The Effect of Ionic Strength on the Sorption and Speciation of Palladium

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Summary

Sedimentary rocks are being considered as potential host rocks for a deep geological repository in Canada. Sedimentary rocks in Canada have been observed to contain brackish, and highly saline solutions and as a result it is of particular interest to determine the effects that ionic strength has on sorption and speciation behavior. This report outlines the method in which the sorption and speciation of Pd, an element of interest due to its presence in used nuclear fuel, can be measured. The Pd sorption onto bentonite MX-80 and shale will be measured using solutions of ionic strengths 0.01M, 0.1M and 1.0M.

1. Introduction

Sedimentary rocksare being considered in Canada as potential host rocks for a deep geological repository (DGR). The two sedimentary rock types being considered for use are argillaceous limestone and shale. The engineered barriers, or seal materials, being considered for use in a Canadian DGR are bentonite, or bentonite and sand mixtures. According to Vilks (2009)[1], sedimentary rocks in Canada have been observed to contain brackish to highly saline fluids. As a result there has been an emphasis on determining the effects that saline solutions have on sorption behaviour.

Sorption data has been collected on several elements of interest, however data gaps still exist between sorption data and various experimental conditions, such as high ionic strength conditions. Palladium (Pd) is one of the elements of interest that is missing important sorption data. Palladium was selected as an element of interest because radionuclides of Pd are present in high-level radioactive waste. Specifically Pd-107 which has a half-life of 6.5×10^{6} years [2]. As a result, when completing the safety calculations for a DGR in Canada, it has the potential to be an important dose contributor [3].

Currently Pb(II) is being used as a chemical analogue of Pd(II) [3] because sorption data for Pd is only available for sorption onto bentonite, when considering materials of interest for a DGR in Canada, and only at low ionic strengths (0.01M and 0.1M) [2]. The aim of this paper is to fill the data gaps surrounding Pd by outlining the method in which the effect of ionic strength has on sorption onto bentonite MX-80 and shale.

2. Experimental Procedure

2.1 Sorption Experiment

2.1.1 Materials

Bentonite used in the experiments is bentonite MX-80, a sodium rich bentonite clay found in Wyoming that is passed through an 80 mesh sieve[3].The bentonite MX-80 was acquired from the American Colloid Company. The shale sample was provided by the Nuclear Waste Management Organization (NWMO) and is a sample of Queenstone shale. Certified ACS calcium chloride dehydrate and sodium chloride were acquired from Ficher Scientific and used to control the ionic strengths of the solutions. The palladium used was 99.999% $PdCl_2$ which was also acquired from Fisher Scientific. The distilled water used during the experiment was produced using a Millipore water system. Nitric Acid and Sodium Hydroxide used for pH adjustment will be purchased from Fisher Scientific.

2.1.2 Kinetics Experiment

A sorption kinetics experiment is being conducted in order to determine the amount of time it takes for Pd sorption to reach equilibrium. The kinetics experiment is being carried out under aerobic conditions at 25˚C. The two different solid samples, bentonite MX-80 and shale, were contacted with distilled water in polyethylene vials. A liquid to solid ratio of $1.0m^3/kg$ was used for both the MX-80 and shale.After a high concentration Pd solution was added to the solutions such that the final concentration of Pd in the samples was 1×10^{-7} M. The high concentration Pd solution was prepared using 99.999% $PdCl_2$ and distilled water and had a concentration of 1×10^{-5} M. The pH and Eh of the solutions were measured before and after adding the Pd to the solutions. The samples were stored in an incubator at 20 rpm and 25˚C up until it was time to take measurements. The pH, Eh and concentration of Pd are being measured after 1 day, 2 days, 3 days, 1 week and 2 weeks. In order to take these measurements the vessels were first placed in a centrifuge for 15 minutes at 3500 rpm. The measurements of pH and Eh were taken first and afterwards 5ml of solution was removed with a pipette. The concentration of Pd will be determined by using inductively coupled mass spectroscopy (Agilent ICP-MS 8800) on the 5ml of liquid phase removed from the samples.

2.1.3 Sorption Methodology

The sorption experiments will be carried out under aerobic conditions at room temperature. The full set of experimental conditions are shown inTable 1. First the Na-Ca-Cl solutions will be prepared of ionic strengths 0.01M 0.1Mand 1.0M using the aforementioned $CaCl_2$ and NaCl compounds acquired from Ficher Scientific. A 1.0Msolution will be made first using a ratio of 50:32 for $NaCl:CaCl_2$ (as outline by NWMO SR-270-PW) [3]. This will then be diluted down to 0.1Mand 0.01M. The two solid samples, bentonite MX-80 and shale, will then be contacted with the Na-Ca-Cl solutions in polyethylene vials. Two liquid to solid ratios will be used; $0.1m^3/kg$ and $1.0m^3/kg$, for both the MX-80 and shale. The samples will then be left for a period of time, as determined by the kinetics experiment, in order for the solid to become saturated and reach equilibrium. During the prequilibration period the pH and Eh will be monitored periodically, and the samples will be placed in an incubator at 20rpm and 25˚C. After the prequilbration period the solution is decanted and the solid remains. A new Na-Ca-Cl solution is added, after which a Pd solution with concentration of 1 × 10 $^{-5}$ M will be added to the samples such that the final concentration of Pd in the samples is 1 × 10 $^{-7}$ M. The 1 × 10 $^{-5}$ M Pd solution will be prepared using 99.999% $PdCl_2$ and distilled water. The pH and Eh of the solutions will be measured before and after adding the Pd to the solutions.The samples will then be left for a period of time, as determined by the kinetics experiment, during which the pH and Eh will be monitored periodically, and the samples will be placed in an incubator at 20rpm and 25˚C. The samples will then be placed in a centrifuge to separate the solid from the liquid. The centrifuge will operate for 15 minutes at 3500 rpm. The concentration of Pd in the liquid will then be measured using ICP-MS.

Table 1: Experimental Parameters used for Sorption Experiment

Parameter	***Values***
Ionic Strength	0.01M, 0.10M, 1.00M
Ionic Strength Adjusted With	NaCl, $CaCl_2$
Liquid-Solid Ratio	0.1 m^3/kg 1.0 m^3/kg
Solid	Bentonite MX-80, Shale
Atmosphere	Aerobic
Temperature	Room temperature

2.1.4 Blank Testing

A blank test will be carried out simultaneously with the above sorption experiment, under the same aerobic conditions at room temperature. Pd will be spiked into the Na-Ca-Cl solution such that the resulting concentration will be 1×10^{-7} M. Since no solid is present, pH will be adjusted using HNO_3 and NaOH such that the pH of the blank solution is comparable to the equilibrium pH of the solid solutions. After a period of time (to be determined by kinetics experiment), during which the samples will be placed in an incubator at 20 rpm and 25˚C and the pH and Ehwill be monitored periodically, 5ml of liquid will be removed using a pipette and the concentration of Pd in the liquid will be measured using ICP-MS. The remainder of the solution will then be decanted and then they will be rinsed gently with the Na-Ca-Cl solution. The Na-Ca-Cl solutions pH should be adjusted to be within in the range of the equilibrium pH of the solid samples using $HNO_3$and NaOH. Then the test tube will be washed using HNO_3 with pH of 0. The adsorbed Pd will then desorb and dissolve into the HNO_3. Using ICP-MS the concentration of Pd in the HNO_3 will be measured. This will check the adsorption of Pd onto the vessel wall.

2.2 Solubility

The concentration of Pd in the samples is confirmed to be lower than the solubility limit of Pd by PHREEQC calculation, using version 3.1.4-8929 [4].This version of PHREEQC was also used to study the speciation of Pd, specifically, the effect that ionic strength has on the speciation of Pd.

3. Discussion

3.1 Calculation of K_d Values

Traditionally the distribution coefficient, or the $K_d$value, is calculated using equation (1).

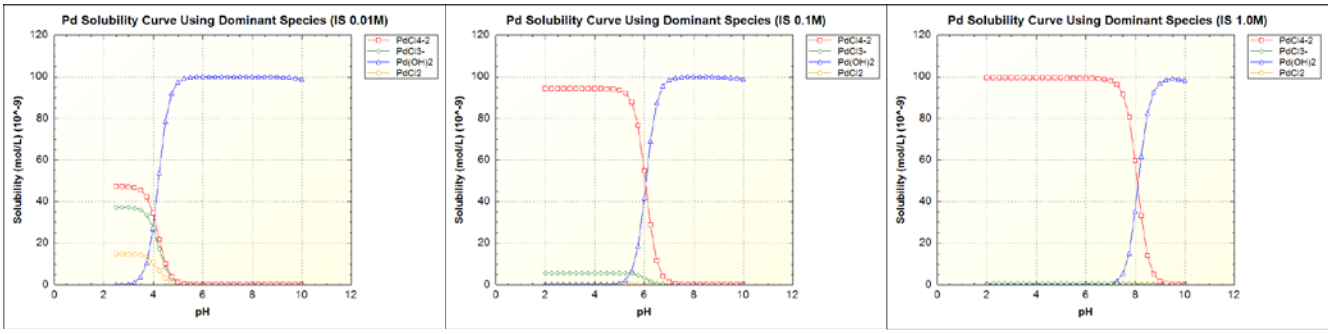
$$K_d = \frac{C_b - C_t}{C_t} \times \frac{L}{S} \tag{1}$$

Where $C_b$is the final concentration of Pd in the blank solution, C_t is the final concentration of Pd in the sample solution and L/S is the liquid to solid ratio used in the sample. However, according to Tachi et. al. (1999)[2], Pd sorption onto vessel wall is only significant in blank solutions, and only a little Pd appears to sorb onto the vessel walls when a solid is present. Tachi concluded that it is inappropriate to use the final concentration in the blank solution to calculate K_d and that it is more appropriate to use C_i, the initial concentration of Pd in the sample. Therefore K_d values in this report will be calculated using equation (2).

$$K_d = \frac{C_i - C_t}{C_t} \times \frac{L}{S} \tag{2}$$

3.2 PHREEQC

PHREEQC, in conjunction with the thermodynamic database is being used.The concentration of Pd in the samples is confirmed to be lower than the solubility limit of Pd by PHREEQC calculationand speciation of Pd under the experimental conditions outlined in Table 1. The thermodynamic data of Pd selected in Japan Atomic Energy's thermodynamic database (JAEA-TDB) [5], which is being used for the calculation of speciation and solubility, are shown in Table 2. The dominant species in Na-Ca-Cl solutions varies with pH and ionic strength. At 0.01M ionic strength the dominant species are chloride complexes; $PdCl_4^{2-}$, $PdCl_3^{2-}$ and $PdCl_2$, below pH 4, and neutral hydroxo complexes, $Pd(OH)_2$, above pH 4. As ionic strength increases the transition point between dominant species increases, this can be seen in Figure 1.



(b) Ionic Strength 0.01M (a) Ionic Strength 0.1M (c) Ionic Strength 1.0M

Figure 1: Dominant species of Pd in Na-Ca-Cl solution as a function of pH. Concentrations for $PdCl_4^{2-}$, $PdCl_3^{-}$, $PdCl_2$ and $Pd(OH)_2$ are shown in red, green, yellow and blue respectively.

Table 2: Thermodynamic Data of Pd(II) Selected in JAEA-TDB [5]

Reactions	***log K***	***Error***
$+1.0\ Pd^{2+} +2.0\ H_2O -2.0\ H+ = Pd(OH)_2$	-3.49	
$+1.0\ Pd^{2+} +3.0\ H_2O -3.0\ H+ = Pd(OH)_3^-$	-15.48	0.35
$+1.0\ Pd^{2+} +1.0\ Cl^- = PdCl^+$	5.00	0.24
$+1.0\ Pd^{2+} +2.0\ Cl^- = PdCl_2$	8.42	0.31
$+1.0\ Pd^{2+} +3.0\ Cl^- = PdCl_3^-$	10.93	0.38
$+1.0\ Pd^{2+} +4.0\ Cl^- = PdCl_4^{2-}$	13.05	0.59
$+1.0\ Pd^{2+} +1.0\ NO_3^- = PdNO_3^+$	0.167	0.024
$+1.0\ Pd^{2+} +2.0\ NO_3^- = Pd(NO3)_2$	-0.762	0.039
$+1.0\ Pd^{2+} +1.0\ NO_3^- +1.0\ H_2O -1.0\ H^+ = PdOHNO_3$	-0.65	0.036
$+1.0\ Pd^{2+} +3.0\ Cl^- +1.0\ H_2O -1.0\ H^+ = PdCl_3OH^{2-}$	3.77	0.626
$+1.0\ Pd^{2+} +1.0\ NH_4^+ -1.0\ H^+ = PdNH_3^{2+}$	0.363	
$+1.0\ Pd^{2+} +2.0\ NH_4^+ -2.0\ H^+ = Pd(NH3)_2^{2+}$	0.026	
$+1.0\ Pd^{2+} +3.0\ NH_4^+ -3.0\ H^+ = Pd(NH3)_3^{2+}$	-1.711	
$+1.0\ Pd^{2+} +4.0\ NH_4^+ -4.0\ H^+ = Pd(NH3)_4^{2+}$	-4.148	
$Pd(cr) = +1.0\ Pd^{+2} +2.0\ e^-$	-32.86	
$Pd(s) = +1.0\ Pd^{+2} +2.0\ e^-$	-29.57	1.12
$Pd(OH)2(am) = Pd^{+2} + 2\ H_2O -2\ H^+$	-3.58	0.36
$Pd(OH)2(colloidal) = Pd^{+2} + 2\ H_2O -2\ H^+$	-2.41	

4. Conclusions

This paper has outlined the method in which the sorption behaviour for Pd will be measured and calculated. Currently the kinetics experiment is underway, the only remaining task is calculating the concentration of Pd in the liquid phase. Once calculated, the data will be used to determine the equilibrium time and reaction time.

5. References

[1] Vilks, P., “Sorption in Highly Saline Solutions” Nuclear Waste Management Organization (NWMO) Technical Report, NWMO TR-2009-18, 2009.

[2] Tachi, Y., T. Shibutani. H. Sato and M. Shibata, “Sorption and diffusion behaviour of palladium in bentonite, granodiorite and tuff,” Japan Nuclear Cycle Development Institute (JNC) Technical Report, JNC TN8400 99-088, 1999.

[3] Vilks, P., “Sorption of selected radionuclides on sedimentary rocks in saline conditions” Nuclear Waste Management Organization (NWMO) Technical Report, NWMO TR-2011-12, 2011.

[4] Parkhurst, D.L., and Appelo, C.A.J, “Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations,” *U.S. Geological Survey Techniques and Methods*, book 6, 2009,p 497.

[5] Kitamura A. et al, “Update of JAEA-TDB: update of thermodynamic data for palladium and tin, refinement of thermodynamic data for protactinium, and preparation of PHREEQC database for use of the bronsted-guggenheim-scatchard model” Japan Atomic Energy Association (JAEA) Data/Code 2014-009, 2014