RADIONUCLIDE SORPTION AND TRANSPORT IN BRINE SOLUTIONS

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ABSTRACT

The Canadian Nuclear Waste Management Organization (NWMO) is responsible for implementing Adaptive Phased Management (APM), Canada's plan for the long-term management of used nuclear fuel produced by Canada's nuclear reactors. The goal of APM is a long-term containment and isolation of used nuclear fuel in a Deep Geologic Repository (DGR) constructed in a suitable crystalline or sedimentary rock formation. Sedimentary rocks in Canada are known to contain Na-Ca-Cl brine solutions with total dissolved solids (TDS) in the range of 200 to300 g/L. The sorption properties of shales and limestone and for clay-based materials used in engineered barriers are required in evaluations of the safety of a deep geological repository in a Canadian sedimentary setting. The process of defining the role of sorption in the transport of radionuclides in these rocks includes: (1) batch sorption experiments in brine solutions to develop an understanding of processes and mechanisms; (2) the establishment of a defensible database of sorption values; and (3) demonstration that sorption values can be applied to explain mass transport processes.

The sorption of Sr, Ni, Cu, Eu and U was measured on bentonite, shale and limestone in Na-Ca-Cl brine solutions with TDS values as high as 300 g/L. Initial results have confirmed that group 1 and 2 elements, which sorb by non-specific coulombic attraction, are not likely to sorb in brine solutions. Transition metals, such as Ni and Cu, and the trivalent Eu and hexavalent U sorb by surface complexation mechanisms to bentonite, shale and limestone. The high concentrations of Ca in the brine were found to compete with Ni for sorption sites and the formation of complexes with carbonate reduced the sorption of Eu and U.

The development of a sorption database for sedimentary rocks (shale and limestone) and bentonite, in a setting that would include Na-Ca-Cl brine solutions at near neutral pH, was initiated. The elements of interest for performance assessment included C, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Sn, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. The process included a search of the international literature for data relevant for bentonite, shale, limestone, illite, chlorite and calcite in high salinity water, and a consideration of results from new batch experiments. The sorption values determined as part of this process are intended as a starting point for the development of a Canadian sorption database for sedimentary rocks. Future work will include batch and mass transport experiments, combined with modelling to fill data gaps and improve understanding of sorption processes during mass transport, and continued development of a sorption database for sedimentary rocks.

1. INTRODUCTION

Sorption of radionuclides onto mineral surfaces within the geosphere, and on the materials making up the engineered barriers of a deep geological repository (DGR) can be an important mechanism for slowing the transport of radionuclides to the surface environment. The treatment of sorption and the derivation of a sorption database for the post closure assessment for a deep geological repository concept in crystalline rock of the Canadian Shield has been described [1, 2, 3, 4]. The sorption database for Canadian crystalline rock [2] was based on literature values and experiments performed in groundwaters whose compositions ranged from a freshwater, with a TDS of 0.1 g/L, to a saline Ca-Na-Cl-SO4 solution with a TDS of 11.3 g/L. The sorption database includes values for sorption onto igneous rocks (grey granite, red granite, gabbro) and a variety of rock forming minerals. The current sorption data are relevant mainly to crystalline rocks and groundwater compositions representative of depths of up to ~ 500 to 1000 m in the Canadian Shield. Deeper groundwaters in the Canadian Shield may include Na-Ca-Cl brines with TDS values between 100 and 320 g/L [e.g. 5].

With the Canadian Government's selection of the Adaptive Phased Management approach for the long-term management of Canada's used nuclear fuel in 2007, the Nuclear Waste Management Organization (NWMO) is considering both crystalline and sedimentary rock as potential host formations [7]. Sedimentary rocks in Canada, for example in the Michigan Basin, have been observed to contain Na-Ca-Cl and Ca-Na-Cl brine solutions with total dissolved solids (TDS) concentrations exceeding 300 g/L. Since the Canadian sorption database was developed primarily for crystalline rocks, there is a need to establish an understanding of sorption process for sedimentary rocks, particularly in the presence of brine solutions [8].

The list of elements of interest for Canada's nuclear waste management program for performance assessment of a DGR in sedimentary rock include C, Cu, As, Se, Zr, Nb, Mo, Tc, Pa, Sn, Pb, Bi, Ra, Th, Pr, U, Np, Pu and Am [9]. The process of defining the role of sorption in the transport of these and other elements must include the following three phases:

1. The development of an understanding of processes and mechanisms that would control sorption on sedimentary rocks and backfill materials (bentonite) in the presence of brine solutions. This would be based to a large extent on results from new laboratory sorption experiments;
2. The establishment of a defensible database of sorption values for sedimentary rock containing brine solutions; and
3. Demonstration that sorption values can be applied to explain and predict mass transport processes.

This paper aims to describe progress toward understanding the role of sorption in radionuclide retardation and mass transport within sedimentary rocks.

2. UNDERSTANDING SORPTION IN BRINE SOLUTIONS

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. An understanding of the sorption mechanisms is required to provide a defensible set of sorption parameters for performance assessment.

2.1 Sorption mechanisms and processes

2.1.1 Non-specific coulombic sorption

Mineral surfaces may acquire a charge either from a permanent charge imbalance in the structure or from potential-determining reactions at surface sites. In the former case surface charge is independent of pH, while in the latter the surface charge will vary with pH, becoming negative above a certain pH value that is specific to the composition of the solid. The electrostatic pull of a negatively charged surface is countered by the accumulation of cations in two types of layers close to the surface. In the outer diffuse layer, which is known as the electric double layer, ions are able to move freely as in the free solution, so that there is minimal entropy decrease with sorption. The inner Stern layer [10] consists of a surface monolayer in which the total amount of adsorbed ions is restricted by their size and available surface area. In the Stern layer, sorption of ions with smaller hydrated radii is preferred because ions must compete for space and because they can approach the surface more closely Coulomb's law predicts that they will be sorbed more strongly.

Coulombic sorption is reversible with rapid sorption and desorption kinetics. It is an important sorption mechanism for group 1 and 2 cations, which do not form as strong bonds with oxygen as the transition metals. Higher valence cations are preferred, but cations of the same valence have only a slight relative selectivity determined by their hydrated radii. In practice, it will probably not be feasible to distinguish non-specific sorption in the diffuse layer from that in the Stern layer. Trace ions sorbed by non-specific coulombic attractions should be displaced by the high ion concentrations of a salt solution and therefore radionuclides that are attached to surfaces only by non-specific coulombic attraction are not likely to sorb in brine solutions.

2.1.2 Specific chemical sorption

Due to the ability of metals to be sorbed on sediments or soils in seawater, specific chemical sorption was operationally defined 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" [11]. Specific chemical sorption is also used to explain the sharp increase in sorption with pH produced in the mid pH ranges. This phenomenon, known as the sorption edge, was described for transition metal sorption on oxides of Si, Al, Fe, and Mn [12, 13, 14, 15, 16, 17]. The cations with the strongest hydrolysis constants have their sorption edge at lower pH values, suggesting the formation of metal oxygen bonds. The most common concept used to explain specific chemical sorption is surface complexation, which involves metal coordination with surface oxygens where broken bonds exist at oxide surfaces or the edges of clay minerals. Surface complexation has been widely proposed to explain metal sorption on oxides [e.g. 13, 16, 17, 18]. The exposed surface 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.

Other mechanisms: Sorption by chemical substitution may occur when a dissolved constituent is removed from solution and incorporated into a solid by replacing a chemically similar constituent that makes up the main component of the solid phase. Structural penetration may occur if an element is able to enter the interlayer of clays or cleavages and structural defects of other minerals. Structural penetration is slow and possibly irreversible. Isotopic exchange involves the exchange of a radioisotope with a stable isotope of the same element in a solid or solution. This mechanism has been proposed for the sorption of ^{14}C in calcite.

2.2 Quantifying Sorption

Sorption data are most commonly reported in the form of a sorption coefficient. If a contaminant's concentration is low enough its sorption may be linear with concentration and a sorption coefficient can be used to describe its distribution between solid and liquid. Sorption coefficients (K_d) are defined as a ratio between the amount sorbed per mass of solid (S) and the amount remaining in solution (C).

$$K_d = \frac{S}{C} \qquad (\mathrm{m^3/kg}) \tag{1}$$

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. Despite an on-going scientific debate on the validity of K_d values, the fact remains that for most practical applications, sorption is measured in batch experiments and reported as K_d values. The understanding of a particular sorption process, as derived from measurements and modelling studies, is usually approximated by a K_d value, which is then used in mass transport calculations.

2.3 Batch Sorption Studies with Sedimentary Rocks and Brine Solutions

An experimental program was initiated to develop an understanding of sorption processes in Na-Ca-Cl brine solutions with Canadian sedimentary rocks [19]. The sorption of Sr^{+2}, Cu^{+2}, Ni^{+2}, Eu^{+3}, and UO_2^{+2} was characterized on bentonite, shale and limestone in Na-Ca-Cl brine solutions with total dissolved solids (TDS) values as high as 300 g/L using batch sorption experiments. In these experiments, strontium is used as a chemical analog to radium and other group 1 and 2 elements. Similarly, nickel is considered as a chemical analog for divalent transition elements and lead, while europium is considered as chemical analog for trivalent actinides. Copper was included because it will be an element of interest if the proposed container for holding the used fuel bundles is copper.

The solids used in the sorption studies were a Na rich bentonite (MX-80), Queenston shale and Cobourg limestone. The shale, limestone and bentonite were crushed and dry sieved to collect a size fraction between 100 and 200 μm. The solutions used in the sorption tests included Na-Ca-Cl brines with TDS values of 10, 25, 100, 200 and 300 g/L, and a Na-Cl brine with a TDS of 100 g/L. Sorption tests were performed with experimental volumes of 10 to 200 mL, and solid/liquid ratios of 0.5 to 10 g/100 mL. Sorption experiments were performed in contact with the atmosphere, and the experimental time frame varied from 3 h to 28 d. Although redox conditions in groundwaters within sedimentary rocks are likely to be reducing, no attempt was made to perform experiments under reducing conditions due to difficulties in maintaining such conditions in the laboratory. At the end of the reaction period, the solids were separated from solution by centrifuging for 15 minutes at 20,000 rpm. Blank solutions, without sorbing solids, were used to account for any sorption losses on container walls. Radioisotope tracers were not used in sorption experiments and analyses were performed using either inductively-coupled plasma (ICP), a colorimetric method or a fluorescence technique [19].

Brine solutions in contact with solids for 1 to 3 days tended to reach equilibrium pH values that were determined by the solution composition and equilibration with carbonate, which was present in all solids. Attempts to manipulate pH values by manipulating solid/liquid ratios, conditioning solids at lower pH and increasing total dissolved carbonate concentration to reduce calcite dissolution were not successful. The use of pH buffers is a possibility, but their use was avoided in this study due to potential effects on sorption reactions. The best way to evaluate the effects of pH on sorption may be through short-term experiments, lasting one to several hours, which are complete before the solution pH has had a chance to be buffered by the rock.

The initial sorption experiments found that Sr^{+2} sorption was not detected on bentonite or sedimentary rocks in the Na-Ca-Cl brine solution. These results confirm that Sr^{2+} sorbs mainly by non-specific cation exchange, and is not able to compete with the high concentration of Ca^{+2} in the brine. Consequently, group 1 and 2 elements will not be sorbed to any significant extent by sedimentary rocks associated with concentrated brine solutions and it should be assumed that elements, such as Ra^{+2}, have a sorption coefficient of 0 in brine solutions.

The sorption of Cu^{+2}, Ni^{+2}, Eu^{+3}, and UO_2^{+2} was affected by brine composition. It should be noted that in this study, the pH and salt concentration were not independent variables because the solids buffered the pH to values that depended upon the salt concentration. Although the sorption of the transition metals, Cu^{+2} and Ni^{+2}, on bentonite, shale and limestone appeared to increase with pH, in the present data set this effect could not be separated from differences in salt concentration. The presence of Ca^{+2} was shown to reduce Ni^{+2} sorption by a factor 2 to 7 and would likely have a similar effect on Cu^{+2} sorption. The sorption of UO_2^{+2} and Eu^{+3} appeared to be independent of pH in the range 6 to 7.5, suggesting that the sorption edge for UO_2^{+2} and Eu^{+3} occurs at a lower pH. The sorption of Eu^{+3} and UO_2^{+2} was not affected by salt concentration, confirming that sorption is by surface complexation. Results confirmed that U sorption is reduced by increasing carbonate concentrations.

An experimental duration of 7 days was arbitrarily chosen as a reference time for determining sorption coefficients. Sorption studies were performed over a 28 day period to determine to what extent the 7 day sorption values represent an equilibrium or steady-state. Nickel sorption continued to increase with time over a 28 day period in all brine compositions. In most cases U sorption appeared to reach equilibrium within 7 to 14 days. Europium sorption on bentonite and shale also appeared to reach equilibrium within 7 to 14 days in most cases. However, in several cases sorption on limestone seemed to keep increasing over longer periods, possibly exceeding 28 days. The reversibility of sorption reactions was tested by diluting the sorbate concentration and measuring the response in K_d values to see whether they would decrease to levels observed before the desorption test. Results indicated that U sorption was reversible, but that of Ni and Eu was not over the duration of the two week desorption tests.

The sorption properties of all the elements included in this study are summarized in Table 1. The reference sorption time was 7 days and therefore, K_d values could be higher if longer sorption times are considered. These average values in Table 1 cover a pH range from 6.0 to 7.5, and ionic strengths of 0.2 to 7.5 (mol/kg).

Table 1. Comparison of element sorption properties.

	Average K_d (m^3/kg)				
Rock Type	**Sr(II)**	**Ni(II)**	**Cu(II)**	**Eu(III)**	**U(VI)**
bentonite	0	0.047 ± 0.026	0.062 ± 0.11	2.2 ± 3.1	0.24 ± 0.23
shale	0	0.023 ± 0.020	0.11 ± 0.21	0.17 ± 0.050	0.020 ± 0.022
limestone	0	0.004 ± 0.004	0.041 ± 0.053	0.18 ± 0.10	0.008 ± 0.007

2.4 Moving forward with sorption studies

Sorption studies are continuing with batch experiments to characterize the sorption properties of Cu, Pb, U, Zr and Se on shale, limestone and bentonite in a reference brine solution. In addition to providing recommended sorption values, these tests are intended to improve process understanding for certain aspects of the sorption process that include pH effects, sorption and desorption kinetics and the effects of microbiology. Sorption modelling will be performed with PHREEQC [20], using the NWMO thermodynamic database [19]. The modelling is intended to relate observed sorption to measured capacity factors such as specific surface area and total estimated surface sites. One and two site surface complexation models will be tested. Sorption measurements will be related to groundwater variables, such as chloride, carbonate, monovalent and divalent cation concentrations, and pH for the purpose of understanding sorption processes and developing the capability to extrapolate sorption to other groundwater compositions that include the effects of Eh and any organic complexes that could be introduced from a potential repository.

3. DATABASE DEVELOPMENT

3.1 Approaches used to develop sorption databases

The data that are used to construct a sorption database for Canada’s nuclear waste management program are commonly derived from a number of different approaches: 1) 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 mass transport experiments with advection and diffusion; 2) Experimental measurements are supplemented with data from the open literature and from international databases, such as the NEA sorption database [21] and the online Japanese sorption database (http://migrationdb.jaea.jp) [22]. Considerations for selecting data from the literature include water chemistry (pH, Eh, major ions, ionic strengths), temperature, radionuclide concentrations, experimental method (batch or dynamic, lab or field), and chemical form. If data gaps exist for certain elements and geologic materials, other lines of reasoning may be used. If sorption data for an element on a particular mineral or rock is not available, data from a similar rock or mineral has been used as an 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 is made that it does not sorb.

3.2 Availability of data for selected elements that is relevant to sedimentary rocks and brine solutions

The international literature and sorption databases were searched to find sorption data that would be relevant to Canadian sedimentary rocks (shale and limestone) and bentonite, in a setting that would include Na-Ca-Cl brine solutions at near neutral pH [9]. The selection process to identify data that could be used in brine solutions involved a comparison of sorption values as a function of ionic strength. This process was used to determine whether an element will sorb in a brine solution, and whether the data from a low ionic strength can be extrapolated to brine conditions. Where possible, data were selected from tests performed in the pH range of 6 to 7. If not, then a judgement was made as to whether a given sorption value is applicable, based on a known trend with respect to pH. For redox sensitive elements, sorption values were obtained for both oxidizing and reducing conditions. Although deep groundwater is generally reducing, it is useful to have data for both oxidising and reducing conditions to illustrate the importance of the redox effect. If sorption values for bentonite, shale and limestone were available for reasonable solution compositions, they were reported as recommended values. Sorption data for bentonite were based on values reported for bentonite, montmorillonite or smectite. If no data was available for shale, data from some other clay rich rock, such as mudstone, was used as an approximation. Alternatively, data for illite or chlorite were used to estimate sorption assuming that shale has a clay content of 70%. Sorption values for marl were used to estimate sorption for limestone. Otherwise, sorption on limestone was approximated by sorption values reported for calcite.

The literature review of sorption values was supplemented with the results of batch sorption measurements previously discussed. Sorption data relevant to brine solution were found for some, but not all elements. Where possible, chemical analog elements were used to fill data gaps. The chemical analog elements included Nb(V), Np(V), and Th(IV), for which published sorption coefficients were used. In addition, the batch sorption data [19] for Sr(II), Ni(II), Eu(III) and U(VI) were used as chemical analogs. Recommended K_d values for sedimentary rocks in brine solutions are summarized in Table 2. These values are intended as a starting point for the development of a Canadian sorption database for sedimentary rocks.

4. MASS TRANSPORT

Mass transport experiments involving sorbing radionuclides have been used extensively to demonstrate the role of sorption in mass transport, to improve our understanding of how sorption works during mass transport and to derive sorption coefficients. Mass transport experiments include diffusion experiments, advection experiments and diffusion combined with advection experiments. Mass transport calculations often involve the combination of a measured physical transport process with measured sorption data to produce an estimate of mass transport. The derivation of sorption parameters from mass transport studies depends 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.

In diffusion experiments, the apparent diffusion coefficient (D_a) is often used to describe diffusive fluxes of sorbing elements and has been defined as [23]:

Table 2. Recommended sorption values for sedimentary rock.

	Range in K_d Values		
Element	**Shale (m^3/kg)**	**Limestone (m^3/kg)**	**Bentonite (m^3/kg)**
C inorganic	0	0.0017 to 0.090	0.00002 to 0.0001
C organic	0	0	0
Ni(II)	0.006 to 0.047	0.0004 to 0.008	0.022 to 0.082
Cu(II)	0.0001 to 0.49	0.0002 to 0.12	0.007 to 0.26
As(V)	0.29 to 0.47	0.079 to 0.57	0.27 to 0.28
As(III)	0.031 to 0.091	No data	0.30
Se(IV)	0.019	0.0013	0.014 to 0.016
Se(-II)	0.027 to 0.039	0.0037	0.015 to 0.17
Zr(IV)	0.05 to 0.5	No data	0.05 to 1.6
Nb(V)	1.4 to 2.8	No data	1.2 to 1.8
Mo(VI)	0.02 to 0.27	0.002 to 0.017	0.01 to 0.40
Tc(VII)	0.00007 to 0.08	0.003 to 0.075	0.00026
Tc(IV)	0.0007	0.017	4.2 to 10
Pd(II)	0.006 to 0.047	0.0004 to 0.008	0.022 to 0.082
Sn(IV)	0.05 to 0.5	0.7 to 10	660 to 2700
Pb(II)	0.006 to 0.047	0.0004 to 0.008	0.022 to 0.082
Bi(III)	0.11 to 0.22	0.093 to 0.29	25 to 50
Ra(II)	0.0070 to 0.032	0	0
Th(IV)	No data	0.7 to 10	0.25 to 6.3
Pa(V)	0.0088 to 0.32	0.001 to 0.20	0.017 to 0.40
U(VI)	0.002 to 0.051	0.002 to 0.017	0.014 to 0.57
U(IV)	0.095	0.035	150 to 180
Np(V)	0.0088 to 0.32	0.001 to 0.20	0.017 to 0.40
Np(IV,V)	0.15 to 2.3	0.70 to 10	0.84 to 23
Pu(IV, V)	1.6 to 3.8	0.020 to 0.50	1.7 to 30
Pu(III)	0.11 to 0.22	0.093 to 0.29	0.088 to 28
Am (III)	0.23 to 42	0.02 to 0.50	0.23 to 46

$$D_a = \frac{D_w \delta \varepsilon_t}{\tau^2} \frac{1}{(\varepsilon_c + \rho_b K_d)} \qquad (2)$$

D_w is the free-water diffusion coefficient. The physical aspects of diffusion, related to pore geometry are accounted by the geometric tortuosity (τ), the constrictivity (δ) and the through-transport porosity (ε_t). Retardation of the diffusing element is determined by the storage capacity of the rock, which is the sum of the total connected porosity (ε_c) and the amount sorbed on rock surfaces as estimated by the product of the sorption coefficient (K_d) and the bulk density (ρ_b). The total connected porosity includes both the transport porosity and the dead end porosity. In the case of a nonsorbing tracer, such as iodide, the rock capacity is equal to the total connected porosity (ε_c). By comparing the total connected porosity estimated by a conservative tracer with rock capacity term determined by a sorbing tracer, one can estimate a K_d value for the sorbing tracer.

In mass transport experiments that include advection, the velocity (v_c) of the sorbing tracer can be compared with the velocity of water (v), as determined with a non-sorbing tracer [24]. The retardation equation (3) provides a general expression that relates sorption to the retardation factor (R) that reduces the velocity of a contaminant, with a sorption coefficient of K_d, that is being transported through a media with a porosity (ε_t) and a bulk density (ρ_b):

$$R = \frac{v}{v_c} = 1 + \frac{\rho_b}{\varepsilon} K_d \qquad (3)$$

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 a continuous injection can be performed 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.

The retardation factor in equation 3 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 3 gives unrealistically high retardation factors because in rocks with low porosity the rock mass available to sorption is significantly reduced compared to that which is available in batch sorption experiments [2]. Assuming that the effects of reduced mass available to sorption counterbalance the increased retardation caused by the reduction in porosity, the following equation was proposed for retardation in rocks with low porosity [2]

$$R = \frac{v}{v_c} = 1 + \rho_b K_d \qquad (4)$$

Another option for accounting for the reduced availability of the rock mass for sorption during transport in fractures or the rock matrix is to reduce the K_d values by a factor, f, which is related to a number of parameters, such as the flow wetted surface available for diffusion, the penetration distance in the rock matrix and transport time [4]. Although it may be possible to estimate the factor f from some basic assumptions [4], in practice it may be better to determine it from transport experiments.

In addition to addressing the issue of determining the fraction of the rock mass available for sorption, the use of sorption coefficient in transport studies assumes that sorption is rapid in the time frame of the transport process, whether experimental or geologic. Furthermore, it is assumed that the sorption process is reversible. For these reasons it is important to compare diffusion parameters derived from batch tests with those estimated from transport experiments.

When comparing K_d values derived from transport experiments with those determined from batch tests one should consider experimental differences in terms of available surface area and water chemistry, as well as the modelling assumptions used to derive K_d values from transport experiments. In many cases, K_d values estimated from transport experiments are lower than determined from batch tests. For example, the K_d values for Ba and Sr determined from column experiments with crushed granite were smaller than those from batch tests [25]. The K_d values derived from Na, Ca and Sr transport experiments in mica gneiss and tonalite were one order of magnitude lower than from batch experiments [26]. The sorption coefficients obtained from Se diffusion experiments on Japanese tuff samples were about an order of magnitude lower than obtained from batch tests, despite attempts to take into account differences in specific surface areas between the two methods [27]. In some cases the results from batch and transport tests are comparable. For example, the sorption behaviour of Na and Sr in Opalinus clay, controlled by cation exchange, was similar in both diffusion and batch tests [28]. In most cases the sorption values of Cs, Ni, Sm, Am, Zr and Np on Kunigel V1 bentonite were higher when measured using batch tests compared with those derived from diffusion experiments [29]. However, the authors point out that the sorption coefficients derived from diffusion studies are usually model dependent. When this is taken into consideration, sorption coefficients derived from diffusion experiments and those calculated from sorption measurements are relatively consistent.

As part of the ongoing program to develop the tools to incorporate sorption processes in predicting transport in sedimentary rocks, dynamic mass transport tests will be undertaken to apply and test current understanding of sorption process in mass transport. These tests will include diffusion studies and advective transport tests in either columns of crushed rock, rock fractures or unfractured rock matrix.

5. CONCLUSIONS

Batch sorption studies were used to evaluate the sorption of Sr, Ni, Cu, Eu and U on bentonite, shale and limestone in Na-Ca-Cl brine solutions with total dissolved solids (TDS) values as high as 300 g/L. Initial results have confirmed that group 1 and 2 elements sorb mainly through coulombic attraction and are not likely to sorb to bentonite, limestone or shale in brine solutions. Transition metals, such as Ni and Cu, and the trivalent Eu and hexavalent U sorb by surface complexation mechanisms to bentonite, shale and limestone. The high concentrations of Ca in the brine reduce the sorption of Ni and probably Cu. As expected, the sorption of Eu and U is reduced with increasing amounts of carbonate in solution. The experimental time required to reach equilibrium depended upon the element, and varied from about 1 week to longer than 4 weeks. The development of a sorption database for Canadian sedimentary rocks and bentonite, in contact with brine solutions at near neutral pH was initiated. The process included a search of the international literature for relevant data and a consideration of results from new batch sorption experiments.

Future work was identified to include batch and mass transport experiments, combined with modelling to fill data gaps, better the understanding of sorption processes during mass transport, and continue the development of a sorption database for Canadian sedimentary rocks.

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