(OH)_6^-$, $Nb(OH)_5$, $Nb(OH)_7^{-2}$
Mo	MoO_4^{-2}	MoO_4^{-2}
Tc	$TcO(OH)_2$	TcO_4^-, $TcO(OH)_2$
Pd	$PdCl_4^{-2}$, *$PdCl_3^-$*	$PdCl_4^{-2}$, $PdCl_3^-$, $Pd(OH)_2$
Sn	$Sn(OH)_4$, *$Sn(OH)_5^-$*	$Sn(OH)_4$, *$Sn(OH)_5^-$*
Pb	$PbCl_4^{-2}$, $PbCl_3^-$, *$PbCl_2$*	$PbCl^+$, $PbCl_2$, Pb^{+2}, $Pb(CO_3)$, *$Pb(SO_4)$, $PbCl_3^-$, $PbCl_4^{-2}$*
Bi	$BiCl_4^-$	$Bi(OH)_2^+$, $Bi(OH)_3$
Ra	Ra^{+2}, $RaCl_2$, $RaCl^+$	Ra^{+2}, $Ra(SO_4)$, *$RaCl^+$*
Th	$Th(OH)_3^+$, $Th(OH)_2^{+2}$, $Th(OH)_4$, *$Th(OH)_3(CO_3)^-$, $Th(OH)_2(CO_3)$, $Th(OH)^{+3}$*	$Th(OH)_3(CO_3)^-$, $Th(OH)_2(CO_3)_2^{-2}$, $Th(OH)_2(CO_3)$
Pa	PaO_2^+, *$PaO_2(OH)$*	PaO_2^+, *$PaO_2(OH)$*
U	$U(OH)_4$, $U(OH)_3^+$	$UO_2(CO_3)_3^{-4}$, $UO_2(CO_3)_2^{-2}$
Np	$Np(OH)_4$, $Np(OH)_3^+$	$Np(OH)_4$, $Np(CO_3)(OH)_3^-$, *$Np(OH)_3^+$*, NpO_2^+
Pu	Pu^{+3}, *$Pu(OH)^{+2}$*	Pu^{+3}, $Pu(SO_4)^+$, $Pu(CO_3)^+$, $Pu(OH)_4$, $Pu(CO_3)_2(OH)_2^{-2}$, $Pu(OH)_3^+$
Am	Am^{+3}, $AmCl^{+2}$, *$AmCl_2^+$, $Am(OH)^{+2}$*	Am^{+3}, $Am(HCO_3)^{+2}$, *$Am(CO_3)^+$, $Am(SO_4)^+$, $AmCl^{+2}$*

Note: Species in italics represent 1 to 9% of the total concentration

The data compiled in this report were for the most part obtained from batch sorption experiments simply because they represent the greatest source of information. An attempt was made to collect data for the highest possible ionic strength conditions, and a range of pH values that would include or span pH 6. Sorption coefficients (m^3/kg) are plotted as function of ionic strength (mol/L) and pH to identify variability with these parameters. If an element's sorption values are close to pH 6 or else do not vary with pH, then sorption at the highest ionic strength is considered. If sorption does not vary with ionic strength, then the focus was on finding values close to pH 6. As discussed previously, some elements are sensitive to redox conditions. In those cases, sorption values are identified for both oxidizing and reducing conditions. In this case, waters with Eh lower than 100 mV are considered to be reducing.

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 an overall comparison of element speciation in the two reference groundwaters.

The reporting of sorption data is initiated 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 a range of ionic strengths that would include seawater and brine solutions. The pH range should include the near neutral values of 6 to 7. The collected sorption data is plotted to identify useful trends with respect to ionic strength and pH. Sorption values of interest for rocks and minerals that best fit water composition for brine solutions are selected. These were not always a good fit with respect to pH and ionic strength. Finally, the selected data were used to compile data that best represents sorption on bentonite, shale and limestone. The tabulated data include a range of sorption coefficients, and for cases where there are three or more values a geometric mean value along with a geometric standard deviation are presented.

The relevant data range of pH and ionic strength are given for the data. No attempt was made here to extrapolate lower ionic strength data to reference groundwater conditions.

3.1 CARBON

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

Ticknor and Vandergraaf (1996) reported that carbon-14 sorption values for calcite varied from 0.022 to 0.090 m^3/kg. Andersson et al. (1982) reported sorption values for calcite in synthetic groundwater at pH 8.1 that varied from 0.0017 to 0.009 mol/L over a 35 day period. Carbon-14 sorption coefficients on Avonlea bentonite determined by diffusion experiments varied between 1×10^{-4} and 3×10^{-4} m^3/kg (Oscarson and Hume, 1994). Carbon-14 sorption on the minerals illite, chlorite and quartz, which are the main components of shale, was assumed to be 0 (Ticknor and Vandergraaf, 1996). Bradbury and Baeyens (2003a) proposed a conservative value of 2×10^{-5} m^3/kg for the sorption of inorganic carbon on MX-80 bentonite over a pH range of 6.9 to 7.25 and an ionic strength of 0.7 mol/L. Sorption of organic carbon was assumed to be 0. Bradbury and Baeyens (2003b) suggested inorganic carbon sorption coefficients for Opalinus clay of 1.6×10^{-3} m^3/kg at pH 6.3 and 6.0×10^{-3} m^3/kg at pH 7.8 (ionic strength was 0.2 mol/L). The main components of Opalinus clay are 20 wt% quartz, 18 wt% illite, 17 wt% kaolinite, 16 wt% calcite, 14 wt% illite/smectite, and 5 wt% chlorite. Since carbon exchange with calcite is assumed, the inorganic sorption values for Opalinus clay may not be appropriate for a carbonate-poor shale. 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 on the assumption that the calcite minerals were not accessible to isotopic exchange with carbon-14.

Table 4 summarizes available sorption values for carbon on bentonite and limestone. The range of sorption values for bentonite is based on the recommendations of Bradbury and

Baeyens (2003) and the transport experiments of Oscarson and Hume (1994). The recommended values for limestone are based on carbon-14 sorption on calcite, reported by Vandergraaf and Ticknor (1996).

Table 4: Recommended Sorption Coefficients for Carbon

CARBON – INORGANIC				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.7**	**6.9 to 7.3**	**2 x 10^{-5} to 3 x10^{-4}**	**8.4 x 10^{-5} (3.9)**
comment	Conservative estimate proposed by Bradbury and Baeyens (2003a) and transport experiments of Oscarson and Hume (1994).			
Shale	**-**	**-**	**0**	**-**
comment	Conservative assumption			
Limestone	**-**	**-**	**0.0017 to 0.090**	**0.030 (5.6)**
comment	Based on calcite data from Ticknor and Vandergraaf (1996) and Andersson et al. (1982).			
CARBON – ORGANIC				
			K_d Values (m^3/kg)	
	I (mol/L)	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.

3.2 COPPER

Copper is a transition element present. Under reducing conditions, copper will be present as a monovalent cation, while under more oxidizing conditions both monovalent and divalent copper ions will be present. Copper solution chemistry is affected by carbonate and hydroxyl complexes, particularly at higher pH values.

Gu et al. (2010) modelled Cu sorption on montmorillonite and found that in the pH range 3 to 6, Cu sorption was very sensitive to the ionic strength because sorption was by outer sphere complexes. At higher pH values, 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 sorption was by inner sphere surface complexation that did not change over a 2.5 year period.

Vilks et al. (2011) reported results of Cu sorption on bentonite, shale and limestone in Na-Ca-Cl solutions with ionic strengths varying from 0.2 to 7.5 mol/L, and pH values between 6 and 8. Copper sorption on bentonite, shale and limestone is affected by brine composition, due to the effects of ionic strength and pH as illustrated in Figure 3. The Ca in solution is likely to compete with Cu for sorption sites. Copper sorption on bentonite over a pH range of 6.8 to 8.0 varied from 0.007 to 0.26 m^3/kg. Sorption on shale at pH 6.4 to 7.5 varied from 0 to 0.49 m^3/kg. Copper sorption values measured with limestone over a pH range of 6.2 to 7.5 varied from 0 to 0.123 m^3/kg. Table 5 summarizes copper sorption values on sedimentary rocks.

Table 5: Recommended Sorption Coefficients for Copper

COPPER (II)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.2 to 7.5**	**6.8 to 8.0**	**0.007 to 0.26**	**0.022 (4)**
comment	Vilks et al. (2011)			
Shale	**0.2 to 7.5**	**6.4 to 7.5**	**0.0001 to 0.49**	**0.008 (23)**
comment	Vilks et al. (2011)			
Limestone	**0.2 to 7.5**	**6.2 to 7.5**	**0.0002 to 0.12**	**0.010 (12)**
comment	Vilks et al. (2011)			

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

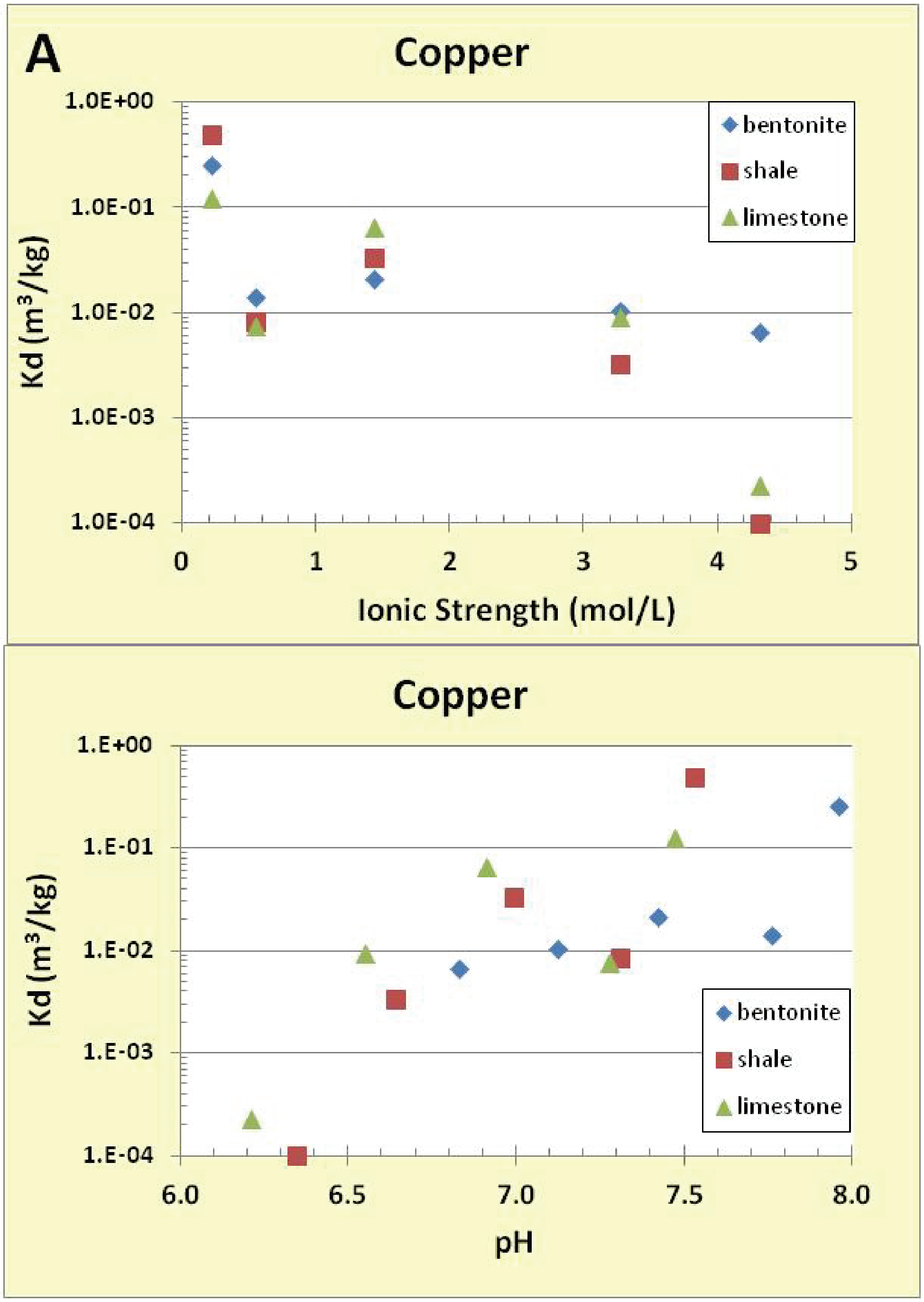


Figure 3: Copper Sorption on Bentonite, Shale and Limestone from Na-Ca-Cl Solutions with Respect to (A) Ionic Strength, and (B) pH (Data are from Vilks et al., 2011)

3.3 ARSENIC

Arsenic is a group 15 non-metal element. PHREEQC (SIT database) predicts that under reducing conditions arsenic is found in the III oxidation state (arsenite) as $H_3(AsO_3)$, while under more oxidizing conditions arsenic is present in both the III oxidation state, as $H_3(AsO_3)$, and in the V oxidation state (arsenate), mainly as the anionic $H_2(AsO_4)^-$ and $H(AsO_4)^{-2}$ species. Arsenite tends to be more mobile than arsenate. Arsenite sorption increases with pH to a maximum around pH 8, while arsenate sorption decreases with higher pH as oxide surfaces become negatively charged.

Data for As sorption was not reported by Vandergraaf and Ticknor (1994), and is not present in the Japanese Sorption Database (http://migrationdb.jaea.jp). Manning and Goldberg (1996) measured As(V) sorption on kaolinite, illite and montmorillonite at a variable pH and an ionic strength of 0.1 mol/L. Goldberg and Johnston (2001) studied As(V) and As(III) sorption on Al and Fe oxide in NaCl solutions with concentrations of 0.01 and 1.0 mol/L. As(V) sorbs by inner sphere complexes on Al and Fe oxides. Sorption of As(V) on Al oxide was independent of salt concentration, while sorption on Fe oxide increased with ionic strength. As(III) sorbed by inner and outer sphere complexes on Fe oxide, but only by outer sphere complexes to Al oxide. Paikaray et al. (2005) reported As(III) sorption on Vindhyen shale at pH 5 and ionic strength 0.01 mol/L. So et al. (2008) reported As(V) sorption on calcite, and noted that As(III) did not sorb on calcite. Manning and Goldberg (1997) reported on As(III) sorption on kaolinite, montmorillonite and illite.

Figure 4 illustrates sorption coefficients for As(V) on calcite, montmorillonite and illite as a function of ionic strength and pH. Figure 5 shows the variation in As(III) sorption coefficients on montmorillonite, shale, illite and Fe oxide in a similar way. The data were extracted from the above mentioned references.

Considering a pH value of 6 to 7 and an ionic strength of 0.1 mol/L, As(V) sorption coefficients (m^3/kg) of interest are 0.27 to 0.28 for bentonite, and 0.42 to 0.67 for illite. Sorption on shale can be approximated with the sorption data on illite, assuming that this data is representative of the sorption properties of the clay making up 60% of the shale. Arsenic sorption on limestone was approximated with sorption data on calcite (0.079 to 0.57 m^3/kg), that was determined with an ionic strength of 0.034 to 0.073 mol/L and a pH range of 7 to 7.5. As(III) sorption coefficients (m^3/kg) of interest at an ionic strength of 0.1 mol/L and a pH range of 6 to 7 are 0.302 for bentonite and 0.6 to 1.03 for illite. Sorption coefficients determined for shale at a pH of 5 and an ionic strength of 0.1 mol/L ranged from 0.031 to 0.091 m^3/kg. The sorption values measured directly with shale are probably the better representation of As(III) sorption on shale. Table 6 summarizes arsenic sorption values for sedimentary rocks.

Table 6: Recommended Sorption Coefficients for Arsenic

ARSENIC (V) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.1**	**6 to 7**	**0.27 to 0.28**	**0.275 (1.0)**
comment	Manning and Goldberg (1996). Range based on 2 values.			
Shale	**0.1**	**6 to 7**	**0.25 to 0.30**	**0.274 (1.1)**
comment	Based on illite from Manning and Goldberg (1996) and assumed 60% illite content in shale. Range based on 2 values.			
Limestone	**0.07**	**7 to 7.5**	**0.079 to 0.57**	**0.222 (2.3)**
comment	Based on calcite data from So et al. (2008).			
ARSENIC (III) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.1**	**6 to 7**	**0.30**	**-**
comment	Manning and Goldberg (1997)			
Shale	**0.1**	**5**	**0.031 to 0.091**	**0.041 (1.6)**
comment	Paikaray et al. (2005); K_d might increase slightly in the pH range 6 to 7.			
Limestone	**-**	**-**	**0**	**-**
comment	So et al. (2008) noted no As(III) sorption on calcite.			

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

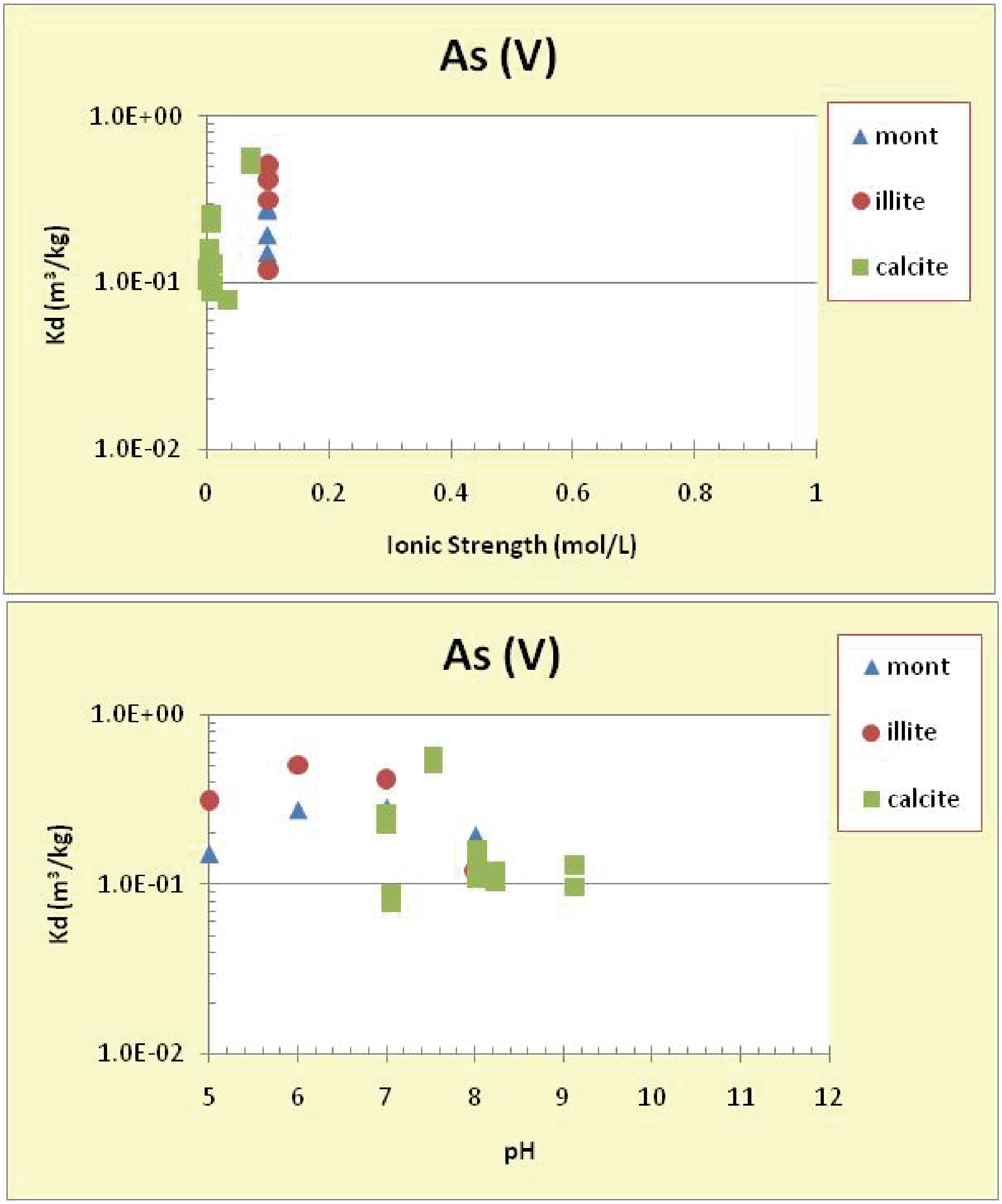


Figure 4: Arsenic (V) Sorption Coefficients on Calcite, Illite and Montmorillonite

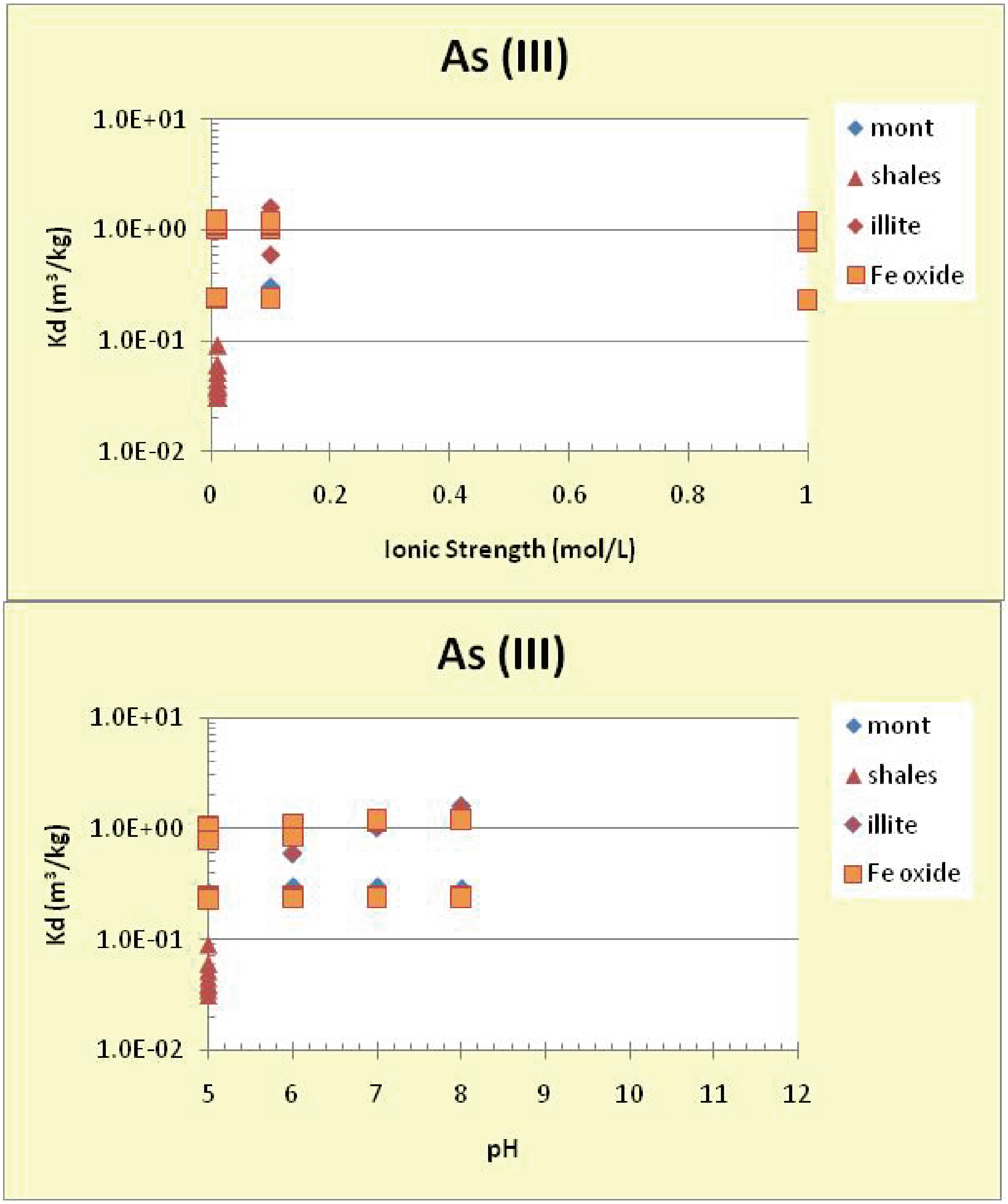


Figure 5: Arsenic (III) Sorption Coefficients on Montmorillonite, Shale, Illite and Fe Oxides

3.4 SELENIUM

Selenium is a group 16 non-metal element, with oxidation states of –II, 0, IV and VI. In oxidizing conditions open to the atmosphere, the VI 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 pH, ionic strength and mineral surface properties (Charlet et al., 2007). Under mildly reducing conditions, the IV oxidation state becomes the dominant dissolved species, producing the anionic $HSeO_3^-$ selenite anion. 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 the 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 –II oxidation state dominates, producing the anionic HSe^- selenide species. The selenium speciation is predicted to be dominated by HSe^- in the reference groundwater SR-300, while, the reference groundwater SR-20 solution chemistry is dominated by Se(IV) as selenite. It should be noted that Se is likely to precipitate as Se(s) in SR-20 if the total Se concentration exceeds 1×10^{-15} mol/L.

Ticknor et al.(1988) measured Se sorption on a number of fracture filling minerals, including calcite, chlorite, illite-muscovite, kaolinite, goethite and hematite under oxidizing and reducing conditions. Ticknor and McMurray (1996) reported Se sorption on goethite and granite under oxidizing conditions. Sorption data on bentonite for oxidizing and reducing conditions was provided by Barney (1981), Tachi et al. (1999), and Shibutani et al. (1994). Selenium sorption data for oxidizing conditions are summarized in Figure 6, while Figure 7 provides data for reducing conditions. Sorption values for oxidizing conditions indicate that Se sorption on chlorite and calcite decreases with increasing ionic strength, while sorption on goethite and hematite is not affected. The Se sorption values do not show any clear trends with pH values. Under reducing conditions, Se sorption values for calcite decreased slightly with higher ionic strength, while data for chlorite, hematite and bentonite did not display any clear trends. Sorption on chlorite appeared to decrease at higher ionic strength, but sorption on calcite and bentonite did not display any clear trends with pH.

Sorption values (m^3/kg) of interest for oxidizing conditions were 0.014 to 0.016 for bentonite (ionic strength of 0.02 mol/L and pH 10), which were determined for an Eh of 200 mV, corresponding to the stability region for selenite. Sorption values for shale were based on chlorite data (0.031 m^3/kg) measured with an ionic strength of 1.27 mol/L and a pH of 7.5. It was assumed that the chlorite content in shale was 60 percent. Sorption values for limestone were based on calcite data (ionic strength of 1.27 mol/L and pH 7.5). The redox conditions for chlorite and calcite corresponded to selenate stability.

Under reducing conditions, sorption values (m^3/kg) of interest are 0.015 to 0.17 for bentonite (ionic strength of 0.1 mol/L and pH 5.9 to 7.9), and sorption for shale was estimated from data for chlorite (0.021 m^3/kg) measured with an ionic strength of 1.54 mol/L and a pH of 7.50. A chlorite content of 60 percent was assumed for shale. Sorption for limestone was based on a value of 0.0037 m^3/kg measured with calcite with an ionic strength of 1.54 mol/L and a pH of 7.5. Table 7 summarizes sorption values for selenium on sedimentary rocks.

Table 7: Recommended Sorption Coefficients for Selenium

SELENIUM (IV, VI) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.02**	**10**	**0.014 to 0.016**	**0.015 (1.1)**
comment	Barney (1981); Likely Se(IV). Value is tenuous since ionic strength is low and pH is high.			
Shale	**1.54**	**7.5**	**0.019**	**-**
comment	Estimated using chlorite from Ticknor et al.(1988), likely Se(VI). Assumed shale contained 60% chlorite.			
Limestone	**1.54**	**7.5**	**0.0013**	**-**
comment	Based on calcite data from Ticknor et al.(1988), likely Se(VI).			
SELENIUM (-II) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.1**	**5.9 to 7.9**	**0.015 to 0.17**	**0.054 (1.1)**
comment	Tachi et al.(1999)			
Shale	**1.54**	**7.5**	**0.0125**	
comment	Estimated using chlorite from Ticknor et al.(1998). Assumed shale contained 60% chlorite.			
Limestone	**1.54**	**7.5**	**0.0037**	**-**
comment	Based on calcite data from Ticknor et al.(1988).			

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

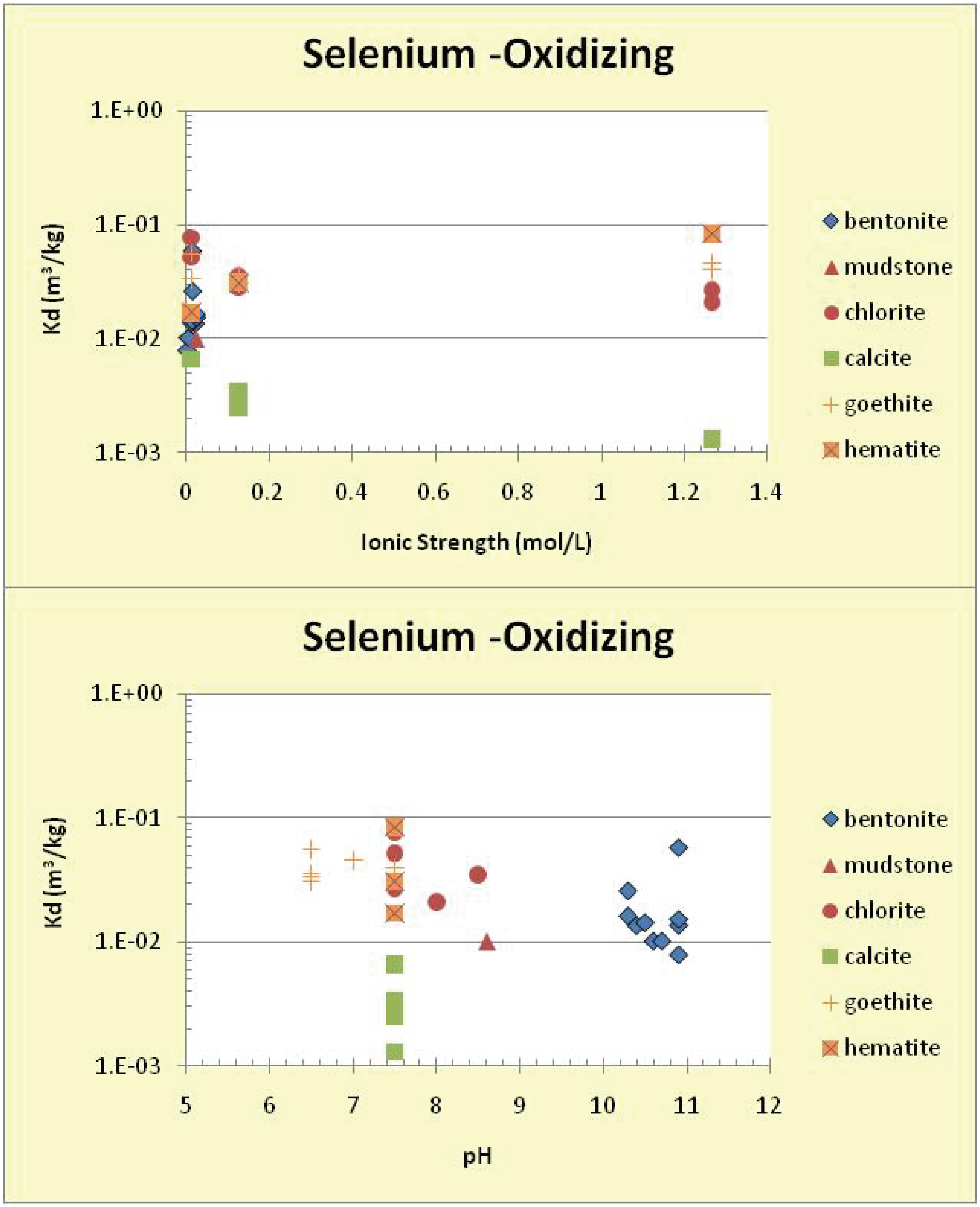


Figure 6: Selenium Sorption Coefficients on Bentonite, Mudstone, Chlorite, Calcite, Geothite and Hematite Under Oxidizing Conditions

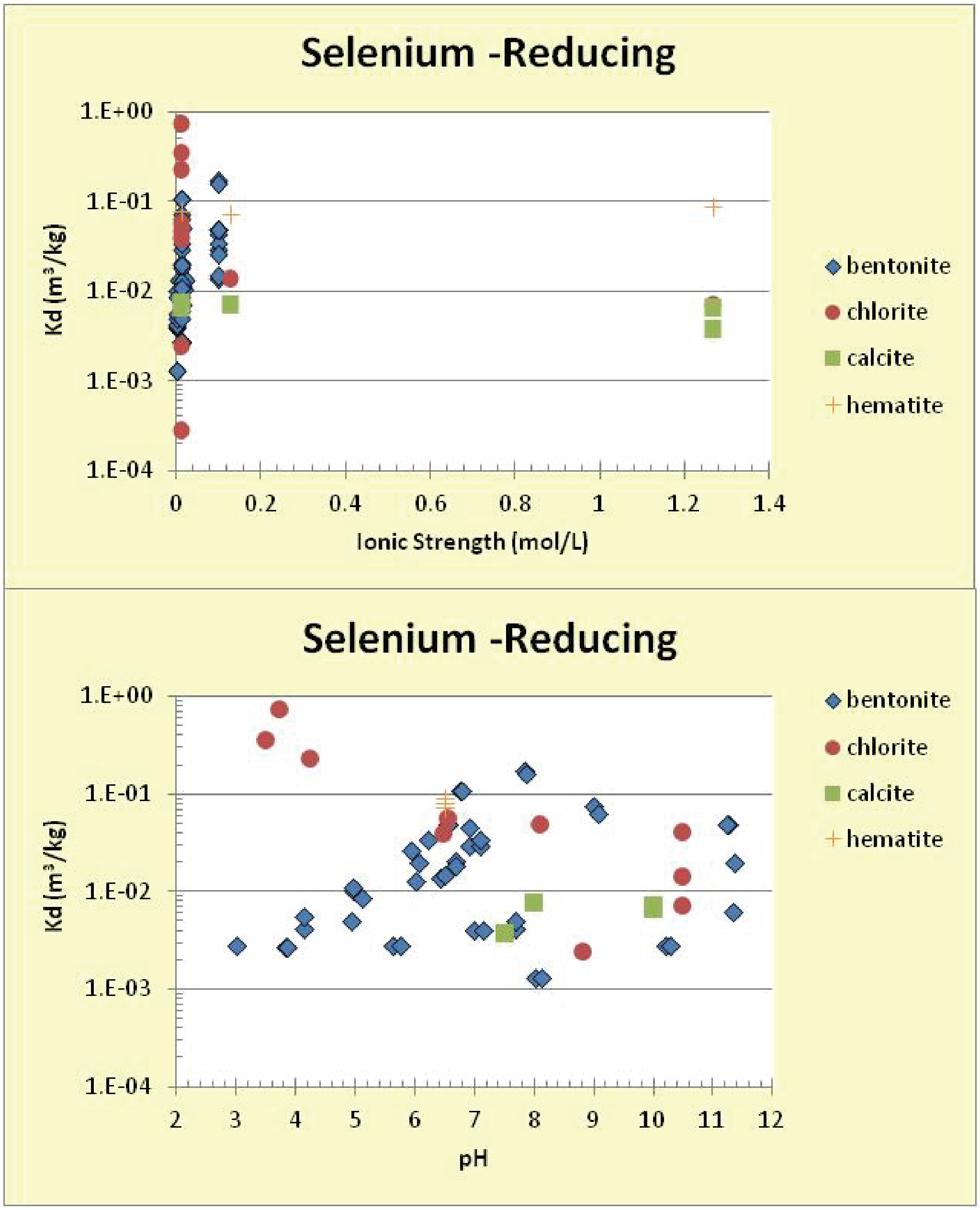


Figure 7: Selenium Sorption Coefficients on Bentonite, Chlorite, Calcite and Hematite Measured Under Reducing Conditions

3.5 ZIRCONIUM

Zirconium is a transition metal element with an oxidation state of IV. 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.

Zirconium sorption data for bentonite were reported by Allard et al. (1979) and Taki and Hata (1991). Rochon et al. (1980) provide date for illite. Zirconium sorption is illustrated in Figure 8, showing that sorption decreases with increasing pH as illustrated by the trend for illite. Salter et al. (1981) predicted that Zr sorption would decrease with pH at pH values above 6.3.

The Zr sorption values determined in seawater were slightly higher than measured in dilute water. The difference might be related to phase separation, or that Zr colloids were not present at higher ionic strength. Since Zr sorption does not decrease with higher ionic strength, all sorption values measured with reaction times of 7 days and lower were considered for bentonite. The sorption coefficient for bentonite ranged from 0.05 to 1.6 m^3/kg. The sorption values for illite were 200 and 1000 m^3/kg, measured at an ionic strength of 0.002 mol/L and a pH of 6 to 8. Although Zr sorption measurements on illite were made at a low ionic strength, it is assumed that it is still valid at high ionic strength since the dominant Zr species in solution are neutral and would sorb by surface complexation. However, the sorption values for bentonite appear to be about 3 orders of magnitude lower than for shale, which is surprising given bentonite's higher surface area. Bradbury et al. (2010) used Hf(IV) as a chemical analog element for Zr(IV) and proposed a K_d value of 42 m^3/kg for generic Swiss argillaceous rocks in contact with solutions with ionic strengths of 0.13 to 0.4 mol/L and a pH value of 6. SKB's Data report for the safety assessment SR-Can (SKB, 2006) reports Zr K_d values for bentonite that range from 0.1 to 134 m^3/kg, with recommended values of 4 and 5 m^3/kg for non-saline, saline (ionic strength of 0.2 mol/L) and highly saline (ionic strength 0.7 mol/L) groundwaters respectively. These values were derived using Th(IV) as a chemical analog (Ochs and Talerico, 2004). The sorption data were considered valid for ionic strengths from 0.2 to 0.7 mol/L and pH values from 7 to 7.4.

Table 8 summarizes recommended Zr sorption values for sedimentary rocks. Using a conservative approach, the measured sorption data was used for bentonite instead of the higher values derived from Th(IV). The recommended data for shale was based on Bradbury et al. (2010) recommendation, combined with measured data for illite.

Table 8: Recommended Sorption Coefficients for Zirconium

ZIRCONIUM (IV)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.72**	**7.1 to 8.2**	**0.05 to 1.6**	**0.36 (4.1)**
comment	Allard et al. (1979); Takki and Hata (1991).			
Shale	**0.002 to 0.4**	**6.0 to 8.3**	**42 to 600**	**159 (6.6)**
comment	Bradbury et al. (2010), using the illite data of Rochon et al. (1980), which is adjusted for 60 wt% content of shale.			
Limestone			**-**	**-**
comment	No data			

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

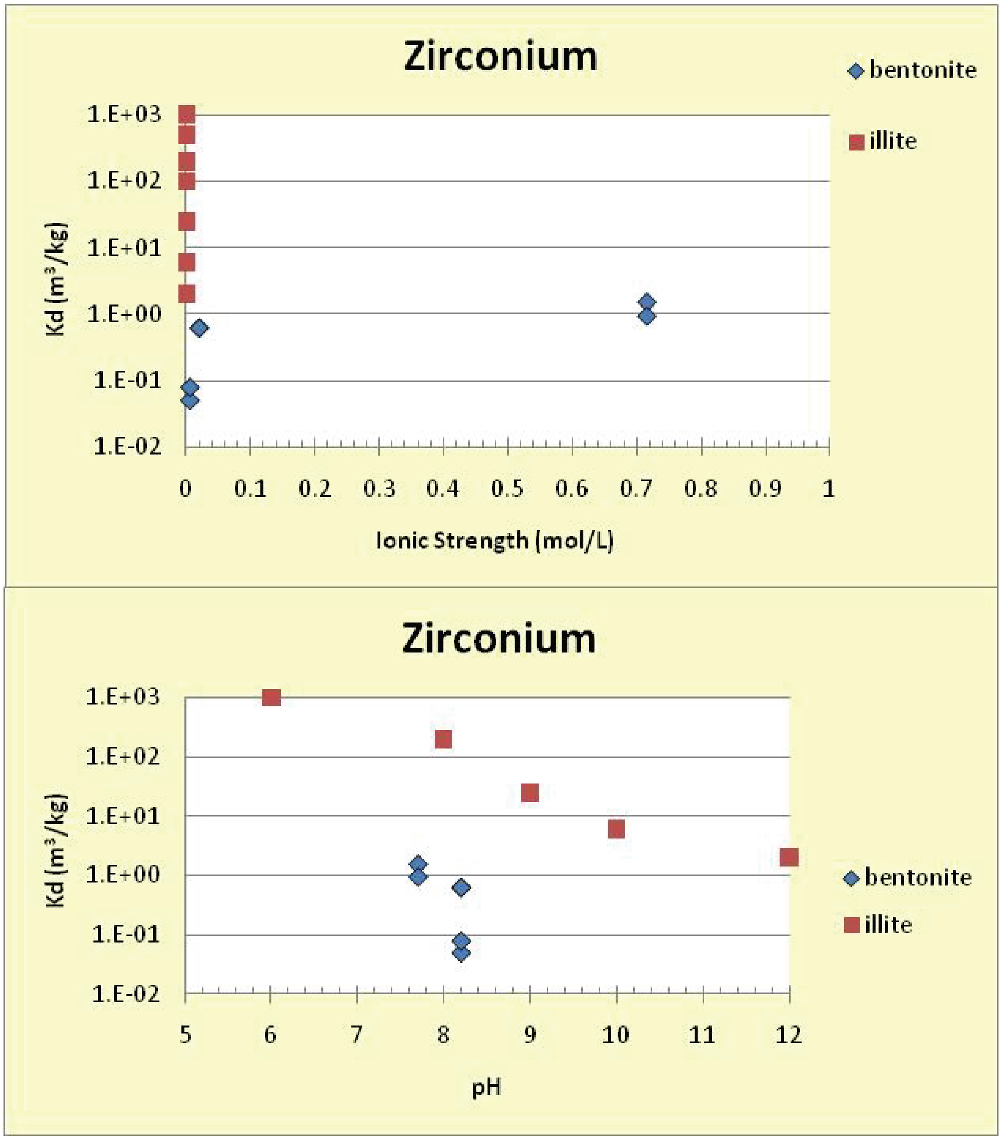


Figure 8: Zirconium Sorption Coefficients on Bentonite and Illite

3.6 NIOBIUM

Niobium is a transition metal element with an oxidation state of V. The dominant solution species in the reference groundwaters are $Nb(OH)_6^-$ and $Nb(OH)_5$ (PHREEQC, SIT database). Niobium solid phases include Nb_2O_5 and niobite $[(Fe,Mn)(Nb,Ta)_2O_8]$.

Niobium sorption on mudstone and bentonite were reported by Duursma and Bewers (1986), Duursma and Bosch (1970), Duursma and Eisma (1973), and Taki and Hata (1991). Ticknor and Vandergraaf (1996) reported niobium sorption values at pH 7.5 and ionic strength of 0.2 mol/L for quartz (0.20 m^3/kg), hematite (16 m^3/kg), and sand-clay mixtures (0.026 to 0.89 m^3/kg).

Niobium sorption coefficients are summarized in Figure 9. The effect of salinity is not clear, and the pH range was too narrow to make conclusions regarding the pH effect. Given niobium's oxidation state and affinity for oxygen, niobium is expected to sorb in brine solutions by surface complexation. Sorption of niobium on mudstone in seawater provides support for the surface complexation assumption. Sorption values measured in sea water (ionic strength of 0.72 mol/L and pH 7.1 to 7.8) are given the highest priority. Sorption values (m^3/kg) of interest are 1.2 to 1.8 for bentonite and 1.4 to 2.8 for mudstone. Sorption value on quartz at an ionic strength of 0.19 mol/L and pH of 7.5 was 0.20 m^3/kg.

Stenhouse (1995) proposed a realistic sorption value of 1.0 m^3/kg for bentonite, based on Zr(IV) data reported by Allard et al. (1979), and a conservative value of 0.1 m^3/kg, based on pH considerations. Stenhouse (1995) proposed a realistic sorption value of 0.5 m^3/kg for marl, based on Nb(V) sorption on marl. Acknowledging that Nb(V) sorption may decrease by an order of magnitude with increasing pH, a conservative sorption value of 0.05 m^3/kg was proposed.

Table 9 summarizes Nb sorption values recommended for sedimentary rocks.

Table 9: Recommended Sorption Coefficients for Niobium

NIOBIUM (V)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.72**	**7.1 to 7.5**	**1.2 to 1.8**	**1.5 (1.3)**
comment	Taki and Hata (1991)			
Shale	**0.72**	**7.8**	**1.4 to 2.8**	**1.7 (1.5)**
comment	Based on mudstone. Taki and Hata (1991).			
Limestone			**-**	**-**
comment	No data			

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

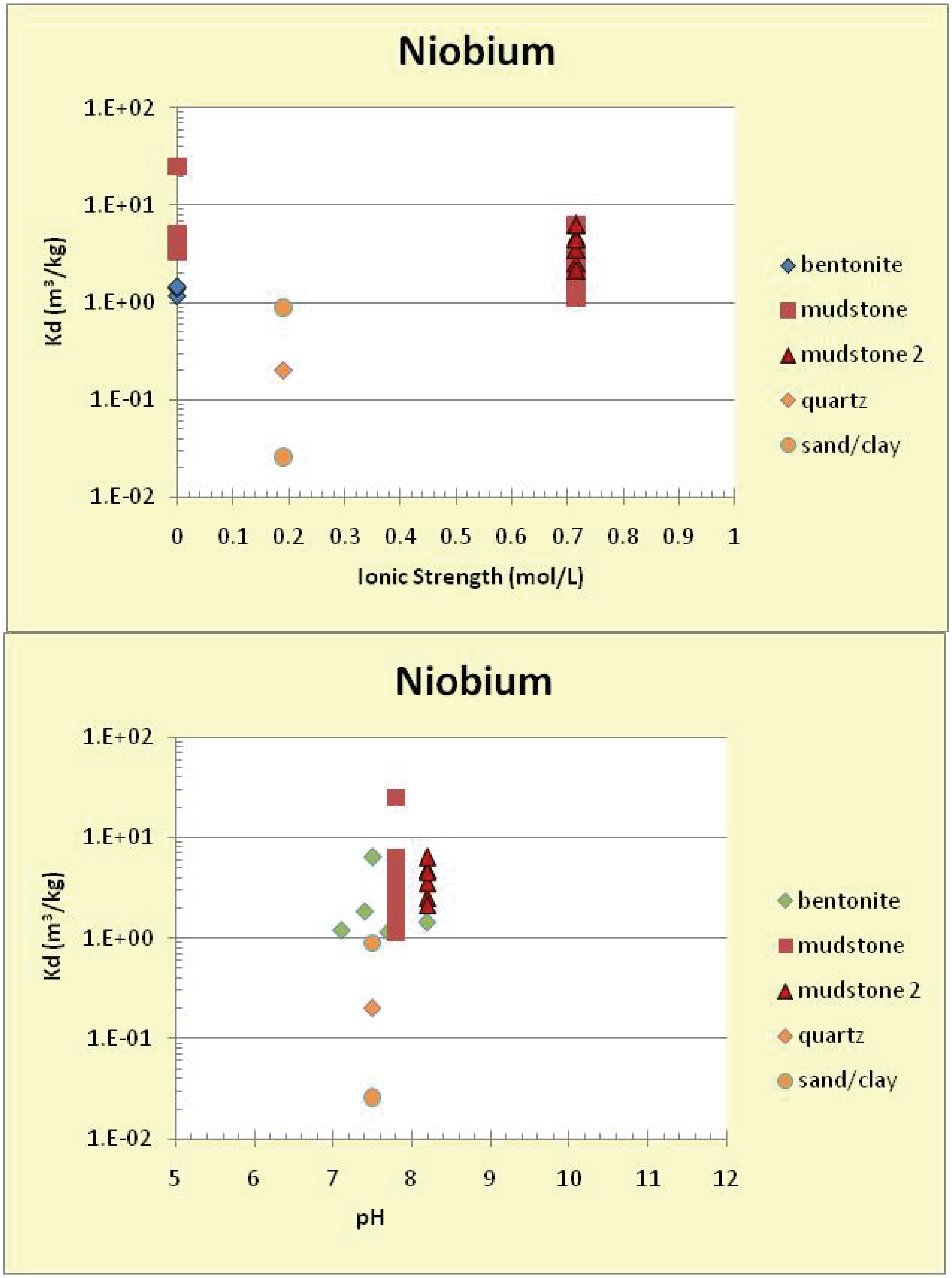


Figure 9: Niobium Sorption Coefficients on Bentonite, Mudstone, Sand/clay and Quartz

3.7 MOLYBDENUM

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

Vandergraaf and Ticknor (1994) assigned a sorption coefficient value of 0 for all minerals of interest. Molybdenum sorption on mudstone was reported by Erdal et al. (1977), and sorption on bentonite was given by Inoue and Morisawa (1975). The data is limited to an ionic strength of 0.0035 mol/L (Figure 10) and an approximate pH range of 4.5 to 8.2. The pH data is not specific enough to permit a plot of K_d versus pH. The Mo sorption coefficient on bentonite was 0.013 to 0.4 m^3/kg, while that on mudstone was 0.016 to 0.27 m^3/kg.

Since molybdenum has a VI oxidation state and has an affinity for oxygen, one might expect to see some coordination to surface oxygens in the form of inner sphere surface complexes. One could consider U(VI) as a chemical analog to Mo(VI). Vilks et al. (2011) determined U(VI) sorption coefficients on bentonite that ranged from 0.014 to 0.51 m^3/kg, and sorption values on shale that were 0.002 to 0.051 m^3/kg. Molybdenum sorption values for bentonite are in a similar range to those of U(VI), and larger than U(VI) sorption on on shale by a factor 10. Given the absence of Mo sorption data for limestone or calcite, U(VI) was used as a chemical anlog for Mo(VI) and the U(VI) sorption data for Ordovician limestone are the recommended Mo sorption values for limestone.

Table 10 summarizes Mo sorption values for sedimentary rocks.

Table 10: Recommended Sorption Coefficients for Molybdenum

MOLYBDENUM (VI)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.004**	**4.5 to 8.2**	**0.01 to 0. 40**	**0.089 (3.3)**
comment	Inoue and Morisawa (1975). Values are tenuous due to very low ionic strength.			
Shale	**0.004**	**4.5 to 8.5**	**0.02 to 0.27**	**0.039 (3.7)**
comment	Based on sorption values reported for mudstone by Inoue and Morisawa (1975) and Erdal et al. (1977). Values are tenuous due to very low ionic strength.			
Limestone	**0.2 to 7.5**	**6.0 to 7.5**	**0.002 to 0.017**	**0.006 (3)**
comment	Based on using U(VI) as a chemical analog. Vilks et al. (2011)			

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

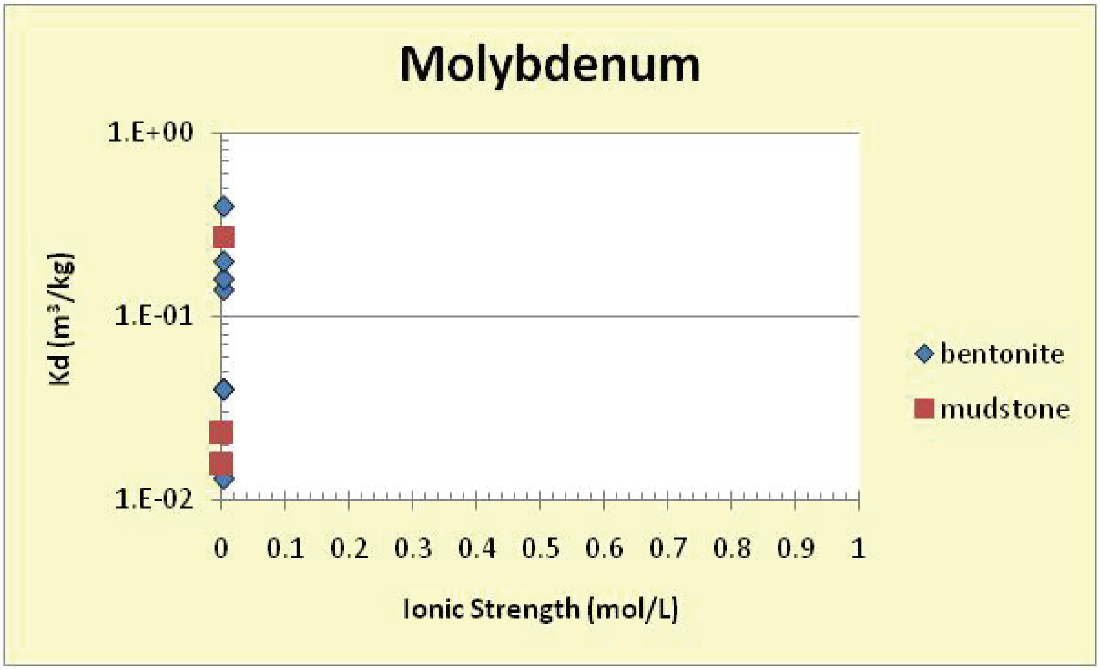


Figure 10: Molybdenum Sorption Coefficients on Bentonite and Mudstone

3.8 TECHNETIUM

Technetium is a transition metal element that may be present in groundwater in several oxidation states (II to VII), 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. Under reducing conditions Tc(IV) forms $TcO(OH)_2$, which has a low solubility and is prone to be strongly sorbed. PHREEQC (SIT database) predicts that in the more reducing reference groundwater Tc will be in the IV oxidation state, while in the less reducing reference groundwater would contain both the Tc(IV) and Tc(VII) species (Table 3). 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 the Fe-containing minerals. 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 data base must consist of two data sets one for oxidizing conditions and one for reducing conditions.

Technetium sorption on bentonite and montmorillonite under oxidizing and reducing conditions were provided by Barney (1981), Jedinakova-Krizova et al. (1998), Allard et al. (1979), Hooker et al. (1986), Baston et al. (1997), Mucciardi et al. (1979), Shade et al. (1984), Henrion et al. (1985), and Sheppard et al. (1990). Sorption on limestone, mudstone, shale and illite were provided by Ito and Kanno (1988), JGC Corporation (1991), Erdal et al. (1977), Mucciardi et al. (1979), Palmer and Meyer (1981), Francis and Bondietti (1979), and MaClean et al. (1978).

Sorption values under oxidizing conditions are given in Figure 11 and Figure 12, while sorption under reducing conditions is shown in Figure 13. Under oxidizing conditions the effect of ionic strength is not clear. Based on sorption values for shale, the ionic strength would have no effect. Sorption on bentonite type clays such as Kunigel clay appears to decrease with higher pH values, but the trend is not clear for the other solids. Under reducing conditions sorption on Kunigel appears to decrease with high pH, but the effect of pH is not clear for the other solids. The ionic strength does not appear to affect Tc sorption.

Sorption values of interest for oxidizing conditions for bentonite, shale, limestone and illite were selected for an ionic strength of 5 mol/L and pH 7.6 (Mucciardi et al., 1979). Sorption coefficients were 2.57×10^{-4} m^3/kg for bentonite, 7.3×10^{-5} to 7.9×10^{-2} m^3/kg for shale, 2.98×10^{-3} to 7.54×10^{-2} for limestone. Under reducing conditions sorption values of 4.2 to 10 m^3/kg were obtained for bentonite at an ionic strength of 0.68 mol/L and pH 8.2. Data report for the safety assessment SR-Can (SKB, 2006) reports Tc(IV) K_d values for bentonite that range from 1.4 to 1764 m^3/kg, with recommended values of 63 and 40 m^3/kg for saline (ionic strength of 0.2 mol/L) and highly saline (ionic strength 0.7 mol/L) groundwaters, respectively. These values were derived using Th(IV) as a chemical analog (Ochs and Talerico, 2004). The sorption data were considered valid for ionic strengths from 0.2 to 0.7 mol/L and pH values from 7 to 7.4. Sorption on chlorite with an ionic strength of 0.02 mol/L and pH 8.2 had a value of 1×10^{-3} m^3/kg. This value was used to estimate sorption on shale, assuming shale contained 60 percent chlorite. A Tc sorption coefficient of 1.72×10^{-2} m^3/kg was determined for calcite at an ionic strength close to 0 and a pH 8.5. Although Tc sorption under reducing conditions appears to be independent of ionic strength, using a single measurement on calcite to approximate sorption on limestone is tenuous.

Recommended Tc sorption values on sedimentary rocks are summarized in Table 11. It should be noted that the upper range of the sorption values used by SKB (2006) are significantly higher than the measured sorption values for bentonite reported by Baston et al. (1995, 1997). It could be that measured Tc(IV) values are low because of the inability to achieve reducing conditions in the laboratory. However, the measured sorption values are recommended to be conservative and since the SKB values were derived using Th(IV) as an analog.

Table 11: Recommended Sorption Coefficients for Technetium

TECHNETIUM (VII) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**5**	**7.6**	**2.6×10^{-4}**	**-**
comment	Based on montmorillonite. Mucciardi et al. (1979).			
Shale	**5**	**7.9**	**7.3×10^{-5} to 7.9×10^{-2}**	**0.0023 (33)**
comment	Mucciardi et al. (1979)			
Limestone	**5**	**7.7**	**3.0×10^{-3} to 7.5×10^{-2}**	**0.012 (5.3)**
comment	Mucciardi et al. (1979)			
TECHNETIUM (IV) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.7**	**8.2**	**4.2 to 10**	**7.2 (1.4)**
comment	Baston et al. (1995, 1997). Data at lower pH would be useful.			
Shale	**0.02**	**8.2**	**0.0007**	**-**
comment	Estimated from sorption measured on chlorite by Allard et al. (1979). Assumed shale contained 60% chlorite. Value seems rather low. Reducing conditions not confirmed.			
Limestone	**0**	**8.5**	**0.017**	**-**
comment	Ito and Kanno (1988); Tenuous due to only 1 data point and very dilute water. Reducing conditions not confirmed.			

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

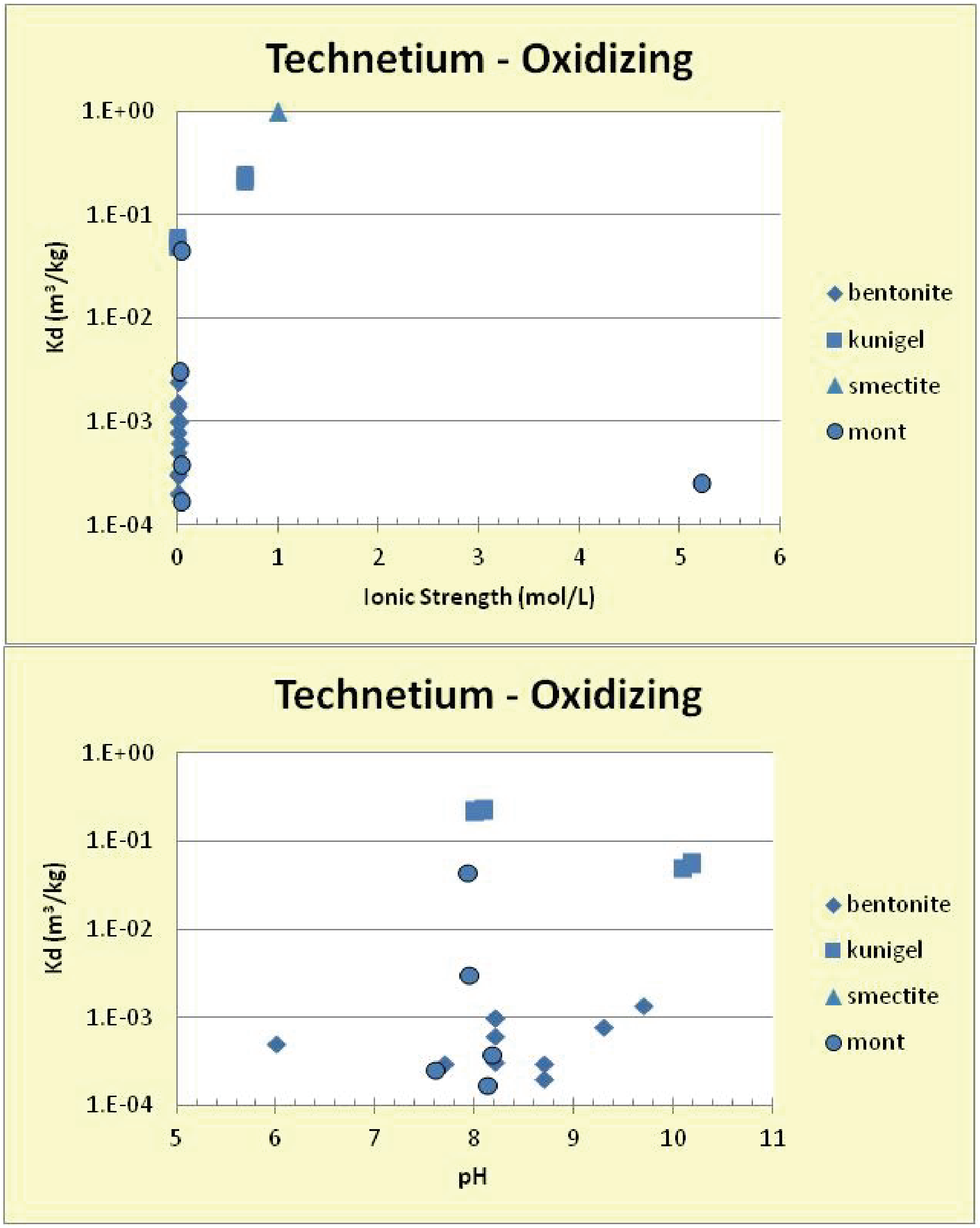


Figure 11: Technetium Sorption Coefficients on Clay Minerals Under Oxidizing Conditions

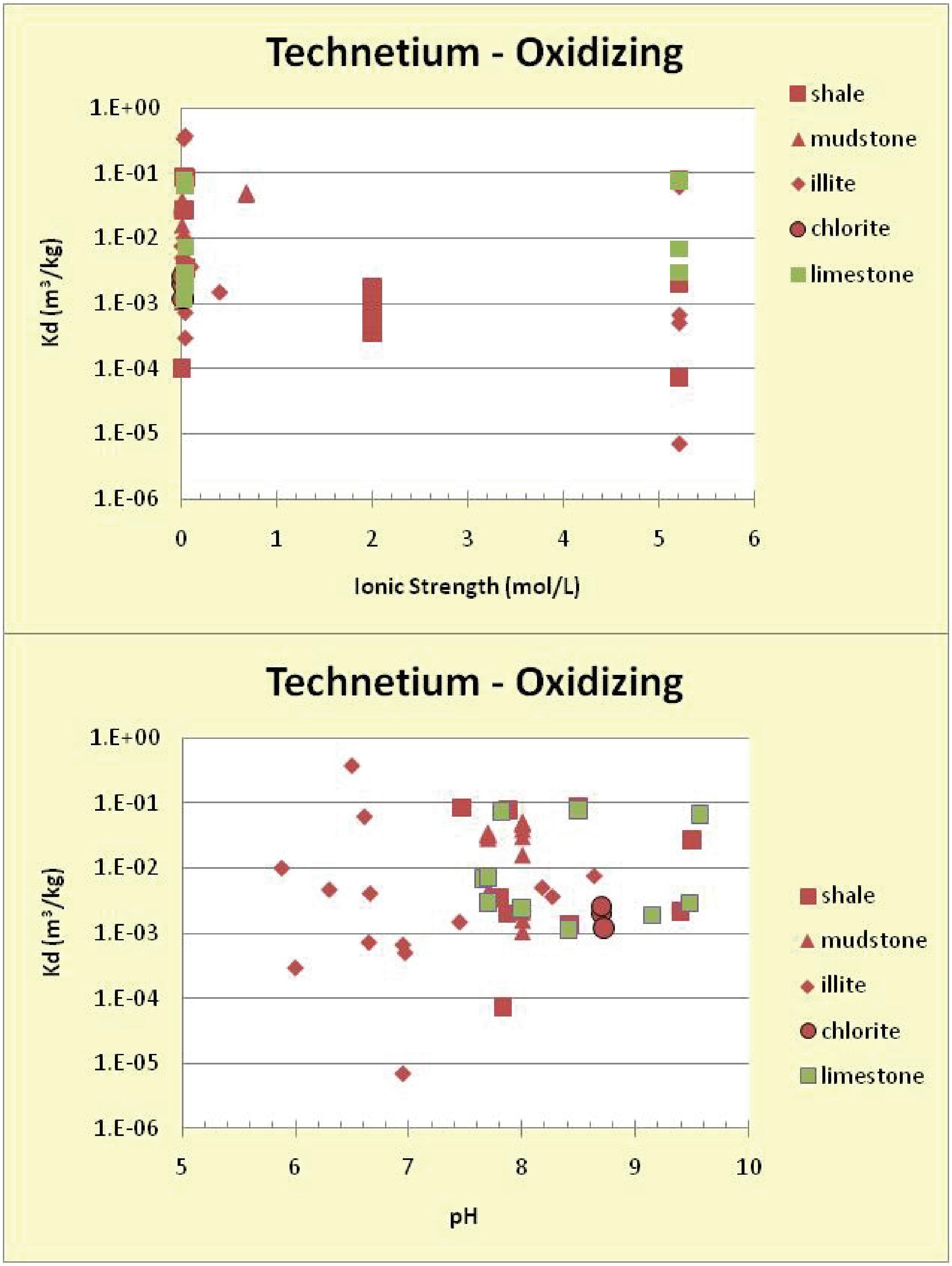


Figure 12: Technetium Sorption Coefficients on Shale, Mudstone, Limestone, Illite and Chlorite Under Oxidizing Conditions

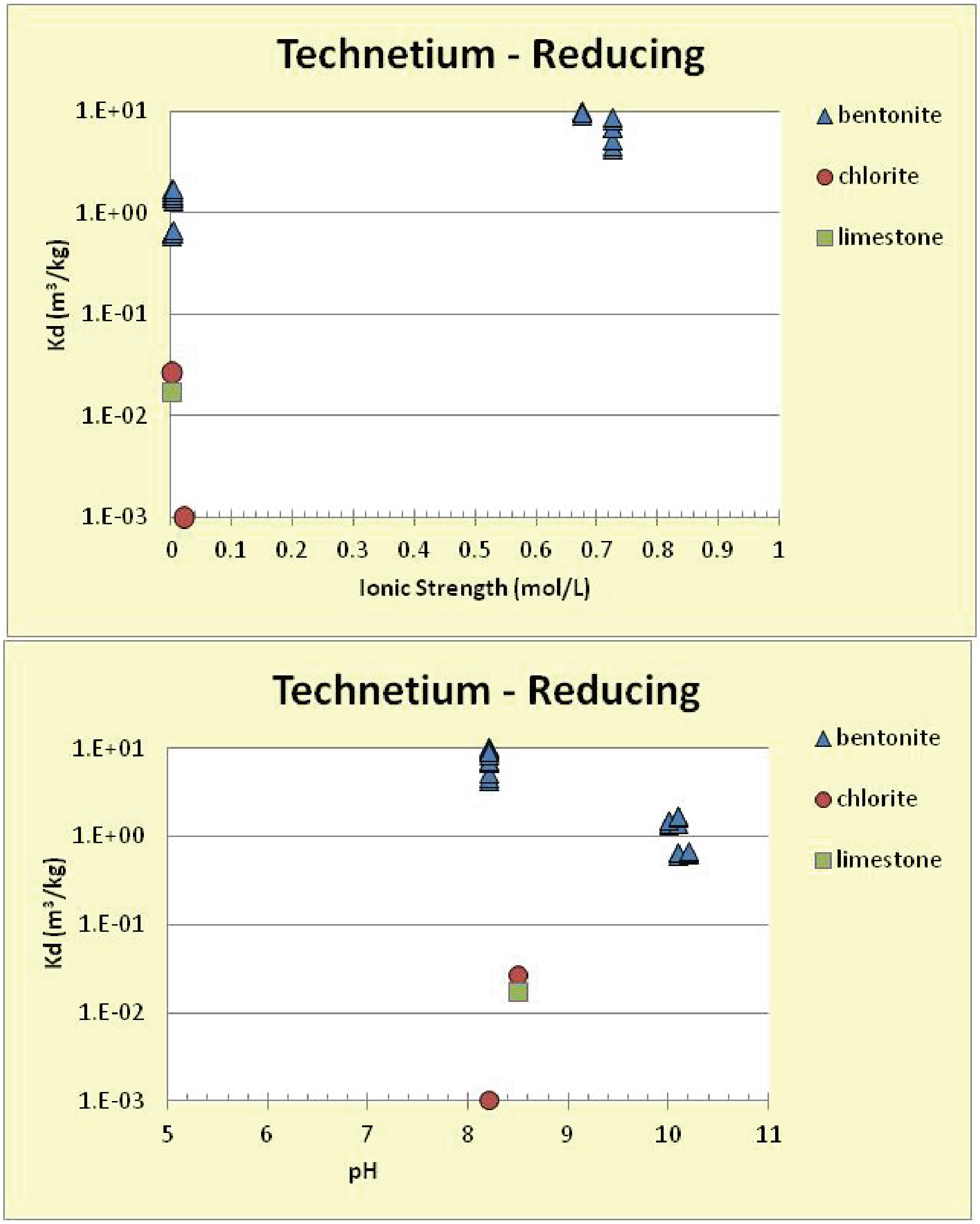


Figure 13: Technetium Sorption Coefficients on Bentonite, Kunigel bentonite, Limestone, and Chlorite Under Reducing Conditions

3.9 PALLADIUM

Palladium is a transition element with several valence states, the II 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 contain mainly the anionic $PdCl_4^{-2}$ and $PdCl_3^-$ species (Table 3). Vandergraaf and Ticknor (1994) suggested that the chemistry of palladium may be similar to that of Ni. However PHREEQC 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 is somewhat limited. Tachi et al. (1999) reported sorption data for bentonite, and granodiorite. The sorption values measured in 0.1 mol/L NaCl appear to be slightly lower than that in the 0.01 mol/L NaCl, possibly due to ionic strength or the complexing effect of chloride (Figure 14). Sorption also appears to decrease slightly with higher pH (Figure 14). Some of the variability in sorption values was created due to the experimental solution to solid ratio since sorption increased when there was more solution for a given solid mass. Sorption values of interest for bentonite were obtained for an ionic strength of 0.1 mol/L and a pH of 5 to 8. Sorption coefficients varied between 0.67 and 61.5 m^3/kg.

Given the lack of Pd sorption data for shale and limestone, one could consider Pb(II) as a chemical analog for Pd(II). Sorption values for palladium on sedimentary rocks are summarized in Table 12.

Table 12: Recommended Sorption Coefficients for Palladium

PALADIUM (II)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.1**	**5 to 8**	**0.67 to 61.5**	**11 (4.3)**
comment	Tachi et al. (1999)			
Shale	**0.25**	**6.0 to 6.5**	**0.59 to 3.38**	**1.41 (3.4)**
comment	Pb(II) sorption on shale used as chemical analog (Table 14).			
Limestone	**0.2 to 7.5**	**6.0 to 7.4**	**0.0004 to 0.008**	**0.0022 (4.2)**
comment	Pb(II) sorption on limestone used as chemical analog (Table 14).			

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

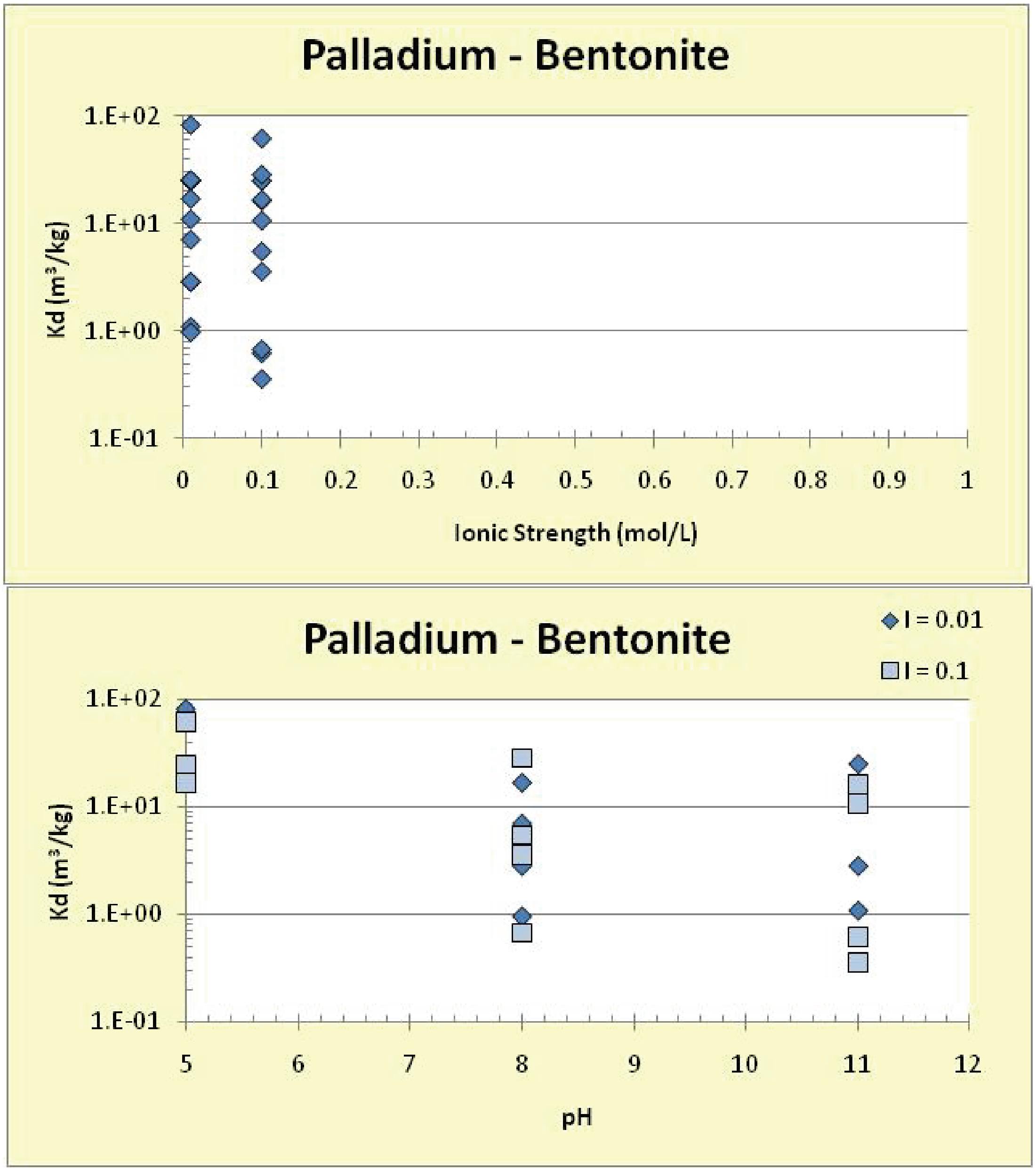


Figure 14: Palladium Sorption Coefficients on Bentonite

3.10 TIN

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

Sorption data for bentonite, clay and montmorillonite were reported by Oda et al. (1999), Baston et al. (1990), and Ikeda et al. (1995). Ticknor and McMurray (1996) presented data for Sn sorption on goethite and granite. Bradbury and Baeyens (2009) reported Sn sorption values on illite (316 and 398 m^3/kg) for an ionic strength of 0.1 mol/L and pH values of 6 and 7. Although the range of ionic strength values in the data sets is not extensive, there does not appear to be a correlation between sorption coefficient and ionic strength (Figure 15). This may suggest that tin could sorb by inner sphere surface complexation with oxygen groups. This could be expected given tin's tendency to form hydroxyl complexes. Sorption on bentonite decreases with pH (Figure 15). Sorption values on bentonite determined at an ionic strength of 0.1 mol/L and pH of 5.8 to 6.4 ranged from 660 to 2700 m^3/kg. Sorption on shale was estimated using Sn sorption values reported for illite, assuming the shale contains 60 percent illite.

Zr(IV) and Th(IV) could be considered as potential chemical analogs for Sn(IV) due to a similarity in oxidation states. Furthermore, just like Sn, both Zr and Th aqueous species are dominated by hydroxyl species in the SR-300 reference groundwater. However, Th has a stronger affinity for carbonate as evidenced by the presence of mixed carbonate-hydroxyl species in the SR-20 reference groundwater (Table 3). Since Sn sorption data are not available for limestone, one could consider using Th(IV) data to estimate Sn(IV) sorption on limestone. Sorption values for tin on sedimentary rocks are summarized in Table 13.

Table 13: Recommended Sorption Coefficients for Tin

TIN (IV)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.1**	**5.8 to 6.4**	**660 to 2700**	**1460 (2)**
comment	Oda et al. (1999)			
Shale	**0.1**	**6 to 7**	**190 to 239**	**213 (1.2)**
comment	Based on 60 wt% illite in shale and Sn sorption data reported for illite by Bradbury and Baeyens (2009). Data range based on 2 values.			
Limestone	**5**	**neutral**	**0.7 to 10**	**2.7 (6.6)**
comment	Based on using Th(IV) as a chemical analog (Table 17).			

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

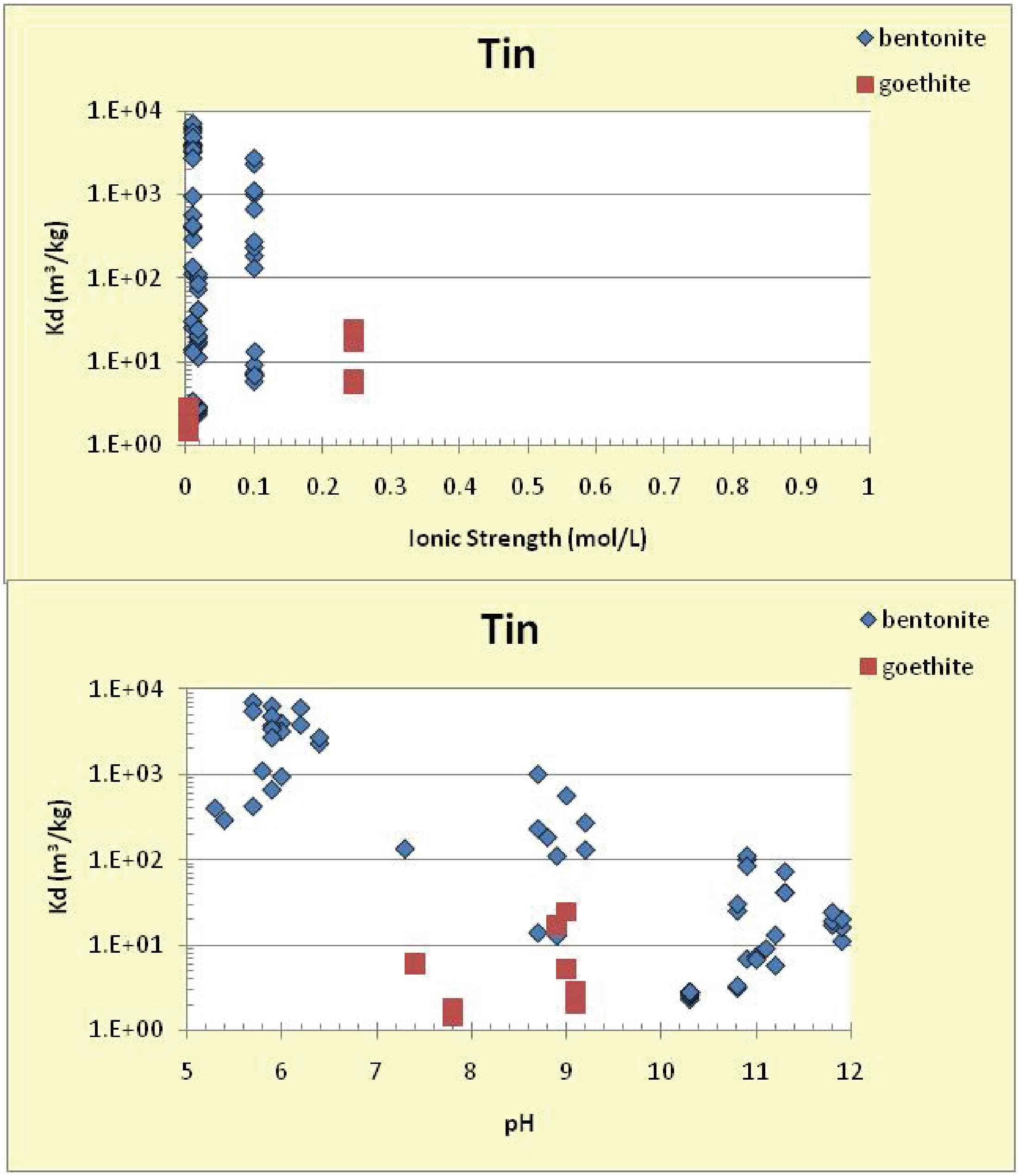


Figure 15: Tin Sorption Coefficients on Bentonite and Goethite

3.11 LEAD

Lead is a group 14 element, which is expected to be in the II oxidation state. 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. PHREEQC (SIT database) predicts that in the concentrated brine reference groundwater SR-300 lead aqueous chemistry will be dominated by $PbCl_4^{-2}$ and $PbCl_3^-$. With a decrease in Cl^- concentration and an increase in SO_4^{-2} and carbonate, the dominant lead species in reference groundwater SR-20 in order of decreasing significance are $PbCl^+$, $PbCl_2$, Pb^{+2} and $Pb(CO_3)$.

Sorption data for bentonite and montmorillonite were reported by Ikeda and Amaya (1998), Ashida et al. (1999), Griffin and Au (1977), Tripathi et al. (1993), Wold and Pickering (1981), Lothenbach et al. (1997), Schulthess and Huang (1990) and Ulrich and Degueldre (1993). Data for illite were reported by Khan and Iqbal (1988) and Wold and Pickering (1981). Ashida et al. (1999), Lieser and Ament (1993) and Gunnerisson et al. (1994) provided sorption data for mudstone and goethite.

Lead sorption appears to decrease with ionic strength, as noted for bentonite, and increases with pH (Figure 16 and Figure 17). However, since lead does sorb at higher ionic strength, the lead sorption process includes a component of surface complexation. Na-montmorillonite and Ca-montmorillonite are used to represent the sorption properties of bentonite, since data are available for Pb sorption on these materials in the pH range 5 to 7. Note that sorption on Ca-montmorillonite was lower than on the Na-montmorillinite, possibly due to competition between Pb and Ca. Lead sorption values of interest were 0.01 to 50 m^3/kg for bentonite, determined at an ionic strength of 0.1 to 0.25 mol/L and pH of 5 to 7. These values included measurements made in $Ca(ClO_4)_2$ solutions where the Ca is likely to suppress Pb sorption. Sorption values on illite, at an ionic strength of 0.25 mol/L and pH 6 to 6.5, ranged from 0.986 to 5.63 m^3/kg. Sorption on mudstone at an ionic strength of 0.2 mol/L and pH 7.4 varied from 1.17 to 60 m^3/kg.

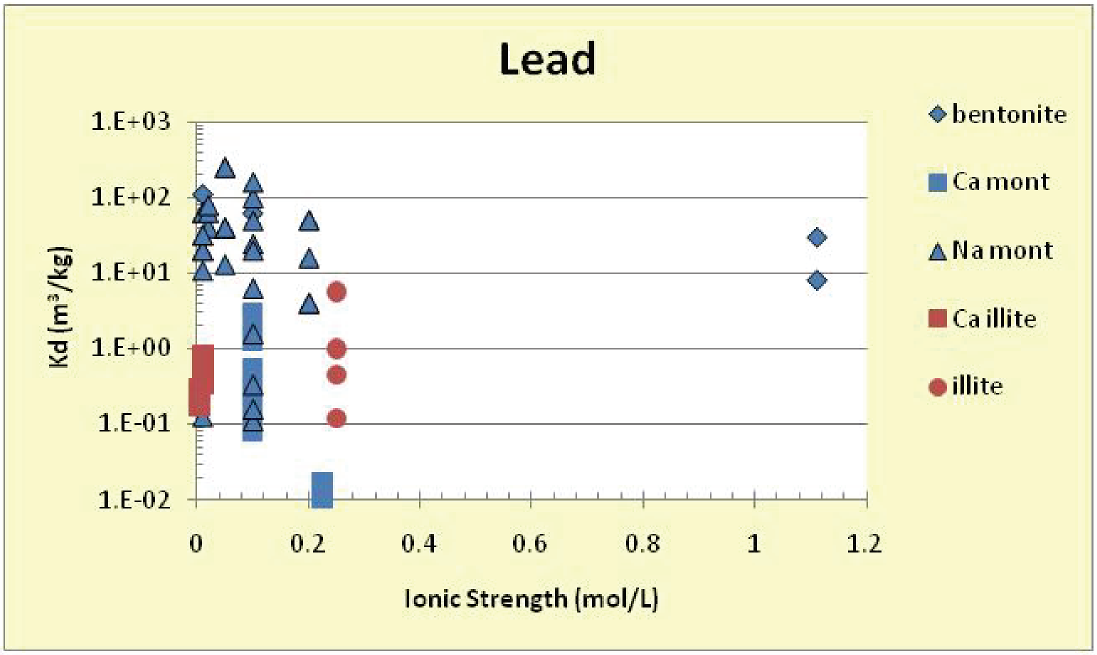
Given the lack of sorption data for limestone, Ni(II) is considered as a chemical analog for Pb(II). Nickel species that are likely to be present in the reference groundwaters are Ni^{+2} and $NiCl^+$. Vilks et al. (2011) measured Ni sorption from brine solutions (similar to the reference groundwaters) onto bentonite and Ordovician shale and limestone. Nickel sorption coefficients, representing ionic strengths of 0.2 to 7.5 mol/L, and pH values of 6.0 to 7.4) were 0.022 to 0.082 m^3/kg for bentonite, 0.006 to 0.047 m^3/kg for shale, and 0.0004 to 0.0080 m^3/kg for limestone. The Ni sorption values on bentonite and shale are significantly lower than Pb sorption values on bentonite, mudstone and illite reported in the literatures. Nevertheless, the Ni sorption values represent measurements on sedimentary rocks in southern Ontario, using representative brine solutions. Therefore, as a conservative assumption the recommended values for Pb sorption are based on measured Ni sorption values.

Lead sorption values for sedimentary rocks are summarized in Table 14.

Table 14: Recommended Sorption Coefficients for Lead

LEAD (II)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.1 to 0.25**	**5.0 to 7.0**	**0.01 to 50**	**0.31 (24)**
comment	Griffin and Au (1977), Tripathi et al. (1993), Wold and Pickering (1981), Ulrich and Degueldre (1993).			
Shale	**0.25**	**6.0 to 6.5**	**0.59 to 3.38**	**1.41 (3.4)**
comment	Based on 60 wt% illite in shale and Pb(II) sorption data from Wold and Pickering (1981). Data range based on 2 values.			
Limestone	**0.2 to 7.5**	**6.0 to 7.4**	**0.0004 to 0.008**	**0.0022 (4.2)**
comment	Ni sorption on limestone used as chemical analog. Vilks et al. (2011)			

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



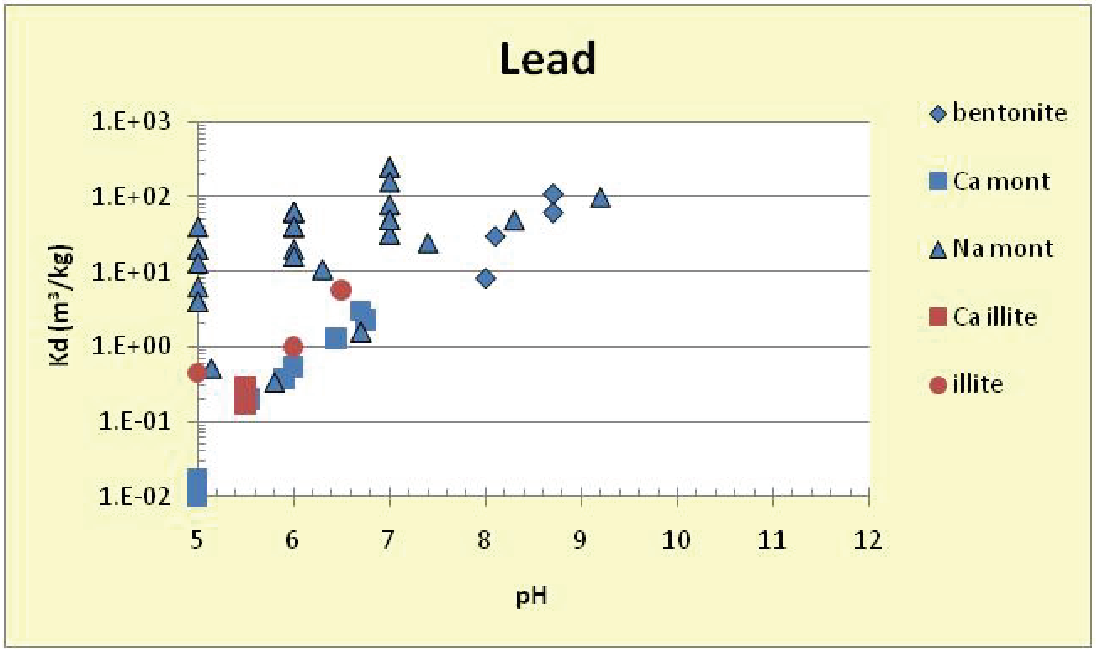


Figure 16: Lead Sorption Coefficients on Bentonite, Montmorillonite and Illite

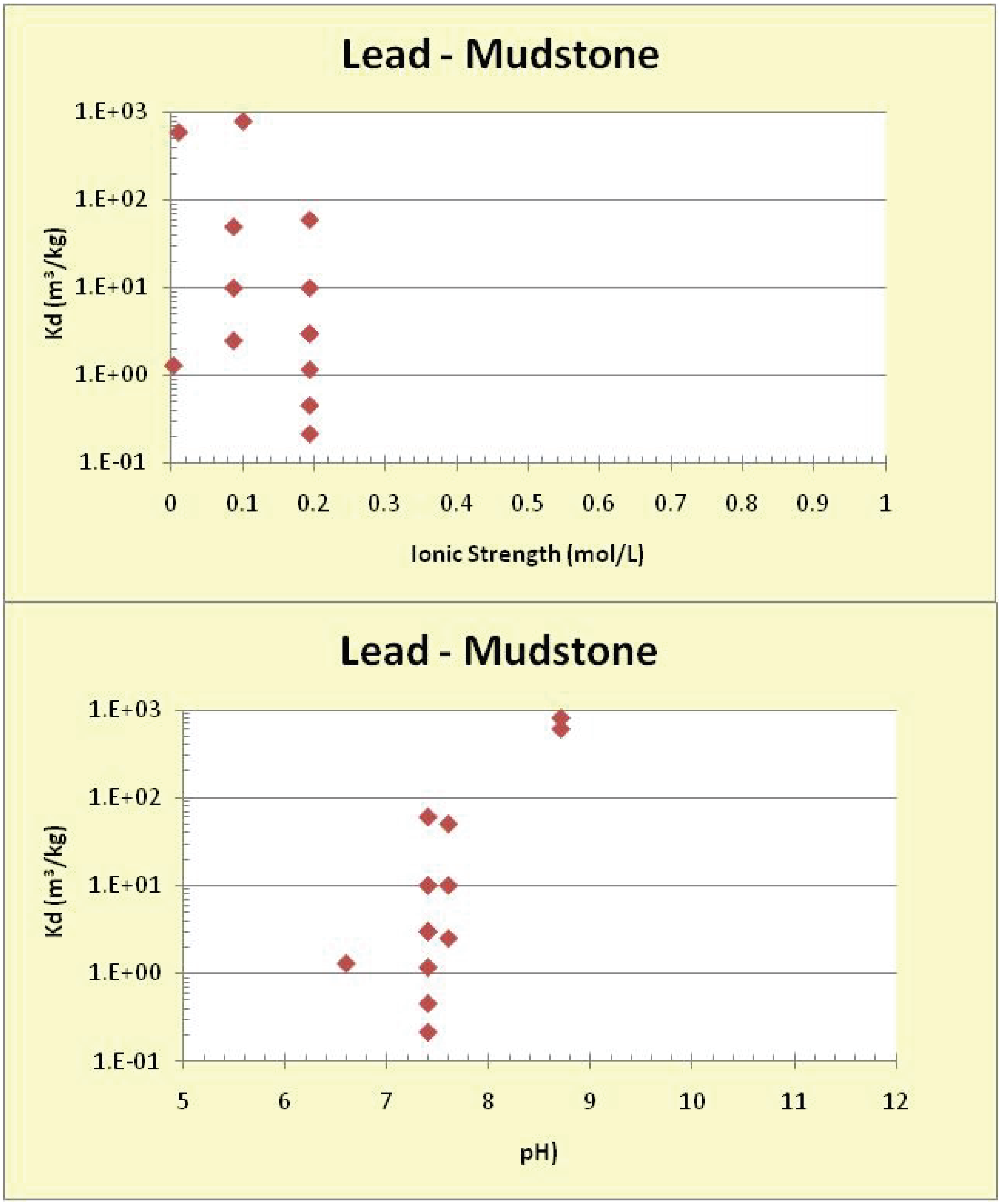


Figure 17: Lead Sorption Coefficients on Mudstone

3.12 BISMUTH

Bismuth is a group 15 element with a dominant III oxidation state, although Bi(V) species are also formed under oxidizing conditions. Calculations with PHREEQC (Japanese thermodynamic database, Kitamura et al., 2010) predict that in the concentrated brine reference groundwater SR-300 bismuth aqueous chemistry will be dominated by the species $BiCl_4^-$, while the dominant species in Sr-20 would be $Bi(OH)_2^+$ and $Bi(OH)_3$. The hydroxyl species suggest that Bi is likely to sorb by surface complexation to oxygen sites coordinated to metals.

Ulrich and Degueldre (1993) and Santshi et al. (1984) reported Bi sorption on Na-montmorillonite and bentonite in sea water. Bismuth sorption on bentonite appears to be independent of ionic strength, but increases with pH (Figure 18). The bismuth sorption coefficient corresponds to an ionic strength of 0.2 mol/L, and the pH range 6 to 7 ranges between 25 and 50 m^3/kg.

Europium (III) could be considered as a chemical analog for Bi(III), although their solution chemistry is slightly different. In SR-300 the dominant Eu(III) species are $EuCl^{+2}$ and Eu^{+3}, and in SR-20 the important species are Eu^{+3}, $EuSO_4^+$ and $EuCl^{+2}$. Vilks et al. (2011) found that Eu sorption values (m^3/kg) were 0.097 to 5.7 for bentonite, 0.11 to 0.22 for shale, and 0.093 to 0.29 for limestone. Based on comparing Eu sorption on bentonite with Bi sorption, it is possible that Eu could underestimate Bi sorption by a factor 5 to 250. As a conservative approximation, Eu sorption could be used to approximate Bi sorption on shale and limestone. Bismuth sorption values recommended for sedimentary rocks are summarized in Table 15.

Table 15: Recommended Sorption Coefficients for Bismuth

Bismuth (III)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.2**	**6 to 7**	**25 to 50**	**35 (1.6)**
comment	Ulrich and Degueldre (1993). Data range based on 2 values.			
Shale	**0.2 to 7.5**	**6.0 to 7.4**	**0.11 to 0.22**	**0.16 (1.4)**
comment	Eu sorption data on shale used as chemical analog. Vilks et al. (2011)			
Limestone	**0.2 to 7.5**	**6.0 to 7.4**	**0.093 to 0.29**	**0.16 (1.8)**
comment	Eu sorption data on limestone used as a chemical analog. Vilks et al. (2011)			

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

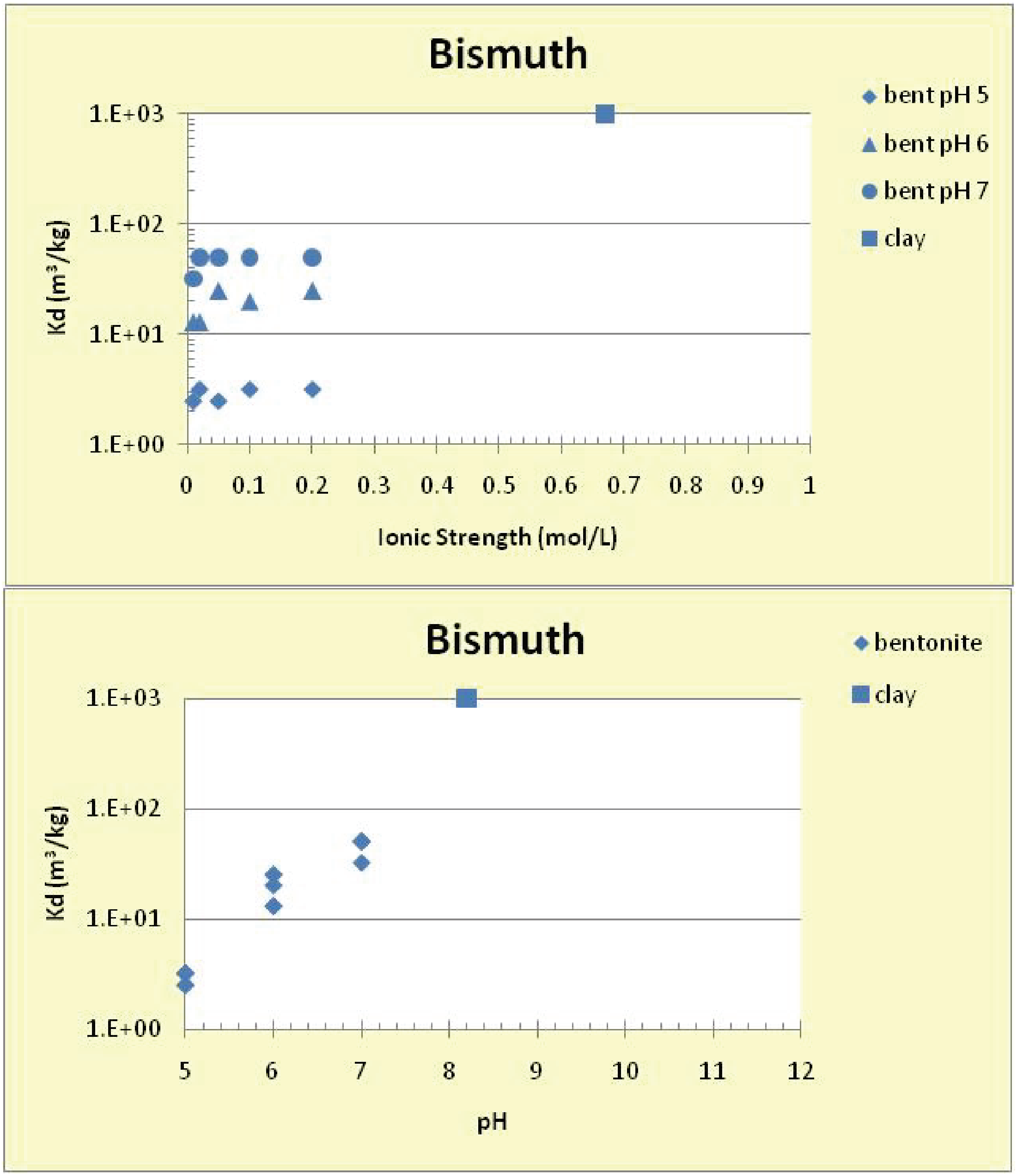


Figure 18: Bismuth Sorption Coefficients on Bentonite and Clay

3.13 RADIUM

Radium is a group 2 element with a II 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 in aqueous solutions. 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 groundwaters the dominant species are predicted to be Ra^{+2}, $RaCl_2$ and $RaCl^+$ in SR-300, and Ra^{+2}, $Ra(SO_4)$ and $RaCl^+$ in SR-20, which has a higher sulphate and a lower chloride concentration (PHREEQC, SIT database). Given radium's affinity for sulphate, it may sorb onto or co-precipitate with barite ($BaSO_4$).

Radium sorption data for bentonite, montmorillonite and smectite was presented by Barney (1981), Allard et al. (1979) Baston et al. (1990), Tachi and Shibutani (1999), Ames et al. (1981, 1983), and Benes et al. (1985). Taki and Hata (1991) provided data for mudstone and Ames et al. (1983) gave results for illite. Radium sorption decreases with ionic strength (Figure 19 and Figure 20) and the effect of pH is not clear. Figure 21 illustrates the effect of temperature on Ra sorption on swelling clays and illite. As can be expected, Ra sorption decreases with increasing temperature. Therefore, sorption values measured at temperatures above 25°C were not considered.

The Ra sorption values that could be considered for bentonite are 0.18 to 0.92 m^3/kg. However, since they were determined with an ionic strength of 0.1 mol/L, it is questionable whether they are relevant for brine solutions. The Ra sorption coefficients for illite, measured at an ionic strength 0.01 mol/L were also not considered. Instead the sorption values measured with mudstone in seawater may be a reasonable approximation of sorption on shale. The Ra sorption values for mudstone were 0.007 to 0.032 m^3/kg.

In the absence of reasonable data for bentonite and limestone, one could consider using Sr(II) as a chemical analog. Vilks et al. (2011) noted that Sr did not sorb from brine solutions (ionic strength of 7.5 mol/L) onto bentonite, shale or limestone. Therefore, as a conservative assumption a sorption value of 0 is recommended for bentonite and limestone. Recommended radium sorption values for sedimentary rocks are summarized in Table 16.

Table 16: Recommended Sorption Coefficients for Radium

RADIUM (II)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**7.5**	**6**	**0**	**-**
comment	Using Sr as a chemical analog, this recommendation is based on measurements of Sr sorption on bentonite in brine solutions by Vilks et al. (2011).			
Shale	**0.72**	**7.8**	**0.0070 to 0.032**	**0.021 (1.6)**
comment	Based on mudstone reported by Taki and Hata (1991). Sorption likely to decrease as the ionic strength increases to 1 mol/L and higher and it may be conservative to assume a value of 0 in brine solutions.			
Limestone	**7.5**	**6**	**0**	**-**
comment	Using Sr as a chemical analog, this recommendation is based on measurements of Sr sorption on Ordovician limestone by Vilks et al. (2011).			

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

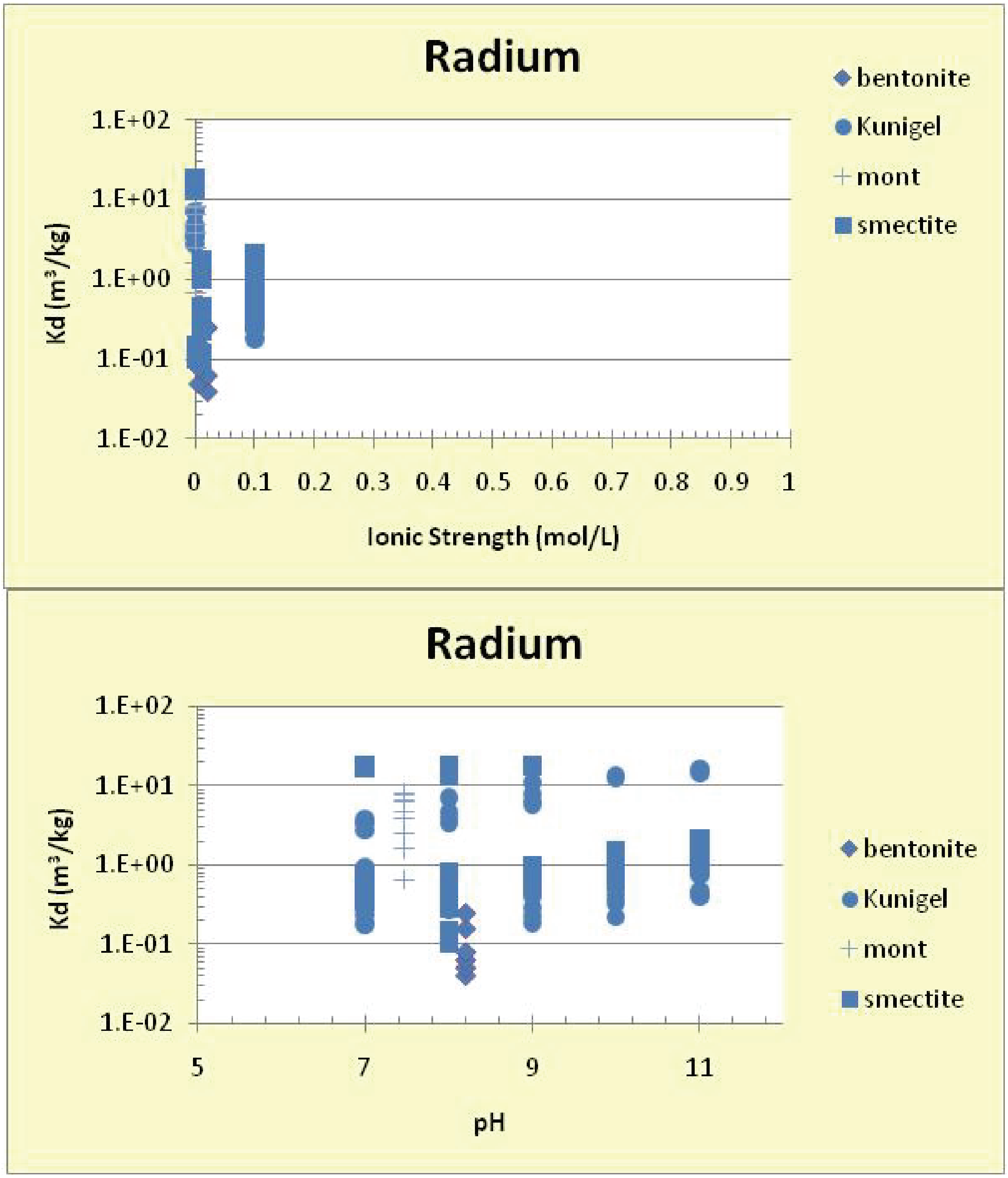


Figure 19: Radium Sorption Coefficients on Bentonite and Swelling Clays

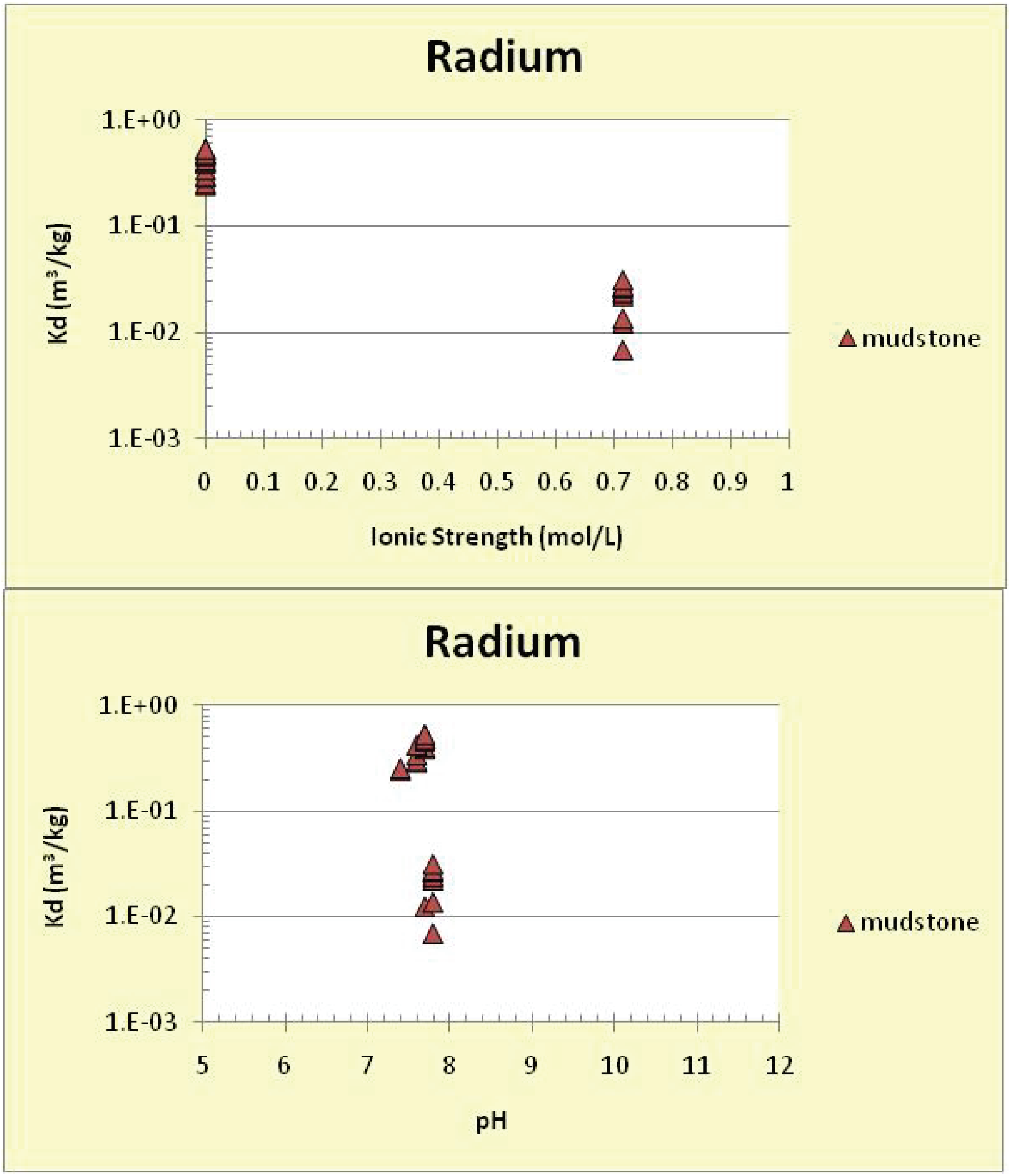


Figure 20: Radium Sorption Coefficients on Mudstone

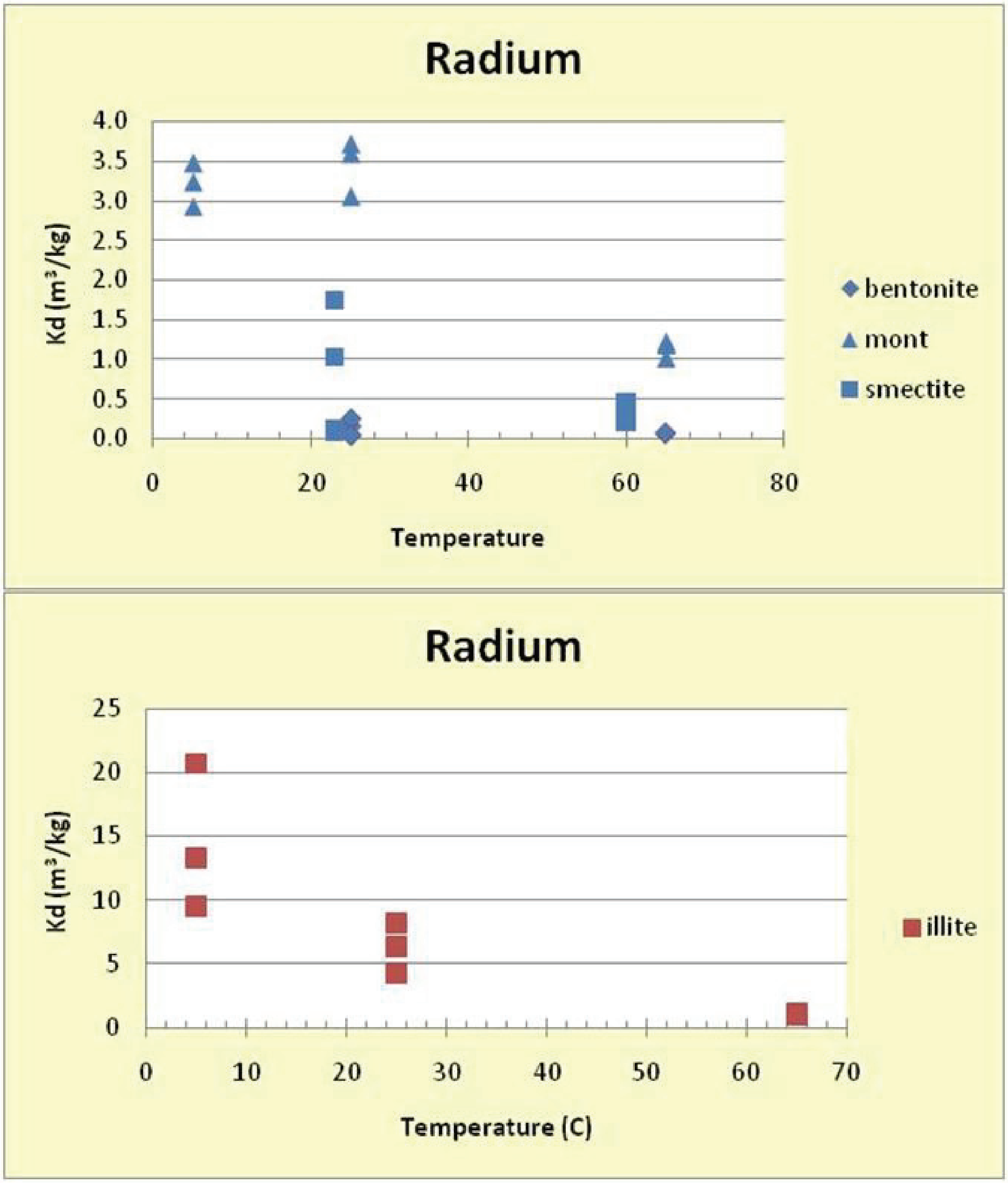


Figure 21: Effect of Temperature on Radium Sorption on Bentonite, Swelling Clays and Illite

3.14 THORIUM

Thorium is an actinide element with a IV oxidation state. Thorium has a very low solubility, making it very difficult to perform sorption measurements without the risk of precipitation. The dominant thorium species predicted by PHREEQC (SIT database) in the reference groundwaters are $Th(OH)_3^+$, $Th(OH)_2^{+2}$, and $Th(OH)_4$ for SR-300 and $Th(OH)_3(CO_3)^-$, $Th(OH)_2(CO_3)_2^{-2}$, and $Th(OH)_2(CO_3)_2^{-2}$ for SR-20. The solubility is limited by ThO_2.

Allard et al. (1979) and Bradbury and Baeyens (2003) presented data for Th sorption on bentonite, and Baston et al. (1991) reported on Th sorption on London Clay, which contains a 70 percent clay content. Sorption on silica and goethite was provided by Osthols (1995), Hunter et al. (1988) and Allard et al. (1982). The sorption of Th does not appear to decrease significantly with the ionic strength, but is affected by pH for Si oxides (Figure 22). Thorium sorption appears to reach a plateau when the pH increases to values between 8 and 12. These observations and the tendency of thorium to form complexes with hydroxyl and carbonate indicate that in brine solutions thorium will likely sorb by surface complexation to oxygen or carbonate sites.

Thorium sorption values (m^3/kg) for bentonite measured at an ionic strength of 0.02 mol/L and a pH of 8.2 ranged from 0.25 to 6.3. Bradbury and Baeyens (2003a) reported that in the pH range of 6.9 to 7.7 and an ionic strength of 0.31 to 0.34 mol/L, the Th K_d value for bentonite is 63 m^3/kg. Data report for the safety assessment SR-Can (SKB, 2006) reports 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 mol/L) and highly saline (ionic strength 0.7 mol/L) groundwaters, respectively. These values were derived using data from Bradbury and Baeyens (Ochs and Talerico, 2004). Sorption values (m^3/kg) measured for London Clay at an ionic strength of 0.02 mol/L and a pH of 8.1 ranged from 0.82 to 1.1 These values were used to approximate sorption on shale after making an adjustment for a lower clay content in shale (60 percent in shale compared to 70 percent in London Clay). The USEPA (1998) recommended Th sorption values for dolomite that ranged from 0.7 to 10 m^3/kg. These values were based on measurements made at near-neutral values in Na-Cl brine solutions with an ionic strength of about 5 mol/L. Stenhouse (1995) used mineral sorption values to estimate sorption on marl and recommended a realistic Th K_d value of 5 m^3/kg and a conservative value of 0.5 m^3/kg.

Table 17 summarizes recommended Th sorption values for sedimentary rock. The recommended K_d values for bentonite are taken from Allard et al. (1979) and Bradbury and Baeyens (2003a), and are consistent with the recommended values by SKB (2006). Measurements on London clay are used to approximate sorption on shale and sorption on limestone is based on recommended values for dolomite.

Table 17: Recommended Sorption Coefficients for Thorium

THORIUM (IV)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.02 to 0.34**	**6.9 to 8.2**	**0.25 to 63**	**5.0 (2.6)**
comment	Allard et al. (1979) and Bradbury and Baeyens 2003a			
Shale	**0.02**	**8.1**	**0.70 to 0.94**	**0.81 (1.2)**
comment	Based on London clay measured by Baston et al. (1991). Data range based on 2 values.			
Limestone	**5**	**neutral**	**0.7 to 10**	**2.7 (6.6)**
comment	Based on dolomite as recommended by USEPA (1998). Data range based on 2 values.			

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

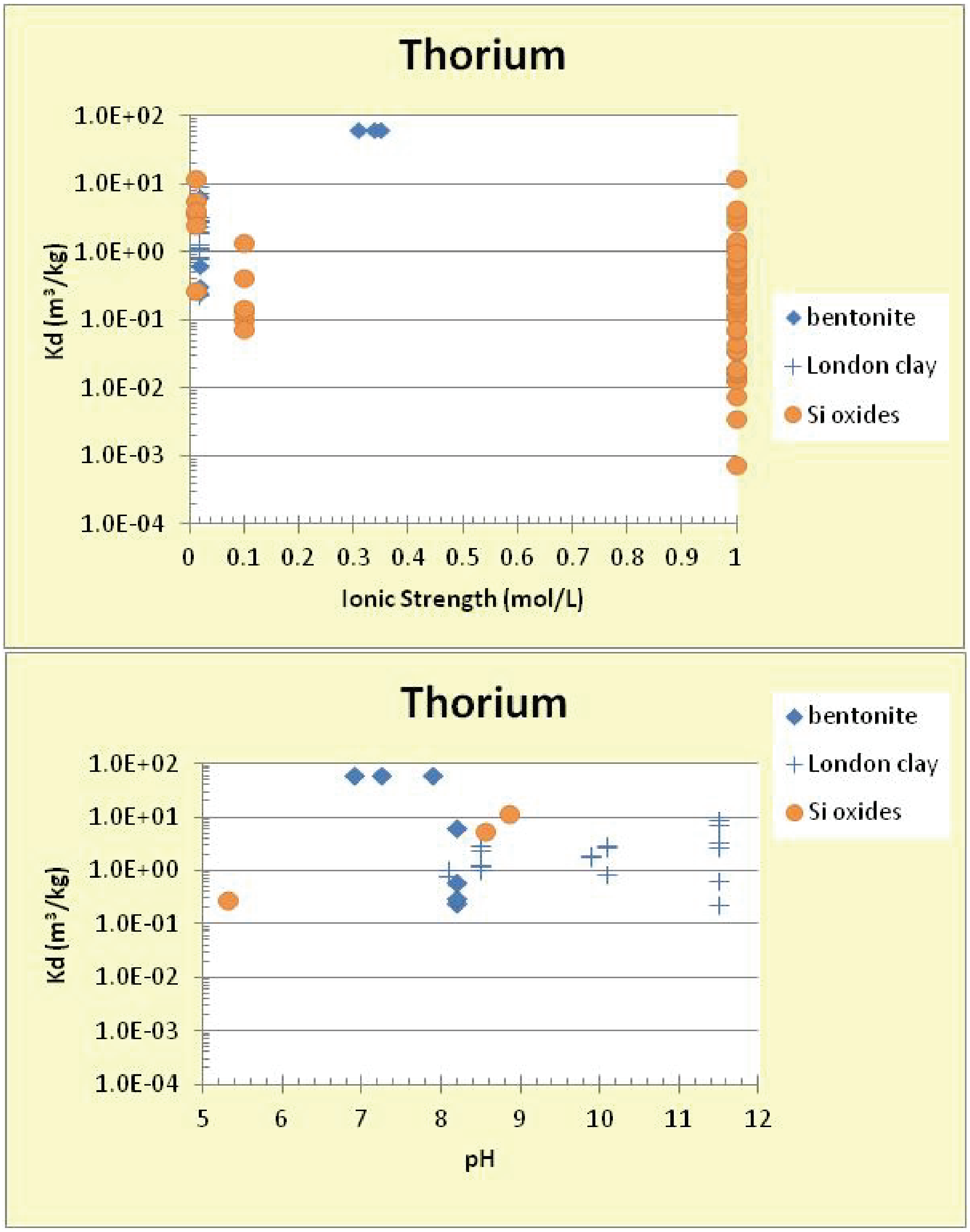


Figure 22: Thorium Sorption Coefficients on Bentonite, Clay and Si Oxides

3.15 PROTACTINIUM

Protactinium (Pa) is an actinide element with oxidation states of IV and V. Pa(IV) is only stable under very strong acid and very reducing conditions. PHREEQC (SIT database) predicts that the V 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). Given its affinity for oxygen, Pa is likely to sorb by surface complexation to surface oxygens coordinated to metals in the solid phases

Allard et al. (1982) and Baston et al. (1999) reported Pa sorption values for montmorillonite and bentonite, while Bode (1989) and Ishii et al. (2001) presented data for marl and mudstone. Sorption data for Pa were determined in solutions with an ionic strength close to 0 (Figure 23). This does not allow one to explore the effect of increasing ionic strength and to say whether or not any of the sorption data could be applicable to brine solutions. Although the amount of data is limited, there appears to be an increase in sorption above pH 9, as indicated by the bentonite data.

The sorption value (m^3/kg) for bentonite, which is closest to a neutral pH (8.5) is 5.0 m^3/kg. The pH conditions for sorption on mudstone and marl were not given. Sorption values for mudstone ranged from 3.5 to 9.4 m^3/kg, while those on marl were between 4.8 and 24 m^3/kg. In summary, although some sorption data for protactinium exists, its applicability to sedimentary rocks in brine solutions is very tenuous.

Neptunium(V) could be considered as a chemical analog to Pa(V). From Table 20, the sorption values for Np(V) on bentonite ranged from 0.017 to 0.40 m^3/kg, which are significantly lower than the reported Pa(V) sorption values on bentonite. Np(V) sorption values on shale range from 0.0088 to 0.32 m^3/kg, while those on limestone are 0.001 to 0.20 m^3/kg. These are also significantly lower than the reported sorption values for Pa(V). Given that Pa sorption measurements, for solution conditions that may not be relevant to brine solutions, are significantly higher than Np(V) sorption coefficients, a conservative recommendation is made that Pa(V) is approximated by Np(V) sorption data.

Recommended Pa sorption values for sedimentary rocks are summarized in Table 18.

Table 18: Recommended Sorption Coefficients for Protactinium

PROTACTINIUM (V)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**1 to 5.2**	**6 to 7.5**	**0.017 to 0.40**	**0.044 (3.6)**
comment	Based on using Np(V) as a chemical analog (Table 20).			
Shale	**1 to 5.2**	**6.1 to 7.2**	**0.0075 to 0.026**	**0.011 (1.7)**
comment	Based on using Np(V) as a chemical analog (Table 20).			
Limestone	**5**	**neutral**	**0.001 to 0.20**	**0.014 (42)**
comment	Based on using Np(V) as a chemical analog (Table 20).			

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

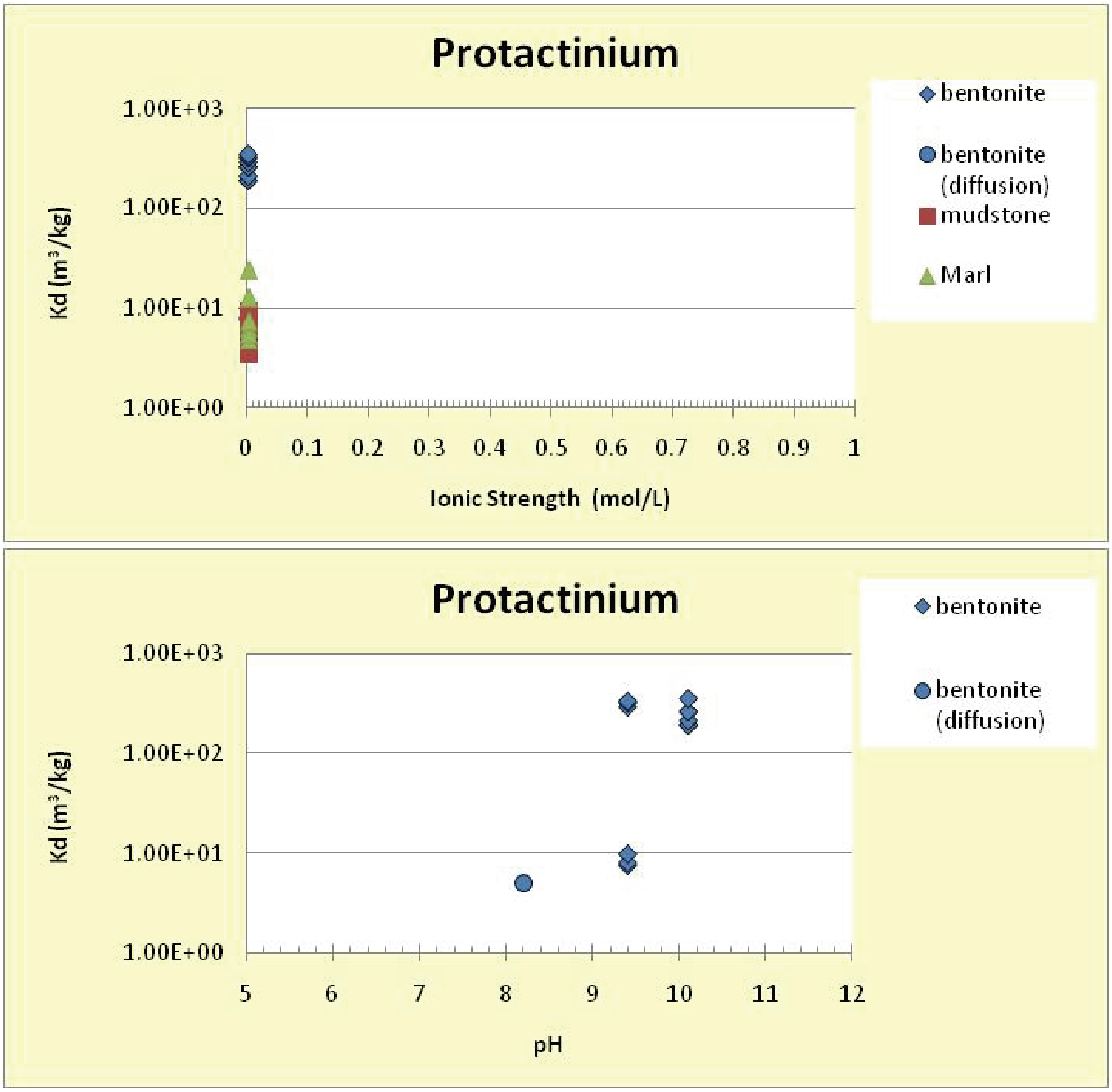


Figure 23: Protactinium Sorption Coefficients on Bentonite, Mudstone and Marl

3.16 URANIUM

Since uranium may occur in the III, IV, V, and VI oxidation states, its chemistry in groundwater is very sensitive to redox conditions. PHREEQC (SIT database) predicts that in the SR-300 reference groundwater, uranium will be mainly in the IV oxidation state with $U(OH)_4$ and $U(OH)_3^+$ being the dominant species. In the SR-20 reference groundwater, uranium would be in the VI oxidation state as $UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$. Under reducing conditions uranium solubility is very low, while under oxidizing conditions solubility is significantly 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.

Uranium(VI) sorption data under oxidizing conditions for bentonite, montmorillonite and smectite were reported by Erdal et al. (1977), Torstenfelt et al. (1988), Morgan et al. (1988), Berry et al. (1989, 1991), Zachara and McKinley (1993), Ames et al. (1981), Salter (1981), Gorgeon (1994) and Berry et al. (1990). Uranium(IV) sorption on bentonite under reducing conditions was given by Baston et al. (1995, 1997). Baston et al. (1991) reported uranum(IV) sorption on London Clay. Ticknor (1993) measured sorption on calcite, illite, chlorite, goethite and hematite under oxidizing and reducing conditions. Sorption values on dolomite and illite were given by Francis and Bondietti (1979) and Gorgeon (1994).

Uranium(VI) sorption data for oxidizing conditions are summarized in Figure 24 and Figure 25. Sorption decreases with higher ionic strength for calcite. Sorption values did not display a consistent variation with pH. Sorption values that could be considered for bentonite and illite were chosen at an ionic strength of 1.0 mol/L and pH ranges of 5.2 to 8.0. Sorption coefficient values for bentonite were between 0.079 and 3.98 m^3/kg, while those for illite ranged from 1.07 to 4.27 m^3/kg. Prospective sorption values for shale ranged from 0.010 to 0.012 m^3/kg, and were measured at an ionic strength of 0.004 mol/L and a pH range of 7.3 to 7.8. Sorption values for chlorite, calcite and goethite were measured at pH 8.25 and an ionic strength of 0.27 mol/L. Respective sorption values for chlorite, calcite and goethite were 0.0058, 0.0069 and 1.40 m^3/kg. Vilks et al. (2011) measured U(VI) sorption on bentonite and Ordovician shales and limestone, in brine solutions with ionic strengths between 0.2 and 7.5 mol/L, and pH values from 6.0 to 7.4. Uranium(VI) sorption coefficients were 0.014 to 0.57 m^3/kg for bentonite, 0.002 to 0.051 m^3/kg for shale, and 0.002 to 0.017 m^3/kg for limestone. These measured sorption values are recommended over those in the literature because they were determined with Canadian sedimentary rocks and brine solutions. Furthermore they are lower than the values selected from the literature, and are therefore more conservative.

Sorption values for U(IV) under reducing conditions are illustrated in Figure 26, showing a decrease in sorption with ionic strength for calcite and illite, and no effect for bentonite. No trend in sorption variation with pH is evident. U(IV) sorption on calcite and illite was significantly lower than on bentonite, although bentonite is expected to have higher sorption capacities. The experimental redox conditions may account for the difference. Experiments with bentonite and London Clay reported Eh values as low as -400 mV, while the tests with the other minerals only reported low O_2 conditions. Uranium(IV) sorption values on bentonite that are most relevant to saline conditions were selected from experiments performed with sea water (pH = 8, ionic strength = 0.68 mol/L), ranging from 150 to 180 m^3/kg. Data report for the safety assessment SR-Can (SKB, 2006) reports U K_d values for bentonite that range from 2.3 to 1113 m^3/kg, with recommended values of 63 and 40 m^3/kg for saline (ionic strength of 0.2 mol/L) and highly saline (ionic strength 0.7 mol/L) groundwaters, respectively. These values were derived using Th(IV) as chemical analog (Ochs and Talerico, 2004). Although K_d values measured with U(IV) are preferred over values determined with the Th(IV) analog, particularly when reducing conditions for the U(IV) tests were well documented, to be conservative the K_d values recommended by SKB (2006) were also considered for sorption on bentonite. Uranium(IV) sorption values for London clay measured at pH 8 and an ionic strength of 0.018 mol/L ranged from 4.3 to 9.0 m^3/kg (Baston et al., 1991). These values were used to estimate sorption on shale, taking account of the 60 percent clay content of shale and 70 percent clay content of London Clay. Sorption on limestone was based on the sorption value of 0.035 m^3/kg (pH = 9.5 and ionic strength = 0.27 mol/L) determined for calcite. The USEPA (1998) recommended U(IV) sorption values for dolomite that ranged from 0.7 to 10 m^3/kg, and were based on measured Th(IV) values. Sorption experiments with Th(IV) overcame the difficulties in maintaining low redox, therefore the Th(IV) data are probably a very reasonable approximation of U(IV) sorption. However, in the interests of being conservative, the U measurement on calcite is recommended.

Uranium sorption values for sedimentary rocks are summarized in Table 19.

Table 19: Recommended Sorption Coefficients for Uranium

URANIUM (VI) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.2 to 7.5**	**6.0 to 7.5**	**0.014 to 0.57**	**0.13 (7)**
comment	Vilks et al. (2011)			
Shale	**0.2 to 7.5**	**6.0 to 7.5**	**0.002 to 0.051**	**0.010 (6)**
comment	Ordovician shale, Vilks et al. (2011)			
Limestone	**0.2 to 7.5**	**6.0 to 7.5**	**0.002 to 0.017**	**0.006 (3)**
comment	Ordovician limestone, Vilks et al. (2011)			
URANIUM (IV) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.2 to 0.7**	**6.9 to 8**	**40 to 180**	**85 (2.9)**
comment	Baston et al. (1995) and SKB (2006).			
Shale	**0.018**	**8**	**3.7 to 7.7**	**5.3 (1.7)**
comment	Estimated from U(IV) sorption on London Clay measured by Baston et al. (1991).			
Limestone	**0.27**	**9.5**	**0.035**	**-**
comment	Based on U(IV) sorption on calcite reported by Ticknor (1993).			

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

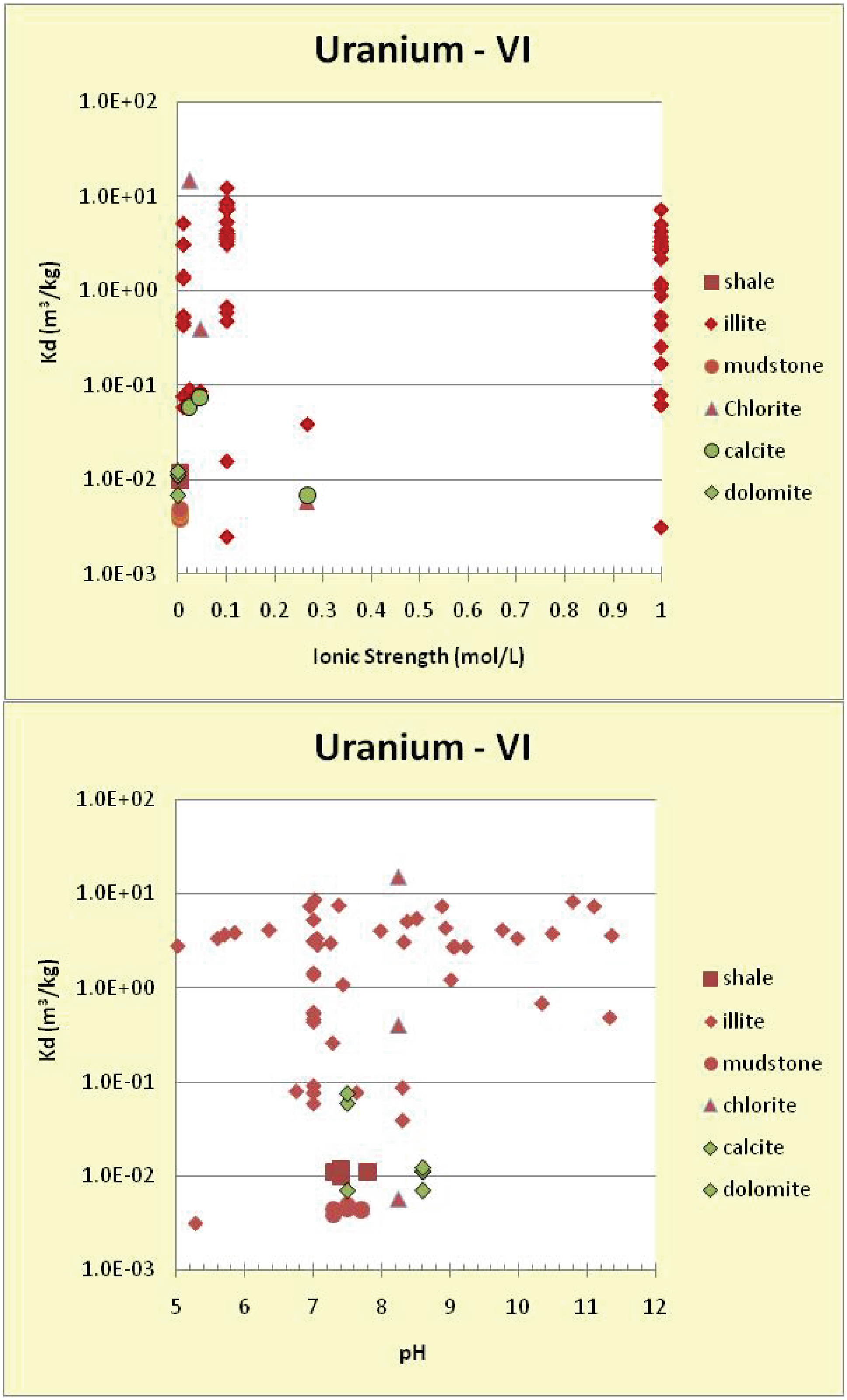


Figure 24: Uranium (VI) Sorption Coefficients on Shale, Calcite, Dolomite, Illite, Mudstone and Chlorite Under Oxidizing Conditions

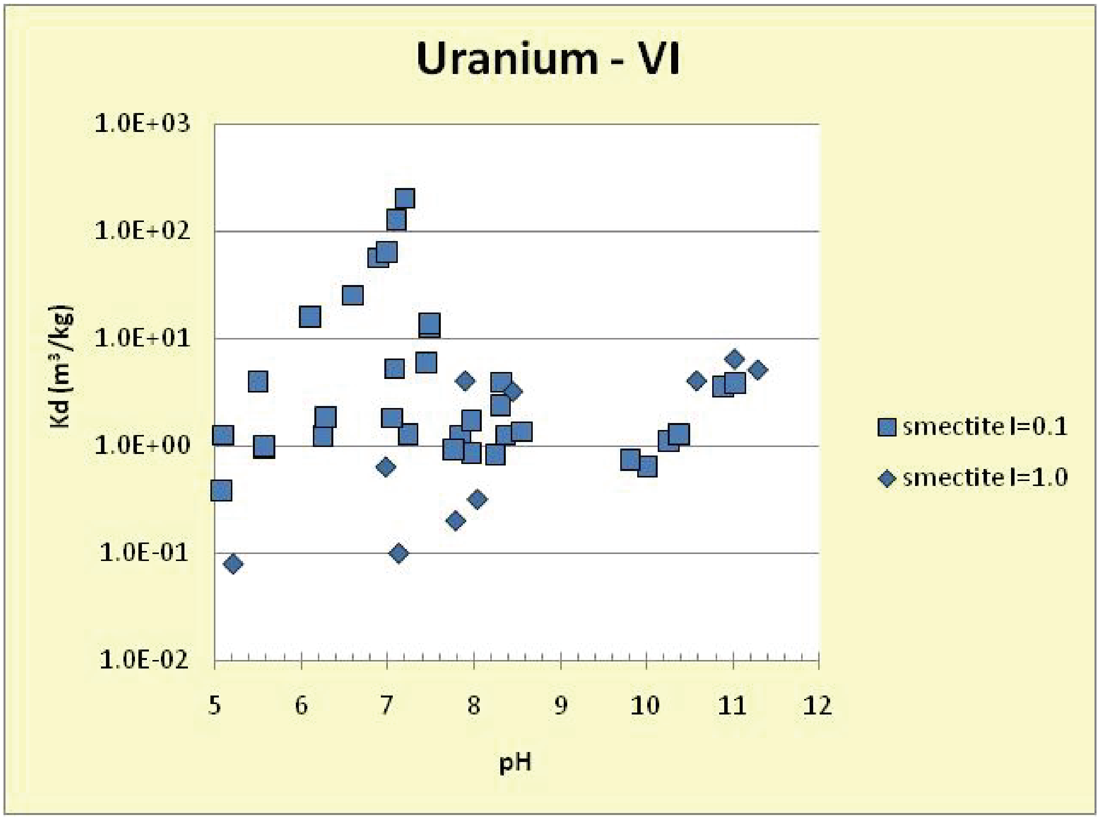


Figure 25: Uranium (VI) Sorption on Smectite Under Oxidizing Conditions

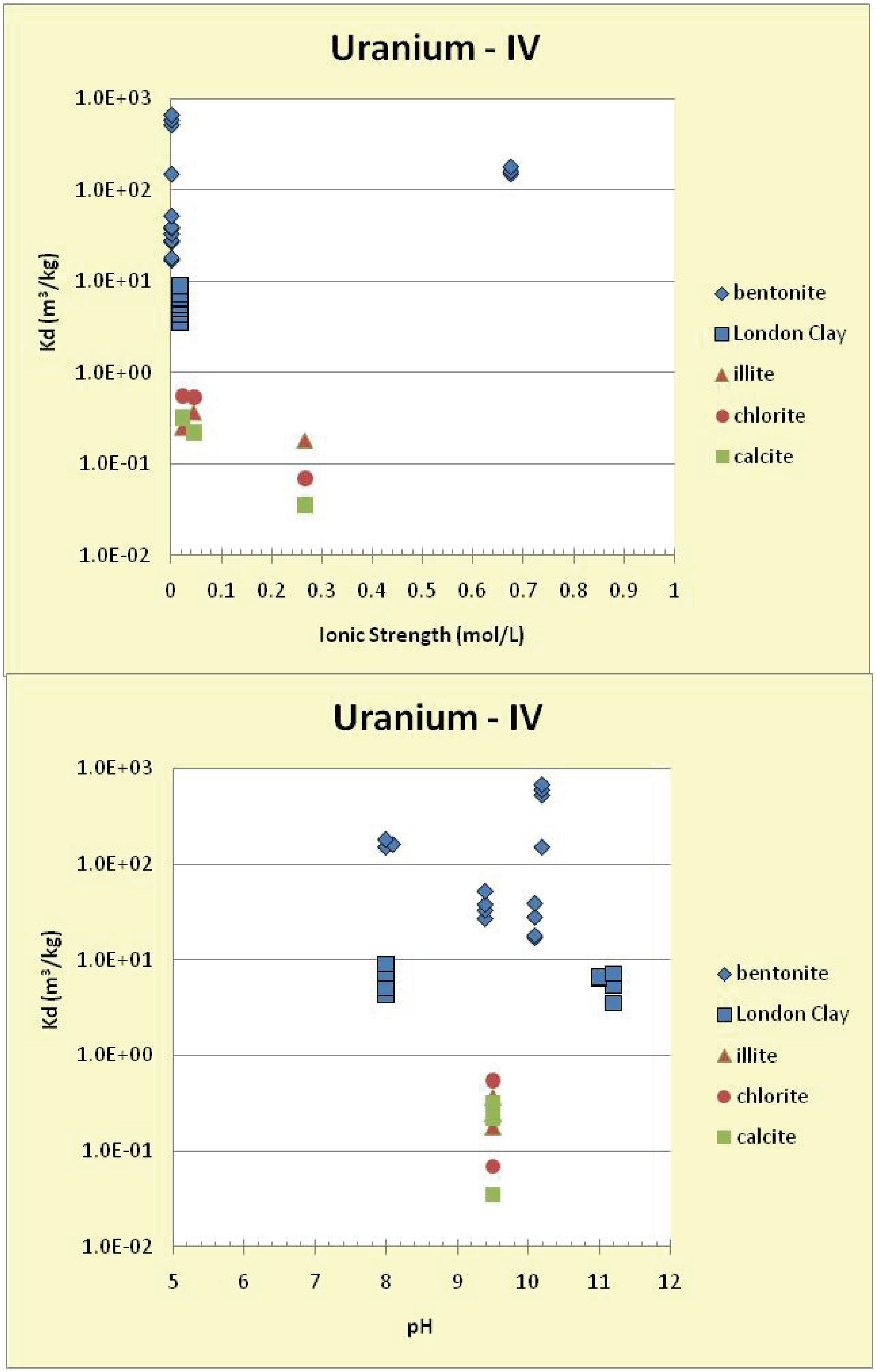


Figure 26: Uranium (IV) Sorption Coefficients on Bentonite, London Clay, Illite, Calcite and Chlorite Under Reducing Conditions

3.17 NEPTUNIUM

Although neptunium has a number of oxidation states (III, IV, V, VI), the IV and V states are more common in groundwater. PHREEQC (SIT database) predicts that the IV oxidation state of neptunium will dominate in the SR-300 groundwater with species $Np(OH)_4$ and $Np(OH)_3^+$. The SR-20 groundwater would likely contain species of both the IV oxidation state ($Np(OH)_4$, $Np(OH)_3^+$, $Np(CO_3)(OH)_3^-$) and the V oxidation state (NpO_2^+). In experiments open to the atmosphere Np(V) will dominate. Given the tendency to form hydrolysis and mixed carbonate-hydrolysis aqueous species, Np will likely sorb by surface complexation to surface oxygen sites associated with alumino-silicate minerals and carbonate.

Neptunium sorption values under oxidizing conditions for bentonite, Montmorillonite, smectite and illite were provided by Barney (1981), Morgan et al. (1988), Tortenfelt et al. (1988), Allard et al. (1979), Stammose et al. (1992), Mucciardi et al. (1979), Gorgeon (1994), Ohe et al. (1993), Meijer et al. (1990), Sakamoto (1990), Salter et al. (1981), Ames et al. (1981), Higgo et al. (1983), and Kitamura and Tomura (2003). Sorption results on bentonite under reducing conditions were reported by Kitamura and Tomura (2003), Ashida et al. (1999), Kitamura et al. (2001), Baston et al. (1997), and Barney (1981). Sorption results on illite were given by Torstenfelt et al. (1988), Mucciardi et al. (1979), Gorgeon (1994) and Ticknor (1993). Barney and Brown et al. (1979), Berry et al. (1990), Higgo et al. (1987) and Tachi et al. (1999) reported sorption values on mudstone.

Under oxidizing conditions Np sorption coefficients do not appear to decrease with increasing ionic strength (Figure 27). However, sorption does increase with pH, so where possible sorption coefficients measured near pH 6 to 7.5 are selected. Under reducing conditions Np sorption coefficients appeared to be independent of ionic strength (Figure 28). There may be a decrease in sorption at pH values above 9. Since neptunium sorption does not decrease with ionic strength, is sensitive to pH, and both Np (IV) and Np(V) form hydroxyl complexes, neptunium sorption is most likely controlled by surface complexation.

Under oxidizing conditions sorption values for bentonite and illite were selected at ionic strengths from 1 to 5.2 mol/L. Sorption values were classified as oxidizing based on a description of the experimental atmosphere and any reported E_h values. Most likely the system would be dominated by Np(V). Neptunium sorption values for bentonite at a pH range of 6 to 7.5 ranged from 0.0165 to 0.398 m^3/kg. Illite displayed sorption values of 0.0125 to 0.0435 m^3/kg, corresponding to a pH range of 6.1 to 7.2. The sorption on illite was used to estimate sorption on shale, assuming the shale contained 60 percent illite. Sorption on mudstone measured in seawater (pH =8.2, ionic strength = 0.68 mol/L) varied from 0.43 to 5.78 m^3/kg. USEPA (1998) proposed Np(V) sorption values ranging from 0.001 to 0.20 m^3/kg for dolomite based on experiments performed at neutral pH and an ionic strength of 5 mol/L, which were selected to represent the sorption values of Np(V) on limestone.

Experiments performed under reducing conditions were identified using reported E_h values that were negative. Under reducing conditions neptunium sorption values, ranging from 0.84 to 23 m^3/kg, were obtained for bentonite at an ionic strength of 1 mol/L and a pH range of 7.4 to 8.0. Sorption values of 0.148 to 2.27 m^3/kg were obtained for mudstone in very dilute water (with the ionic strength around 0 mol/L) and a pH of 9.3. Sorption on mudstone at more neutral pH conditions is likely to be lower than the values at pH of 9.3. USEPA (1998) recommended sorption values for Np(IV) on dolomite that ranged from 0.70 to 10 m^3/kg. These values were based on using Th(IV) as a chemical analog and selected to represent the sorption values of Np(IV) on limestone (see Table 17).

Neptunium sorption values for sedimentary rocks are summarized in Table 20.

Table 20: Recommended Sorption Coefficients for Neptunium

NEPTUNIUM (V) – Oxidizing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**1 to 5.2**	**6 to 7.5**	**0.017 to 0.40**	**0.044 (3.6)**
comment	Mucciardi et al. (1979) and Stammos et al. (1992).			
Shale	**1 to 5.2**	**6.1 to 7.2**	**0.0075 to 0.026**	**0.011 (1.7)**
comment	Based on illite (60%) and assuming no sorption on quartz.			
Limestone	**5**	**neutral**	**0.001 to 0.20**	**0.014 (42)**
comment	Based on values recommended for dololmite by USEPA (1998).			
NEPTUNIUM (IV) – Reducing Conditions				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**1**	**7.4 to 8.0**	**0.84 to 23**	**4.5 (2.9)**
comment	Kitamura and Tomura (2003)			
Shale	**0**	**9.3**	**0.15 to 2.3**	**2.1 (1.1)**
comment	Based on values reported for mudstone by Tachi et al. (1999). The low ionic strength and high pH make this a rough estimate.			
Limestone	**5**	**neutral**	**0.70 to 10**	**2.7 (6.6)**
comment	Based on using Th(IV) as a chemical analog (See Table 17).			

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

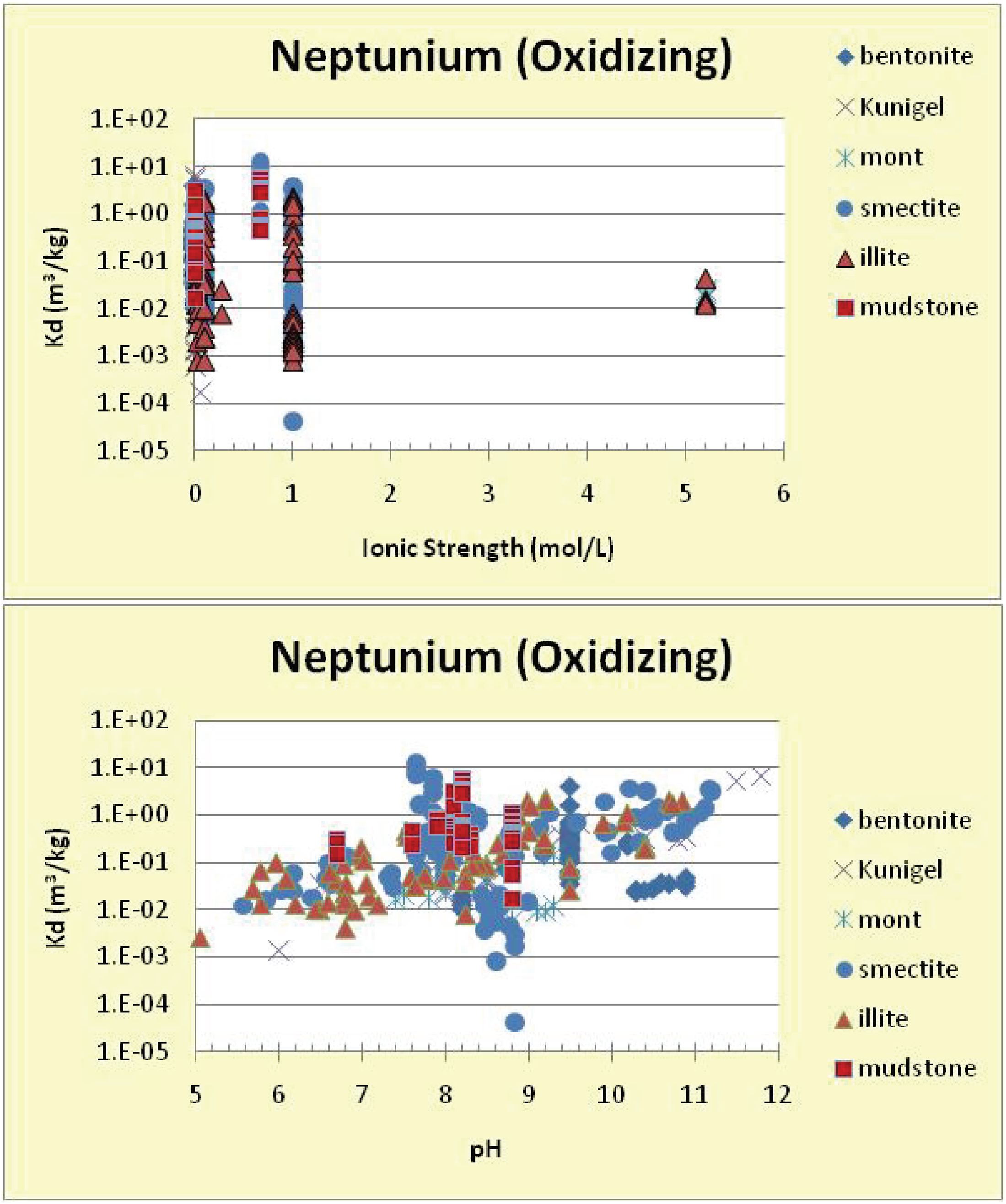


Figure 27: Neptunium Sorption Coefficients on Bentonite, Swelling Clays, Illite and Mudstone Under Oxidizing Conditions

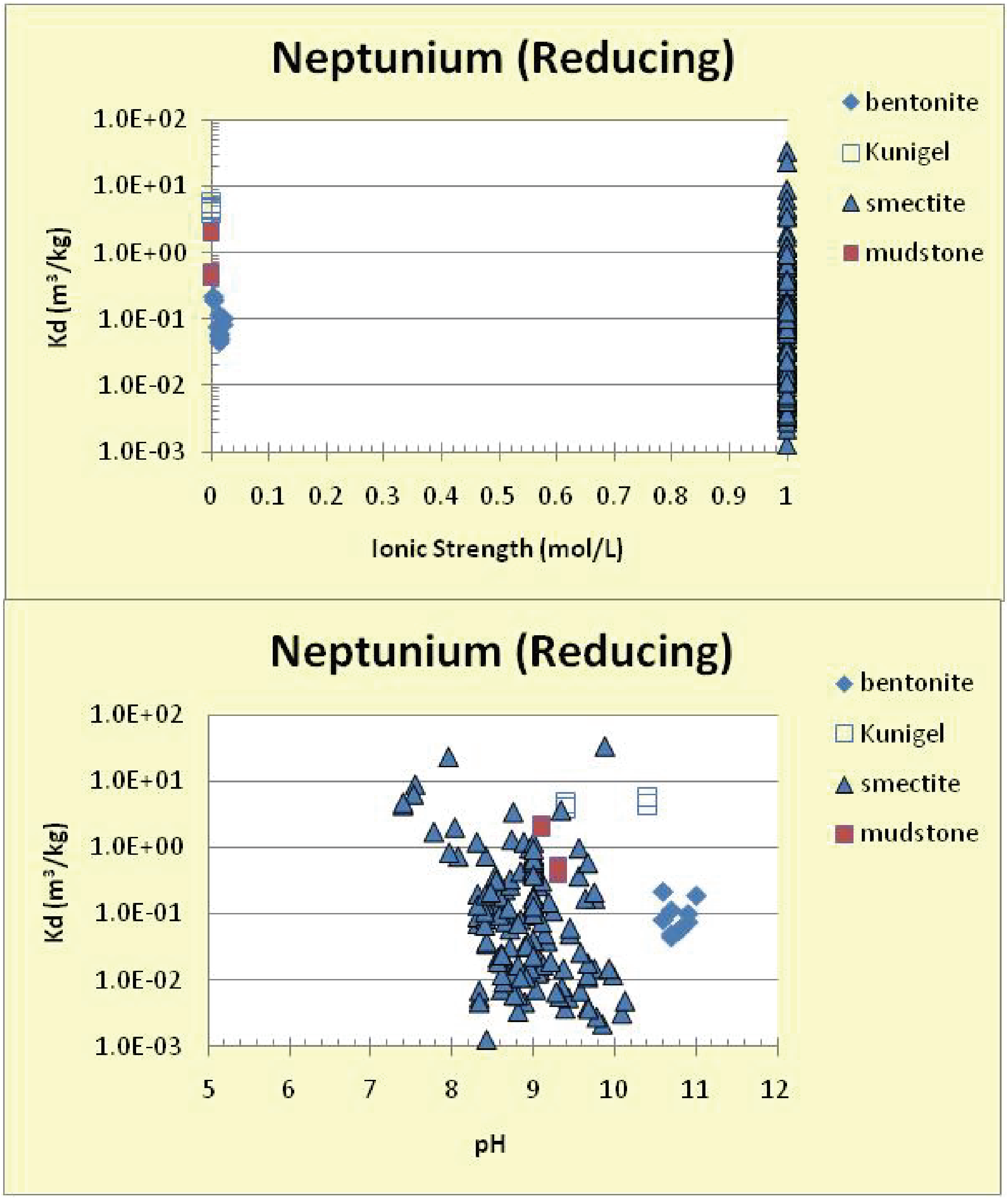


Figure 28: Neptunium Sorption Coefficients on Bentonite, Swelling Clay and Mudstone Under Reducing Conditions

3.18 PLUTONIUM

Plutonium has multiple oxidation states (III, IV, V, VI) and a complex chemistry. PHREEQC (with SIT database) predicts that under reducing conditions the III oxidation state will dominate, while under oxidizing conditions the IV and V states will dominate. The dominant aqueous plutonium species for the SR-300 reference groundwater are Pu^{+3} and $Pu(OH)^{+2}$, while SR-20 is likely to contain both Pu(III) species (Pu^{+3}, $Pu(SO_4)^+$ and $Pu(CO_3)^+$) and Pu(IV) species ($Pu(OH)_4$, $Pu(CO_3)_2(OH)_2^{-2}$ and $Pu(OH)_3^+$). In reducing dilute waters, one could expect that sorption would include cation exchange with the Pu^{+3} cation. However, in brine solutions such as SR-300, 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 database for use in the reference groundwaters should focus on measurements made with plutonium in the III oxidation state. As an alternative, one could consider using sorption results for Am(III) and Eu(III) as chemical analogs.

Plutonium sorption values under oxidizing conditions were reported by Tachi et al. (1999), Allard et al. (1979), Shibutani et al. (1994), Mucciardi et al. (1979), Salter et al. (1981), Nowak (1979), Torstenfelt et al. (1988), Morgan et al. (1988), Berry et al. (1991, 1989), Shibutani et al. (1998), and Ames et al (1981). Ticknor (1993) reported sorption values for chlorite, illite, goethite, calcite, and hematite. Sorption on mudstone was reported by Erdal (1980), Tanaka and Muraoka (1999), Daniels (1981) and Higgo et al. (1987). Francis and Bondietti (1979) reported sorption on dolomite. Maclean et al. (1978) reported sorption on limestone, and Torstenfelt et al. (1988) reported sorption on illite. Sorption under reducing conditions on bentonite was given by Shibutani et al. (1998).

Under oxidizing conditions, the sorption coefficients of Pu(IV, V) do not display a clear trend with increasing ionic strength or pH (Figure 29 and Figure 30). Under oxidizing conditions sorption values on bentonite ranged from 1.69 to 30 m^3/kg, for an ionic strength of 5 to 7 mol/L and a pH range of 6.6 to 7.7. Sorption on mudstone in seawater (ionic strength = 0.68 mol/L and pH = 8.2) ranged from 0.133 to 107 m^3/kg. Sorption values for illite (ionic strength = 0.25 to 6.4 mol/L and pH = 6.2 to 8.3) ranged from 2.26 to 5.4 m^3/kg. One sorption measurement on chlorite at an ionic strength of 0.25 mol/L and a pH of 8.25 produced a sorption coefficient of 0.57 m^3/kg. The sorption values for illite were selected to represent shale (assuming shale contains 60 percent illite) because they were determined at higher ionic strengths and a more relevant pH range compared to the measurements made with mudstone in seawater.

Sorption on limestone at an ionic strength of 5 mol/L and a pH of 6.5 had a sorption coefficient of 0.45 m^3/kg, while sorption on calcite at an ionic strength of 0.25 mol/L and a pH range of 8.3 to 9.5 produced a narrow range of sorption coefficients from 0.019 to 0.02 m^3/kg. The lower sorption on calcite compared to limestone suggests that the limestone may have contained another mineral, such as a clay, leading to an increase in its plutonium sorption. The USEPA (1998) reported Pu(V) sorption results for dolomite, which ranged from 0.020 to 0.50 m^3/kg for an ionic strength of 5 mol/L and neutral pH. Since the results for dolomite are applicable to brine solutions and span the sorption results for limestone and calcite, they have been selected to represent Pu(V) sorption on limestone.

Plutonium sorption under reducing conditions was only reported for bentonite. 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). The range of ionic strength values only extends up to 0.1 mol/L, and the sorption coefficients of Pu(III) on bentonite do not show any clear variation with ionic strength

(Figure 31). Sorption on bentonite appears to vary with pH, with the highest sorption coefficient around pH 8. Under reducing conditions plutonium sorption values for bentonite at an ionic strength of 0.1 mol/L and a pH range of 5.4 to 7.4 are 0.088 to 28 m^3/kg. The lower sorption value suggests that Pu(III) may not sorb as strongly as Pu(IV) and Pu(V). Vilks et al. (2011) measured Eu(III) sorption from brine solutions (ionic strength of 0.2 to 7.5 mol/L, and pH of 6.0 to 7.4). Eu(III) sorption coefficients were 0.097 to 5.7 m^3/kg on bentonite, 0.11 to 0.22 mol/L on shale, and 0.093 to 0.29 m^3/kg on limestone. Comparing Eu(III) sorption on bentonite with reported Pu(III) sorption values, it seems that Eu(III) could be used as a chemical analog for Pu(III). Therefore, recommended Pu(III) sorption values for shale and limestone are based on Eu(III) sorption properties.

Plutonium sorption values for sedimentary rocks are summarized in Table 21.

Table 21: Recommended Sorption Values for Plutonium

PLUTONIUM (IV, V) – Oxidizing Conditions					
			K_d Values (m^3/kg)		
	I (mol/L)	pH	Range		Geometric Mean
Bentonite	**5 to 7**	**6.6 to 7.7**	**1.7 to 30**	**4.4 (3.2)**	
comment	Muccardi et al. (1979); Nowak (1979).				
Shale	**0.3 to 6**	**6.2 to 8.3**	**1.4 to 3.2**	**2.2 (1.8)**	
comment	Based on Pu sorption on illite reported by Ticknor (1993) and Muccardi et al. (1979).				
Limestone	**5**	**neutral**	**0.020 to 0.50**	**0.10 (9.7)**	
comment	Based on Pu(V) sorption on dolomite as recommended by USEPA (1998).				
PLUTONIUM (III) – Reducing Conditions					
			K_d Values (m^3/kg)		
	I (mol/L)	pH	Range	Geometric Mean	
Bentonite	**0.1**	**5.4 to 7.4**	**0.088 to 28**	**1.6 (59)**	
comment	Shibutani et al. (1998). Data range based on 2 values.				
Shale	**0.2 to 7.5**	**neutral**	**0.11 to 0.22**	**0.16 (1.4)**	
comment	Based on Eu(III) sorption on Ordovician shale by Vilks et al. (2011).				
Limestone	**0.2 to 7.5**	**neutral**	**0.093 to 0.29**	**0.16 (1.8)**	
comment	Based on Eu(III) sorption on Ordovician limestone by Vilks et al. (2011).				

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

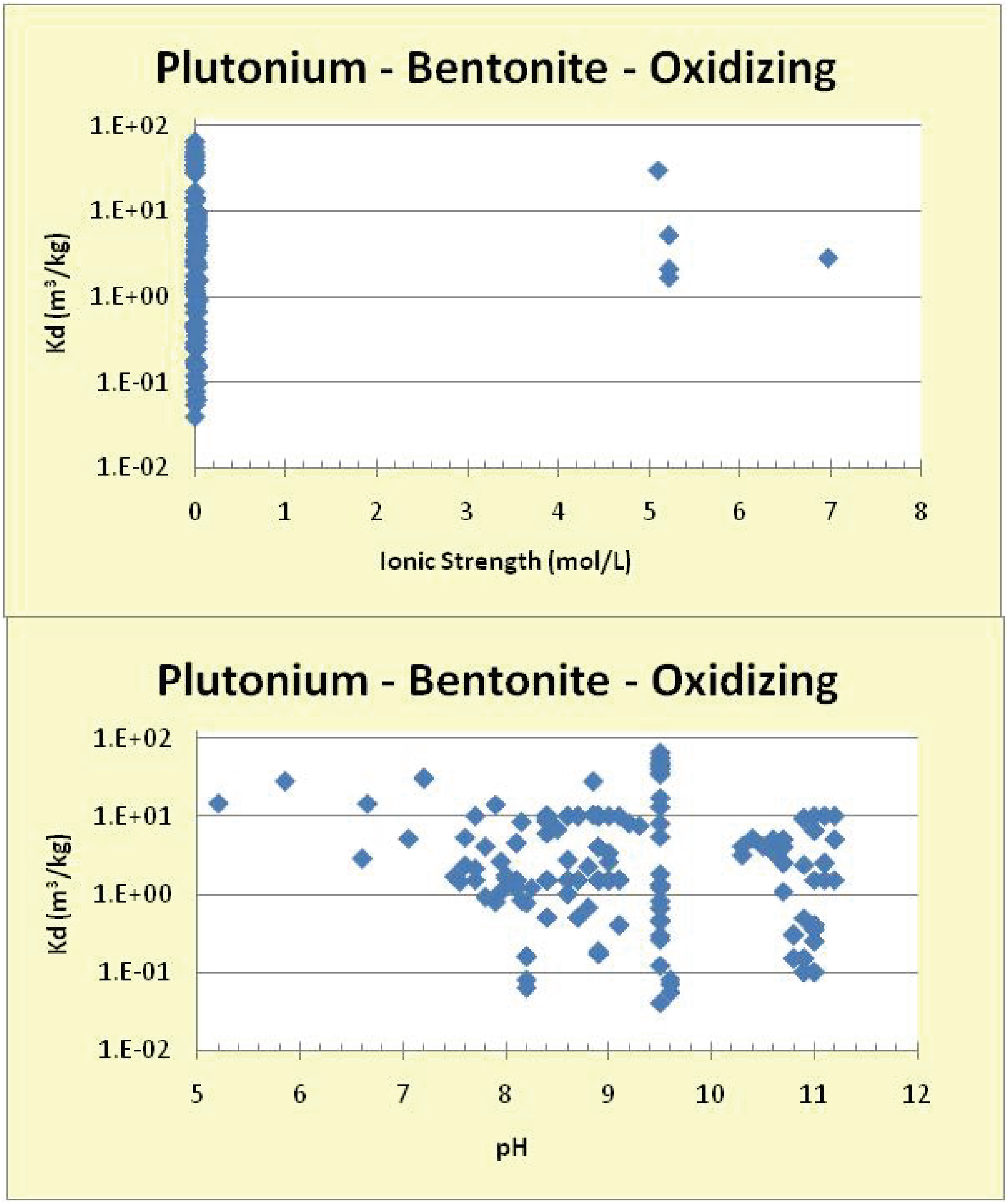


Figure 29: Plutonium Sorption Coefficients on Bentonite Under Oxidizing Conditions

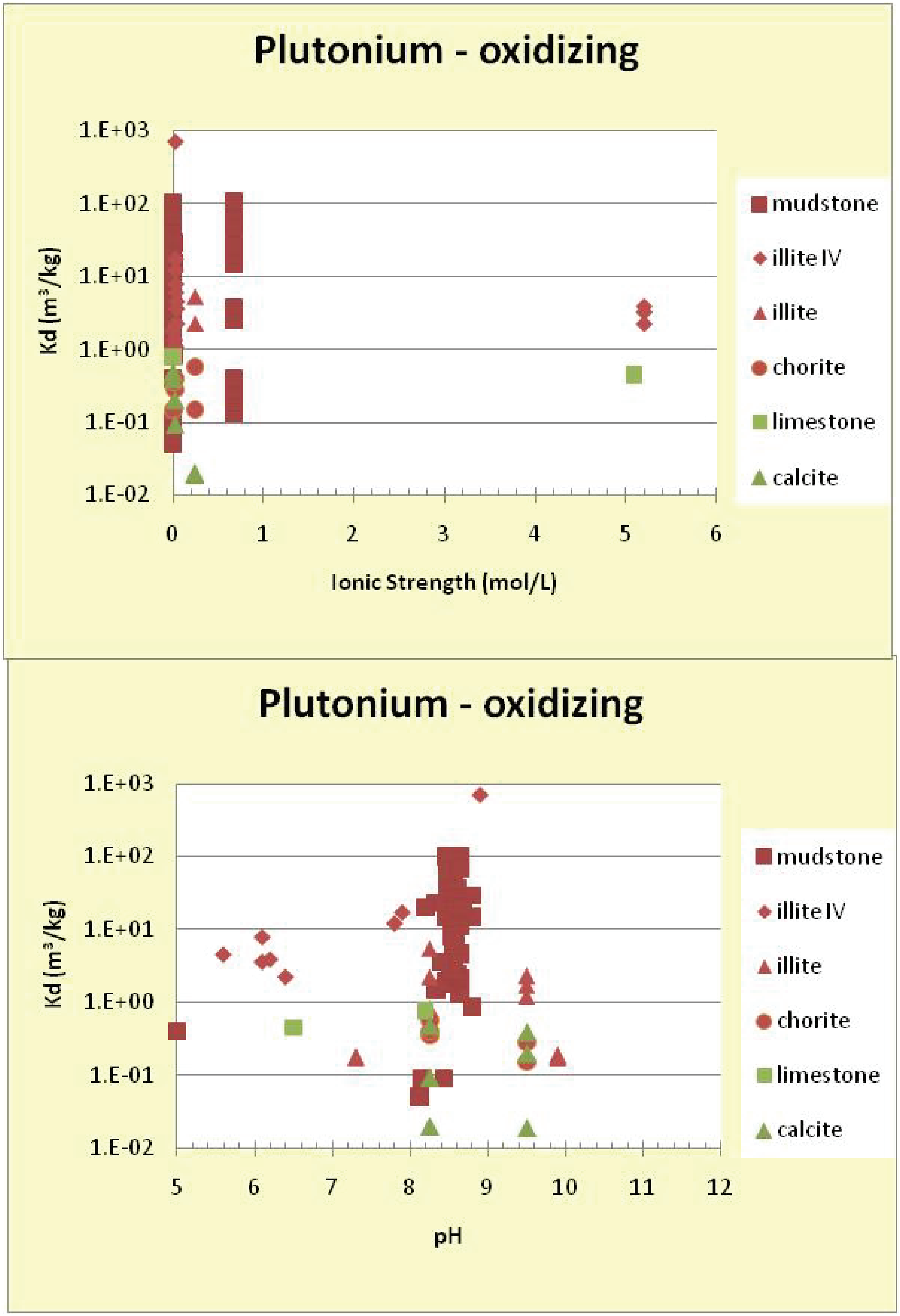


Figure 30: Plutonium Sorption Coefficients on Illite, Mudstone, Calcite, Chlorite and Limestone Under Oxidizing Conditions

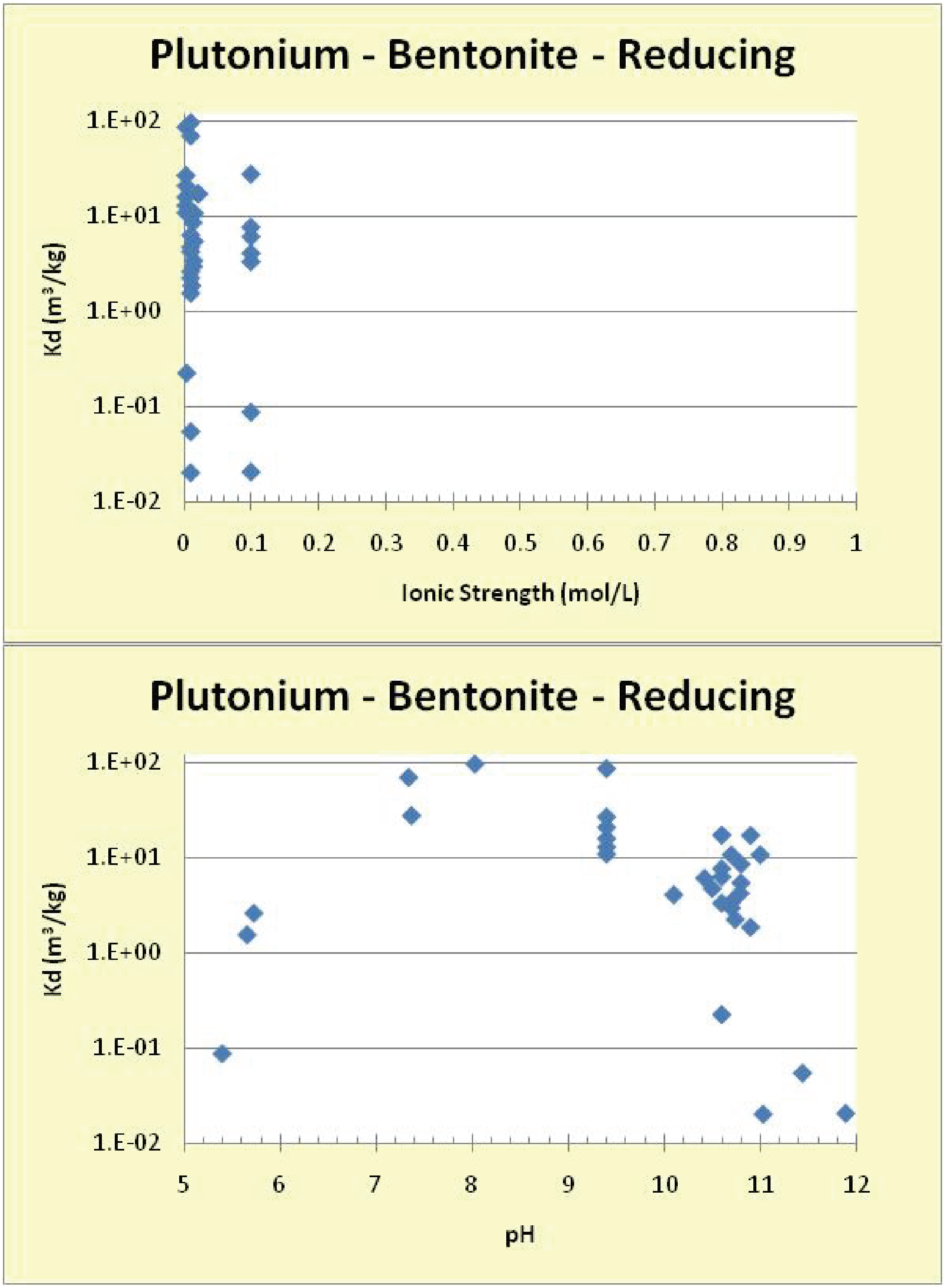


Figure 31: Plutonium Sorption Coefficients on Bentonite Under Reducing Conditions

3.19 AMERICIUM

Americium is an actinide element with a dominant oxidation state of III. PHREEQC (SIT database) predicts that in a brine solution the dominant americium aqueous species are Am^{+3} and $AmCl^{+2}$ for SR-300 and Am^{+3} and $Am(HCO_3)^{+2}$ for SR-20. 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.

Americium sorption data for bentonite, montmorillonite and smectite were reported by Barney (1981), Ikeda and Amaya (1998), Konishi et al. (1988), Morgan et al. (1988), Nowak (1979), Allard et al. (1979), Fukumoto et al. (2000), Stammose and Dolo (1990), Stammose et al. (1992), Degueldre et al. (1994), Mucciardi et al. (1979), Gorgeon (1994), Higgo et al. (1983), Ames et al. (1981), Nagasaki et al. (1997, 1994), Sato and Shibutani (1994) and Salter et al. (1981). Sorption data for illite were provided by Degueldre et al. (1994), Mucciardi et al. (1979), Gorgeon (1994) and Higgo et al. (1983). Sorption results on mudstone were given by Higgo et al. (1987). Sorption coefficients on quartz were provided by Erdal et al. (1979), Kitamura et al. (1999) and Mucciardi et al. (1979).

The large number of measured values for Am sorption coefficients onto bentonite is illustrated in Figure 32. Light blue squares are the data points recommended to represent Am sorption on bentonite in brine solutions. The selected Am sorption values are for an ionic strength range of 0.68 to 5 mol/L and pH range of 5.9 to 7.8. They range from 0.23 to 46 m^3/kg. Considering the entire data set, there are no clear trends of Am sorption on bentonite with ionic strength or pH. However, if one focuses on only the selected data, there is a slight decrease in sorption with ionic strength. At the highest ionic strength the lowest sorption coefficients were determined in a $CaCl_2$ brine, suggesting that Ca^{+2} will reduce Am(III) sorption.

Americium sorption on illite appears to increase with pH and might be slightly lower in brine solutions (Figure 33). Americium sorption on calcite in sea water appears to reach a plateau after 7 days, but then slowly increases over a time period of 56 days (Figure 34). The high americium sorption values on aluminosilicates and carbonate in the presence of high salinity suggests that americium sorbs by surface complexation to oxygens coordinated with aluminum or silica, and to carbonate surface sites.

Americium sorption on mudstone was measured in seawater (ionic strength = 0.68 mol/L, and pH = 8.2) using a large range of solid to liquid ratios, which accounts for the wide range of sorption values (11 to 1810 m^3/kg). Sorption values for illite, ranging from 0.33 to 60 m^3/kg, were taken from an ionic strength range of 1 to 5 mol/L and a pH range of 5.8 to 7.2. Americium sorption on quartz in an ionic strength of 5.2 mol/L and a pH of 7 was significantly lower (0.046 to 0.197 m^3/kg).

Recommended Am sorption values for shale were based on illite as opposed to using mudstone, because the measurements with illite were performed with brine solutions. It was assumed that shale contained 60 percent illite. Americium sorption on calcite in seawater at a pH of 7.7 was rather high, ranging from 97 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 Np(V) measurements as a chemical analog because actual tests with Am failed to produce values that could be used with confidence. The values proposed by the USEPA (1998) are recommended for Am sorption on limestone in the interests of being conservative and since they represent brine solutions as opposed to seawater.

Table 22 summarized sorption americium sorption values for sedimentary rocks.

Table 22: Recommended Sorption Values for Americium

AMERICIUM (III)				
			K_d Values (m^3/kg)	
	I (mol/L)	pH	Range	Geometric Mean
Bentonite	**0.7 to 5**	**5.9 to 7.8**	**0.23 to 46**	**6.9 (4.9)**
comment	Mucciardi et al. (1979); Gorgeon (1994); Ikeda and Amaya (1998); Nowak (1979); Stammose and Dolo (1990).			
Shale	**1 to 5**	**5.8 to 7.2**	**0.23 to 42**	**4.5 (4.5)**
comment	Based on Am sorption on illite reported by Mucciardi et al. (1979) and Gorgeon (1994).			
Limestone	**5**	**neutral**	**0.020 to 0.50**	**0.10 (9.7)**
comment	Based on Am sorption values recommended for dolomite by USEPA (1998). Data range based on 2 values.			

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

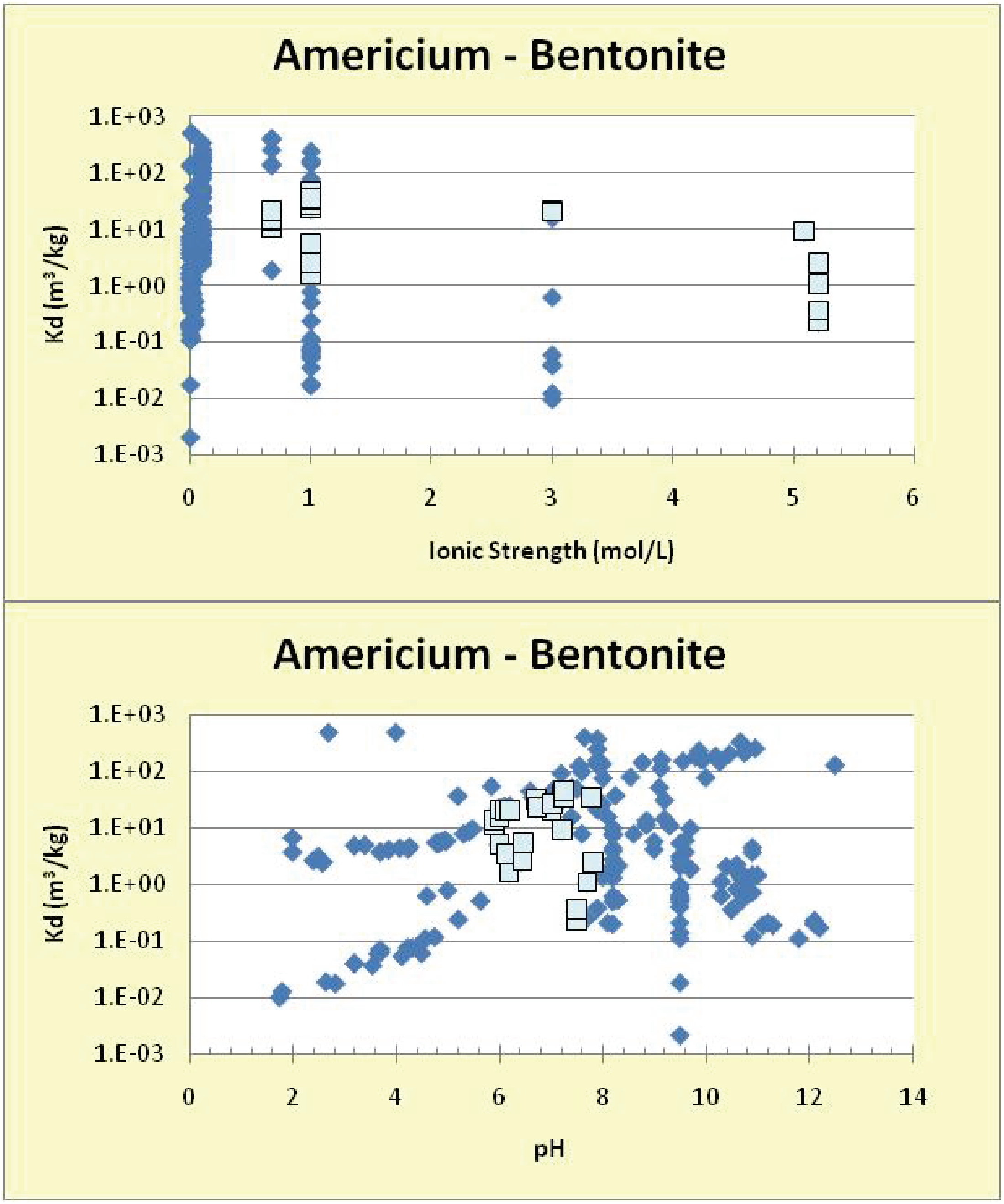


Figure 32: Americium Sorption Coefficients on Bentonite. Light Blue Squares Identify Recommended Data

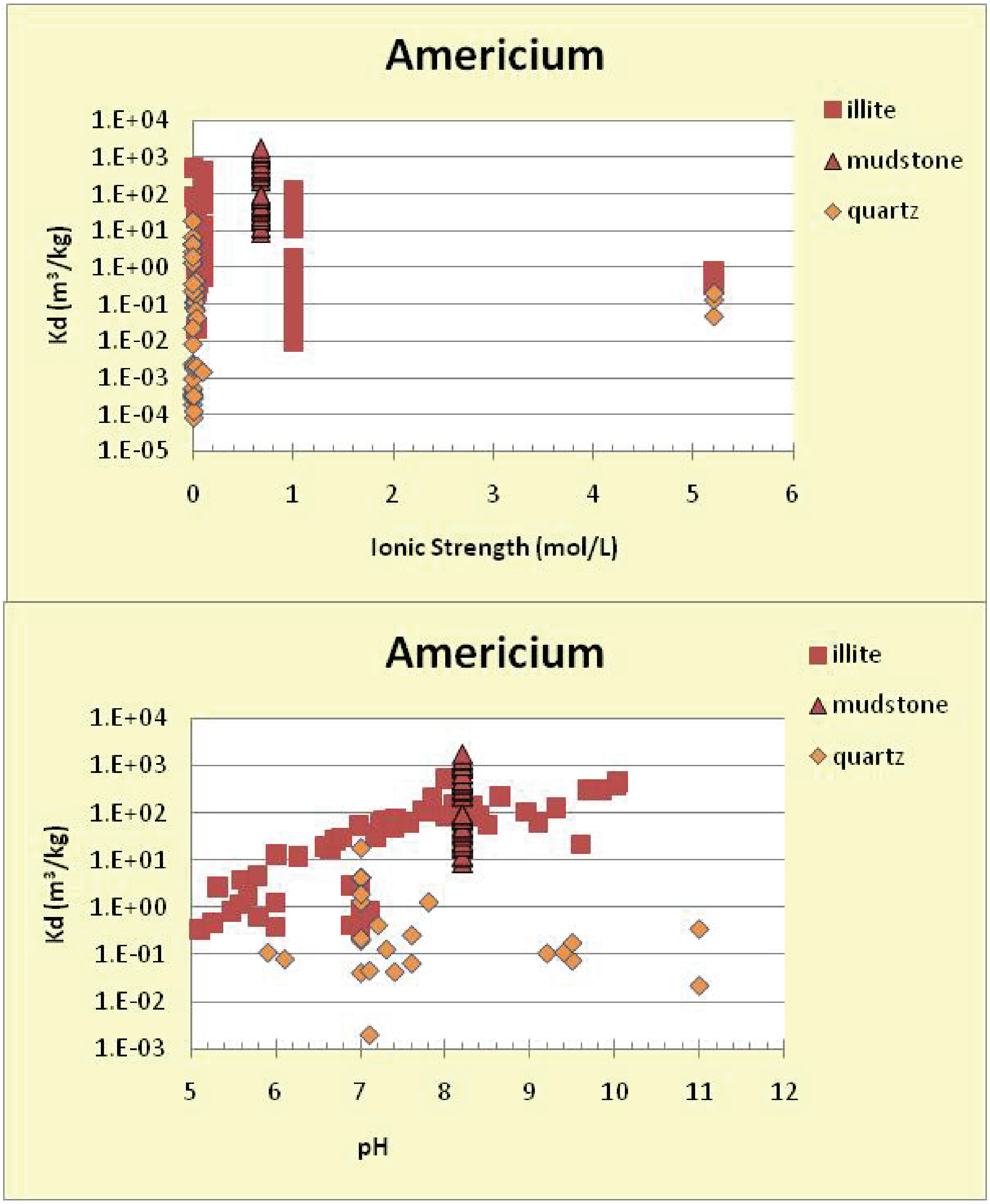


Figure 33: Americium Sorption Coefficients on Illite, Mudstone and Quartz

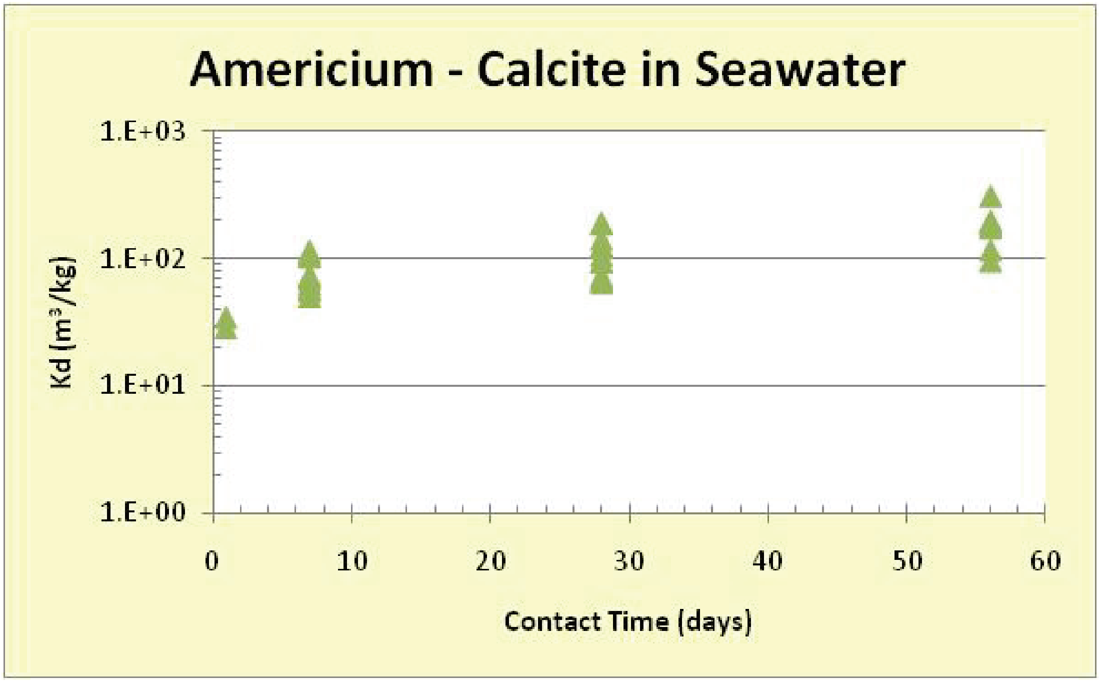


Figure 34: Americium Sorption Coefficients on Calcite in Seawater

4. SUMMARY

The international literature and sorption databases were searched to find sorption data 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. Redox conditions were factored for those elements that are redox sensitive. The elements of interest included C, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. Their recommended sorption values are summarized in Table 23.

Table 23: Summary of Recommended Sorption Values for Sedimentary Rock

	Range in K_d Values		
Element	**Bentonite (m^3/kg)**	**Shale (m^3/kg)**	**Limestone (m^3/kg)**
C inorganic	0.00002 to 0.0003	0	0.0017 to 0.090
C organic	0	0	0
Cu(II)	0.007 to 0.26	0.0001 to 0.49	0.0002 to 0.12
As(V)	0.27 to 0.28	0.25 to 0.30	0.079 to 0.57
As(III)	0.30	0.031 to 0.091	0
Se(IV)	0.014 to 0.016	0.019	0.0013
Se(-II)	0.015 to 0.17	0.0125	0.0037
Zr(IV)	0.05 to 1.6	42 to 600	no data
Nb(V)	1.2 to 1.8	1.4 to 2.8	no data
Mo(VI)	0.01 to 0.40	0.02 to 0.27	0.002 to 0.017
Tc(VII)	0.00026	0.000073 to 0.079	0.003 to 0.075
Tc(IV)	4.2 to 10	0.0007	0.017
Pd(II)	0.67 to 61.5	0.59 to 3.38	0.0004 to 0.008
Sn(IV)	660 to 2700	190 to 239	0.7 to 10
Pb(II)	0.01 to 50	0.59 to 3.38	0.0004 to 0.008
Bi(III)	25 to 50	0.11 to 0.22	0.093 to 0.29
Ra(II)	0	0.0070 to 0.032	0
Th(IV)	0.25 to 6.3	0.70 to 0.94	0.7 to 10
Pa(V)	0.017 to 0.40	0.0075 to 0.026	0.001 to 0.20
U(VI)	0.014 to 0.57	0.002 to 0.051	0.002 to 0.017
U(IV)	40 to 180	3.7 to 7.7	0.035
Np(V)	0.017 to 0.40	0.0075 to 0.026	0.001 to 0.20
Np(IV)	0.84 to 23	0.15 to 2.3	0.70 to 10
Pu(IV, V)	1.7 to 30	1.4 to 3.2	0.020 to 0.50
Pu(III)	0.088 to 28	0.11 to 0.22	0.093 to 0.29
Am (III)	0.23 to 46	0.23 to 42	0.02 to 0.50

Sorption data relevant to brine solutions were found for bentonite, shale, limestone, illite, chlorite and calcite for some, but not all elements. Where possible, chemical analog elements were used to fill data gaps. The chemical analog elements included Np(V), Th(IV), and Pb(II) for which published sorption coefficients were used. In addition, sorption data for Sr(II), Ni(II), Eu(III) and U(VI) measured on bentonite and Ordovician shales and limestone in the presence of brine solutions were used as chemical analogs. Chemical analogs were used to derive 8% of the sorption values for bentonite, 15% for shale and 35% for limestone. The recommended sorption values are intended as a starting point for the development of a Canadian sorption database for sedimentary rocks.

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