Sorption in Highly Saline Solutions – State of the Science Review

NWMO TR-2009-18

July 2009

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ABSTRACT

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Abstract

The sorption of radionuclides onto mineral surfaces within the geosphere, and on the materials making up the engineered barriers of a deep geologic repository is an important mechanism for slowing the transport of radionuclides to the surface environment. A Canadian sorption database for the post closure assessment of a hypothetical repository in the Canadian Shield with groundwater compositions having up to 11 g/L TDS was finalized in 1996. With the Canadian Government's selection of the Adaptive Phased Management approach for the long-term management of Canada's used nuclear fuel, both crystalline and sedimentary rock formations are under consideration as potential host formations (NWMO, 2005). Sedimentary rocks in Canada, for example in the Michigan basin, have been observed to contain Na-Ca-Cl and Ca-Na-Cl brines with TDS concentrations reaching 300 g/L. Deep groundwaters in the Canadian shield may also contain brines with TDS values up to 400 g/L. Therefore, there is a need to establish an understanding of how brine solutions affect sorption on sedimentary and crystalline rocks. The purpose of this report is to describe the results of a literature survey to evaluate the state-of-science knowledge of sorption processes and their contribution to mass transport, with a particular focus on processes that would occur in high salinity water. The report identifies data gaps that need to be addressed for understanding sorption in brine solutions and proposes an experimental strategy to address these gaps.

The international literature contains data for radionuclide sorption on sedimentary formations at the Gorleben site, Germany, for a range of groundwaters that include NaCl brines with TDS as high as 159 g/L. Actinide sorption on dolomite in the presence of NaCl brines with TDS up to 338 g/L has been described for the WIPP site, New Mexico. Information from these programs, combined with our current understanding of sorption mechanisms indicates that in brine solutions the mass action effects of Na^+ and Ca^{2+} will significantly reduce or eliminate the sorption of elements such as Cs^+, Sr^{2+} and Ra^{2+} that are sorbed by coulombic attraction. Elements with a strong tendency to hydrolyse at pH values above 6 will be sorbed by surface complexation with minimal effects from TDS. Although this information provides valuable background knowledge, existing sorption databases can only be adapted to high salinity solutions after one has acquired an understanding of sorption processes in Na-Ca-Cl brine solutions with Canadian sedimentary and crystalline rocks. To address this need a two-stage program of sorption experiments has been proposed, starting with sedimentary rocks and eventually including crystalline rocks. Following the approach used to establish international sorption databases, the program proposes the initiation of "in-house" experiments using Canadian sedimentary rocks, and a range of brine compositions. The experimental program includes batch experiments to address sorption specific issues, and dynamic transport experiments designed to relate sorption processes to mass transport. The first stage would develop experimental protocols and collect scoping data. Stage 2 would build on the understanding gained in the first stage to improve the understanding of sorption processes and to develop predictive abilities through modelling efforts.

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1. INTRODUCTION

The sorption of radionuclides onto mineral surfaces within the geosphere, and on the materials making up the engineered barriers of a deep geologic repository is an important mechanism for slowing the transport of radionuclides to the surface environment. It is widely recognized that the only likely pathway for radionuclides to be transported from a deep geologic repository to the surface environment is through the water that occupies the connected fracture network that is present to varying degrees in rock formations. If the concentrations of dissolved radionuclides remained unchanged in water conducting fractures, the rate of radionuclide mass transport to the surface environment would be determined mainly by the rate of groundwater flow. If radionuclide concentrations in groundwater are decreased, the transport of radionuclide contaminants by groundwater is reduced or slowed down. Processes that reduce radionuclide concentrations in fractures include physical mechanisms such as matrix diffusion and dispersion, and chemical processes such as precipitation, coprecipitation and sorption. While precipitation and coprecipitation are important mechanisms for limiting the total dissolved radionuclide concentrations and removing radionuclides from solution when there is a sudden change in groundwater chemistry, sorption reactions remain the most important process for reducing dissolved radionuclide concentrations, particularly when the contaminants are present at trace concentrations.

Sorption reactions involve complex processes that depend upon the properties of individual radionuclides, dissolved radionuclide concentrations, the properties of sorbing minerals, groundwater chemistry (pH, Eh, ionic strength, complexing ligands), and time. The sorption of a given radionuclide onto a mineral may be determined by a number of different mechanisms, whose relative importance is determined by radionuclide concentration, water chemistry and time. Sorption mechanisms include non-specific coulombic sorption (diffuse layer and Stern layer), specific chemical sorption, surface induced precipitation, structural penetration and chemical substitution and isotopic exchange. This complicates the understanding of sorption processes. Furthermore, certain experimental techniques that could provide insight into the mechanisms that bond radionuclides to mineral surfaces may require high radionuclide concentrations and experimental conditions that are not relevant to natural systems.

Although sorption processes may involve a number of complex mechanisms, the performance assessment calculations that make use of sorption data require simplifications and approximations. Performance assessment models usually require sorption properties to be incorporated in the form of distribution coefficients that are specific to certain rock types and may be given as a function of radionuclide concentration and groundwater chemistry. The use of distribution coefficients in performance assessment calculations makes the assumption of equilibrium and reversible sorption, which may not always be valid. A good understanding of sorption mechanisms is required to determine what sorption data and assumptions can be used to consider sorption effects in performance assessment.

The treatment of sorption and the derivation of a sorption database for the postclosure assessment for the previous Canadian deep geological repository concept in plutonic rock of the Canadian Shield has been described by Vandergraaf (1982), Davison et al. (1994), Vandergraaf and Ticknor (1994), Ticknor and Vandergraaf (1996), and Ticknor and Vandergraaf (1997). The sorption database took the form of a parametric equation that calculated a distribution coefficient (R_d) as a function of Total Dissolved Solids (TDS) and contaminant or radionuclide concentration ([RN]). The use of pH and Eh as independent variables was rejected because of the uncertainties associated with controlling these parameters in sorption experiments. The sorption database compiled by Vandergraaf and Ticknor (1994) was based on literature values and experiments performed in groundwaters whose compositions ranged from a freshwater Ca-Na-HCO_3-SO_4-Cl solution with a TDS of 0.1 g/L to a saline Ca-Na-Cl-SO_4 solution with a TDS of 11.3 g/L. The freshwater composition was representative of shallow granitic groundwater, while the saline solution was representative of water from a depth of ~ 500 to 1000 m in the Canadian Shield (McMurry, 2004). The sorption database includes values for sorption onto igneous rocks (grey granite, red granite, gabbro) and a variety of minerals (biotite, calcite, chlorite, epidote, gypsum, goethite, hematite, illite, kaolinite, microcline, muscovite, plagioclase, and quartz). The sorption database also includes several parameters that account for the uncertainty associated with the natural variability of rock and water compositions and a normalizing factor for different geologic materials to account for their specific surface area.

Although the range of groundwater compositions used to define the sorption database compiled for the Canadian nuclear waste management program was believed to be representative of groundwater chemistries likely to be encountered at the depth of a deep geologic repository, deeper groundwaters in the Canadian Shield may have significantly higher salt contents. Frape et al. (1984) and Gascoyne et al. (1987) reported the existence of Ca-Na-Cl brines at mines in Thompson, Sudbury and Yellowknife, with TDS values of 100 to 418 g/L. Granite rocks from depths of 400 to 1000 m have been found to contain saline waters with compositions of Ca-Cl, Ca-Na-Cl, and Ca-Na-Cl-SO_4, and TDS values ranging from 12 to 90 g/L (Gascoyne et al., 1987, and Vilks et al., 2004). The existence of brines and groundwaters with higher salinity indicates that the sorption database for Canadian Shield crystalline rocks compiled by Vandergraaf and coworkers may need to be revised to be valid for assessing the safety case for a deep geologic repository that is sited in rocks containing highly saline and possibly brine solutions.

Currently both sedimentary and crystalline rocks are considered as potential hosts for a deep geologic repository (NWMO, 2005). A geoscientific assessment was completed on the suitability of the Paleozoic sedimentary rock sequence occurring beneath southern Ontario to host a Deep Geologic Repository (DGR) for used nuclear fuel (Mazurek 2004). Based on an initial assessment using simple criteria (existence of low hydraulic conductivity rock mass, formation depth below ground surface, formation thickness, and simple formation geometry), suitable bedrock formations were identified as the Middle/Upper Ordovician age (ca. 470 - 443 Ma) shales (Blue Mountain, Georgian Bay and Queenston Formations) and underlying limestones (Simcoe Group, i.e*.,* the Gull River, Bobcaygeon, Verulam and Lindsay Formations). Mazurek (2004) indicated that future work to determine the suitability of Ordovician sediments to host a DGR should include the acquisition of formation specific data to support the quantification of solute transport retardation, such as mineralogy, porosity, diffusivity, ion exchange and sorption characteristics, pore-water composition and redox state. The Ordovician sedimentary rocks underlying the Bruce Nuclear site are currently being considered as a site for a low and intermediate level radioactive waste DGR (Heystee and Jensen, 2005). The pore waters and groundwaters of Ordovician shales and limestones of southern Ontario have high salinities, with TDS values ranging from 30 to 304 g/L (McNutt et al., 1987, Sherwood and Frape, 1989, Vilks and Miller, 2007). The major element compositions of these waters are either Na-Ca-Cl or Ca-Na-Cl.

Since it is possible that a DGR will be sited in a formation, either crystalline or sedimentary, containing groundwater with high salinity, there is a need to improve the understanding of sorption reactions in waters with high salt concentrations.

In this report the definitions of water types will be consistent with conventions used by Kharaka and Hanor (2004), Frape et al. (1984), and Carpenter et al. (1974). Fresh water is considered to be any water with a TDS < 1 g/L, which includes many shallow groundwaters. Brackish water has a TDS ranging from 10 to 35 g/L. The term saline water is applied to waters with a TDS from 10 to 100 g/L, keeping in mind that seawater has a TDS of 33 to 37 g/L. The term brine is reserved for waters with a TDS > 100 g/L. The term salinity ($^{0}/_{00}$) "is defined as the weight in grams of the dissolved inorganic matter in 1 kg of seawater after all Br^- and I^- have been replaced by the equivalent quantity of Cl^- and all HCO_3^- and CO_3^{-2} have been converted to oxide" (Stumm and Morgan, 1981). Salinity is synonymous with Total Dissolved Solids, often reported as mg/L or g/L. Groundwater compositions are often classified in a form like "Ca-Na-Cl-SO_4", where the major cations are listed first in order of decreasing concentration, followed by anions in order of decreasing concentration. An element is listed only if its mass concentration is ≥ 5 % of the total TDS concentration (Kharaka and Hanor, 2004).

The purpose of this report is to present the results of a state of the science review of sorption processes with the aim of identifying a strategy to move forward on establishing a scientifically defensible methodology for quantifying the effects of sorption in mass transport and performance assessment calculations with an emphasis on highly saline solutions. The NWMO has not identified a specific site or rock formation as a potential host for a DGR for used fuel. Therefore, at this time the performance assessment requirements for the Canadian Adaptive Phase Management of used nuclear fuel are limited to understanding sorption on general sedimentary and crystalline rock types, without reference to a specific formation. Since sorption on Canadian crystalline rock has been extensively studied, there is an urgent need to obtain sorption data for sedimentary rock, such as the Ordovician shales and limestones of southern Ontario. The specific objectives of this report are to:

- Evaluate current understanding of sorption mechanisms and how they influence mass transport.
- Determine performance assessment requirements for quantifying the effects of sorption, particularly with respect to data types and useful mathematical expressions.
- Identify state of the art methodologies for studying sorption.
- Assess the availability of sorption data for highly saline solutions to formulate initial concepts of sorption at high salinity, and identify information gaps.
- Develop an experimental strategy for moving forward on furthering the understanding of sorption processes and establishing a sorption database that is relevant for quantifying the effects of sorption on radionuclide transport in the presence of highly saline solutions.

2. SORPTION CONCEPTS

Chapter 2 is intended to summarize the current understanding of sorption concepts to provide a foundation for understanding sorption behaviour in brine solutions, and for formulating a plan to develop a sorption database that is relevant to simulating contaminant transport in highly saline conditions. These concepts include what is known about sorption mechanisms, mathematical models for quantifying sorption, models used for predicting sorption, and experimental methods for studying sorption processes.

2.1 PROCESSES TO CONSIDER

The observed transfer of dissolved radionuclides or contaminants (sorbate) to a solid phase (sorbent) may be the net result of a number of different processes occurring in a number of different locations on the solid. Sorption is a general term that is used to describe this process, without specifying the location(s) or mechanism(s) responsible for the attachment. Adsorption is defined to be the attachment of a dissolved species to the surface of the solid. A dissolved species is considered to be absorbed if it enters the interior of the solid through a defect or a network of capillaries. The total adsorption capacity of a solid is determined by the solid's available surface area, while the total capacity for absorption depends on the solid's total volume that is accessible to diffusion. Adsorption is likely to be faster and more reversible than absorption since diffusion through a solid is not required. Co-precipitation involves the incorporation of a dissolved species into a mineral structure at the time of mineral formation. It may not involve diffusion through a solid and is probably even less reversible than absorption.

Although sorption may involve a number of different processes, performance assessment calculations require a simplification in the form of an overall sorption reaction that is valid for a given set of minerals and water chemistry. A good understanding of the mechanisms that provide a significant contribution to the sorption process is required to provide a defensible set of sorption parameters for performance assessment. Different sorption processes respond to changes in water chemistry in different ways, and may lead to different forms of attachment that may or may not be subject to desorption. A consideration of sorption mechanisms is also a key component for the design of any experimental program.

The sorption of metals is very pH dependent (Figure 1), often with sharp increases in sorption between pH 4 and 8 (O'Connor and Kester, 1975; Payne and Pickering, 1975; and Farrah and Pickering, 1977). This sharp increase in sorption for a given element over a narrow pH range has been called the sorption edge. At very high pH sorption may decrease again because of the formation of soluble hydroxyl species. The effect of pH on the sorption of a given metal depends upon which mineral is controlling the sorption. For example, sorption on kaolinite and illite is more affected by pH than sorption on montmorillonite. The pH may affect sorption by (1) the effect of H^+ as a counter ion in non-specific adsorption, (2) the dependence of some surface charges on pH, (3) the dissolution of Al at low pH, and (4) the effect of H^+ on the complexing capability of surface sites and the precipitation of hydroxides. The presence of complexing ligands will complicate sorption reactions, particularly their relationship to pH (Farrah and Pickering, 1977). Ligands can reduce sorption by keeping a metal in solution or they may enhance adsorption if the ligand has an affinity for the surface.

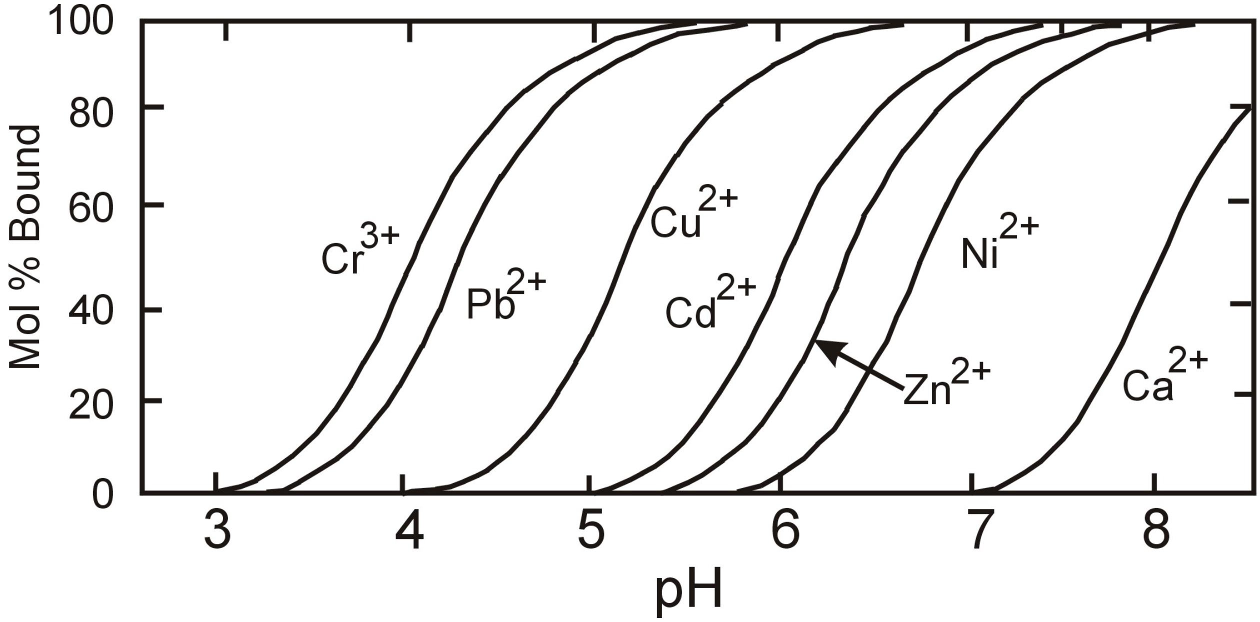


Figure 1: The pH Dependence of Metal Sorption on Fe Oxide (After Stumm, 1992).

Sorption of trace elements is reduced by increasing salinity, but is not eliminated (O'Connor and Kester, 1975, and Garcia-Miragaya and Page, 1976). As the salt concentration is increased trace elements held by non-specific electrostatic forces will be displaced by the major salt ions. The amount of divalent metal ions held by non-specific sorption in the presence of a salt solution can be predicted (Babcock, 1963). If the quantity of sorbed metal exceeds this predicted value, as in the case of trace metals in seawater, then specific chemical sorption must be significant. Seawater can also reduce the sorption of a metal if the metal is complexed by the chloride ion as in the case of Cd.

Sorption is also a function of sorbate concentration. In some cases if the sorbate concentration is very low or if the concentration range of interest is not large, the amount of sorbed metal may increase linearly with metal concentration in solution. In this simple situation the sorption isotherm can be described by a distribution coefficient given by the ratio of sorbed element to the element still in solution. When sorption is considered over a wider range of sorbate concentrations the amount of sorbed element can no longer be described by a linear relationship with the element concentration in solution. Section 2.2 describes various mathematical approaches and models to describe the relationship between the amount of sorbate attached to the solid and the concentration of sorbate in solution (as expressed by the sorption isotherm).

There are other factors that should be considered when designing and interpreting sorption experiments. Surface area is very important because the amount of area at the interface ultimately determines the quantity of sites available for adsorption. Surface area is determined by a mineral's crystallinity, surface morphology and grain size. It has been observed that the concentration of sorbed metals decreases as the concentration of solid particles is increased, particularly in suspension with low solid/liquid ratios. Our choice of experimental solid/liquid ratio is limited by the need to have enough solid to produce a measurable change in solution sorbate concentration. In salt solution, clay-sized particles may coagulate into flocs that may affect the sorption process by either blocking sorption sites or by enhancing sorption by raising metal concentrations in the interstitial water of the clay flocs. Another problem encountered by sorption studies on minerals, such as clays, is the purity of the mineral sample. It is possible that sorption is masked by the presence of surface oxides of Fe, Mn or Al and/or surface complexing ligands (Jenne, 1977, and Lim et al., 1980). Procedures have been developed for removing some impurities (Ostram, 1961; Fordham, 1969, and Anderson and Jenne, 1970), but in some cases severe treatments can alter the mineral surface and create new sorption sites.

Table 1 summarizes some of the parameters which must be considered in experimental design and which must be consistent with any sorption theories.

Table 1: Factors Important to Sorption

Parameter	Comment
pH	Strong increase in sorption within the middle pH range.
Sorbate concentration	Depending on sorbate concentration the increase in sorption can be linear or non-linear with concentration.
Temperature	In many cases increased temperature is likely to reduce sorption
Pressure	Important if sorption leads to a volume change
Salt concentration	Reduces non-specific sorption through mass action effects.
Complexing ligands	Can reduce or enhance sorption
Eh	Affects the chemistry of redox sensitive sorbates, sometimes significantly affecting sorption.
Solid/liquid ratio	Can influence measured sorption at low solid concentrations.
Specific Surface area	Determines the amount of available surface sites.
Exchange capacity	Determines the total amount of sorption by ion exchange
Type and density of surface sites	Determines the total amount of sorption by surface complexation.
Mineral pre-treatment	Can standardize a surface, but can also produce artefacts. Sorption results can be affected by the amount of time the mineral is conditioned in the experimental ionic medium.

2.1.1 Sorption Mechanisms

Sorption is not a simple process, and there are differing views as to which mechanisms control sorption properties. For example, McBride (1976) demonstrated that in his experiments Cu sorbed on kaolinite was mobile and was held by electrostatic attractions, while Farrah and Pickering (1976a) suggest that in their experiments Cu may be taken up by kaolinite by a surface induced precipitation. This is a good example of how experiments carried out under different experimental conditions can emphasize different sorption mechanisms and lead investigators to differing conclusions regarding the sorption of a given metal on a certain mineral.

Non-specific coulombic sorption: Most mineral surfaces, which are immersed in water, carry some sort of charge. If the charge is positive it will be compensated by anion adsorption at the surface. This simple type of coulombic attraction has been used to account for many reversible ion exchange reactions. It is also the underlying principle of more complicated models, which describe ion accumulation as a function of distance from a charged surface. These models have been used to explain the flocculation behaviour of clay suspensions (Stumm and Morgan, 1981), the effect of surface charge on surface coordination reactions (Schindler and Gamsjager 1972: Hohl and Stumm, 1976), electrophoretic mobilities, osmotic pressures, surface conductances and membrane potentials (Van Olphen, 1977). Coulombic adsorption is probably very important for group IA and IIA elements, which do not form very strong oxygen bonds in most aqueous environments.

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 clay minerals this condition is fulfilled at those upper or lower faces that consist of the inert basal oxygens of the tetrahedral layer. Hydroxyls from the gibbsite layer, which are exposed at the upper or lower faces may also satisfy this condition. On the other hand, the edges of clay crystals contain broken bonds resulting from the interruption of the gibbsite and silica sheets. Once exposed to water the reduced coordinations of oxygen atoms at the surface will be quickly satisfied by coordinations with one or two hydrogen ions. Any exposed silica or alumina will coordinate with oxygen in water molecules. In either case the result is the formation of a surface containing oxygens, which can coordinate with one or two hydrogen ions. If this surface is dominated by oxygens with two hydrogens, then it will be positively charged. If no hydrogens are bound to the oxygens a negative charge will result. If only one hydrogen is bound to each oxygen, or if the positive and negative sites are equal, then no net charge will result.

Kaolinite provides an example of clay mineral whose crystal structure can be used to explain the heterogeneous charge distribution on its surfaces. Follet (1965) used electron microscopy and the sorption of negatively charged gold sols to demonstrate that kaolinite grains have positively charged edges and negatively charged faces. Since the kaolinite edges are made up of alternating silica and alumina (gibbsite) layers, one could expect that any variable charge developed there could be predicted by mixing the charges of silica gel with that of gibbsite, both of which have been determined independently. Above pH 2.5, silica is negatively charged, so that the edge surface of the silica sheet should carry a negative charge under most natural pH conditions. However, the alumina layer in exposed kaolinite edges has been shown by alkalimetric-acidimetric titrations to have a variable charge with a pH of zero charge (pH_{pzc}) around 7.5. The intrinsic acidity constants of the ≡MOH groups on the edges of the alumina layer were found to be $pK_{a,1} = 6.3$ and $pK_{a,2} = 8.7$, which are comparable to the values determined for γ-Al_2O_3, $pK_{a,1} = 7.4$ and $pK_{a,2} = 10$ (Stumm, 1992). The silica faces on kaolinite carry a negative charge due to the substitution of Si^{+4} by Al^{+3} in the silica sheet. The exposed ≡MOH groups on gibbsite faces are different from edge sites, and with a pH_{pzc} of about 4 have a negative charge under most natural pH conditions. In summary, the crystal structure of kaolinite can be used to explain the existence of a variable (often +) charge on the edges and negative charges on Si and Al faces.

The distribution of cations around a negatively charged surface can be described by the Gouy-Chapman theory of the diffuse-double layer, in some combination with the Stern theory of an adsorbed monolayer at the surface (Bolt, 1955, 1955b, Overbeek, 1952, Stern, 1924, van Raij and Peech, 1972, Dixon and Weed, 1977, and Stumm, 1992). The diffuse layer and the Stern layer are two distinct regions surrounding a charged surface (Figure 2). Although cations in both of these regions may be held by electrostatic forces, it is worthwhile to make the distinction between these zones because the properties of an ion in the diffuse layer may be slightly different from an equivalent ion in the Stern layer. The concept of a diffuse layer in combination with a surface monolayer is important for surface science because these theories attempt to describe the transition from a solution to the space immediately adjacent to the solid surface.

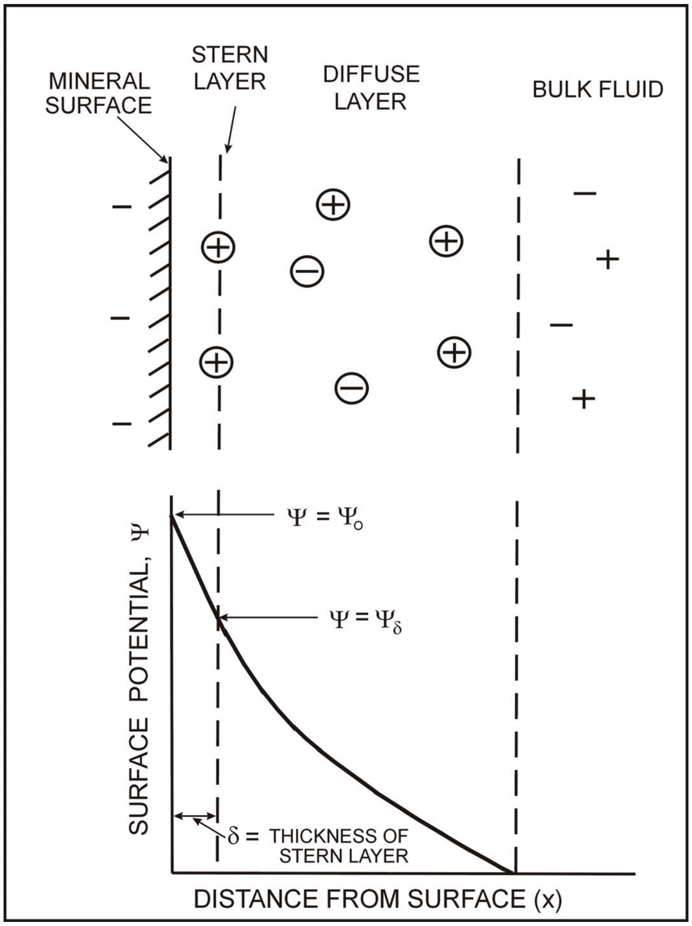


Figure 2: The Distribution of Ions and Electric Potential with Distance from a Charged Surface According to Stern's Model.

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. Ions that have the opposite sign as the surface and which balance the surface charge are known as counter ions, while ions which have the same charge as the surface are known as co-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). Dixon and Weed (1977) and Stumm (1992) give good summaries of equations used to calculate surface charge. The influence of the diffuse layer can extend more than 100 Angstroms away from the solid surface. As the electrolyte concentration is increased or if dominant monovalent cations in solution are replaced by divalent cations, then the thickness of the double layer will decrease to 20 Angstroms. The decrease in double layer thickness affects the stability of colloidal particles, the porosity available to mass transport in rocks, and is likely to have some influence on sorption reactions.

Coulombic sorption in the Stern layer: The Gouy-Chapman theory of the diffuse layer does not work for surfaces with very large potentials because the theory does not account for the volume taken up by ions in solution. At high potential surfaces Gouy-Chapman theory predicts unreasonably high cation concentrations. To overcome this problem, 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. Therefore, Stern theory includes a term for maximum sorption capacity. 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.

Double-layer theory does predict that ions with a higher charge will be preferred over ions of a lesser charge. Erickson (1952) derived from double layer theory an equation which calculates the fraction of the surface charge neutralized by monovalent ions in a mixture of monovalent and divalent salts (Gast, 1977).

$$\frac{\Gamma_1}{\Gamma} = \frac{r}{\Gamma\sqrt{B}}\sinh^{-1}\left(\frac{\Gamma\sqrt{B}}{r + 4v_d\sqrt{m_2}}\right) \qquad (1)$$

where:

Γ_1 = charge neutralized by monovalent cations
Γ = total surface charge density (meq/cm^2)
r = the "reduced ratio" = $m_1/(m_2)^{-1/2}$
m_1 = monovalent salt molar concentration in bulk solution
m_2 = divalent molar salt concentration in bulk solution
B = $8000\pi F^2/DRT$, where F = 2.982×10^{-11} esu/meq and D is the dielectric constant, R=the gas constant, T=the absolute temperature.
At 25° C, $B = 1.08 \times 10^{15}$ cm mole/meq^2
ν_d = cosh y at the midplane between clay particles (assumed to be 1), where
y = $z_i e\, \psi / k$T (z_i is the valence, e is the electric charge, ψ is the electrical potential, k is the Boltzman constant and T is the absolute temperature).

Gast (1977) gives an example calculation with equation 1. Upton Wyoming bentonite with a surface charge density of 5.17 x 10^4 esu/cm^2 is placed in a solution containing 0.004 mol/L Ca^{+2} and 0.012 mol/L Na^+. Even though there is about three times as much Na, the Na neutralizes only 11 percent of the surface charge.

In summary, coulombic sorption has very rapid sorption and desorption kinetics and is very reversible. It is an important sorption mechanism for group IA and IIA 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.

Specific chemical sorption: There are several sorption phenomena, which are distinct from non-specific coulombic attraction. For example, positively charged metal ions have been known to sorb onto positively charged goethite at pH values below 7. 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. Selectivity produced by differences in hydrated radii and by the divalent charge on metals will not be great enough to allow significant non-specific trace metal sorption in the presence of salt solution. O’Connor and Kester (1975) were able to measure significant amounts of Cu and Co sorption onto illite in the presence of seawater. Due to this 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”.

Another feature that is difficult to explain by non-specific coulombic interaction is the sharp increase in sorption with pH produced in the mid pH ranges (Figure 1). 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). A similar sorption relationship with pH has also been described for clays by Hodgson (1960), O’Connor and Kester (1975), Payne and Pickering (1975), and Farrah and Pickering (1976a, 1976b, 1979). The sharp increase in metal sorption cannot result from a non-specific competition from H^+ ions because in some experiments metal concentrations (10^{-4} mol/L) greatly exceed hydrogen ion concentrations. The sorption jump for different metals occurs at different pH values, which would not be the case if the sorption jump was caused by a change in the surface charge. The cations with the strongest hydrolysis constants have their sorption jumps at lower pH values, suggesting the formation of metal oxygen bonds. These sorption jumps cannot be explained away as simple hydroxide precipitation since metal solubility was not exceeded in the bulk solution.

Further evidence for the existence of specific chemical sorption comes from the observed irreversibility of metal sorption reactions as noted by Hodgson (1960) and Farrah and Pickering (1978). As pH is raised sorption may exceed a clay’s cation exchange capacity, which is attributed to the permanent negative charge of the clay structure. Kaolinite has low cation exchange capacities, which may fall in the range of 2 to 15 meq/100g. Farrah and Pickering (1978) measured 30 mmoles Cu/100 g (60 meq/100 g) on kaolinite exposed to 1.6 x 10^{-4} mol/L Cu at pH 6.5.

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.

Surface induced precipitation: Surface induced precipitation occurs when the solubility product of a potential precipitate is exceeded at the surface, but not in the free solution. This mechanism is conceptually distinct from surface precipitation, but unfortunately the effects are very similar, particularly when the precipitating species are hydroxides. Surface precipitation of metals has been proposed by Farrah and Pickering (1976a, 1976b, 1979), Payne and Pickering (1975), and Bingham et al. (1964). Surface precipitation by silicic acid has been described by Tiller (1967). The solubility product of a metal precipitate will be exceeded if the metal concentration and/or the complexing anion concentration are raised. Metal concentrations higher than the free solution are found at the negatively charged faces of clay grains. Clay edges may be positively charged so that concentrations of anions such as OH^- are concentrated at edge sites. The higher pH values found near the edges of clay grains may promote the precipitation of metal hydroxides, particularly if there is a collision between a clay face, enriched with metal, and an edge, with a higher pH. Although OH^- is probably the most common anion to produce precipitation, Farrah and Pickering (1976a, 1976b) have shown that phosphate will produce Cu and Pb precipitation, and sulphate will precipitate Pb. Bingham et al. (1964) measured increased Cu and Zn precipitation in the presence of acetate.

Although surface precipitation by some anions such as phosphate and SO_4 can be demonstrated, the more general case of precipitation with OH^- is very difficult to distinguish from complexation reactions with surface oxygens. It has been observed that cations with the stronger first hydrolysis constants are also more strongly adsorbed by silica (Dugger et al., 1964), and transition metals with stronger hydrolysis constants have their sorption jump at lower pH values. Unfortunately this observation supports the precipitation mechanism as well as surface complexation. The first hydrolysis constants give a measure of the relative ability of metals to bind with oxygen bonds. Farrah and Pickering (1979) found that metal sorption to cellulose was similar to that on clays whose surface oxygens are expected to be different from those on cellulose. Precipitation reactions, which are less dependent on the type of surface sites, could be used to explain the observed similar sorption properties of clays and cellulose.

Further evidence for precipitation comes from the work of O'Connor and Kester (1975), who found similar sorption relationships to pH for Cu on illite and polyethylene, and for Co on illite and sand.

McBride (1982) used Electron Spin Resonance (ESR) to distinguish a surface complexation reaction and a precipitation reaction controlling Cu sorption by Al hydroxides. The Cu fraction, which was believed to coordinate to surface sites, was sorbed more rapidly and, according to the ESR spectra, was spaced evenly on the mineral surface. Precipitated Cu fraction was sorbed more slowly (hours) and the ESR spectra indicated that the Cu ions were bunched together at nucleation sites. When the Al hydroxides were subjected to NH_3 vapor it was found that the precipitated Cu was easily desorbed, while the Cu bound to surface sites resisted desorption. McBride also found a correlation between mineralogy and the type of sorption mechanism. Poorly crystalline Al and boehmite have large surface areas where the exposed oxygens are bound to one Al, while the better-crystallized gibbsite has fewer edge sites with oxygens bonded to only one Al. The minerals, with more oxygens bonded to one Al, had higher sorption capacities and were dominated by surface coordination, whereas sorption on gibbsite was dominated by surface precipitation. Oxygens bonded to only one Al are prime candidates for active surface sites (Parfitt et al, 1977).

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., 1987), 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.

The fixation of a metal by a mineral does not prove that it has entered the crystal structure unless it can be shown that the desorption method releases all forms of metal fixed on the surface. Farrah and Pickering (1978) carried out a series of desorption studies of Pb, Cu, Cd, and Zn adsorbed to kaolinite, illite, and montmorillonite. The metals were sorbed at pH 5 and 7, over a 24 hour period so that most of the sorbed metal was probably still on the surface. Ammonia acetate, ammonia oxalate, and acetic acid did not remove all the sorbed metals. EDTA was completely successful at pH 5 in removing sorbed metals, but was not successful at pH 7 (Although the authors felt that a stronger dose of EDTA would have been more successful). Studies of metal fixation provide evidence for structural penetration, but they do not prove it because it is likely that a portion of the fixed metal is still on the surface.

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 then these size restrictions may no longer be valid.

Due to the large enthalpies of hydration (-2494 to –322 kJ/mole) McBride and Mortland (1974) believe that under most conditions at the earth's surface, cations will not dehydrate and therefore will only enter clay structures during diagenetic conditions, where higher temperatures may favour dehydration. Dehydration might be favoured by the formation of hydroxy complexes or bonds with surface oxygens. If this were the case, structural penetration would be favoured by higher pH, making the process difficult to distinguish from a slow surface precipitation reaction.

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 radio-contaminants 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). Although isotopic exchange is usually not considered as a separate mechanism when evaluating contaminant transport, its effects may influence the understanding of sorption processes in experiments and in mass transport. Since certain radioisotopes have very high specific activities, their actual mass concentrations may be extremely low in experimental studies. Consequently, it is good practice to include and report the concentrations of the stable isotope (carrier) used with the radioisotope in the experimental study. The sorption process determined in the experiment will likely be driven by the concentration of the stable isotope, which may exceed that of the radioisotope by many orders of magnitude. A complication in using radioisotopes to monitor an element's distribution between solid and solution is that isotopic fractionation could occur during the sorption process. Juillot et al. (2008) determined that during sorption on goethite and ferrihydrite, Zn isotopes are fractionated by 3 to 5 percent, with the heavier isotope favouring the solid phase.

Table 2: Principal Sorption Mechanisms

Commonly Used Term	Process Description	Properties
Non-specific coulombic sorption in diffuse layer	- Balance between the electrostatic pull of a surface on oppositely charged counter ions and the kinetic energy of the counter ions pulling them away from the surface. - Counter ion concentration decreases with distance from surface.	- Higher valence cations are preferred, particularly at low salt concentrations. - Rapid and reversible - Independent of - Temp - Dependent on - pH - Competition with major ions
Coulombic sorption in Stern layer	- Coulombic forces hold counter-ions in a monolayer at the solid surface (Stern layer). - Ion volume affects sorption capacity and selectivity. - Outer-sphere complex	- Higher valence cations are preferred, particularly at low salt concentrations. - Rapid and reversible - Dependent on - pH - Sorbent composition - Temperature - Competition with major ions -Volume limitation could favour ions with smaller hydrated radii.
Specific chemical sorption in Stern layer	- Bonds formed with surface oxygens, analogous to interactions with oxygens in hydroxyls or other species. - Inner-sphere complex.	- Rapid and perhaps reversible - Evenly distributed on surface - Less dependent on salt concentration - Dependent on - pH - temperature - Sorbate chem. - Sorbent chem. - number of surface sites
Surface induced precipitation	The solid/solution interface contains higher ion concentrations, a slightly different pH, and perhaps redox affecting elements (Fe). These may induce a precipitation reaction that would not normally occur in free solution.	- Slow and perhaps not reversible - Unevenly distributed - Sorption capacity not limited by surface sites. - Depends on - Sorbate concentration - redox - pH

Chemical substitution	Ion exchange of sorbate with a constituent in the mineral structure of a solid phase, possibly reducing the solubility of the solid.	- Slow and partially reversible. - Dependent on - Temp - Sorbate chem. - Sorbent chem.
Structural penetration	Sorbate migrating into defects or the interlayer spaces of clay particles.	- Slow - Irreversible or slow diffusion-controlled desorption.
Isotopic exchange	Exchange of a radioisotope with a stable isotope of the same element on the solid.	- Kinetics would depend upon the location of the exchange reaction. - Something to consider when using radioisotopes in experiments. - Radioisotope could decrease in solution without having a significant impact on element mass balance between solution and solid.
Physical sorption or Physisorption	- Long-range forces of attraction involving the entire electron shells of the sorbate and sorbent (Van der Walls) - Sorption of neutral species (i.e. neutral OH complexes) onto neutral surfaces	- Non-specific - Rapid and reversible - Independent of - Temp - Sorbent composition - Ionic strength - Dependent on - pH

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 contaminant 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.

The principal sorption mechanisms and their properties are summarized in Table 2.

2.1.2 Kinetics

The understanding of sorption kinetics, with respect to the rates of forward and reverse reactions, is important for several reasons. Sorption rates affect experimental design by determining reaction times and setting practical limits on what can be achieved in an experimental program. Desorption studies help to determine whether equilibrium has been achieved, and to what extent sorption is reversible. The assumption of equilibrium is commonly used to estimate mass transport in performance assessments. Irreversibility on the experimental time scale might not be a factor for performance assessment simulations based on geologic time scales. Sorption kinetics may be a more important factor when comparing the results of short-term laboratory batch and transport experiments. Kinetics may help to identify the existence of more than one sorption mechanism, and may even be used to experimentally focus on a given mechanism. This section provides a general background to kinetic studies and then reviews examples of sorption studies that have included kinetics.

General background: Kinetic theory has been described in considerable detail by Benson (1960), Edwards (1965), and Sykes (1966). Condensed reviews of kinetic theory can be found in Lasaga and Kirkpatrick (1981) and Stumm and Morgan (1981). Most reactions are made up of a combination of elementary reactions, which each represent a single step in the overall reaction. Unlike the chemical process under study, each elementary step is path independent. The mechanism or mechanisms, which control the overall reaction are made up of some combination of elementary steps. The overall reaction rate is given if all the elementary reaction rates are known. If an overall reaction is described by equation 2, and if the stoichiometry is correct then the rate law is given by equation 3.

$$aA + bB \ldots \rightarrow pP + qQ \tag{2}$$

$$rate = \frac{1}{a}\frac{d[A]}{dt} = \frac{1}{b}\frac{d[B]}{dt} = \ldots = -\frac{1}{p}\frac{d[P]}{dt} = -\frac{1}{q}\frac{d[Q]}{dt} \tag{3}$$

The concentration terms in rate laws, [X] can be in mol/L if the reaction is homogeneous. Heterogeneous processes, which involve reactions across phase boundaries, should be described by rate laws in which the concentration terms include the specific area between the phases (i.e. mol/cm^2/L or mol L/cm^2). Often rate laws can also be expressed as follows.

$$rate = k[A]^{nA}[B]^{nB}\ldots[P]^{nP}[Q]^{nQ} \tag{4}$$

In equation 4, k is the rate constant, which must be determined by experiment. The exponents, nX, can be positive or negative integers, or fractions, and must also be determined by experiment. The order of a rate expression is given by the sum of these exponents. If the sum of the exponents is zero, then the rate is zero-order, and if it is n, the overall reaction is considered to follow nth order kinetics. The unimolecular reaction given by equation 5 follows a first-order rate law given by equation 6.

$$A \xrightarrow{k} B \tag{5}$$

$$-\frac{d[A]}{dt} = k[A] \tag{6}$$

The first-order rate constant, k, has units of time^{-1}, and relates the disappearance of A to the remaining concentration of A. First-order rate laws are commonly used to describe many reactions in solution, and they have widespread use in the description of radioactive decay. Reactions which involve the interaction of two reactant molecules (equations 7 and 9), can be described by second-order rate laws (equations 8 and 10).

$$A + B \xrightarrow{k} C \tag{7}$$

$$-\frac{d[A]}{dt} = k[A][B] \tag{8}$$

$$A + A \xrightarrow{k} C \tag{9}$$

$$-\frac{d[A]}{dt} = k[A]^2 \tag{10}$$

In equation 8 the overall rate law is second-order, with a rate constant, k, which may have units of concentration^{-1}time^{-1}. However, with respect to the individual species A and B, the disappearance of A is still first-order. Since equation 9 involves two molecules of A, the rate law given by equation 10 is second-order with respect to A. Some reactions appear to have a constant rate, which is independent of concentration. If reaction 11 is controlled by such zero-order kinetics the rate law in equation 12 can describe it. The rate constant for the zero-order rate law will have units of concentration per unit time.

$$A \xrightarrow{k} P \tag{11}$$

$$-\frac{d[A]}{dt} = k \tag{12}$$

In order to work with rate expressions and to determine rate constants it is necessary to integrate rate laws. Some complex rate expressions can be very tedious to integrate. The following are some simple examples of integrations for the previously mentioned rate laws. The zero-order rate law shown in equation 12 is easily integrated to equation 13.

$$[A] = [A]_0 - kt \tag{13}$$

The original concentration of A is $[A]_0$. The half-life for this reaction is given by

$$t_{1/2} = \frac{[A]_0}{2k} \tag{14}$$

The first-order rate law described by equation 6, is integrated to

$$\ln[A] = \ln[A]_0 - kt \tag{15}$$

The half-life for a first-order reaction is given by

$$t_{1/2} = \frac{\ln 2}{k} \tag{16}$$

The integrated form of higher order reactions, where n is the order, is given by

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt \qquad (17)$$

When reactions of first-order and higher begin to approach equilibrium, or a steady state, reverse reactions may start to influence the rate. If the reaction is so fast that it cannot be monitored far enough away from equilibrium for the forward reaction to dominate then one must account for the reverse reaction in the rate expression. When the forward and reverse rates have equal magnitude the first order kinetics must be written as

$$\frac{d[A]}{dt} = k([A]_{equil} - [A]) \qquad (18)$$

$$\ln \frac{[A]_{equil} - [A]}{[A]_{equil} - [A]_0} = -kt \qquad (19)$$

$[A]_{equil}$ = equilibrium concentration of A
$[A]_0$ = initial concentration of A

In order to understand the reaction mechanism one tries to analyze the overall reaction rate by determining the contribution of each species to the rate law. Unfortunately many reactions are so complex that it is difficult to obtain a meaningful rate constant, not to mention worrying about the order of the participating species. Two experimental strategies have been developed to simplify the rate laws so that the kinetics can be evaluated. One of these is the initial rate method, which can be used if the overall reaction is slow or if the concentrations of some species can be buffered. The basic strategy is to measure the initial rate after the reaction has been started. At this point the concentrations of the reactants have not changed much and significant amounts of products have not been built up to initiate reverse reactions. In order to determine the contribution of a given reactant to the rate law, experiments are started with different initial amounts of that reactant, while the concentrations of the other reactants remain constant. The relation between the initial rate and the initial concentration of A will tell us what contribution A will make to the overall rate law. If the rate law for the following reaction is given by equation 21,

$$A + B + C \xrightarrow{k} P \qquad (20)$$

$$\frac{d[P]}{dt} = [A]_0^{nA} [B]_0^{nB} [C]_0^{nC} \qquad (21)$$

then holding the initial concentrations ($[B]_0$, $[C]_0$) constant the rate becomes

$$rate = \frac{d[P]}{dt} = k'[A]_0^{nA} \qquad (22)$$

or

$$\log(rate) = \log(k') + nA\log([A]_0) \tag{23}$$

In equation 22 the rate law assumes a first-order form with respect to the initial concentration of A. The rate constant, k', is conditional to fixed concentrations of B and C. Plotting log rate against log $[A]_0$, gives nA as the slope. This procedure can be repeated with the other reactants to get nB and nC.

Many natural reactions are too complex for the initial rate method. Plots of concentration versus time are curved and there is no way of unambiguously defining the initial rate. For this situation one can employ the method of isolation. The objective is to try to find a condition where one or more of the components will remain constant. This can be accomplished by having some of the reactants in excess, by having them buffered, or by adding more reactant as it is being consumed. For example, if the reaction is

$$A + B = C + D \tag{24}$$

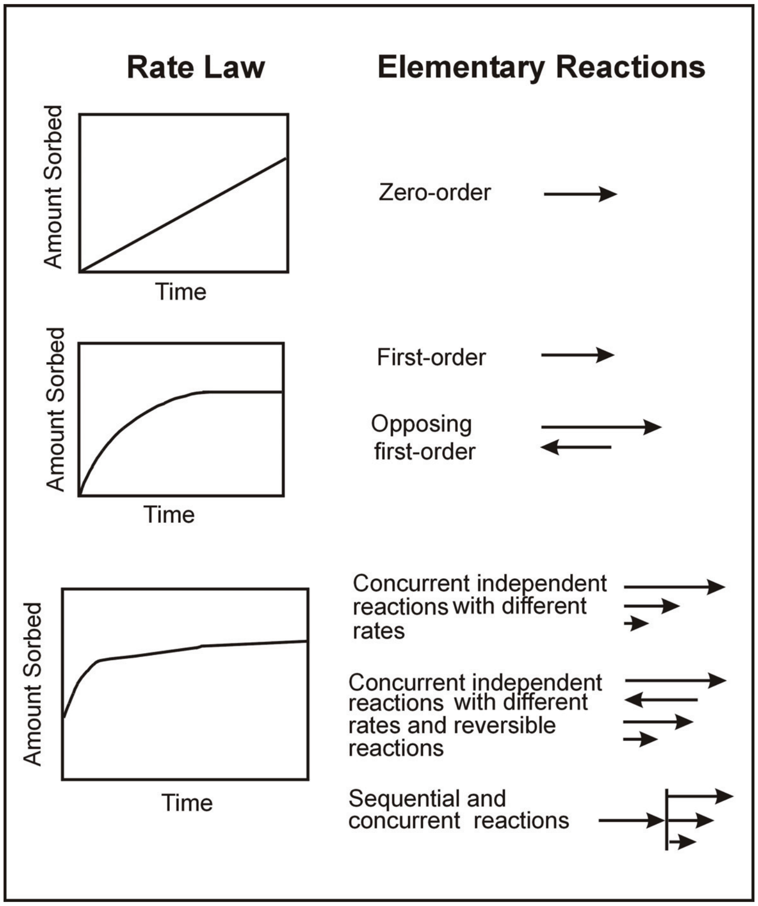
$$-\frac{d[A]}{dt} = k[A][B] \tag{25}$$

If $[B]_0 >> [A]_0$ then

$$-\frac{d[A]}{dt} = k[B]_0[A]_0 = k'[A] \tag{26}$$

By simplifying equation 25 the order of the reaction has been reduced, making it easier to determine the rate constant. The rate constant is determined from the integrated form of equation 26, by plotting ln [A] versus time. The slope of this line will give the rate constant, k'.

There are various possible combinations of elementary reactions which can make up a rate law. Each combination can give the rate law a different form. Figure 3 illustrates several examples of how elementary reactions can combine to make up a rate law observed in sorption reactions. A single zero-order reaction gives a distinct rate law. However, a single first-order reaction produces a rate law that is similar to that of two opposing first-order reactions. Rate laws that do not appear to reach equilibrium can be the product of several reactions in different combinations.



Arrow lengths indicate relative reaction rates.

Figure 3: Possible Rate Laws which Might Be Encountered in Sorption Reactions.

Reaction rates can be determined either by transport processes, such as diffusion, or by chemical reactions, which might involve breaking or forming bonds, and/or changes in various entropy contributions. In solution fast reactions are usually only limited by transport mechanisms, while chemical processes control slow reactions. If the rate of a reaction is only limited by the collision frequency of reacting molecules, then a calculation of this collision rate will give us the speed of the reaction. The Smoluchowski expression for encounters through diffusion will give us the collision rate for two uncharged molecules in solution.

$$\text{collision rate} = k = \frac{4\pi N}{1000}\left(D_A + D_B\right) r_{AB} \qquad (27)$$

The separation distance upon a collision between A and B is r_{AB}, and N is Avogadro's number. The diffusion coefficients, D_A and D_B, can be calculated with the Stokes-Einstein equation for spherical particles.

$$D = \frac{RT}{6\pi \eta r N} \qquad (28)$$

The radius of the spherical particle is r, and the viscosity is given by n. Collision rates calculated from equation 27 fall into the range of 10^{10} $(mol/L)^{-1}s^{-1}$, which is in the range of many observed hydrolysis reactions. If the intersecting particles have like charges, the collision rates will be reduced, while if they have opposite charges the reaction rate will increase. Reactions, with rate constants as low as 10^{-11} $(mol/L)^{-1}s^{-1}$, are much too slow to be controlled by transport processes in solution and must be limited by chemical reactions. The two theories, which have been devised to evaluate these chemical processes, are collision theory and transition state theory. According to collision theory a reaction will only take place when the reactants come together in the proper orientation and configuration, and with enough energy to become an activated complex. The rate constant for two molecules to interact is given by

$$k = pZe^{-E/RT} \tag{29}$$

The term p is an empirical, dimensionless steric factor, which accounts for the fraction of collisions having the right orientation and configuration to permit the reaction to take place. The term Z is the specific collision rate with units of $(mol/L)^{-1}s^{-1}$. The energy associated with the fraction of collisions having enough energy to enter the activated state is given by E, which is approximately equal to the activation energy. In transition state theory the reaction doesn’t happen until the reactants form an activated complex, which then readily transforms itself into products. The difference from collision theory comes from the fact that transition state theory assumes that the reactants are in equilibrium with activated complex. If the energy required to form the activated complex is very large, so that its formation constant is very low, the reaction will be slow.

The change in the rate constant with temperature is related to the activation energy. Arrhenius used the Van’t Hoff equation as an analogy to develop the following expressions to relate the temperature dependence of the rate constant to the activation energy.

$$\frac{d\ln k}{dt} = \frac{E_a}{RT^2} \tag{30}$$

If the activation energy is temperature independent then equation 30 can be integrated to the following

$$k = A\exp\left(-\frac{E_a}{RT^2}\right) \tag{31}$$

In equation 31, A is the probability factor, and may be a function of temperature, T. E_a is the activation energy, which can be expressed as

$$E_a = -\frac{Rd\ln k}{d\left(1/T\right)} \tag{32}$$

The activation energy will be given by the slope of a plot of In *k* versus temperature. If the plot is curved then E_a is a function of temperature. The activation energy of the overall reaction is made up of the sum of activation energies from the elementary reactions. Not only do activation energies give the temperature dependence of the reaction rate, but they also give an indication of the reaction mechanism. Fast reactions tend to have large probability factors and/or small activation energies. For example, the activation energy for diffusion in water is < 5 kcal/mol, while that for surface controlled reactions is between 10 and 20 kcal/mol. The activation energy for diffusion in minerals varies between 20 and 120 kcal/mol.

Sorption reactions will have similarities to ion interactions in solution. In both cases metal will experience electrostatic interactions with other ions, and they may undergo coordination changes by forming or breaking metal oxygen bonds. The main difference is that reactions in solution are homogeneous, while sorption reactions are heterogeneous, involving two phases. The kinetics of sorption should be similar to ion interactions in solution, except that sorption process will be slowed down by (1) the availability of surface area, (2) the transport of ions to and from the surface, and (3) a significant change in entropy produced by sorption. Factors 1 and 2 will determine the collision probability between a metal and surface sites. With these reservations, it is still useful to compare sorption kinetics to the kinetics of ion interactions in solution. Acid-base reactions, and the formation of ligand complexes can be very fast. Therefore, reactive edge sites on clays, which are easily accessible, may be expected to rapidly coordinate metal ions and to quickly respond to changes in hydrogen ion activity. On the other hand, reactions which require a ligand exchange with a previously existing complex can be very slow. Metals bound to some surface sites may be slow to react with ligands added to the system because the metal-mineral bonds are hard to break.

Sorption kinetics: Chen et al. (1973) found that phosphate sorption on kaolinite and Al oxide was controlled by a fast reaction, lasting from 12 to 24 hours, and a slow mechanism, which continued for 60 days. The slow reaction increased with a larger surface area and a lower pH. The activation energy for this reaction was 10 kJ/mole, and at pH 5 the first order rate constant was 2×10^{-4} d^{-1}. Nucleation and growth were believed to be the limiting factors. Griffin and Jurinak (1974) also found two sorption reactions in the uptake of phosphate by calcite. The fast mechanism had a second order rate constant of 0.26×10^{-1} mol/L^{-1} s^{-1}, and was believed to represent the adsorption of phosphate on the calcite surface. The slower reaction had a first order rate constant of 0.15×10^{-4} s^{-1} and was probably controlled by the surface arrangement of phosphate clusters into Ca phosphate heteronuclei.

Rophael and Malati (1972) measured Ca sorption on Mn dioxide with an electrode and observed that there were two first order sorption mechanisms. A fast reaction, lasting up to 6 minutes, had an activation energy of 18.1 kJ/mol. A slower reaction was measured from 6 to 18 minutes and had an activation energy of 32.9 kJ/mol. Ahrland et al. (1960) measured the sorption of Na^+, Ca^{+2}, Ba^{+2}, UO_2^{+2}, Gd^{+3}, Zr(IV), Nb, U(IV), and Pu(IV) on silica gel. The sorption of nonhydrated ions was rapid (5 min), while the uptake of hydrolysed ions was slow (2 to 50 h). From the plots of sorption versus time, there was an initial fast sorption. Kinniburgh (1983) looked at the H/Zn and H/Ca exchange stoichiometries on ferrihydrite. Upon addition of Zn or Ca to a suspension of ferrihydrite there was an instantaneous drop in pH. As base was added the pH stopped dropping after one minute. The ratio of H^+ released to Zn^{+2} sorbed remained constant with time. The H/Ca ratio was constant for 900 min and then slowly increased with time. After an initial rapid sorption lasting 6 min, the amounts of sorbed Zn and Ca continued to increase with time (about 2 d).

Bunzl et al. (1976) measured the sorption of Pb, Cu, Cd, Zn and Ca by peat from deionized water. Sorption kinetics were monitored by conductivity and showed that equilibrium was reached after about 2 minutes. Sorption rates increased with higher metal concentration. Absolute sorption rates decreased with different metals according to the order Pb>Cu>Cd>Zn>Ca. The authors believed that film diffusion was the limiting step.

Singhal and Gupta (1978) measured Zn sorption on dickite using a centrifuge separation, and observed two reaction rates. The faster mechanism lasted for an hour and had a first order rate constant of (2 to 7) x 10^{-3} min^{-1}. The mechanism was believed to result from an ion exchange and was limited by film or particle diffusion. The slower reaction, lasting from 1 to 6 h, was attributed to structural penetration or to a surface fixation. With higher Zn loadings the sorption kinetics increased and the sorption became more sensitive to pH. Inskeep and Bham (1983) looked at Cu and Cd sorption on Na montmorillonite at pH's of 4, 5, and 6. Cu sorption was complete within a 2 minute time frame, and it was completely reversible. Sorption displayed a slight dependence upon pH, which was significantly less than for oxides. Malcolm and Kennedy (1969) investigated Ba, Ca and Mg exchange for K and Na on kaolinite, illite, montmorillonite, and vermiculite, using electrodes. Ba/K exchange on kaolinite and illite was 75 percent complete in three seconds. Ca/K, Mg/K, Ca/Na, and Mg/Na exchange on the above clays was also very rapid. Vermiculite, however, showed a fast and slow exchange. The slow exchange probably resulted from diffusion in the interlayer spaces, as indicated by a linear plot of exchange versus the square root of time.

Shainberg (1973) used conductivity measurements to monitor the hydrolysis of montmorillonite when it was dialyzed. When a clay is exposed to a large supply of deionized water, surface cations are replaced by hydrogen ions. Fast and slow reactions were observed. The fast reaction was postulated to be the initial exchange of hydrogen ion for surface cations. The slower reaction probably resulted from a penetration of the structure by hydrogen ion, followed by the release of octahedral Al or Mg. The activation energies for the second reaction ranged from 96 to 119 kJ/mol.

Griffin and Burau (1974) found that boron desorption from western California desert soil followed three rates. The fastest desorption reaction was complete in less than one hour and had a pseudo-first-order rate constant of 0.5 to 0.9 h^{-1}. The second pseudo-first-order reaction was complete in 20 h and had rate constant of 0.04 to 0.11 h^{-1}. Both of these reactions were believed to represent exchange on different surface sites, and desorption measured within their time frame followed a two site Langmuir model. From 20 to at least 72 h, a slow boron desorption was observed, which may have represented diffusion from interior clay sites.

Harter and Lehman (1983) observed that within the first 20 minutes the exchange of Cu, Ni, Ca, Mg and hydrogen ion on soil showed three separate adsorption regions. First there was an instantaneous reaction, which was attributed to cation exchange. This was followed by an exponential region for the next six months, after which time there was a slow sorption drift. The authors wanted to look at only ion exchange reactions so they used sorption kinetics to extrapolate the sorption back to the time of the instantaneous reaction attributed to ion exchange.

Du et al. (2007) studied the sorption/desorption of radioruthenium on marine sediments. They observed a fast reaction that was complete in about 60 min, followed by a slow reaction lasting for 113 days. Sorption was somewhat irreversible, with an 81.5 % hysteresis coefficient. Jannasch et al. (1988) measured the sorption of ^{46}Sc, ^{113}Sn, ^{65}Zn, and ^{230}Th by particles in seawater. Four distinct processes were noted with times of < 1 min, ~ 20 min, ~ 4 h, and several days. Two uptake models were presented and sorption rates were attributed to processes such as surface reactions, diffusion, and mass transfer. Desai et al. (1994) investigated the desorption of ^{137}Cs from marine sediments in seawater. They found that there were three modes of desorption, irrespective of ^{137}Cs contact time with sediment before desorption. A fast reaction, with a half life of 30 to 50 min was attributed to ion exchange. A medium rate reaction, with a half life of 25 to 50 h, was believed to be a slower exchange reaction, while the slowest reaction (half life of 31 to 112 days) was believed to represent ^{137}Cs trapped within mineral lattices.

The results of kinetic studies of sorption processes are summarized in Table 3. Most of the studies on metal sorption on soil materials revealed that two or more sorption rates are controlling the metal uptake, suggesting that more than one mechanism is responsible for sorption. Some studies, which have used fast measuring techniques, have reported instantaneous sorption reactions. These very fast sorption reactions may have similar rates to acid-base or complex formation reactions in solution. They have been also attributed to ion exchange and are probably limited by film or particle diffusion. Some of the slow reactions are believed to result from surface precipitation, fixation reactions or even structural penetration. Desorption times ranged from minutes to over a hundred days.

The best way to deal with kinetic sorption data may be to plot the logarithm of the sorbed ions versus time. Regions, which plot as linear segments, could be interpreted as being controlled by pseudo-first-order reactions. Regions, which cannot be linearized in this way could be treated by reversible first-order kinetic expressions, or by some other model. Before kinetic data can be divided into mechanisms it must be shown statistically that the rate for each mechanism is significantly different from the other rates.

The half lives for various sorption mechanisms reported in the literature vary from instantaneous to many days. The reported rates will of course be a function of the sorbate and sorbent used in the study. However, experimental conditions will also influence the observed sorption kinetics because factors such as ionic medium and pH can determine which mechanism(s) will control the overall sorption rate. The method of measuring sorption will also influence the observed kinetics. If samples have to be separated by filtration or centrifugation, the very fast mechanisms cannot be followed. Also, errors introduced by the separation process may mask subtle changes produced by very slow reactions. The use of specific ion electrodes or conductivity measurements is essential to follow very fast kinetics.

Table 3: Summary of Selected Kinetic Sorption Studies Reported in the Literature

			Sorption Rates		
Ref.	**Sorbate**	**Sorbent**	**1**	**2**	**3**
1	phosphate	kaolinite	12 to 24 h 2×10^{-7} sec^{-1}	Steady-state drift for at least 60 d.	
2	phosphate	calcite	< 10 min 0.026 sec^{-1}	Up to 2 h	
3	Ca	Mn dioxide	6 min 1st order	At least 18 min 1st order	
4	Na, Ca, Ba, Gd, Zr, Nb, U(IV, VI), Pu	silica gel	5 min	2 to 50 h	
5	Zn, Ca	ferrihydrite	< 6 min	At least 6 d	
6	Pb, Cu, Cd, Zn, Ca	peat	2 min		
7	Zn	dickite	1 h 8×10^{-5} sec^{-1}	6 h $(0.03 \text{ to } 2) \times 10^{-5}$ sec^{-1}	
8	Cu, Cd	montmorillonite	< 2 min		
9	Ba, Ca, Mg	Kaolinite Illite Montmorillonite vermiculite	instantaneous instantaneous instantaneous instantaneous	100 s 100 s 100 s 1000 s	
10	H	montmorillonite	instantaneous	At least 170 h First order	
11	B desorption	Desert soil from western California	1 h 2×10^{-4} sec^{-1}		
12	Cu, Ni, Ca, Mg, H	Soil (Paxton A, Christiana B)	instantaneous	6 min (curved)	Slow drift for 20 min.
13	Radio-Ru	Sediments in seawater	60 min (40%)	113 d (80%)	
14	^{113}Sn ^{230}Th ^{46}Sc ^{65}Zn	Marine particles	30 d^{-1} 5 d^{-1} 2 d^{-1} 0.07 d^{-1}	-0.5 d^{-1} 0.005 d^{-1} -0.005 d^{-1} 0.16 d^{-1}	
15	Cs desorption	Marine sediments	30 to 50 min	25-50 h	31-112 d

1. Chen et al. (1973)
2. Griffin and Jurinak (1974)
3. Rophael and Malati (1972)
4. Ahrland et al. (1960)
5. Kinniburgh (1983)
6. Bunzl et al. (1976)
7. Singhal and Gupta (1978)
8. Inskeep and Baham (1983)
9. Malcolm and Kennedy (1969)
10. Shainberg (1973)
11. Griffin and Burau (1974)
12. Harter and Lehman (1983).
13. Du et al. (2007)
14. Jannasch et al. (1988)
15. Desai et al., (1994)

Soil scientists have recognized that many reactions in soil are slow and therefore they have found the need to develop mathematical models to account for sorption kinetics. Some of these models are based on opposing sorption and desorption reactions, while others are just empirical expressions. Travis and Etnier (1981) give an excellent review of various kinetic expressions used in soil science literature. The following is a summary of these models.

First-order kinetic sorption models include reversible linear (equation 33) and reversible non-linear (equation 34) expressions.

$$\frac{dS}{dt} = k_1 (v/d) C - k_{-1} S \tag{33}$$

S = sorbed sorbate
C = dissolved sorbate
k_1 = forward rate constant
v = soil water content
d = soil bulk density
k_{-1} = reverse rate constant

$$\frac{dS}{dt} = k_1 (v/d) C^n - k_{-1} s \tag{34}$$

n = constant

Both the reversible linear and non-linear models have found use in modelling sorption reactions of organics, herbicides, pesticides and phosphate. Enfield (1974) devised a kinetic product model (equation 35) to describe phosphate sorption in soil. This model is empirical with no theoretical basis and it has no way of accounting for sorption capacity. However, for phosphate it seemed to reproduce the sorption better than the first-order kinetic models. In equation 35 a, b, and d are empirical constants.

$$\frac{dS}{dt} = a C^b S^d \tag{35}$$

The bilinear adsorption model (equation 36) is a kinetic version of the Langmuir isotherm.

$$\frac{dS}{dt} = k_1 C (b - S) - k_{-1} S \tag{36}$$

b = sorption capacity

Two-site kinetic models have been developed by Selim et al. (1976), Fujikawa and Fukui (1991), and Cameron and Klute (1977). These models assume the existence of fast (1) and slow (2) sorption sites. The total sorption rate is given by the sum of the sorption rates on the two sites. Either a Freundlich or a linear isotherm can describe the sorption on the fast site since equilibrium is attained quickly. On the slow site sorption is controlled by a linear first-order model. Under fast flow conditions in soil sorption is dominated by site 1, while if the flow is slow, site 2 will have a greater influence on sorption.

In summary, although in most studies sorption reactions appear to be complete within a week, there are reports of sorption reactions lasting as long as 2 months. Two or more sorption rates are commonly reported, suggesting the operation of more than one sorption mechanism. Some sorption reactions appear to be only partially reversible for periods of over 100 days. Although this slow reversibility is likely to affect laboratory migration experiments, it might not necessarily be a factor for time scales of many years. Although kinetic sorption models do exist, it is beyond the scope of this report to evaluate their applicability to performance assessment.

2.2 CONCEPTUAL MODELS FOR QUANTIFYING SORPTION

When studying sorption phenomenon or making use of sorption data one needs to describe the sorption process with some mathematical expression that relates the amount of sorbate attached to the sorbent to the amount of sorbate remaining in solution (Figure 4). The following section describes some of the more common approaches used to describe sorption under assumed equilibrium conditions. Travis and Etnier (1981) provide a more complete description and set of references describing sorption equations. Babcock (1963) gives a good review of cation exchange equations. Each of the following expressions is an attempt to present the sorption data in a meaningful way. Some expressions give more insight to the sorption process than others, but they all have their uses, depending upon the objectives of the study or application.

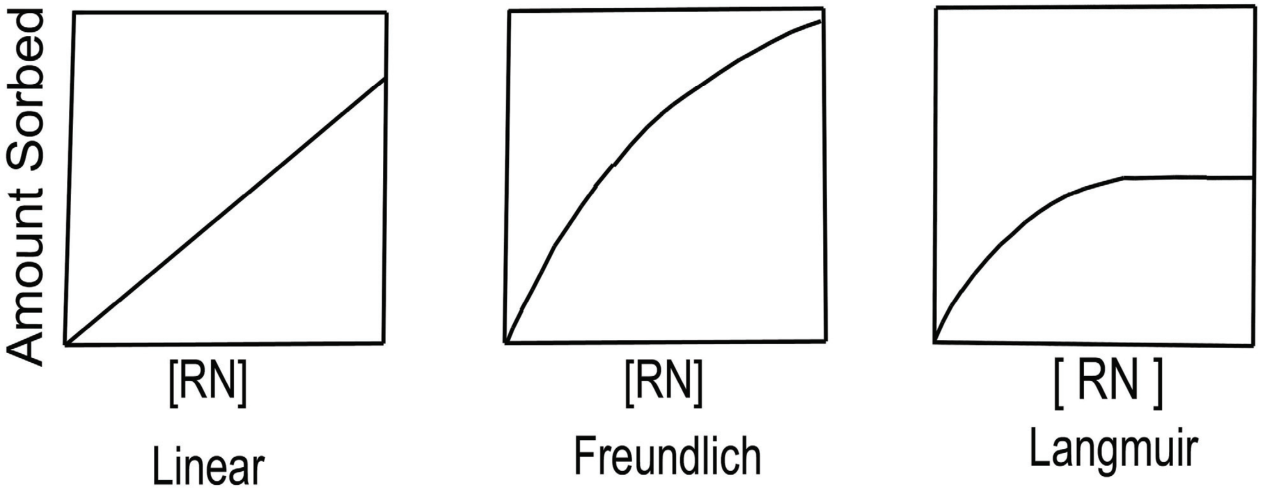


Figure 4: Typical Sorption Isotherms Showing the Variation in the Amount Sorbed with Sorbate Concentration ([RN]) in Solution.

2.2.1 Sorption Coefficients

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

$$K_d = \frac{S}{C} \quad \text{or} \quad R_d = \frac{S}{C} \tag{37}$$

where S is the concentration of sorbed sorbate (mol/g)
C is the concentration of sorbate in solution (mol/cm^3)
K_d is the distribution coefficient (cm^3/g)

The sorption coefficient is a convenient and simple way of expressing sorption. However, it is empirical 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 distribution 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 measurements are originally measured as 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 (cm^2/g). In this case the sorption coefficient is defined as K_a or R_a where

$$K_a = \frac{S}{C} \approx R_a \quad \text{(cm)} \tag{38}$$

The value of R_a is related to R_d by the following

$$R_a = \frac{R_d}{A_{sp}} \tag{39}$$

2.2.2 Isotherm Models

Since the amount of surface or internal sites available for sorption on solids may be limited, increases in sorbate concentration will induce competition for these sites and may decrease the value of the measured sorption coefficient. The variation of the sorption coefficient with sorbate concentration is known as a sorption isotherm, which can be described with a number of different approaches.

Langmuir isotherm: Soil scientists have adopted the use of the Langmuir isotherm to account for the changes in sorption when the surface becomes loaded with sorbate. The Langmuir isotherm was originally developed to describe monolayer adsorption of gases onto solids. When it was adapted for adsorption from a liquid to a solid, it retained two useful parameters, which were the maximum adsorption capacity, S_{max}, and a constant, b, related to the binding energy. The following are examples of Langmuir equations for the sorption of a single ion (equation 40), more than one ion (equation 41), and several ions on two different sites (equation 42).

$$S = \frac{(S_{\max} bC)}{(1 + bC)} \tag{40}$$

S = sorbate on surface C = sorbate in solution

$$S = \frac{(S_{\max} b_1 c_1)}{(1 + b_1 c_1 + b_2 c_2)} \tag{41}$$

$$S = \underset{\text{(site 1)}}{\frac{(S_{\max 1} b_{11} c_1)}{(1 + b_{11} c_1 + b_{12} c_2)}} + \underset{\text{(site 2)}}{\frac{(S_{\max 2} b_{21} c_1)}{(1 + b_{21} c_1 + b_{22} c_2)}} \tag{42}$$

b_{ij} = binding constant for sorbate j on site i
c_j = concentration of sorbate j in solution.
s_i = sorption capacity for site i.

The Langmuir equation has the advantage of giving a maximum sorption capacity, which represents the adsorption energy. Also the equation can be expanded to account for competition from other ions (equation 41). The sorption model can also include several adsorption sites with different capacities and binding constants (equation 42).

Freundlich Isotherm: The Freundlich isotherm (Freundlich, 1926) is an empirical expression that is useful for describing sorption on multi-site surfaces. If it is assumed that the heat of sorption decreases exponentially with increased surface coverage then the Freundlich isotherm can be derived from a multi-site Langmuir equation (Kinniburgh and Jackson, 1981). The Freundlich equation has been useful for describing sorption on clays and some oxides. Unfortunately this isotherm does not have a parameter to express maximum sorption and at low sorbate concentrations it does not become linear, as predicted by Henry's law. Also, like the sorption coefficient, the Freundlich isotherm is only valid at a given ionic strength and pH. The Freundlich isotherm is described by equation 43,

$$S = KC^{1/n} \tag{43}$$

S = concentration of sorbed species (mol/g)
K = constant

n = dimensionless constant
C = concentration of sorbate in solution (mol/mL)

Expressing the Freundlich equation in log form gives

$$\log S = 1/n \log C + \log K \tag{44}$$

A plot of log S versus log C gives a straight line with a slope of 1/n, which often has a value of unity or less. If n is unity then K becomes identical to a sorption coefficient (R_d). Values of n greater than unity suggest precipitation from solution rather than sorption (Vandergraaf and Ticknor, 1994).

Dubinin-Radushkevich Isotherm: The Dubinin-Radushkevich isotherm, originally developed for charcoal by Dubinin and Radushkevich (1947), is described by equation 45. This isotherm has been used to estimate the maximum sorption capacity of the solid by plotting ln S versus ε^2, and extrapolating to infinite concentration, where ε has a value of zero. This isotherm is usually used as an empirical fit to sorption data.

$$S = be^{-B\varepsilon^2} \tag{45}$$

ε = the Polyani potential = $RT\ln\left(1+\frac{1}{C}\right)$
S = concentration of sorbed species (mol/g)
C = concentration of sorbate in solution (mol/mL)
b = maximum sorption capacity (mol/g)
R = gas constant (8.3 J mol^{-1} K^{-1})
T = temperature (K)
B = sorption energy (mol^2 J^{-2})

2.2.3 Mass Action Models

Mass action models may be more appealing than isotherms and sorption coefficients because they can be related to thermodynamics. This provides an opportunity to characterize the type of reactions and to predict sorption reactions based on previously measured thermodynamic values, provided that the solution and sorbed species can be properly defined. Ion exchange is a mass action approach, which has been popular for describing sorption reactions because it is recognized that geologic materials, such as soils, can exchange one ion for another. Furthermore, the concept of ion exchange does not allow for the creation of a charge imbalance at the surface or in solution. Ion exchange is most useful when a surface's total cation exchange capacity is filled by two exchanging cations in roughly similar proportions. An ion exchange reaction as shown in equation 46, can be described by a Nernst-Berthelot distribution coefficient (equation 47)

$$bC_A^{+a} + aS_B^{+b} = bS_A^{+a} + aC_B^{+b} \tag{46}$$

$$K_{A/B} = \frac{\left(S_A^{+a}\right)^b \left(C_B^{+b}\right)^a}{\left(S_B^{+b}\right)^a \left(C_A^{+a}\right)^b} \qquad (47)$$

C = ion in solution
S = sorbed ion
a and b are the valences of the sorbing and exchanged ions

The Nernst-Berthelot distribution coefficient ($K_{A/B}$) usually changes with the composition of exchanging ions and it is the starting point for all thermodynamic treatments of cation exchange (Gaines and Thomas, 1953, Eberl, 1980). El-Sayed et al. (1970) looked at the thermodynamics of Cu/Ca exchange on bentonite. Maes and Cremers (1975) measured Co and Zn exchange on montmorillonite, and Egozy (1980) looked at Cd/Co reactions on clays. Aluminum and Ca exchange on smectite was investigated by McBride and Bloom (1977). In situations where one cation occurs at trace levels and only covers a small fraction of the surface exchange capacity the use of an ion exchange technique is no longer justified. Ion exchange is also impractical if it is not clear which ions, if any, the sorbing ion replaces.

2.2.4 Surface Complexation Models

This method treats sorption with a stability constant approach in which solid surfaces are considered to have sites that can complex metal ions. Using this approach these sites can be treated as complexing ligands. Using the specific area available for sorption (cm^2/g) of a solid for a known mass of the solid suspended in solution, the concentration of surface sites can be converted from mol/kg or mol/cm^2 to mol/L. Sorption can then be described as in the form of conditional stability constants as used in solution chemistry. For example, stability constants for the following reactions

$$M^{+z} + iC^{=} = MC_i^{z-i} \qquad (48)$$

$$M^{+z} + iHC = MC_i^{z-i} + iH^{+} \qquad (49)$$

can be written as

$$B_i = \frac{\left[MC_i^{z-i}\right]}{\left[M^{+z}\right]\left[C^{-}\right]^i} \qquad (50)$$

and

$$^{*}B_i = \frac{\left[MC_i^{z-i}\right]\left[H^{+}\right]^i}{\left[M^{+z}\right]\left[HC\right]^i} \qquad (51)$$

B_i and $^{*}B_i$ are conditional stability constants

$[C^-]$ = concentration of deprotonated sites (mol/L)
$[HC]$ = concentration of protonated surface sites (mol/L)
$[MC_i^{z-i}]$ = concentration of sorbed metal (mol/L)
$[M^{+z}]$ = dissolved metal concentration in solution (mol/L)
$[H^+]$ = hydrogen ion concentration in solution

The presence of a MC complex implies that the metal only binds to one surface site, while in a MC_2 complex the surface metal coverage is low enough that each metal can complex with two sites. This adsorption formulation is easy to use in speciation calculations that may want to take into account the presence of suspended particulate matter in a body of water. The constant B_i can be evaluated using similar techniques, which are employed in the determination of stability constants with dissolved constituents. Competition for surface sites by hydrogen and other metal ions can also be accounted for. This mathematical expression has similar modelling capabilities to the multi-site Langmuir isotherm.

Surface complexation models take into account the acid-base properties of mineral surfaces through equilibrium reactions involving amphoteric surface functional groups. Equations describing these reactions can be written as follows, with XOH^o representing the amphoteric surface site.

$$XOH^0 + H^+ = XOH_2^+ \quad \text{(protonation reaction, } K_+\text{)} \tag{52}$$

$$XOH^0 = XO^- + H^+ \quad \text{(deprotonation, } K_-\text{)} \tag{53}$$

The activities of ions and H^+ at the mineral surface are corrected for the charge effects of the surface using the exponential Boltzmann relation, which relates surface activities, $[C^{+z}]_{surface}$, to activities in the bulk solution, $[C^{+z}]_{bulk}$.

$$\left[C^{+z}\right]_{surface} = \left[C^{+z}\right]_{bulk}\left(\exp\left(-\frac{\psi_J F}{RT}\right)\right)^2 \tag{54}$$

where ψ_J is the electrostatic potential of the layer J
F is the Faraday constant
R is the ideal gas constant
T is the temperature (K)

Various models based on the surface complexation approach to sorption have found extensive use in the literature to help understand sorption on metal oxides and other rock-forming minerals. Many studies have used this approach in conjunction with double layer theory to describe cation sorption on oxide surfaces and the effect of this sorption on surface charge (Schindler and Gamsjager, 1972, Hohl and Stumm, 1976, and Davis and Kent, 1990). These models include the Diffuse Layer Model (DLM) and the Constant Capacitance Model (CCM) (Dzombak and Morel, 1990). Other models have employed the Stern layer in which the charge of the potential determining ions has been reduced by the adsorption of inert electrolyte (Yates et al., 1974, and Davis et al., 1978). These models are known as Triple Layer Models (TLM). Surface complexation models can include one or more types of surface sites and can consider several different sorbate complexes with different affinities for the surface.

Payne and Waite (1991) used a TLM to study uranium sorption on rock samples from the Koongara uranium deposit, Australia. Uranium sorption data obtained by isotope exchange techniques was fitted to a TLM applied to ferrihydrite, which was believed to be the dominant mineral responsible for uranium sorption. The isotopic exchange technique was able to identify the fraction of natural uranium in the rock samples that participated in the sorption process.

Arnold et al. (2001) used sorption measurements and a DLM to study sorption behaviour of U(VI) on phyllite. The rock sorption properties of phylite were derived from those of constituent minerals that included quartz, chlorite, muscovite, albite, and Fe oxide/hydroxides. Site densities were evaluated from adsorption isotherms at pH 6.5

Marmier et al. (1997) used a CCM to study Yb(III) sorption and desorption on hematite and alumina. They found that sorption was reversible when surface loading was small, and less reversible at higher loadings. The surface complexation model was used to interpret this phenomenon by taking into account hydroxylation of the surface complexes.

Bradbury et al. (2005) used a two-site protolysis, non electrostatic surface complexation and cation exchange model to study sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. This model included cation exchange of Eu^{+3} with Na^{+} or Ca^{+2}, and inner sphere surface complexation of three Eu complexes. Eu speciation of was assumed to mimic that of Cm, whose complexes were studied with time resolved fluorescence spectroscopy.

Christl and Kretzschmar (1999) studied the competitive sorption of copper and lead at the oxide-water interface, by fitting experimental data to different model types. One was a TLM and the other was a 2 pK basic Stern model. They showed that surface site density was key to obtaining model fits to data.

Davis et al. (1998) and Davis et al. (2004) describe a Component Additivity model (CA) and a Generalized Composite model (GC). In a CA model it is assumed that the bulk properties of a rock are the sum of the properties of its mineral constituents. One can then derive the sorption properties of the rock by adding up the sorption properties of the major mineral phases in proportion to their occurrence in the rock. The GC approach assumes that the sorption properties of individual minerals are not known in sufficient detail, particularly since sorption data is not available for every mineral. Instead, sorption is described by the operation of generic surface complexation sites (>SOH). The site densities and formation constants for these sites are determined by fitting whole rock experimental data.

Tertre et al. (2008) studied rare earth element (REE) sorption on basaltic rock as a function of pH, ionic strength (0.025 mol/L and 0.5 mol/L NaCl), and REE concentration. Sorption results were interpreted with a Generalized Composite (GC) non-electrostatic model that contained exchange sites (affected by exchange with Na) and specific sites (not affected by Na competition). The total site density of exchange and specific sites was estimated with a cation exchange measurement (CEC = 52 $\mu mol/m^2$). Estimates of exchange sites (22 $\mu mol/m^2$) and specific sites (30 $\mu mol/m^2$) were obtained from Langmuir fits to REE and phosphate sorption data. While all of the REE were fitted to a single exchange constant, there was considerable variation in the surface complexation constant for each element.

Surface complexation models are elegant, and under the right conditions can provide insight into sorption processes. However, they do have their limitations. Their main drawbacks are their complexity and no linearity. Models often require many model specific parameters that are not precisely known and are often used as fitting parameters (Turner and Sassman, 1996). Morel et al., 1981, warn of the risk of over interpreting model fits, particularly if the models contain a large amount of fitted parameters. Often several models can be fitted to a single data set, and without other lines of evidence a model fit may prove nothing. To help deal with this problem, Dzombak and Morel, 1990, recommend the adoption of a standard set of parameters that is uniformly applied. Although this approach is not exact, it tends to limit the number of adjustable parameters. An example of this approach is given by Turner and Sassman, 1996, in their study of U sorption on goethite. They compared model fits to three different models (CCM, DLM, and TLM), which were able to account for sorption in the presence of CO_2 and in varying ionic strengths up to 1 M.

2.2.5 Parametric Models

Parametric sorption models are empirical relationships that attempt to relate sorption coefficients to independent parameters such as sorbate concentration, pH, Eh, solid/liquid ratio, total dissolved solids and ionic strength (Vandergraaf and Ticknor, 1994). Parametric models require experimental data from carefully designed experiments in which the variables are truly independent of each other and their variability is significant. The selected data are then fitted to a polynomial equation using multiple linear or non-linear regression. Since this approach is totally empirical, the application of the calibrated equation cannot be extrapolated beyond the data ranges of the parameters to which the equation was fitted. Parametric equations must be designed with some care; otherwise there is a risk that the regression analysis will not converge to a unique solution.

A parametric model was designed by Vandergraaf and Ticknor (1994) in an attempt to define sorption coefficients used in the Geosphere model for the 1990 Assessment of the Whiteshell Research Area. The parametric model had the following form.

$$\begin{aligned} R_d &= b_0 + b_1 \log TDS + b_2 \log[RN] + b_{11} \log^2 TDS \\ &\quad + b_{22} \log^2[RN] + b_{12} \log TDS \log[RN] \end{aligned} \tag{55}$$

where TDS is the total dissolved solids
[*RN*] is the dissolved radionuclide concentration
b_{ij} are coefficients determined by data fitting

In practice, Vandergraaf and Ticknor (1994) had difficulties in finding sorption data in the literature that would meet statistically valid criteria for an adequate fit to the proposed parametric model. Therefore, for a majority of elements in the database the b_{ij} coefficients have a value of 0, and the sorption data take on the form of mineral-specific sorption coefficients (Rd). If there was a significant increase in the availability of sorption data as a function of TDS and sorbate concentration, the parametric approach could be useful.

2.3 MODELS USED FOR PREDICTING SORPTION PROCESSES

Thermodynamic Sorption Models (TSMs) are of interest to performance assessment because they have the potential ability to describe sorption under variable geochemical conditions and to integrate geochemical and sorption equilibria in a single coherent model (Davis et al.,2005,; Ochs et al., 2006). The transfer of data determined in the laboratory to in-situ conditions is fully quantitative and traceable. The transfer of sorption data from the conditions used for measurement to performance assessment-specific conditions is fully quantifiable, as opposed to a semi-quantitative approach, taking account of differences in CEC and radionuclide speciation, or a qualitative expert judgement. TSMs allow a direct coupling of sorption with variable solution chemistry and mineralogy in a thermodynamic framework. TSMs involve some form of a surface complexation model, which may include ion exchange. An attempt is made to relate components of the model to standard states and express parameters as thermodynamic constants.

Bradbury and Baeyens (2005,2005b) modelled Mn(II), Co(II), Ni(II),Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) sorption on montmorillonite, using a two-site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model to establish a basis for developing a thermodynamic sorption database. Cation exchange selectivity coefficients for metal exchange with Na and Ca were determined at low pH values where surface complexation does not take place. Protolysis constants for surface sites were determined by titration and site capacities estimated by the ^{22}Na isotopic dilution method (Baeyens and Bradbury, 1995, 1997). Non-electrostatic weak and strong surface complexation constants were determined by modelling “in house” and literature sorption edge data. Surface complexation constants for Pd(II), Pb(II), Pu(III), Zr(IV), U(IV), Np(IV), Pu(IV) and Pa(V) were estimated using linear free energy relationships (LFER). LFER are relationships that can be found between the free energies of formation of aqueous or surface metal complexes and thermodynamic properties of the metal ions or ligands.

Arthur (1996) demonstrated the use of a Generalized Two-Layer (GTL) surface complexation model with surface complexation constants for Np(V) to predict sorption on rocks as a function of pH, and concentrations of Ca, Cl and HCO_3. It was assumed that the rock surface was coated with a film of hydrous ferric oxide that controlled sorption reactions. The calculated K_d values from the GTL model were consistent with values reported in the literature for similar geochemical situations, although the calculated values were slightly higher.

Turner and Pabalan (1999) used a diffuse-layer surface complexation model to predict ranges of sorption values for Np(V) and U(VI) that could be used to better define lognormal Probability Distribution Functions (PDFs) for use in performance assessment calculations for the proposed high-level radioactive waste repository at Yucca Mountain. Groundwater compositions in the vicinity of Yucca Mountain were used to define the range of parameters that could affect sorption. These parameters were used to predict sorption coefficients for different groundwater compositions. Changes in groundwater chemistries over periods of days to years caused variations in sorption that were almost five orders of magnitude for Np(V) and nine orders of magnitude for U(VI).

Brendler et al. (2003) described the RES^{3}T digitized thermodynamic sorption database for use in TSM’s. Data are mineral specific and therefore useful for additive models (CA). Data records include mineral properties, specific surface areas, surface binding site characteristics and sorption ligand information. In 2002 the database included 81 solid phases, 269 specific surface area values, 399 surface site property data sets and 845 records for surface complexation reactions. The database has a lot of information on oxides and clay minerals, but is lacking in major rock forming minerals, such as feldspars, mica, pyroxene, amphiboles and olivine. It contains a large amount of data on commonly studied contaminants such as U, Cu, Cd, Th and Pb. However, other actinide data is lacking.

Davis et al. (2005) and Ochs et al. (2006) discuss the results of the NEA Sorption Project Phase II TSM comparative modelling exercise designed to test the effectiveness of TSMs in predicting sorption under variable geochemical conditions. The exercise evaluated a number of simple systems that included single oxide minerals (carbonate, goethite, quartz), clay minerals and bentonite, and soils and sediments. The elements used in the exercise included U(VI), Se(IV/VI), Np(V), Ni(II), Np(V), U(VI), and Co(II). The groundwater parameters considered in the modelling were pH, P_{CO2}, ionic strength, ligand concentrations and radionuclide concentration. The participants in the exercise used a variety of models that included surface complexation, and surface complexation with ion exchange. Project findings included that TSM's were able to reproduce trends and the magnitude of K_d. Average absolute errors of model predictions were 0.5 to 1 log K_d unit. Modelling personnel and their decisions and preferences had a significant influence on model design and performance. The type of model used depends upon the complexity of the system (Ochs et al., 2006). The most defensible models use an adequately detailed experimental database, which allows proper calibration and sufficient constraint of model parameters. They also need a detailed description and understanding of the solid/solution interface, which may not be available for complex systems. A more directly applicable approach is to use a Generalized Composite (GC) approach in which models are parameterized directly with macroscopic data from complex substrates. These models tend to be simpler, use generic surface sites, may neglect electrostatic corrections, and emphasise the best fit to achieve more direct application to natural systems.

One of the problems with TSMs is that many of the parameter values used in typical surface complexation models are conditional, model-dependent values, rather than true thermodynamic constants. Standard states for surface complexes are more difficult to define than for aqueous species.

2.4 EXPERIMENTAL APPROACHES TO MEASURING SORPTION

2.4.1 Batch Methods

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 are 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 and the liquid (or solid) are characterized for sorbate concentration or chemical form. Batch methods have been used for both sorption and desorption reactions.

The vessels used in sorption tests are used from materials, such as polyethylene, polypropylene or Teflon, which are assumed to sorb a minimum of sorbate. Ticknor et al. (1996) found that polycarbonate was a better material for reaction vessels, compared to glass and polyethylene. Reaction vessel volumes can vary from about a litre (Vilks and Degueldre, 1991) to 10 or 20 mL scintillation vials or centrifuge tubes (Ticknor, 1994, Erten et al., 1988). If small experimental containers are used, usually tests are performed in triplicate, along with blanks to test for sorption on container walls (Ticknor, 1994). If larger vessels are used it may be possible to take multiple samples from the same experiment as a function of time.

The method(s) applied to phase separation need to be considered carefully to properly determine the amount of sorbate that is in solution from that which is on the solid. Suspended solids are removed from solution by gravitational settling, centrifugation (Ticknor, 1994, Erten et al., 1988, Berry et al., 1988) or by some form of filtration such as cross-filtration with a 0.2 µm polycarbonate filter (So et al., 2008) or tangential-flow filtration (Vilks and Degueldre, 1991). Whichever method is used must succeed in removing the smallest particles, which may include colloids. Otherwise, the true dissolved concentration of the sorbate is not properly defined. If sorbate concentrations can be determined with an electrode it may not be necessary to perform a phase separation and kinetic studies can be performed even on short time scales. Heidmann et al. (2005) used potentiometric titrations and specific ion electrodes to study Cu and Pb sorption on kaolinite-fulvic acid colloids. Fulvic acid enhanced metal sorption on kaolinite. It should be remembered that specific ion electrodes respond to the activities of free ions, and may not measure the total sorbate concentration which includes complexes.

Solid mineral or rock material is commonly crushed and sized to a given particle size such as 100 to 200 µm (Berry et al., 1988). Since the crushed rock has freshly exposed surfaces with broken bonds, it is sometimes deemed necessary to condition the solid material by exposing it to the experimental ionic medium before starting sorption tests (Ticknor et al., 1996). Some sorption experiments have been performed on solid rock coupons. For example, Pinnioja et al., 1983, compared batch sorption with autoradiography to measure sorption of ^{89}Sr, ^{58}Co, ^{134}Cs and ^{241}Am on samples of granite and tonalite. The autoradiography method was able to identify which minerals were responsible for sorption and produced K_a (cm) values that were of the same order of magnitude as those produced by batch experiments. Kamineni et al., 1983, studied the sorption of ^{137}Cs, ^{90}Sr, ^{147}Pm, ^{241}Am, and ^{95m}Tc on thin sections of granitic rock (Eye Dashwa Lakes Pluton, Atikokan, Ontario) containing fractures. They found that there was enhanced sorption on fracture filling secondary minerals as compared to primary minerals in the rock matrix.

If an element is sorbed in a batch experiment its concentration in solution will decrease by a few percent to 100 percent. Probably the optimum experimental design will produce a drop in sorbate concentration that is just large enough to determine the amount sorbed with a minimum of error. If the reduction in sorbent concentration is large and approaches 100 percent it will be difficult to establish the equilibrium dissolved concentration responsible for sorption. Not only will detection limits be a problem, but it may not be clear whether some of the sorption that took place was triggered by the high sorbate concentration at the start of the experiment. If reverse reactions are slow, the resulting sorption coefficient may not be representative of an equilibrium state. Furthermore, when the dissolved sorbate concentration approaches 0, small changes in concentration result in large variability with derived sorption coefficients, as well as uncertainty associated with approaching detection limits. One can influence the drop in sorbate concentration by manipulating the solid/solution ratio in the experiment. If an element is sorbed very strongly, one could reduce the solid/liquid ratio to reduce the amount of sorbate removed from solution.

Changes in experimental solid/liquid ratio have been reported to affect measured sorption coefficients in some cases. Oscarson and Hume (1998) argued that reduced Sr^{2+} and Cs^+ K_d values that they observed for sorption on bentonite at higher solid/liquid ratios were due to particle-particle interactions, which may lead to the blocking of some sorption sites. After presenting their work on Cd sorption on Fe oxyhydroxide and reviewing the literature, McKinley and Jenne (1991) argued that the reported "solids concentration" effect was caused by inappropriate experimental design or errors in data interpretation. Phillippi et al. (2007) presented a theoretical discussion of why K_d values determined in batch experiments for multicomponent systems may become dependent on the solid/liquid ratio, and why the choice of solid liquid ratio may be important for extrapolating the results of batch experiments to column experiments and then to the field. Their modelling of U(VI) sorption on Fe oxyhydroxides showed that when the adsorption isotherms of strongly interacting sorbates, which may be independent of solid/liquid ratio in monocomponent systems, are combined in multicomponent systems the resulting isotherm may become dependent upon the solid/liquid ratio.

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 additions 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.

Sorbate solubility and chemical speciation must also be considered in experimental design. Sorption experiments must be performed with sorbate concentrations that are well below solubility limits. Otherwise they become precipitation experiments. This may be a challenge for elements with very low solubilities, such as Am(III) and Th(IV), because of analytical detection limits and the danger of precipitating colloids. Chemical speciation affects the type of sorbate complexes that may sorb and the overall sorbate concentration in solution. Therefore, sorption experiments must accurately report parameters such as pH, pCO_2 and the presence of any other complexing ligands.

2.4.2 Spectroscopy and Surface Science

The understanding of sorption processes can be improved by looking at changes in the sorbate's bonding environment as it becomes attached to the surface, or at changes in the structure of the sorbing solid, such as a clay, caused by sorption process. X-ray diffraction (XRD) has often been used to study the effect of cation exchange on the interlayer spacing of montmorillonites and vermiculites (Grim, 1968). Infrared spectroscopy (IR) has been used to study the changes in the orientation of clay hydroxyls, as the octahedral layers are penetrated by sorbing cations (McBride et al., 1984). Electron spin resonance spectroscopy (ESR) has been used to study the bonding environment of adsorbed Cu. McBride, 1976, used ESR to show that Cu loaded onto kaolinite existed as square planar complexes, which could move freely on the surface. On the other hand, Cu sorbed onto Al hydroxides was shown to be either bonded to surface oxygens or was precipitated at nucleation centres (McBride, 1982, McBride et al., 1984).

Chen and Hayes (1999) used X-ray absorption spectroscopy (XAS) to study the chemistry of Co and Sr sorbed on clays. At low pH the Co was shown to be in the form of an outer sphere mononuclear complex, easily desorbed by Na. At higher pH XAS indicated that Co had formed a precipitate that was hard to desorb. Sr appeared to be in the form of outer sphere mononuclear complexes at all pH conditions. Grafe et al. (2008) used extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate the chemistry of Cu(II) and As(V) sorbed on goethite and jarosite. Results showed that Cu and As can form surface precipitates from under-saturated solutions. Elzinga et al. (2006) used EXAFS to study the coordination chemistry Cu(II), Zn(II) and Pb(II) sorbed to the calcite surface. The metals are likely to remain available for exchange for extended sorption times (2.5 years). Dähn et al., 2002, studied Th(IV) uptake on montmorillonite with polarized-EXAFS to identify Th coordination chemistry under unsaturated conditions (pH 2 and 3) and under saturated conditions (pH 5). When Th was saturated EXAFS was able to identify the presence of $Th(OH)_4$. Under unsaturated conditions Th was found coordinated with two oxygen shells and one silica shell. Therefore, in the absence of precipitation Th is bound to montmorillonite by sharing double corners with Si tetrahedra. Dahn et al. (2003) used polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy to study the chemistry of Ni(II) sorption to edge sites on montmomorillonite. Results demonstrated that the formation of an inner sphere mononuclear Ni surface complex at edge sites is a possible sorption mechanism. Uranyl sorption by montmorillonite was studied by Catanano and Brown (2005) using EXAFS to evaluate binding sites and the effects of carbonate complexation. At low pH (~4) and low ionic strength (0.001 M), uranyl cation was found to sorb by cation exchange. At higher pH (~7) and ionic strength (1 M) U(VI) was sorbed to inner sphere Fe and Al octahedral edge sites. In the presence of carbonate the sorption of uranyl-carbonato ternary complexes was identified.

Carroll et al. (2002) combined traditional batch and flow-through experiments with multinuclear nuclear magnetic resonance (NMR) to study the chemistry of the silica-water interface to evaluate the surface speciation of amorphous silica as a function of pH and NaCl and CsCl concentrations. Scott et al. (2007) studied U sorption on fresh and weathered pyrite surfaces, and used X-ray photoelectron spectroscopy (XPS) to indicate a partial reduction of uranium at the pyrite surface, and a heterogeneous distribution of U(IV) and U(VI) species. Duff et al.(2001) used microautoradiography (MAR) and a synchrotron-based micro-X-ray fluorescence (micro-SXRF) for detecting the spatial distributions of Pb sorbed on tuff from Yucca Mountain. The Pb was found associated mainly with smectite and Mn oxides.

Although analytical tools, such as XRD, IR, ESR and EXAFS, can tell us something about the bonding environment of a sorbed metal they may not be applicable to trace element systems because these techniques require a heavy metal loading on the mineral surface to create measurable changes in the mineral structure and to have enough sorbate present for spectroscopic measurements. To perform measurements the mineral may have to be separated from suspension and partially dried. The bonding conditions for a trace metal in a mineral suspension may be totally different from those in a partially dried mineral plug that has been saturated with sorbate. Therefore, although spectroscopy and surface science can provide valuable clues regarding sorption mechanisms, one must consider the chemical and physical parameters used in these measurements when extrapolating the results for sorption reactions at trace sorbate concentrations.

2.4.3 Mass Transport

Mass transport experiments involving sorbing radionuclides have been used extensively to demonstrate the role of sorption in mass transport, improve our 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 process during mass transport.

Ticknor and Vandergraaf (1997) compared the treatment of sorption and retardation in performance assessments used in Canada, Finland, Sweden, Switzerland and the United Kingdom. Berry et al. (1988) studied ^{36}Cl, ^{45}Ca, ^{63}Ni, ^{85}Sr, and ^{137}Cs sorption on sandstones and mudstones using batch methods, through diffusion, in diffusion and high-pressure convection. In a through diffusion experiment one quantifies the mass of tracer that has diffused through a rock sample. The in diffusion method determines the penetration depth of the tracer and does not require tracer to pass through a rock sample. Through diffusion as a method to evaluate sorption was effective for weakly sorbing radionuclides, and the in diffusion method had potential for strongly sorbing radionuclides. The high-pressure convection method was better than diffusion due to its reduced timescale requirements. The sorption properties of Am, Cs, and Sr observed with high-pressure convection method were comparable to batch sorption results. Hatipoglu et al. (1994) studied Ba(II) and Sr(II) interactions with granite using batch experiments and transport measurements in a column of crushed granite. The sorption coefficients determined from column experiments were smaller than those from batch tests. Hölttä et al. (2001) studied Na, Ca and Sr diffusion and transport in mica gneiss and tonalite. They found that sorption coefficients derived from transport experiments were one order of magnitude lower than from batch experiments. Wellman et al. (2008) studied U(VI) in saturated and unsaturated porous media. Under saturated conditions exclusion of conservative tracers was noted and U sorption was lower than predicted from batch experiments. However, under unsaturated conditions, conservative tracer was not excluded and sorption was greater than predicted from batch experiments. Van Loon et al. (2005) compared the sorption behaviour of Na and Sr in Opalinus clay derived from diffusion measurements and batch tests. The agreement between both methods was good and the uptake mechanism was identified as cation exchange. Lefèvre et al., 1996, studied the migration of ^{45}Ca and ^{90}Sr in clayey and calcareous sand. Provided that the pH and concentrations of major cations are stable, it was possible to calculate distribution coefficients as a function of major cations. Cation exchange and Ca – HCO_3 equilibrium controlled Ca and Sr transport.

Kirchner and Nageldinger (1996) studied the kinetics of ^{137}Cs sorption and desorption in a soil pellet with a diffusion experiment. The best model fit to the diffusion data was achieved with first-order kinetics and a Freundlich isotherm. Desorption displayed a marked hysteresis. Rundberg et al. (1991) studied ^{85}Sr, ^{137}Cs, and ^{133}Ba transport in tuff samples from Yucca Mountain. The experimental results showed greater tailing than could be explained with the conventional advection dispersion equation. Sr transport could agree with batch sorption measurements provided the dispersion was adjusted to a significantly larger value than observed for tritiated water. Similar agreement was found for Cs and Ba using Gelhar's dispersion model for a stratified medium. André et al. (1998) analyzed the breakthrough curves of Np(V) in clayey sand packed columns in terms of mass transfer kinetics. Values of K_d at various pH values were measured from the first-moment of peaks. Results were interpreted in the framework of linear chromatography theory.

Bradbury and Baeyens (2003) compared diffusion measurements of Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V) in Kunigel V1 bentonite with predicted diffusion properties derived from batch sorption measurements. In most cases the batch sorption values are higher, with surface diffusion and anion exclusion being called upon to explain the difference. The authors point out that the sorption coefficients derived from diffusion studies are usually model dependent. The authors concluded that the differences in diffusion coefficients derived from diffusion experiments and those calculated with the help of sorption measurements are not that great. An important consideration is performing sorption measurements and diffusion experiments with a similar pore water chemistry.

Perkins and Lucero (2001) studied the transport of ^{22}Na, ^{241}Am, ^{239}Np, ^{228}Th, ^{232}U, and ^{241}Pu through intact cores of Culebra dolomite using a synthetic brine solution as the eluant. The ^{22}Na was used as a conservative tracer to define the apparent porosity and dispersion coefficient of the core. While, ^{239}Np and ^{232}U were moderately sorbed and eluted from the column, ^{241}Am, and ^{241}Pu were not eluted. Destructive and non-destructive analyses of the an intact core sample showed that ^{241}Am was concentrated at the inlet, while ^{241}Pu was dispersed throughout the core with a strong retardation. A retardation factor for ^{241}Pu was obtained using a single porosity advection-dispersion model.

Tachi et al. (1998) studied Se sorption on Japanese tuff samples using through-diffusion and batch experiments. The sorption coefficients obtained from diffusion experiments were about an order of magnitude lower than obtained from batch experiments, despite attempts to take into account differences in specific surface areas between the two methods. Vandergraaf (1997) discussed the effects of available surface areas and porosities on the sorptive capacities of moderately and sparsely fractured rock. Vandergraaf also noted that since pore fluid compositions may have TDS values that are orders of magnitude higher than groundwater in fractures, sorption for certain elements is likely to be significantly lower in the rock matrix compared to sorption in fractures. Therefore, sorption values based on dilute groundwater are likely to overestimate sorption within the rock matrix.

Jakob et al. (2009) investigated the effects of sorption competition on Cs diffusion through a sample of Opalinus clay from the Mont Terri underground laboratory (Switzerland). The results from both a through diffusion phase and the following out diffusion phase were simulated with a simple single-species model, in which diffusion and non-linear sorption of Cs were considered, and a more complex multi-species model, where pore water chemistry and the sorption/desorption of competing cations were also considered. Although the simple model could explain the results of the through diffusion measurements, the more complex model had to be used for the out diffusion experiment.

The derivation of sorption parameters from mass transport studies depends very much on the nature of the transport process and the understanding of the physical processes involved. Transport models of various complexities have been used to simulate the results of transport experiments and to explore the role of sorption and/or estimate sorption parameters. It is not the role of this report to review all the approaches that have been used. However, to illustrate the role of sorption in mass transport and contaminant retardation, several simple approaches used for diffusion and advective transport are presented.

Diffusive mass transport: The effective or empirical diffusion coefficient (D_e) is commonly used to describe diffusive fluxes, and is defined as (Choi and Oscarson 1996, Skagius and Neretnieks 1982, and Ohlsson and Neretnieks 1995):

$$D_e = \frac{D_w \delta \varepsilon_t}{\tau^2} \tag{56}$$

D_w is the free-water diffusion coefficient, τ is the geometric tortuosity, and δ is the constrictivity. The through-transport porosity (ε_t) determines the diffusive flux through rock when steady state has been achieved. However, the storage capacity of the rock must also be considered. The storage capacity results from sorption for those species, which are likely to adsorb onto mineral surfaces and from the total connected (ε_c), which includes both the transport porosity and the dead end porosity. The storage capacity is quantified by the rock capacity factor (α), which has been defined as (Bradbury and Green 1985):

$$\alpha = \varepsilon_c + \rho \cdot K_d \tag{57}$$

where ρ is the bulk density of the rock, K_d is the sorption coefficient.

The apparent diffusion coefficient (D_a) incorporates the capacity factor and has been defined as (Bradbury and Green 1985, Choi and Oscarson 1996, Oscarson and Hume 1994 and Ohlsson and Neretnieks 1995):

$$D_a = \frac{D_e}{\alpha} = \frac{D_p \varepsilon_t}{(\varepsilon_c + \rho K_d)} \tag{58}$$

In the case of a nonsorbing tracer, such as iodide, the rock capacity term (α) is equal to the total connected porosity (ε_c).

In a through diffusion experiment, in which tracer is allowed to diffuse through a rock sample, tracer breakthrough is monitored as a function of time. Following the initial breakthrough of tracer, the amount of tracer diffusing through the sample into the elution reservoir eventually reaches a steady-state, provided that the physical properties of the rock remain constant during the diffusion experiment (Figure 5). The mass of tracer (M_t) diffusing through the sample under steady-state conditions at time (t) is described by the following equation:

$$M_t = D_e(C_oA/L)\, t - \alpha(ALC_o/6) \tag{59}$$

where

D_e = effective diffusion coefficient for a given tracer in the rock sample,
A = surface area through which the tracer diffuses,
L = diffusion path length (i.e., thickness of rock sample),
C_o = concentration of a given tracer in the tracer reservoir, and
α = rock capacity factor

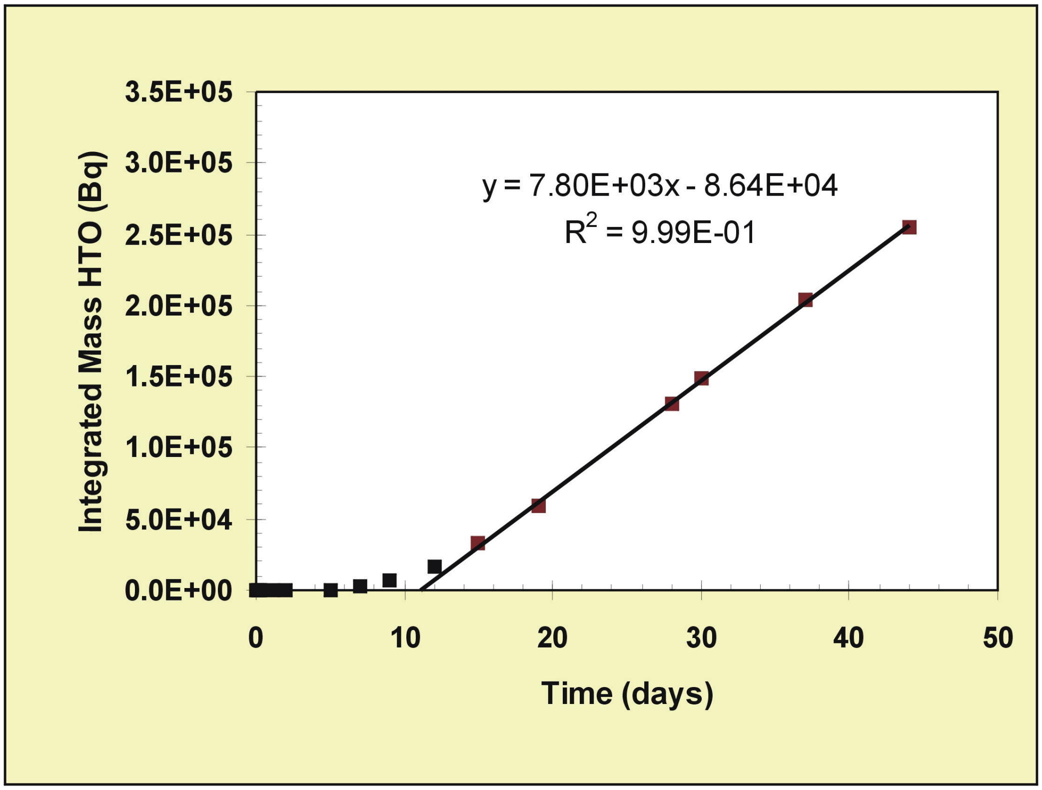


Figure 5: Example of Tracer Mass Diffusion in a Through-diffusion Experiment (Vilks and Miller, 2007)

When steady-state has been achieved a plot of M_t versus time will produce a straight line with a slope:

$$\text{Slope} = D_e(C_oA/L) \tag{60}$$

and an intercept:

$$\text{Intercept} = -\ \alpha(ALC_o/6) \tag{61}$$

Because C_o, A and L are known, the slope of the line can be used to calculate D_e. The intercept of the straight line can be used to calculate the dimensionless rock capacity factor (α), which represents the amount of tracer retained in the rock sample before steady-state is achieved. The magnitude of α depends upon the total connected porosity accessed by the tracer (ε_c) and on the amount of tracer that is adsorbed by the rock sample. The value of ε_c

can be determined by the diffusion of a non-sorbing tracer. In the case of a sorbing tracer the rock capacity factor will be higher than ε_c by an amount that is determined by the distribution coefficient, allowing one to calculate a sorption coefficient from equation 57.

Advective mass transport: In mass transport experiments that include advection one can compare the velocity of the sorbing tracer with the velocity water, as determined with a non-sorbing tracer. The retardation equation (Freeze and Cherry, 1979) provides a general expression that relates sorption to the reduction in the velocity of a sorbing contaminant

$$R=\frac{v}{v_c}=1+\frac{\rho_b}{\varepsilon}*K_d \tag{62}$$

Where

R = retardation factor
v = average linear water velocity
v_c = average linear velocity of sorbing contaminant
ε = porosity
ρ_b = the bulk mass density of the media through which transport is taking place

The bulk mass density is determined to the density (ρ) of the solids or minerals, and by the porosity of the transport media.

$$\rho_b = p*(1+\varepsilon) \tag{63}$$

In a given migration experiment the average linear velocities of the water (non-sorbing tracer) and the sorbing tracer are determined with the same protocol. For example, in column migration tests one can do a continuous injection with a tracer of constant concentration, C_0, until eluted tracer concentrations, C, reach a C/C_0 value of close to 1. The times at which eluted C/C_0 concentrations reach 0.5 are used to determine tracer velocities and calculate the sorption coefficient with equation 62.

The retardation factor in equation 62 was developed for porous media with porosities around 0.5. If transport occurs in unfractured rocks with low porosities (below ~ 0.1) the retardation factor given by equation 62 gives unrealistically high retardation factors because in rocks the available sorption is significantly reduced (Vandergraff and Ticknor, 1994). Instead Vandergraaf and Ticknor (1994) propose equation 64 for retardation in rocks with low porosity. Equation 64 may be used to calculate sorption coefficients from transport experiments using unfractured rock cores.

$$R=\frac{v}{v_c}=1+\rho*K_d \tag{64}$$

2.4.4 Natural Analog Studies

Natural analog studies can provide estimates of element distribution ratios between solids and natural groundwaters under in-situ conditions over geologic time scales. McKinley and Alexander (1993) provide an overview of the uses and abuses of natural analog studies for extracting information on radionuclide sorption and retardation. Considerable effort must be made to characterize and identify the key geochemical processes before meaningful conclusions can be derived regarding sorption processes. One example of an attempt to characterize the geochemistry of uranium in an ore body and to identify the fraction of the natural uranium, which interacts with groundwater is described by Payne et al. (2001) and Payne and Waite (1991). The accessible uranium was identified with a chemical extraction technique and verified with an isotopic exchange technique (^{238}U exchanged with ^{236}U before extraction). The accessible uranium comprised about 20 percent of the total uranium. Field-derived partitioning ratios (P_{acc}), based on accessible uranium, were similar to laboratory measured sorption ratios (R_d), provided the laboratory measurements were made under comparable pH and pCO_2 conditions.

As part of a natural analog study, Zukin et al. (1987) investigated uranium-thorium series radionuclides in brines and reservoir rocks from two deep geothermal boreholes in the Salton Sea Geothermal Field, southestern California. Rock/brine concentration ratios (Rc) were close to unity for Ra, Pb and Rn. Rc ratios for Th and U were 5×10^5 and 5×10^4, respectively. The low sorption of Pb was attributed to the formation of chloride complexes. The low sorption of Ra was explained by a combination of chloride complex formation, mass action effect of high salinity and the high temperature of the brines (~300 C, TDS ~ 250 g/L).

The IAEA (1999) reviewed the use of natural analogs to support radionuclide transport models used for the safety assessments for deep geologic repositories. Confidence in our conceptual models or radionuclide behaviour in natural systems is improved by considering processes observed in the study of natural systems. These processes may operate over large spatial and temporal scales that cannot be reproduced in the laboratory. The detailed characterization of natural migration systems, coupled with the testing of thermodynamic databases, enhances our understanding of mineralogical and hydrochemical controls on radionuclide solution chemistry and sorption/migration behaviour. Natural analogs also provide a useful means for identifying and scoping the principle uncertainties associated with applying geochemical models to complex natural systems.

In summary, natural analog studies can provide a benchmark data set that reflects the effects of natural processes that take into account in-situ geochemical and physical conditions and possibly the effects of geologic time scales. Such data cannot be easily produced in the laboratory. However, geologic uncertainties pose a formidable challenge for the use and interpretation of data from natural analog studies.

2.4.5 In-situ Experiments Involving Batch or Mass Transport Techniques

One of the main challenges for natural analog studies is to precisely define processes that have operated over very long time scales. Although in-situ experiments are restricted by time scales of several years, they permit one to better define the experimental system and identify the dissolved and sorbed or precipitated species participating in a particular reaction. In-situ experiments also permit one to sample the effects of geosphere variability and unique geochemistry not permitted in laboratory tests. One of the difficult challenges for laboratory tests is to recreate the often poorly buffered reducing conditions of many groundwater systems.

One solution to this problem was to move the laboratory to the field and perform experiments using groundwater taken directly from the rock. Kumata and Vandergraaf (1998) performed an experiment at AECL's Underground Research Laboratory to study Np transport in crushed granite using in-situ groundwater. Results demonstrated that the reducing conditions achieved by using in-situ groundwater resulted in Np(V) reduction to Np(IV) and increased Np retardation by an order of magnitude. Yamaguchi et al. (2008) describe radionuclide migration experiments with Br, ^{3}H, ^{85}Sr, ^{237}Np, ^{238}Pu and ^{95}Tc performed in a fracture of a 1 m^{3} granite block using in-situ groundwater. Np retardation was less than observed in a column experiment with crushed granite (Kumata and Vandergraaf, 1998) because the granite fracture did not have the fresh rock surfaces that facilitated Np reduction in the column of crushed granite.

In-situ advective transport experiments that include sorbing tracers are also a possibility. Some laboratories, such as SKB's Äspö Hard Rock Laboratory, Sweden, and Nagra's Grimsel Test Site, Switzerland, have licences to use radioactive tracers. An example of in-situ tracer tests is given by Andersson et al. (2007), who describe the TRUE Block Scale Continuation Project, performed at the Äspö Hard Rock Laboratory. Tracer tests were performed in a fracture system with separation distances of 20 and 22 m between injection and withdrawal boreholes. Sorbing tracers included ^{22}Na and ^{85}Sr as slightly sorbing, ^{86}Rb and ^{133}Ba as moderately sorbing, and ^{137}Cs and ^{54}Mn as strongly sorbing tracers. Conservative tracers, assumed not to sorb, included ^{131}I, $^{3}H_2O$, ^{160}Tb-HDTPA, and ^{155}Eu-DTPA. Although field-scale tracer tests are able to test the effects of geosphere uncertainty and in-situ chemical and physical conditions, they do require flow rates (on the scale of metres/min) which may be several orders of magnitude higher than natural flow rates. Extending experimental travel distance to 100 m for sorbing tracers is prohibitive due to the long time frames required, and the low mass recoveries.

In-situ diffusion experiments that involve longer reaction times and better-controlled geometry have been performed at AECL's Underground Research Laboratory (Vilks et al., 2004) and at SKB's Äspö Hard Rock Laboratory (Vilks et al., 2005 and SKB, 2008). At AECL's Underground Research Laboratory a conservative tracer (I) and weakly sorbing tracers (Li, and Rb) were allowed to diffuse into granite and granodiorite for a 15 month period, after which test sections were over cored to determine tracer diffusion profiles into the rock matrix. Results showed that Rb was sorbed more strongly than Li. Sorption decreased significantly as the pore water TDS increased from 0.58 to 90 g/L. At the highest salinity Li sorption appeared to be eliminated, while a small amount of Rb sorption was still apparent. The Long Term Sorption Diffusion Experiment (LTDE-SD) at the Äspö Hard Rock Laboratory involved the diffusion of sorbing and non-sorbing radiotracers into an altered fracture surface and a section of rock matrix. Diffusion into the rock and sorption were determined by monitoring tracer losses from the reservoirs in contact with rock, and by the over coring the test rock sections to recover tracer penetration profiles. The in-situ part of the experiment is complete and analysis of penetration profiles is underway.

3. APPLICATION TO PERFORMANCE ASSESSMENT

Performance assessments include mass transport calculations in which contaminant transport velocity is decreased relative to groundwater velocity by chemical retardation. The retardation factor, R, which is defined as the ratio between groundwater velocity and the contaminant velocity, is related to an assumed linear and reversible sorption coefficient, K_d, by equation 62 for porous media or by equation 64 for low porosity rocks (Section 2.4.3). Although debate continues regarding the merits of using the K_d approach to describe retardation, sorption coefficients remain the primary tool for quantifying the effects of sorption in performance assessment calculations.

With the Canadian Government's selection of Adaptive Phased Management as the long-term management approach for used nuclear fuel, both sedimentary and crystalline rocks are considered as potential hosts for a deep geologic repository (NWMO, 2005). While sorption on Canadian crystalline rocks has been extensively investigated, sorption on sedimentary rocks has not. Therefore, a priority for the Canadian program is to increase the understanding of sorption on sedimentary rocks to a similar level to that of crystalline rocks. Some crystalline rocks and sedimentary rocks such as the Ordovician sedimentary rocks of southern Ontario, have salinities that may be as high as 300 g/L. Consequently the Canadian program also needs to consider sorption behaviour in brine solutions.

Since the NWMO has not yet selected a specific site or sites for a DGR for used nuclear fuel, its performance assessment needs require the development of an understanding of sorption in highly saline solutions, with an immediate emphasis on generic sedimentary rocks that may include shales and limestones. Ultimately this may require the development of an up to date sorption data base, following the approaches used by other international programs.

3.1 DATABASES USED IN NUCLEAR WASTE MANAGEMENT PROGRAMS

Canada: Vandergraaf and Ticknor (1994) described the sorption database that was used in the Geosphere Model of SYVAC (System Variability Analysis Code) for the 1990 assessment of the Whiteshell Research Area. The sorption database was fixed in 1990, and the data reported as R_d values (mL/g) in the form of a parametric equation that was a function of TDS and radionuclide concentration. The pH was not used as an independent variable because pH variations (7.5 to 8.5) are generally small, and pH is difficult to control experimentally during sorption reactions. The Eh was also not used as an independent variable because of the great difficulty in achieving low Eh conditions without compromising the sorption reactions. However, R_d values were given for both oxidized (Eh +200 mV) and reduced conditions (Eh –300 mV). The database was considered valid for granitic groundwater with Total Dissolved Solids (TDS) ranging from 0 to 11.3 g/L, and groundwater compositions ranging from Ca-Na-HCO_3-SO_4-Cl to Ca-Na-Cl-SO_4. Sorption data was provided for grey granite, red granite, gabbro, and individual minerals that included biotite, calcite, chlorite, epidote, gypsum, goethite, hematite, illite, kaolinite, microcline, muscovite, plagioclase, and quartz. The parametric equation for R_d values also included factors to estimate data uncertainty, and a normalizing factor for different geologic materials to account for specific surface area and is equivalent to mass density of the solid. It should be noted that for most combinations of radionuclide with sorbing solid, the factors accounting for uncertainty and variation with TDS are not given due to a lack of sufficient data to properly define these factors.

The data used by Vandergraaf and Ticknor (1994) to compile the sorption database came from (1) static batch sorption experiments performed at Whiteshell, (2) the Sorption Data Base compiled by the Nuclear Energy Agency (NEA) (Rüegger and Ticknor, 1992), (3) sorption data from published literature, (4) laboratory transport experiments in columns or intact cores, and (5) other lines of evidence from the literature not directly related to the R_d concept. If sorption data for an element on a particular mineral or rock were not available, sorption data from a similar rock or mineral were used as an estimate. If no mineralogical similarity could be established for the solid of interest, sorption data for quartz were used as a conservative estimate, since sorption on quartz tends to be low. Chemical homologs were used to estimate sorption properties for elements for which there were no sorption measurements. Chemical homologs are elements with similar chemical properties to the element of interest. In an ideal situation two or more homologs are used to bracket the chemical properties of the element of interest. If the chemistry of a multivalent element is either very complex or poorly known, a conservative assumption was made that it does not sorb. Short-lived radionuclides were not included in the database.

Ticknor and Vandergraaf (1996) updated the sorption database used in the Canadian Nuclear Fuel Waste Management Program to include data obtained after 1990. Montmorillonite was added as an additional solid, and data was added for twelve additional elements that included P, Cl, Y, Ru, Rh, Ag, In, Sb, Te, I, Os, Ir, Pt, Po and Rn. The form of the parametric equation presented by Vandergraaf and Ticknor (1994) remained the same.

United States: The U.S. Environmental Protection Agency (USEPA, 1998) documents the sorption database used by the U.S. Department of Energy for conducting performance and compliance assessments evaluating the radioactive waste containment capabilities of the Waste Isolation Pilot Plant (WIPP) in New Mexico. The report focused on the sorption of actinide elements on Culebra dolomites in the presence of NaCl brine (TDS of 338 g/L). Based on initial quantities, half-lives and specific radioactivity, the calculated releases from the WIPP site are dominated by Th, U, Am and Pu (Perkins et al., 1998). Data are presented in the form of K_d (mL/g) ranges for Am(III), Pu(III), Pu(IV), U(IV), U(VI), Th(IV), Np(IV) and Np(V). 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).

Voudrias and Means (1993) determined uranium retardation factors for halite and carbonate using batch and column sorption experiments. Lucero et al., 1998, reported on the transport of ^{3}H, ^{22}Na, ^{241}Am, ^{239}Np, ^{228}Th, ^{232}U, and ^{241}Pu through cores of Culebra dolomite using NaCl brine solutions. Both ^{3}H and ^{22}Na behaved as conservative tracers in the brine solutions. The ^{239}Np and ^{232}U were eluted from the cores, showing moderate retardation. The ^{241}Am, ^{228}Th, and ^{241}Pu were strongly sorbed and not eluted. Single and dual porosity models produced similar results for the conservative tracers. Compared to packed cores, the intact cores showed significantly more dispersion probably due to channelling. Minimum retardation factors were predicted for the non-eluted species using a modelling approach combined with minimum detection limits for Am, Th and Pu (Perkins et al., 1998). Changing brine composition did not significantly affect transport properties in the dolomite.

Krupka et al. (2004) provide sorption data in the form of K_d (mL/g) values as part of the Geochemical Data Package for the 2005 Hanford Integrated Disposal Facility performance assessment. Sorption data were based on experiments using site specific solids and groundwaters. Near-field water chemistry has high pH, ionic strength and radionuclide concentrations, while far-field chemistry has a pH ~ 8 and much lower ionic strength (0.01 mol/L). The types of solids considered were near-field vitrified waste and cementations secondary waste, and far-field sediments.

The U.S. Environmental Protection Agency (USEPA, 1999a) discusses the conceptualization, measurement and use of the distribution coefficient K_d (mL/g) in formulating the retardation factor (R) for application in site remediation and waste management decisions. The capabilities of EPA's geochemical reaction model, MINTEQA2, and its different sorption models are also reviewed. The second volume of this report (USEPA, 1999b) provides useful reviews of the geochemistry of a number of contaminants and provides minimum and maximum K_d values for application to various sediments and rocks. Tables providing K_d values as a function of pH were provided for Cd, Th and U. Sorption K_d values for Sr were provided for a range of pH, CEC and clay content values. Sorption values for Pu were give as a function of clay content and soluble carbonate. Sorption of Pb was given as a function of Pb concentration and soil pH. K_d values for Cr were given as function of extractable Fe and soluble sulfate. Sorption for Cs was given for a range of clay contents for conditions of low ionic strength ($I < 0.1$ mol/L). USEPA (2004) reviewed the geochemistry and published sorption K_d values for Am, As, Cm, I, Np, Ra, and Tc.

Finland: Hakanen and Hölttä (1992) summarize the sorption and diffusion parameters used in the Finnish updated safety assessment TVO-92. The sorption data is presented as K_d (m^3/kg) and K_a (m^3/m^2) values for crystalline rocks, and as K_d (m^3/kg) values for sand (90%)/bentonite (10%) mixture. Values for oxidizing and reducing conditions are given for redox sensitive elements. Reference waters at pH 8 were a dilute granite groundwater (TDS = 0.27 g/L) and a brackish water with a TDS of 9.6 g/L. Except for Se, Pd, Ra and Sn the sorption coefficients in the database were based on experimental work performed at the University of Helsinki. The other sorption data were taken from the NEA sorption database. As in many other databases, the sorption coefficients are tabulated as conservative and realistic values.

Sweden: Carbol and Engkvist (1997) compiled a database of sorption coefficients (K_d) that are relevant for conditions found at candidate sites for a future Swedish spent nuclear waste repository. Sorption data were selected from Swedish measurements made with reference groundwater types, and from the international literature with a focus on matching Swedish groundwater types. K_d values for 28 relevant radionuclides were reported for non-saline and saline groundwaters. Non-saline waters were defined as having a chlorinity of < 0.5 g/L Cl, while saline waters had a chlorinity between 0.5 and 6.5 g/L Cl. Sorption data were selected for reducing waters (Eh < -200 mV), with pH values > 7. Selected K_d values had to be deemed reliable, meaning that their values had to demonstrate a consensus between different experimental groups. Elemental chemistry was also considered, so that for example, a K_d value for U(IV) should be much like that for Th(IV). Also, K_d values for an element are compared to values for similar elements in order to eliminate outliers. The Swedish concept of sorption considered ion exchange and surface complexation mechanisms. The sorption of elements controlled by ionic exchange reactions are considered to be the most susceptible to reduction by high salt content, while those elements affected by surface complexation are most susceptible to pH changes. Only elements that had isotopes with half-lives longer than 5.27 years, were considered for the sorption database. Crawford et al.(2006) reviewed the available data on sorption coefficients (K_d) and provided uncertainty assessments for input into the Swedish interim safety report, SR-Can. Although the review focused on Cs, Sr, Ra, Ni, Th, U, Np and Am, the final database in the report included data for an additional 19 elements taken from the compilation of Carbol and Engkvist (1997). The recommended sorption values are intended for use in typical Swedish groundwater conditions and rock types found on the Simpevarp peninsula and Forsmark.

Savage and Stenhouse (2002) compiled sorption K_d (m^3/kg) values for the SFR 1 Vault Database, for use in radionuclide and assessment calculations by SKI. The solids considered for sorption included the waste matrix (porous cement), cementations materials, sand, sand-bentonite, and rocks in the near and far field. The reference water was assumed to be saline.

Switzerland: Stenhouse and Pöttinger (1994) reviewed three databases from European high level waste management programs for crystalline rock and bentonite-porewater systems, as well as the Canadian database. In general there was good agreement between the different programs. However, a number of elements, such as Pd, Sn, Tc, U and Np, have limited or no sorption data.

Stenhouse (1995) assembled sorption databases for use by Nagra for performance assessments of crystalline rock, marl and bentonite. Sorption data in the form of K_d values (m^3/kg) were presented for two types of crystalline rocks (fractured infill and altered wall rock), three types of marl (1. fault gauge and shaley marl, 2. vein infill, and 3. limestone/limey marl), and bentonite. Reference groundwaters included two non-saline types for crystalline rock, a $Na\text{-}HCO_3$ (TDS~1.4 g/L) type and a saline Na-Cl (TDS~28 g/L) type for marl, and a $Na\text{-}HCO_3\text{-}SO_4$ (TDS~5.3 g/L, pH 9.0) type for bentonite. In the marl database, different sorption values for Na-Cl and $Na\text{-}HCO_3$ were given for some elements (Cs, Se, and Ra). Since sorption values were required for a number of different rock types, the approach used was to compile K_d values for constituent minerals, which were used to derive whole rock values based on the mineral content of the rocks. The process for selecting sorption values considered (1) water chemistry (pH, Eh, major ions, radionuclide concentrations, temperature), (2) experimental method (batch or dynamic, lab or field), and (3) chemical speciation (whether identified or not). Preference was given to batch experiments, which provide the greatest data volume and amount of useful information.

Bradbury and Baeyens (2003) describe the near-field sorption database for compacted MX-80 bentonite to be used by Nagra for performance assessment of a high-level radioactive waste repository in Opalinus Clay host rock. The database, in the form of distribution ratio (R_d) values, was compiled from “in house” sorption isotherm data measured for Cs(I), Ni(II), Eu(III), Th(IV), Se(IV), and I(-I), as well as sorption data from the open literature. A main concern for developing the sorption data base for bentonite was to establish the correct pore water composition in terms of major ions, pH and Eh. Sorption databases were developed for the reference bentonite pore water with a pH of 7.25, as well two additional pore waters with pH values of 6.9 and 7.9 to establish upper and lower bounds for water composition. Although the reference pore waters were reducing, Nagra was also considering a scenario where oxidizing conditions (Eh of +635) exist in the near-field. The safety-relevant radionuclides that would be affected by the oxidizing conditions were identified as Tc, Se, U, Np and Pu. It was noted that R_d values are obtained from batch experiments, using dispersed clay suspensions. Arguments were presented why these R_d values should be relevant to modelling transport in compacted clay.

Wieland and Van Loon (2003) report on a near-field cement sorption database for performance assessment of an intermediate level waste repository in Opalinus Clay. Sorption data were reported as R_d values (m^3/kg) for oxidizing and reducing conditions for pore waters corresponding to stage I (pH = 13.3) and stage II (pH = 12.5) of cement degradation. The major elements in the pore water were OH^- and Na (0.11 mol/L) and K (0.18 mol/L). Reported data were derived from in-house experimental studies and the open literature.

Germany: Warnecke et al. (1994) summarizes the results of batch sorption and radionuclide migration experiments (column and diffusion experiments) that were completed with Gorleben waters and sediments over the previous 10 years. Sorption coefficients (mL/g) are provided for sandy sediments and clayish sediments for fresh water and saline water. The elements included in the database are Sr, Tc, I, Cs, Pb, Ra, Th, Np, U, Pu, Ac, and C. Sorption coefficients for Sr, I, Cs, Ra, Np and C were lower in saline water. The effect of salinity on Tc, Th, U, Pu and Ac was negligible or inconclusive. Interestingly, the sorption of Pb increased in saline water. The presence of varying amounts of complexing humic substances in Gorleben groundwaters may have affected the behaviour of some elements, such as Pb.

Lieser and Mühlenweg (1988) determined Np sorption from column experiments using Gorleben sediments and waters ranging from dilute to Na-Cl brine (TDS = 160 g/L) at neutral pH. Under aerobic conditions the sorption ratio R_S of Np(V) varied from 1 to 6 mL/g. Under anaerobic conditions most of the neptunium was sorbed as Np(IV) with an R_s value > 10^3 mL/g. The water composition did not appear to have a significant effect on Np sorption for both redox conditions. Meier et al. (1994) reported the results of batch sorption experiments of ^{233}U, ^{226}Ra, ^{228}Th, ^{210}Pb, ^{227}Ac and ^{90}Sr on Gorleben sediments in saline and weakly saline water. Meier et al. (1991) presented sorption ratios (R_s) for ^{233}U, ^{226}Ra, and ^{63}Ni for sediments from Gorleben as a function of ionic strength and temperature. Meier et al. (1988) reported on the diffusion and sorption of ^{233}U, ^{237}Np, and ^{63}Ni in sedimentary rock samples from the Konrad, Asse and Gorleben sites, using fresh, weakly saline, and saline waters. Sorption coefficients (Kd, mL/g) that were extracted from diffusion results were similar to sorption (R_s) and desorption (R_D) coefficients determined from batch experiments. The R_D values tended to be a factor 1.1 to 3.6 higher than R_s values. Meier et al. (2003) discussed the effect of humic colloids on radionuclide transport in groundwater aquifers at the Gorleben site. Sorption and desorption ratios are provided for Ni, Pb, Ra, Ac, Th and U in dilute water, and for Ac and Th in saline water.

Japan: The Japan Nuclear Cycle – Sorption DataBase (JNC-SDB) has been compiled by the Japan Atomic Energy Agency (JAEA) from a number of sorption databases (Shibuatani et al., 1999). The JNC-SDB was updated with more recent literature by Suyama and Sasamoto, 2004, and Saito et al., 2007. The database is a compilation of K_d values from the literature for bentonite and rocks under a variety of groundwater compositions. Elements in the database include Am, U, Th, Pa, Cm, Ac, Cs, Np, Pb, Pu, Se, Tc, Bi, Eu, I, Mn, Mo, Ni, Po, Sm, Sn, Sr, Ra, Zn, Ag, Ba, Co and Fe. Ochs et al. (2008) extracted sorption data from the JNC-SDB and from the literature to develop K_d values for Th, Np, Cs, and Sc sorption on Horonobe rocks (mudstones and shales). The approach was to assume that sorption was controlled by smectite, chlorite, kaolinite and illite, with other rock forming minerals having a negligible effect. The sorption properties of the rocks were derived from the sorption characteristics of these minerals, taking into account of their abundance, specific surface area and cation exchange properties. The effects of pH, complexing ligands and competing major cations were also considered.

Nuclear Energy Agency: The NEA sorption database collected more than 10,500 K_d values (Ruëgger and Ticknor, 1992). Among them, 1,525 K_d values were measured under reducing conditions. The elements include Ag, Am, Ba, C, Ce, Co, Cs, Eu, Fe, I, Mn, Mo, Nb, Ni, Np, Pd, Pm, Pu, Ra, Ru, Sb, Se, Sn, Sr, Tc, Th, U, Y, Zn, Zr. The solids include granite, tuff, sandstone, bentonite, minerals and clay. Beginning in 1997, OECD/NEA launched a sorption project with ANDRA, Posiva Oy, NRC, ANSTO, ONDRAF, RAWRA, GRS, JAEA, etc. as project partners. A report was published in 2001 on using thermodynamic sorption models for guiding the selection of radioelement distribution coefficient investigations (NEA 2001).

3.2 KEY RADIONUCLIDES

The term “key radionuclide” may be applied to those elements whose potential radiological dose from used fuel is high enough to be of interest to performance assessment. The list of key radionuclides would be used to identify a much smaller number of elements that could be the focus of a program to study sorption in highly saline waters. Grouping key radionuclides with similar properties, and selecting representative elements that are practical for use in sorption experiments accomplishes this. Certain elements are selected because they may be representative of one or more sorption mechanisms. With an understanding of how these mechanisms operate under saline conditions it may be possible to determine to what extent existing sorption data bases can be used to derive sorption properties in brine solutions for the full list of key radionuclides. Experimental work with some elements may be avoided for practical reasons, such as the need for redox control, analytical difficulties, or solubility limits.

Table 4 lists a select number of elements that are reported in international sorption databases. Note that some databases, such as the Canadian one, contain other elements not listed in the table. These elements have at least one radioisotope with a half-life longer than 5.27 years (^{60}Co). The importance of elements listed in Table 4 is variable, depending upon initial quantities in the waste form, radio-toxicity, and sometimes toxicity. Elements that have received a high interest include Cs, Sr, Zr, I, Tc, and the actinides. The TDS values for the highest salt concentrations considered by the databases are reported, along with the major element components of the high salinity reference groundwaters.

Tritium, krypton (a noble gas), and the halogens, Cl and I, do not sorb or are very weakly sorbing. As a result, the halogens are often used as conservative tracers in transport experiments to define the transport properties of water and provide a reference for the breakthrough curves of sorbing tracers. However, since ^{129}I is an important contributor to dose in performance assessment calculations, considerable attention has been given to defining the sorption properties of I as even a small amount of well-defined sorption may increase predicted retardation.

The alkali and alkali earths, including Cs, Sr, and Ra, are soluble and are known to sorb mainly by cation exchange. It is known that mass action effects at high salt concentrations significantly reduce sorption of these elements. For example, transport experiments with dolomite and brine solutions have demonstrated that ^{22}Na behaved as a conservative tracer, similar to $^{3}H_2O$ (Lucero et al., 1998).

The transitional elements, including Cr, Ni, Zr, Nb, Tc, Pd and Ag, have a variable chemistry. However, in addition to sorption by ion exchange, they also form inner-sphere surface complexes to varying degrees. Therefore, many transition elements could be expected to sorb to some extend at high ionic strength. However, complexation reactions with chloride could increase solubility and reduce sorption for some elements in brine solution.

Table 4: Reporting of Elements in International Sorption Databases

Element	Canada (1,2)	Sweden (3)	Finland (4)	Switzerland (5)	Switzerland (6)	Gorleben (7)	WIPP (8, 9)
	Crystal.	Crystal.	Crystal.	Crystalline Marl Bentonite	Cement	Sediments	Dolomite
H (as H_2O)	yes				yes		yes
C (as CO_3^{-2})	yes	yes	yes	yes	yes	yes	
Cl (-I)	yes		yes	yes			
Ni (II)	yes	yes	yes	yes	yes	yes	
Se (-II,IV,VI)	yes	yes	yes	yes	yes		
Kr	yes	yes					
Sr (II)	yes	yes		yes	yes	yes	
Zr (IV)	yes	yes	yes	yes	yes		
Nb (V)	yes	yes	yes	yes	yes		
Tc (IV,VII)	yes	yes	yes	yes	yes	yes	
Pd (II)	yes	yes		yes			
Ag (I)	yes	yes					
Cd (II)	yes	yes					
Sn (IV)	yes	yes	yes	yes	yes		
I (-I, V)	yes	yes	yes	yes	yes	yes	
Cs (I)	yes	yes	yes	yes	yes	yes	
Sm (III)	yes	yes			yes		
Eu (III)		yes			yes		
Ho (III)		yes					
Pb (II)	yes			yes	yes	yes	
Ra (II)	yes	yes	yes	yes	yes	yes	
Ac (III)	yes	yes		yes	yes	yes	
Th (IV)	yes	yes	yes	yes	yes	yes	yes
Pa (IV,V)	yes	yes	yes	yes	yes		
U (IV,V,VI)	yes	yes	yes	yes	yes	yes	yes
Np (IV,V)	yes	yes	yes	yes	yes	yes	yes
Pu (III,IV,V,VI)	yes	yes	yes	yes	yes	yes	yes
Am (III)	yes	yes	yes	yes	yes		yes
Cm (III)	yes	yes	yes	yes			yes
max. TDS (g/L)	11.2	11	21	28	9	159	338
Saline comp.	Na-Ca-Cl-SO_4	Na-Ca-Cl-SO_4	Na-Ca-Cl	Na-Cl	Na-OH	Na-Cl	Na-Cl

1. Ticknor and Vandergraaf, 1996
2. Vandergraaf and Ticknor, 1994
3. Carbol and Engkvist, 1997
4. Hakanen and Hölttä, 1992
5. Stenhouse, 1995
6. Wieland and Van Loon, 2003
7. Warnecke et al, 1994
8. USEPA, 1998
9. Lucero, et al., 1998

The lanthanides, including Sm, Eu and Ho, are trivalent and are strongly hydrolysed at pH levels above 6. As a result, at pH values of 8 to 9 lanthanides are fully hydrolysed, leading to the formation of strong inner-sphere surface complexes, as well as precipitates. Lanthanides are expected to sorb in brine solutions. The actinides also have a tendency to form strong hydrolysis complexes, leading to the formation of inner-sphere surface complexes, and extremely low solubilities. Salinity is expected to have a minor effect on sorption. The main difficulties with performing experiments with actinides are their tendency to form colloids, their low solubility, and the limited availability of short-lived isotopes, making it more difficult to quantify the very low dissolved concentrations imposed by solubility limits.

The redox sensitive elements in Table 4 are Se, Tc, I, Pa, U, Np, and Pu. Working with these elements under reducing conditions may be very difficult, requiring the use of in-situ groundwater or the addition of redox buffers that may create experimental uncertainty. Some elements are used as 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 that include 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.

In summary, the selection of elements to use at the beginning of an experimental program to understand sorption behaviour in brine solutions should focus on a small number of elements that would define the key sorption mechanisms. With this understanding it will be possible to make better use of sorption in existing databases, and to plan for future experiments as required. Table 5 summarizes categorization of key radionuclides into groups with similar sorption properties, and the selection of elements that could be used to experimentally test these properties.

Table 5: Selection of Elements that Could Be Used in Sorption Experiments

Group	**Key Radionuclide**	**Experimental Representative**
Non-sorbing elements	Tritium, Kr, Cl, I	I
Alkalies and alkali earths	Cs(I), Sr(II), Ra(II)	Cs(I), Rb(I), Sr(II), Ba(II)
Transition elements	Cr, Ni, Zr, Nb, Tc, Pd, Ag(I)	Cu(II), Ni(II)
Lanthanides	Sm (III), Eu(III), Ho(III)	Sm (III), or Eu(III)
Actinides	Ac(III), Th(IV), Pa(IV,V), U(IV,V,VI), Np(IV,V), Pu(III,IV,V,VI), Am(III), Cm(III)	Eu(III), U(VI)

3.3 APPROACHES TO CONSTRUCTING SORPTION DATABASES

Despite the ongoing debate over the advantages of surface complexation models, sorption databases in international waste management programs still consist of data in the format of sorption coefficients, with units of mL/g or m^3/kg. Sorption data are selected to be site specific for the geologic host materials, which are intended to make up the host rock for the repository being considered. Some databases only include sorption parameters for rocks, while others provide data for minerals as well. Sorption data for minerals are useful since they can be used for predicting sorption on rocks after making assumptions regarding rock mineral content. Data are specific to one or more reference groundwaters that have a fixed pH and ionic strength. Although a parametric model has been used in the Canadian sorption database that would account for the effect of TDS (over a limited range), the effect of TDS was only calibrated for a limited number of elements due to a lack of data available in the literature. Usually sorption data are given for reference oxidizing and reducing conditions for redox sensitive elements. Sorption databases include parameters that describe data uncertainty due to measurement errors and geosphere variability. Some databases include both conservative and best estimate sorption values.

The data that are used to construct a sorption database are commonly derived from a number of different approaches, which include:

1. In-house experiments performed with geologic materials and groundwater compositions taken from the geologic setting proposed for the geologic repository. Sorption measurements include batch experiments as well as dynamic transport experiments with advection and diffusion. Batch experiments provide the bulk of the data due to their lower cost and ability to measure sorption under more controlled conditions without the complication of mass transport. Mass transport measurements require a model to interpret the results and extract sorption parameters. On the other hand, dynamic experiments provide the ability to integrate sorption reactions with mass transport and to demonstrate our ability to apply our understanding of sorption to mass transport.
2. The NEA sorption database (Rüegger and Ticknor, 1992) has been used as a source for additional sorption values, using the assumption that sorption on similar geologic materials is applicable to a site being considered for performance assessment.
3. The open literature is used for to obtain data that is not in the NEA database and to provide additional confidence to existing sorption values. Considerations for selecting data from the literature may include water chemistry (pH, Eh, major ions, radionuclide concentrations), temperature, experimental method (batch or dynamic, lab or field), and chemical speciation (whether identified or not).
4. If published data do not exist or are not practical to obtain for particular elements and geologic materials other lines of reasoning may be used. For example, if sorption data for an element on a particular mineral or rock is not available, sorption data from a similar rock or mineral has been used as an estimate. If no mineralogical similarity could be established for the solid of interest, sorption data for quartz has been used as a conservative estimate. Chemical homologs have been used to estimate sorption properties for elements for which sorption measurements were not practical. If the chemistry of a multivalent element is either very complex or poorly known, a conservative assumption was made that it does not sorb.

4. SORPTION IN HIGHLY SALINE SOLUTIONS

4.1 THE GAP BETWEEN CURRENT DATABASES AND OUR NEEDS

Table 6 summarizes the groundwater compositions and the types of solids for which sorption is reported within international sorption databases used by nuclear waste management programs. The highest reference salt concentration reported for crystalline rock sorption data is 28 g/L for Na-Cl water at the Wellenberg site in Switzerland. The only sorption data available for brine solutions is for sedimentary rocks for the Gorleben area in Germany, and for the WIPP site in New Mexico, USA. The brines at both of these locations have Na-Cl composition. Sorption data are also available for cement-based waste forms from Switzerland and the Hanford site. Both of these waters have high TDS and are very alkaline.

Table 6 shows that a geologic repository for nuclear waste in Canada could possibly be hosted by sedimentary or crystalline rocks that may have groundwater brine compositions with TDS values reaching 300 or 400 g/L. Although actinide sorption on sedimentary rocks (dolomite) has been studied with groundwater compositions with TDS as high as 338 g/L at the WIPP site, Table 4 shows that other radionuclides were not included in the WIPP database. Data for some other key radionuclides is available from the Gorleben studies, but the maximum TDS values reached only 159 g/L. Therefore, although the Gorleben and WIPP databases provide a good start for defining actinide sorption for Canadian sedimentary rocks, work is needed to define the sorption properties of the other radionuclides for TDS values as high as 300 mg/L for sedimentary rocks. While the WIPP and Gorleben brines have a Na-Cl composition, the Canadian sedimentary and crystalline brines have a very significant Ca component. This needs to be taken into account when using data from the WIPP and Gorleben sites. The WIPP and Gorleben databases do not provide data for Canadian crystalline rocks.

Table 6: Summary of Sorption Water and Rock Types Addressed by Various Nuclear Waste Management Programs Compared to Canadian Requirements.

Location	TDS (g/L)	Water Compositions	Solids
Canadian granite	0 to 11.3	Ca-Na-HCO_3-SO_4-Cl Ca-Na-Cl-SO_4	granite, gabbro, minerals
Aspo, Sweden	< 0.8 0.8 to 11	Na-Ca-Cl-HCO_3 Na-Ca-Cl-SO_4	granitic rock
Finland	0.27 9.6	Na-Ca-HCO_3-Cl Na-Ca-Cl-SO_4	crystalline rock (tonalite, granite, granodiorite, mica gneiss) sand (90%)/bentonite
Wellenberg, Swiss	1 28	Na-HCO_3 Na-Cl	crystalline rock, marl, bentonite
Swiss	9	Na-OH	cement
Hanford leachate	98	Na-NO_3-OH	sediments, cement waste, vitrified waste
Gorleben, Germany	dilute to 159	Na-Cl	limestone, clay-rich, sandstone
WIPP, USA	338	Na-Cl	dolomite
Water and rock compositions that need to be considered for inclusion to the Canadian database			
Sedimentary Rocks (eg. Michigan Basin, Williston Basin, Western Canadian Sedimentary Basin)	30 to 300	Na-Ca-Cl Ca-Na-Cl	limestone, dolomite, shale
Canadian Shield deep groundwaters	11 to 420	Ca-Na-Cl Ca-Cl Ca-Na-Cl-SO_4	granite, gabbro

Canadian sedimentary rocks may have somewhat different characteristics compared the WIPP and Gorleben host rocks. Therefore, before applying sorption data from these sites to these sedimentary rocks it is important to characterize the differences in basic sorption properties, such as the types of surface sites, site densities, cation exchange capacities, and specific surface areas. This characterization requires “in house” experiments using sedimentary rocks from Canada. Sorption data for igneous rocks, in contact with brine solutions ranging up to 300 to 400 g/L are required. This would help determine to what extent current databases can be extrapolated to brine solutions.

Although the sorption of I, C (as CO_3), and Cl is likely to be very minimal in brine solutions, an attempt should be made to investigate their transport and retardation because even a very small amount of well-defined sorption may reduce predicted radionuclide doses.

4.2 UNDERSTANDING OF SORPTION IN BRINE SOLUTIONS

Table 2 (Section 2.1.1) is useful when considering how sorption reactions would likely be affected by the presence of Ca-Na-Cl brines. The mass action effect of dissolved Na^+ and Ca^{2+} in the brine is likely to displace any monovalent and divalent cations held by non-specific coulombic sorption in the diffuse layer and coulombic sorption in the Stern layer. The divalent Ca in Canadian Ca-Na-Cl brines will displace monovalent cations to a greater extent than the Na-Cl waters at WIPP or Gorleben. Even though volume limitations in the Stern layer could favour Sr and Ra over Ca, the trace concentrations of Sr and Ra would be overwhelmed by the mass of Ca. The mass action of Cl^- is also likely to reduce the sorption of I^- and any radioisotopes of Cl. Specific chemical sorption that depends upon the elements ability to hydrolyse with dissolved OH and surface oxygen sites is not likely to be significantly affected by competition with Na and Ca. Therefore, depending upon pH, inner-sphere surface complexation sorption reactions are likely to dominate in brine solutions. The sorption of neutral species by physical sorption might not be affected significantly by the high salt concentration. Neutral species could include OH complexes.

Alkali and alkali earth elements that sorb mainly by coulombic attraction are likely to have their sorption reduced to close to zero. Transitional elements that may sorb by both coulombic and specific chemical sorption may have their sorption significantly reduced. Since the lanthanides and actinides sorb mainly through surface complexation, the mass action effect of brine may be negligible to their sorption properties. These concepts are backed up by experimental findings in the literature, as described in Chapter 2. At Gorleben the sorption coefficients for Sr, I, Cs, and Ra were lower in saline water, while the effect of salinity on Tc, Th, U, Pu and Ac was negligible or inconclusive. In the WIPP program changing brine composition did not significantly affect transport properties of actinides in the dolomite. Ra is highly soluble and not retarded in Wolfcamp brine aquifers, Palo Duro Basin, Texas (Laul et al., 1985).

The high Cl^- concentration in brine solutions will produce chloride complexes with many of the transition elements. This will further reduce their sorption. The effect of chloride complex formation can be accounted for and explored by surface complexation models.

The techniques used to study sorption in brine solutions are not fundamentally different from methods used for more dilute waters. The analyses of trace elements in brine solutions may pose an analytical challenge due to salt interferences. This problem has been overcome in many studies by the use of radioisotopes.

Table 7: Predicted Sorption Properties of Sedimentary Rocks and Bentonite

Rock	Minerals	Rock Properties	Predicted Sorption		
			Alkalies	Transition Element	Lanthanides & Actinides
limestone (unpubl. XRD data)	Calcite Quartz Dolomite Clay – minor inclusion	Low CEC (determined by clay) Carbonate dominated SC sites	Low in dilute and brine	Reduced in brine	Similar in brine and dilute. Depends on SC site density from calcite & clay. High sorption for elements with affinity to carbonate.
Shale (Barone et al., 1990)	Illite (40%) Chlorite (10%) Quartz(26%) Feldspar (4%) Calcite (13% Dolomite (5%) Hematite (tr.)	Moderate CEC (12.5 meq/100g) SC sites from clay minerals and Fe	Moderate in dilute, Low in brine	High to moderate in dilute. Reduced in brine	High in brine and dilute. Depends on SC site density from clay
Bentonite (MX-80) (Lajudie et al., 1995)	Montmorillonite (75%) Quartz (15.2%) Feldspar (5 to 8%) Calcite (1.4 %) Organic matter (0.4%)	High CEC = 75 meq/100 g SC sites from edge sites	High in dilute, Low in brine	High to moderate in dilute. Reduced in brine	High in brine and dilute. Depends on SC site density from clay

As an example, Table 7 summarizes the author’s opinion on how salinity could effect the sorption properties of Ordovician sedimentary rocks of southern Ontario. Table 7 gives approximate mineral contents and summarizes expected sorption behaviours of different element classes for sedimentary rocks and bentonite in dilute and saline waters. Except for a different mineral content, the same principles would apply to igneous rocks. The Ordovician limestone composition is dominated by calcite and quartz, along with some dolomite and a possible argillaceous (clay) component. Due to the low clay content, the limestone is expected to have a low cation exchange capacity (CEC), and surface complexation (SC) would likely involve mostly carbonate, along with some silica sites. As a result the sorption of alkali elements would likely be low in both dilute and brine solutions. The sorption of transition elements, lanthanides and actinides would depend on their affinity for carbonate, and on how much clay was present. While the brine solution is not likely to reduce the sorption of lanthanides and actinides, the sorption of transition elements may be reduced in brine by mass action effects and chloride complexation. Mainly the illite, chlorite and hematite would determine the sorption properties of the shale. Due to the higher CEC, one would expect that in comparison to the limestone, the shale would sorb more alkalies from dilute waters, but not from brine solutions. The shale would have a higher concentration of SC sites associated with Al and Si sites, producing a higher sorption of transition elements, lanthanides and actinides, particularly for elements with low affinity of carbonate. Due to the high concentration of montmorillonite in the bentonite, this clay would have a high CEC, producing a high alkali sorption in dilute waters. The bentonite would also have SC sites, which would sorb elements as inner sphere complexes even in brine solutions.

5. EXPERIMENTAL STRATEGY TO MOVE FORWARD

The quantification of mass transport in Canadian sedimentary and crystalline rocks that contain brine solutions requires an understanding of sorption process that occur in Na-Ca-Cl brine solutions. This understanding would determine to what extent existing databases can be used to derive sorption parameters that are applicable to brine solutions and Canadian rocks. To improve the understanding of sorption processes one needs to address the following questions:

- Is the mass action effect of Na, Ca, Cl in brine solutions able to completely eliminate the sorption of alkali and alkali earth elements, or are alkali/alkali earth elements able to become fixed within some mineral site not accessible to Na and Ca?
- Does the effect of ionic strength on the activity coefficients of dissolved ions have a significant influence on sorption?
- To what extent does the formation of chloride complexes affect sorption?
- How is the likely change in dominant sorption mechanism going to affect sorption kinetics and reversibility? Will sorption be less reversible with dominance of specific chemical sorption?

The ultimate purpose of studying sorption is to evaluate its potential effect on mass transport. The only way to really understand sorption processes and how they operate during mass transport is to perform batch experiments along with transport experiments that use the same waters and rock types. This approach would help clarify issues of reversibility, relevant time scales, specific surface areas available to sorption, alteration of surfaces participating in sorption, and whether the relationship between sorption and mass transport is different in brine solutions compared to dilute water. Most international programs have included batch experiments and transport studies. Batch sorption measurements have the advantage of not being complicated by a transport process, being able to study kinetics and reversibility, and can generate a large number of measurements at a reasonable cost. Their drawbacks include questions of surface alteration during the crushing of rock samples, and the relevance of specific surface areas, solid/liquid ratios and reactions times to mass transport. The advantage of mass transport studies is that they demonstrate the effectiveness of sorption by combining it with other transport processes. Sorption coefficients can be extracted from transport experiments and when these values are compared with batch test results insight is gained into sorption processes. Mass transport experiments may include advective transport in columns of crushed rock or rock cores, diffusion tests with rock core, or transport through rock fractures which may include both advective and diffusive transport.

5.1 OBJECTIVES

With an understanding of sorption processes it is possible to move forward toward developing a sorption database. The development of every international sorption database has included “in-house” experiments with rock types and water compositions typical of conditions for a proposed host rock. These experiments have included both batch and dynamic experiments. The "in-house" studies provide a measure of site specific sorption properties for selected elements that build an understanding of sorption process in the host rock. The "in-house" data is supplemented with information from the NEA sorption database and the literature, using reasoned arguments to justify the selection of data. More recently, mechanistic sorption models are being applied to help justify data selection and to improve the process of extrapolating sorption data to in-situ conditions not readily accessible to experimentation.

Bearing in mind the requirements for establishing a sorption database, the objectives of an experimental program to define sorption in Canadian brine solutions should include:

- Perform batch sorption experiments with limestone and shale, using variable brine concentrations to determine site specific sorption coefficients and evaluate the effect of TDS. Elements used in the sorption tests are selected to characterize the sorption mechanisms that affect the radionuclides that are relevant to performance assessment.
- Perform kinetic studies to determine appropriate sorption times and the reversibility of sorption reactions.
- Perform a set of batch experiments to evaluate the effect of the Na(I)/Ca(II) ratio.
- Evaluate the effect of chloride complex formation by performing batch tests with a Cl-free brine composition (Ca-Na-NO_3).
- Perform transport experiments in rock cores to investigate the role of sorption in mass transport in brine solutions of various compositions.
- Characterize the properties of shale and limestone samples that may be required for mechanistic sorption modelling. Optimize datasets for eventual application in sorption modelling.

5.2 EXPERIMENTAL STRATEGY

A two-stage experimental strategy is proposed to achieve the objectives that were identified for improving the understanding of sorption in brine solutions. The first stage, lasting one to two years, would establish experimental protocols and gather scoping information that would help to define stage two. Stage two would expand the sorption experiments to other elements, rock types and brine solutions, focus on refining the understanding of sorption in mass transport, make use of mechanistic sorption modelling, and begin establishing the framework for a sorption database.

5.2.1 Stage 1

Stage 1 is intended to initiate an experimental program to address sorption in brine solutions. The first task is to create and formalize an experimental plan to provide the framework and sufficient details to start Stage 1 experiments. The plan would also provide a vision of what the Stage 2 experimental program would look like.

Research in Stage 1 would focus on Ordovician shale and limestone samples from southern Ontario to develop experimental protocols and to provide scoping sorption data for Canadian sedimentary rocks. Some experiments with bentonite may also be considered since a wealth of sorption data is available for bentonite and bentonite would be a key component of the engineered barrier system. Experiments will be performed with Ca-Na-Cl solutions with TDS (g/L) values of 10, 25, 100, 200 and 300 to assess the impact of TDS on sorption processes. Some tests would be performed with variable Na(I)/Ca(II) ratios to test the effect of changing the divalent cation concentration, and to help establish a link to studies for the WIPP site, which contains Na-Cl brine solutions. These studies will determine the magnitude of R_d reductions for increasing TDS for specific types of elements. The changes in R_d values for specific types of elements will reveal the effect of TDS on different types of sorption mechanisms operating on shale and limestone.

Initial experiments will include studies of sorption kinetics to help define reaction times to be used in experimental protocols. The sorption kinetic studies will be complemented by desorption studies to test sorption reversibility with respect to decreased sorbate concentrations. This information will determine whether measured R_d values represent equilibrium element distributions or just steady-state rock/water distribution ratios. The sorption rates derived from kinetic studies may provide some insight into the nature of sorption mechanisms operating in brine solutions.

Table 5 lists some of the key radionulides that are of interest to performance assessment, along with the elements that can be used to scope the sorption properties of these radionuclides. The elements of interest include I because ^{129}I features prominently in dose calculations for many performance assessments, and the characterization of I sorption is always of interest, even if the R_d value is low. Iodide will test the ability of Cl^- to compete with the sorption of other halides. Cs^+ and possibly Rb^+ will be included to define the ability of monovalent alkali elements to compete in cation exchange reactions with Na^+ and Ca^{2+} in brine solutions. Sr^{2+} and Ba^{2+} (analog to Ra^{2+}) will be included to test their ability to compete with Ca^{2+} in cation exchange reactions. Cu^{2+} and Ni^{2+} will be included as examples of transition elements, which will sorb mainly by surface complexation, with their possibilities for cation exchange having been significantly reduced by Ca^{2+}. These transition metals are also likely to display effects of complexation with chloride. Sm^{3+} or Eu^{3+} may be included as examples of trivalent cations with strong surface complexation that may be independent of TDS. These lanthanides can be considered as analogs to trivalent actinides. U(VI) may be included as a representative actinide.

In addition to measuring R_d values, an effort will be made to characterize representative rock samples for properties that will be needed for surface complexation modelling. These parameters include an estimation of cation exchange capacity, even though it is likely to be mostly occupied by Na^+ and Ca^{2+}. The type and site density of surface complexation sites will be estimated by titration and rationalization with known mineral compositions. This information, along with initial sorption results, will be evaluated through the application of surface complexation models.

The majority of sorption experiments will be in the form of batch experiments, probably with crushed rock samples. Since surface complexation is expected to play a major role in brine solutions, the groundwater pH in sedimentary formations could have a significant effect on sorption. The pH of experimental solutions in contact with rock will be buffered by the rock, and can be controlled to some extent by the use of buffers. The problem with using pH values that are significantly different from the value that is in apparent equilibrium with the rock is that rock dissolution or weathering may occur with long exposure times. The initial approach will be to determine the equilibrium pH values of solutions in contact with shale, limestone and bentonite. Initial sorption studies will focus on using these equilibrium pH values, particularly if they are consistent with pH values determined for groundwater from sedimentary rocks. Depending upon whether or not the experimental “equilibrium” pH values are in a very sensitive region with respect to changes in sorption, the effects of pH will be evaluated either with surface complexation modelling or by experimentally varying the pH. At this stage sorption experiments will be performed under ambient atmospheric conditions of pO_2 and pCO_2 .The intention is to keep the experiments simple by avoiding uncertainties due to variable redox conditions and changes in pCO_2. The experimental volumes, solid/liquid ratios, reaction times and other experimental protocols are to be determined after initial testing and will depend upon the elements being tested and experimental objectives.

Dynamic sorption experiments with convective flow in rock cores will be performed using the High Pressure Radionuclide Migration (HPRM) apparatus (Vandergraaf et al., 1986; Vilks and Miller, 2007). These tests will provide information on core porosity, permeability, and transport properties of sorbing and nonsorbing tracers. Sorption coefficients extracted from these tests will be compared to values determined from batch tests.

The experimental results will be evaluated at the end of Stage 1 to assess the need to expand the experimental scope to include other elements and radioisotopes. This will provide an opportunity to refocus the work scope to address missing gaps and make plans for Stage 2.

5.2.2 Stage 2

Stage 2 will be initiated with well-defined experimental protocols and a sufficient understanding of sorption processes in brine solutions to define meaningful experimental strategies to characterize the role of sorption in mass transport. The experimental work scope could be expanded to include crystalline rocks and brine solutions with TDS values up to 400 g/L. The work scope could be expanded to other elements that would help in the adaptation of existing sorption databases to sedimentary rocks and brine solutions.

The scope of transport experiments could be expanded to include transport tests in fractures, allowing for the possibility of advective transport and matrix diffusion. Longer-term diffusion experiments with sorbing and nonsorbing elements could be performed to improve the understanding of sorption in diffusion processes as a function of pore water composition. The comparison of R_d values measured in batch experiments with those derived from transport experiments through intact core could be complicated by issues of effective surface areas, and fresh versus conditioned surfaces. These issues could be addressed with transport experiments in columns of crushed rock, which contain fresh mineral surfaces and effective surface areas similar to batch experiments.

More extensive kinetic studies could be devised to evaluate forward and reverse reactions to provide further insight toward identifying sorption mechanisms. Longer term tests may evaluate the possibility that some elements could become fixed by penetrating mineral structures or forming more stable configurations on mineral surfaces with prolonged contact.

An attempt will be made to apply mechanistic surface complexation modelling to brine composition to demonstrate a better understanding of sorption processes and to develop the capability to predict sorption for reactions that are difficult to measure experimentally.

6. SUMMARY

Ordovician sedimentary rocks in the Michigan basin of Southern Ontario are known to contain Na-Ca-Cl and Ca-Na-Cl brines with TDS concentrations reaching 300 g/L. Deep groundwaters in the Canadian Shield contain Ca-Na-Cl brines with TDS values exceeding 400 g/L. The existing Canadian sorption database, updated in 1996, is only valid up to a TDS value of about 11 g/L. The sorption data in the international literature reported for brine solutions comes from the WIPP site, New Mexico, and includes data for actinide sorption on dolomite in NaCl brines with TDS values up to 338 g/L. Data for actinide and other radionuclide sorption onto sediments in the presence of dilute waters to NaCl brines (159 g/L) is available for the Gorleben site, Germany. If sedimentary rocks with highly saline waters, such as those in the Michigan basin, or deep crystalline rocks of the Canadian Shield are to be considered as potential host rocks for a nuclear fuel waste repository, it is necessary to develop an understanding of sorption processes in Ca-Na-Cl brine solutions with TDS values ranging up to 300 or 400 g/L.

If one were to adapt current sorption databases to brine solutions one could anticipate the following effects:

- The high concentrations of Na^+ and Ca^{2+} in brine solutions are likely to displace any trace elements that sorb in cation exchange sites by coulombic attraction. This would significantly reduce or eliminate the sorption of alkali and alkali earth cations, such as Cs^+, Sr^{2+} and Ra^{2+}.
- The dominant sorption mechanism in brine solutions is likely to be inner-sphere surface complexation because Na^+ and Ca^{2+} do not have strong hydrolysis constants and will not be able to compete effectively with certain other elements for these sites.
- Actinides and trivalent elements, such as lanthanides, hydrolyse at pH values above 6 and form very strong surface complexes. The sorption of these elements might not be significantly affected by increasing TDS concentrations.
- Transition elements may sorb to some extent in brine solutions because they are likely to participate in surface complexation. However, their sorption is likely to be reduced by the reduction in their coulombic sorption and by the formation of chloride complexes.

As part of the Canadian Government’s Adaptive Phased Management approach for the long-term management of Canada’s used nuclear fuel, both crystalline and sedimentary rock formations are under consideration as potential host formations. Since host sites for either rock type have not yet been chosen it is not possible at this time to address performance assessment requirements that are specific to a particular host rock. The current approach is to improve the capability for addressing future performance assessment requirements by improving the understanding of mass transport in generic Canadian sedimentary and crystalline rocks, which might contain brine solutions. Since the sorption properties of Canadian crystalline rocks under conditions of lower salinity have already been extensively studied, priority is being given to determining the sorption properties of sedimentary rocks in contact with waters with a wide range of TDS.

To address the anticipated performance assessment requirements, a two-stage program of sorption experiments has been proposed to develop an understanding of sorption processes in brine solutions, starting with sedimentary rocks and eventually including crystalline rocks. Following the approach used by international programs to establish sorption databases, the program proposes the initiation of “in-house” experiments using sedimentary rocks from the Michigan Basin, and a range of brine compositions representative of groundwaters in the Michigan basin. The experimental program would include batch experiments to address sorption specific issues (kinetics, effect of TDS, and Cl complexation), and dynamic transport experiments designed to relate sorption processes to mass transport. The first stage would develop experimental protocols and collect scoping data to lay the foundations for understanding sorption in brine solutions. Stage 2 would build on the understanding gained in the first stage and possibly expand the work scope to crystalline rock and a more complete set of elements. More emphasis would be placed on experiments that address kinetics, reversibility, and mass transport. The use of mechanistic surface complexation models would be evaluated to improve the understanding of sorption processes and to develop the ability to make predictions for radionuclides under in-situ conditions, which are difficult to reproduce experimentally.

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