SORPTION DATABASE FOR SELECTED RADIONUCLIDES ON SEDIMENTARY ROCKS IN SALINE CONDITIONS

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Abstract

The Nuclear Waste Management Organization's (NWMO) Adaptive Phased Management (APM) Technical Program is intent on advancing the understanding of solute migration in deep-seated sedimentary and crystalline groundwater systems. In these systems, matrix porewaters and groundwaters have been observed to contain Na-Ca-Cl brine solutions with total dissolved solids (TDS) ranging between 200 and 400 g/L. A database of sorption distribution coefficients (K_d) for 28 elements (C, Cl, Ca, Ni, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Ag, Cd, Sn, I, Cs, Eu, Hg, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am) has been developed as relevant to Canadian sedimentary rocks (shale and limestone) and bentonite clay in saline, near neutral pH environments. The database was compiled following extensive reviews of the open literature and international sorption databases, and has been augmented by measuring sorption values for 15 elements including Ni, Cu, Eu, Pb, As, Se, Zr, Cs, Tc, Pd, Sn, U, Th, Np and Pu with Canadian sedimentary rocks (shale and limestone) and bentonite in a range of high salinity solutions that include a synthetic porewater brine (with a TDS of 275 g/L). The sorption measurements for elements Ni(II), Pb(II), Cu(II), Zr(IV), U(VI), Cs(I), Pd(II), Sn(IV) and Th(IV) were performed by both batch sorption tests and long-term diffusion tests. The sorption measurements for redox sensitive elements As, Se, Tc, U, Np and Pu were conducted under reducing conditions.

1. Introduction

An enormous amount of effort has been devoted over the last a few decades to measuring sorption distribution coefficient (K_d) values for a large number of elements on a variety of engineered and natural materials pertinent to radioactive waste disposal under different water chemistry conditions. These data are contained in a variety of reports and databases (see reviews in [1-5]). The United States, Finland, Sweden, Switzerland, Germany, Japan, and NEA have compiled sorption databases used for nuclear waste management programs (see reviews in [5]). A Canadian sorption database for the postclosure assessment of a hypothetical repository in the Canadian Shield with groundwater compositions having up to 11 g/L TDS concentration was reported by Ticknor and Vandergraaf [6].

In Canada, sedimentary rocks are being considered as potential formations to host a deep geologic repository for long-term management of radioactive waste. Within deep-seated low

permeability groundwater systems these sediments have been observed to contain Na-Ca-Cl brine solutions with TDS concentrations ranging between 200 and 400 g/L. A state-of-the-science review was conducted to review available knowledge with respect to understanding and quantifying the sorption properties of rocks in saline waters [4]. In 2009, NWMO initiated the development of a sorption database with a review of the open literature and international sorption databases to find sorption data that would be relevant to Canadian sedimentary rocks (shale and limestone) and bentonite clay, in a setting that would include Na-Ca-Cl brine solutions at near neutral pH [5]. The database is being augmented by measuring sorption values for elements of importance to the safety assessment [7-12]. It is the first comprehensive sorption database for radionuclides focusing on shale, limestone and bentonite under saline conditions. The purpose of this paper is to document the approach for developing the sorption database for Canadian sedimentary rocks and bentonite clay in highly saline waters.

2. Elements and solids included in the sorption database

2.1 Considerations for the selection of elements

The identified list of 28 elements of potential interest to safety assessment calculations include C, Cl, Ca, Ni, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Ag, Cd, Sn, I, Cs, Eu, Hg, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. These elements are of interest either because (1) radionuclides of the elements are potentially important dose contributors in the safety assessment calculations (C, Cl, Ca, Ni, Se, Tc, Pd, Sn, I, Cs, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am); (2) the elements are potentially important chemical toxins (As, Ag, Cd, Mo, Eu and Hg); or (3) the mass of the element in a used fuel container is large (Cu, Zr and Nb) [13-17]. Some of the elements are both potential important dose contributors and chemically hazardous (e.g., Ni, Se, I, Pb and U). Of these elements, Cu, As, Se, Mo, Tc, Sn, I, Pa, U, Np and Pu are redox sensitive.

2.2 Criteria for data selection

Sorption is a complex process, depending on many factors. The following parameters seem to strongly influence the sorption K_d values: (1) the properties of radionuclide; (2) groundwater chemistry conditions (pH, Eh, ionic strength, major ion composition, complexing ligands); (3) the properties of sorbing minerals/rocks (i.e., the properties of the available sorption reacting surfaces); (4) radionuclide concentration; and (5) temperature.

Although batch sorption tests are commonly used to determine K_d values, mass transport experiments, such as diffusion tests can also be used to estimate K_d values. In batch tests, the most sorption sites may be available to the sorbing element because the rock has been crushed, whereas in a diffusion test the availability of sorption tests in the intact rock coupon may be limited. A comparison of K_d values determined from batch and diffusion experiments provided insight on the effects of sorption on diffusive mass transport and provides confidence that K_d values can be used to simulate mass transport [7-9]. Diffusion experiments (e.g., through-diffusion experiments) may be difficult to perform, particularly in the case of certain strongly sorbing radionuclides that require very long time frames to diffuse distances that are long enough to be characterized experimentally. For this reason the availability of sorption

data generated by diffusion tests was limited. Batch tests remain the most practical means of conducting a large number of experiments on a variety of rocks and radionuclides under different water chemistry conditions and radionuclide concentrations. Among the published sorption K_d data, more than 95% was produced by the simple batch sorption method.

It is apparent that sorption K_d data from the general literature must be justified when input data for safety assessment calculations is sought: (1) the data should be obtained on rocks having similar (if not identical) mineralogy; (2) water chemistries (pH, Eh and compositions) should be those pertaining to the rock formation; and (3) expert judgements must be made as to whether the data is justifiable and "conservative'.

This section describes some of the factors that are considered in the selection of sorption values for sedimentary rocks from the literature and international sorption databases. These include: (1) water chemistry used in sorption measurements in comparison to groundwater observed in deep-seated low permeability Canadian sedimentary rocks; (2) rocks and minerals of interest in the sedimentary environment; (3) experimental techniques; and (4) chemical analogs and sorption modelling.

2.2.1 Water chemistry

Formation groundwater chemistry plays a key role in sorption reactions and is given a high priority in selecting sorption data. Sedimentary rocks in Canada, for example in the Michigan Basin [18] and Western Canada Sedimentary Basin [19, 20], have been observed to contain brackish to high saline fluids with a neutral pH (i.e., pH of 6 to 7). The expected geochemical conditions for the repository at depth will be reducing. Table 1 summarizes the reference groundwater compositions which are used as a guide to establishing the range of water chemistries for which sorption data must be relevant. Except for the reference groundwater SR-20 which represents oxidizing conditions, other reference groundwaters represent reducing conditions in deep-seated sedimentary rocks in Canada, having Na-Ca-Cl, Ca-Na-Cl or Na-Cl type chemistry. The Eh value of -200 mV for the reference groundwaters is an assigned value to define the reducing environment at the depth in sedimentary basins for a deep geological repository (DGR). The deep-seated sedimentary rocks are reducing but the in-situ Eh values could be different. For example, the Eh values are -141.9 mV and -165 mV for Guelph formation groundwater samples OGW-9 and OGW-12, and -123 mV and -159 mV for Cambrian formation groundwater samples OGW-10 and OGW-13, collected from the Bruce nuclear site near Kincardine, Ontario on the eastern flank of the Michigan Basin [21].

The ionic strength of solution was used to identify the effect of salt concentration on sorption because it represents both ion concentration and the influence of ion charges. In compiling sorption data from the literature, saline conditions were considered for ionic strengths equal to or greater than 0.7 mol/L (seawater). The presence of anions, such as HCO_3^-, may complex with metals and reduce sorption. Therefore, the most reliable sorption measurements are obtained from solutions that contain the complexing anions found in natural groundwater. Emphasis is placed on brines with similar compositions to the reference groundwaters (Table 1).

Table 1: Reference Sedimentary Groundwater Compositions

Water Name	SR-300	SR-270-PW	SR-270-NaCl	SR-160	SR-20
Nominal pH	6.0	6.0	6.1	6.5	6.5
Redox state	Reducing	Reducing	Reducing	Reducing	Oxidizing
Nominal Eh (mV)	-200	-200	-200	-200	90
Solutes (mg/L)					
Na	43,100	50,100	101,200	37,000	4,300
K	3,600	12,500	-	1,780	130
Ca	57,300	32,000	3,700	14,700	1,500
Mg	9,900	8,200	1,300	3,900	900
HCO_3	40	110	180	50	330
SO_4	160	440	2,470	420	1,100
Cl	199,500	168,500	165,000	97,600	11,300
Br	2,000	1,700	-	570	80
Sr	900	1200	-	510	30
Li	7	5	-	7	-
F	2	2	-	5	-
I	90	3	-	90	-
B	-	80	-	-	-
Si	5	4	-	10	-
Fe	30	30	-	30	0.1
TDS (mg/L)	317,000	275,000	273,000	157,000	20,000
***Ionic Strength (M)**	7.8 (8.7)	6.0 (6.7)	5.4 (5.5)	3.2 (3.4)	0.40 (0.43)
Water type	Ca-Na-Cl	Na-Ca-Cl	Na-Cl	Na-Ca-Cl	Na-Cl

*Ionic strength was estimated using PHREEQC version 3.3.5 with SIT thermodynamic database (THERMOCHIMIE version 9a). The ionic strength in the bracket was estimated with Pitzer thermodynamic database (pitzer.dat) [22].

2.2.2 Solid

Sedimentary rocks in Canada, including shales and limestone, are being considered as potential host rocks for a DGR for radioactive waste. The primary seal material considered in Canada for engineered barriers is Na-rich Wyoming bentonite clay, which may also be mixed with sand (e.g., in backfill materials). Table 2 summarizes the mineralogical compositions of limestone, shale and clay-based engineered barriers (bentonite) considered for the literature review.

Table 2: Mineralogical Compositions of Reference Rock/Clay

	Properties	Mineral compositions (wt%)
Argillaceous Limestone	2% porosity	Calcite 80 Dolomite 7 Illite 5 Chlorite 5 Quartz 2 Other 1
Shale	7% porosity	Clay 60 - Illite 60 - Chlorite 40 Quartz 30 Feldspars 3 Dolomite 2 Other 5
Bentonite clay seal	100% MX-80 clay Dry bulk density 1.6 Mg/m^3	Montmorillonite 82 Quartz 3 Feldspar & mica 8 Cristobalite/tridymite 4 (pyrite, calcite, illite, gypsum) 3
Bentonite/sand seal	70% MX-80 clay with 30% silica sand. Dry bulk density 1.6 Mg/m^3	See previous row for MX-80, diluted by 30 wt% silica sand

In selecting sorption data, the first priority was given to bentonite, shale, and limestone. If sorption values for bentonite, shale, and limestone are available for solutions with reasonably similar compositions to the reference groundwater (Table 1), they were selected as recommended values. Since the sorption of many elements was not measured on shale, limestone and bentonite, the initial selection process also focused on key minerals making up the reference bentonite, shale, and limestone (Table 2). Bentonite is composed mainly of the swelling clay montmorillonite; the principle components of shale are illite, chlorite, and quartz; and limestone is composed mostly of calcite and dolomite [7, 21]. If sorption values for bentonite, shale, and limestone are not available for solutions with reasonably similar compositions to the reference groundwater, sorption data from montmorillonite were considered to approximate sorption on bentonite; sorption values for marl or calcite were used to estimate sorption for limestone. Sorption data for some other clay rich rock such as mudstone were used to estimate sorption for shale, assuming the remaining minerals (quartz, feldspar and carbonate) do not sorb significantly compared to the clay content. Sorption data for illite and/or chlorite were also used as an approximation for shale, assuming that the total illite content of clay is 60% (Table 2). Vilks and Miller [9] found that, in the case of Ni(II), Cu(II), Pb(II) and U(VI), if calculated sorption values for illite were reduced to 60%, they would match measured sorption values for shale. Nagasaki et al. [11] found that the K_d values of Np(V) on shale were larger than 60% of the K_d values on illite, suggesting that Np(V) also

sorbs onto other minerals in shale (e.g., chlorite). Disregarding the sorption onto other minerals in shale (such as chlorite), the assumption that the sorption value of illite is reduced to 60% of its original value to estimate shale sorption value is conservative. If reasonable sorption data for both illite and chlorite are available, a weighted average (60% illite and 40% chlorite) was used to represent sorption on the clay fraction of the shale.

2.2.3 Experimental techniques

Sorption experimental techniques impact the measured K_d values, for example, experimental methods (batch and diffusion), liquid/solid ratios, particle size distribution, element initial concentration, duration of the experiment, and controlled atmosphere under which the experiments were conducted. In selecting sorption data from the literature, when possible the priority was given to K_d values measured by a diffusion method, under controlled atmosphere conditions, and at the optimal liquid/solid ratio (e.g., at which the K_d value reached a plateau in the K_d versus liquid/solid ratio plot).

2.2.4 Chemical analogs and sorption modelling

Chemical analogs are used for elements without measured sorption data because they are difficult to study experimentally due to redox control, low solubility and detection issues, or problems with licensing the use of radioisotopes. Lanthanide elements, such as Sm, Eu and Ho, have been used as chemical analogs for trivalent actinides Ac(III), Pu(III), Am(III) and Cm(III). Th(IV) has been used as an analog for tetravalent actinides U(IV), Np(IV) and Pu(IV), which require strictly controlled reducing conditions during sorption experiments. For example, the USEPA [23] established sorption data for Am(III), Th(IV), Np(V) and U(VI) by batch sorption tests and transport experiments using dolomite cores. The oxidation-state analogy approach was used to extrapolate the established sorption ranges to represent Pu(III) by Am(III); and Pu(IV), U(IV) and Np(IV) by Th(IV) for performance assessment for the Waste Isolation Pilot Plant (WIPP) site.

For the NWMO sorption database, measurements of Sr(II) sorption in brine solution were used as a chemical analog for Ra(II) sorption on bentonite, shale and limestone. Eu(III), whose K_d values were measured in brines [7], was used as a chemical analog for trivalent Bi(III), Pu(III) and Am(III) sorbing on limestone. Thorium (IV), whose K_d values were measured in brines [8], was used as an analog for tetravalent actinides, as in the case of U(IV) and Np(IV) sorbing on limestone [5]. The sorption measurements for Pu(III), U(IV) and Np(IV) under saline, reducing conditions are ongoing and their K_d values will be updated with the measured values. The sorption data for Ra(II), Bi(III) and Am(III) will also be updated with the K_d values measured in brines when available.

Sorption modelling is a useful tool for furthering the understanding of sorption mechanisms and extrapolating sorption results to different conditions. Using montmorillonite and illite to approximate bentonite and shale (with 60% illite), surface complexation modelling was performed for these minerals using a 2-site protolysis non-electrostatic surface complexation

and cation exchange model (2SPNE SC/CE) [24-27]. Sorption modelling was applied to fill data gaps for a few elements whose measured sorption values are not available, for example, Bi(III) on bentonite and shale, and Pa(V) on shale [5, 10]. The sorption data for these elements will be updated when measured K_d values in saline solutions are available.

3. Data Extraction

The sorption data compiled were taken from the open literature and from published sorption databases. Sorption databases that were consulted included: (1) the Canadian sorption database for crystalline rock [6, 28]; (2) the Swedish sorption database for granite [29, 30]; (3) the Swiss sorption database for Opalinus clay and bentonite [31, 32]; (4) the sorption database for the WIPP site in dolomite [23, 33]; (5) the Japanese sorption database for a broad range of rocks and minerals [34-36]; and (6) the existing sorption data for OPG's proposed deep geological repository for low and intermediate level nuclear waste (DGR) in sedimentary rock [37].

The development of a sorption database relies to some extent on a mechanistic understanding. Sorption values of an element as a function of pH may help to determine the sorption mechanisms (ion exchange, surface complexation). The selection of the sorption value will become simpler if the sorption of a given element does not vary with pH in the pH range of interest. In an ideal situation, sorption data can be selected in the pH range of 6 to 7 (note that most of the reported pH values in the literature are electrode measured values). If not, then a judgement must be made as to whether a given sorption value is applicable, based on the known trend of sorption with respect to pH.

Sorption values of an element as a function of ionic strength may help to determine whether the element will sorb in a brine solution. The initial data selection process tries to capture sorption values over a range of ionic strengths, including brine if possible by plotting K_d values for the given element as a function of ionic strength. The recommended sorption data for an element is focused on the values measured in brines. When possible, the recommended sorption data for an element considers the values obtained by both diffusion and batch tests, the initial radionuclide concentration in solution not exceeding its solubility, and experiments conducted in a controlled atmosphere.

Reducing conditions are assumed to exist within both the repository and the host rock soon after closure. Although deep groundwater is generally reducing, it is useful to have sorption data for oxidizing conditions to compare with sorption data for reducing conditions to illustrate the effect of the redox on sorption. Some elements have varied dominant oxidation states depending upon the redox conditions (e.g., Cu, As, Se, Mo, Tc, Sn, I, Pa, U, Np, Pu). For these redox sensitive elements, it is important to report sorption values for both oxidizing and reducing conditions, and to distinguish between those measurements made in an aerobic atmosphere from those made in solutions where redox has been controlled and maintained as reducing.

In the course of the compilation of the sorption data for the 28 elements of interest from the literature, sorption data gaps were identified for some of the elements. The sorption data for

redox sensitive radionuclides in saline solutions under reducing conditions are scarce [4, 5]. As such, NWMO initiated the sorption measurements for 15 elements (Ni, Cu, Eu, Pb, As, Se, Zr, Cs, Tc, Pd, Sn, U, Th, Np and Pu) with the Canadian sedimentary rocks (including shale and limestone) and bentonite in Na-Ca-Cl brines since 2009 [7-9, 11, 12]. Both batch sorption and long-term (1-year) through-diffusion tests were performed to measure sorption K_d values for Ni, Cu, Eu, Pb, Zr, Cs, Pd, Sn, U(VI) and Th [7-9]. Sorption measurements for redox sensitive elements As, Se, Tc, U, Np and Pu were performed under reducing conditions using batch tests [12]. The measured sorption data for these 15 elements were compared to the published literature data. Sorption measurements for the key redox sensitive elements under saline, reducing conditions will be continued to obtain defensible K_d values for safety assessment calculations. The NWMO sorption database for sedimentary rocks will continue to be updated with the measured sorption values.

4. Database Contents

The NWMO sorption database is described in NWMO technical reports which present the sorption data on an element by element basis [5, 10]. It starts with a collection of sorption data for rocks and minerals most closely representing the sedimentary rocks of interest. Emphasis is placed on collecting data for relevant water compositions that include: (1) a range of ionic strengths that would include seawater and brine solutions, and (2) a pH range that would include the near neutral values (6 to 7) of interest. The collected sorption data is plotted to identify useful trends with respect to ionic strength and pH. Sorption values for rocks (i.e., shale, limestone and bentonite) and minerals of interest (e.g., montmorillonite, illite, chlorite, dolomite and calcite) that were measured in solutions that best fit reference groundwater conditions are selected and presented in tables that provide information on water compositions, ionic strength, pH, experimental time, redox conditions, atmosphere, experimental methods (batch, diffusion, in-situ), and literature references.

A table of “recommended sorption coefficients” is presented for each element for shale, limestone and bentonite based on scientific reasoning. The SR-270-PW groundwater composition was a target reference, even though some reference groundwaters have lower salinities with ionic strengths as low as 0.4 mol/L (Table 1). The data selection focuses on the highest salinities on the assumption that sorption generally does not decrease with lower ionic strength and values determined at highest salinities are conservative. Sorption data measured with SR-270-PW brine and Canadian sedimentary rocks and bentonite have the highest priority for recommended sorption coefficients. The sorption of some elements is very sensitive to the ionic strength of the solution, while the sorption of other elements is not affected by the ionic strength. The table of “recommended sorption coefficients” for each element includes the range of ionic strengths used to derive sorption values and the corresponding pH values of the solutions. The tabulated data include a range of sorption coefficients.

In a few cases when experimental data was not available for higher ionic strength solutions, surface complexation modelling was used to estimate sorption in brine solutions, for example, Bi(III) sorption on shale and bentonite, and Pa(V) sorption on shale were estimated by

sorption modelling [10]. In those cases where no experimental or modelling results were available for higher ionic strength solutions and there was no scientific basis for extrapolating measured sorption values to saline conditions, the recommended K_d values were assumed to be 0. For example, K_d value of 0 was recommended for organic C, Ca, Cu(I), As(V), Ag(I), Cd(II) and Ra(II) [10]. The sorption data for these elements will be updated when measured values in saline solutions are available.

5. Summary

A database of sorption K_d values for Canadian sedimentary rocks (shale and limestone) and bentonite clay in highly saline waters has been developed. The goal was to provide sorption data for Canadian sedimentary rocks in a setting that would include Na-Ca-Cl saline solutions at near neutral pH. The NWMO sorption database for sedimentary rocks includes K_d values for 28 elements C, Cl, Ca, Ni, Cu, As, Se, Zr, Nb, Mo, Tc, Pd, Ag, Cd, Sn, I, Cs, Eu, Hg, Pb, Bi, Ra, Th, Pa, U, Np, Pu and Am. The main approaches used for developing the sorption database were (1) an extensive literature review of published sorption data with a focus on higher ionic strengths; (2) an incorporation of sorption measurement values with Canadian sedimentary rocks and bentonite clay in brines for 15 elements including Ni, Cu, Eu, Pb, As, Se, Zr, Cs, Tc, Pd, Sn, U, Th, Np and Pu; (3) the use of chemical analogs for a few elements without measured sorption data (e.g., Sr(II) for Ra(II); Eu(III) for Bi(III), Pu(III) and Am(III) sorbing onto limestone; Th(IV) for U(IV) and Np(IV) sorbing on limestone); and (4) sorption modelling to fill data gaps for shale and bentonite (e.g., Bi(III) sorbing on shale and bentonite; Pa(V) sorbing on shale). The sorption measurements for elements Ni(II), Pb(II), Cu(II), Zr(IV), U(VI), Cs(I), Pd(II), Sn(IV) and Th(IV) were performed using both batch sorption tests and long-term diffusion tests. A comparison of K_d values determined from batch and diffusion experiments provided insight on the effects of sorption on diffusive mass transport and provides confidence that K_d values can be used to simulate mass transport. The sorption measurements for redox sensitive elements As, Se, Tc, U, Np and Pu were conducted under reducing conditions.

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