SORPTION AND SPECIATION OF PALLADIUM UNDER HIGH IONIC STRENGTH CONDITIONS

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Abstract

Both crystalline and sedimentary rocks are being considered as potential host rocks for a deep geological repository in Canada. Deep-seated sedimentary rocks in the Michigan Basin,Ontario, Canada contain highly saline ground and pore waters.The relatively high ionic strength (*I*) of these waters may influence speciation and rock matrix sorption properties. To this end, laboratory sorption experiments were conducted to examine sorption of palladium (Pd (II)) on sodium bentonite, illite and Ordovician age shale as a function of pH and solution ionic strength. Solutions with pH values in the range of 5 to 9 and *I* ranging from 0.1 to 4 Mwere considered. Experiments were performed under aerobic conditions at 25˚C, and the Eh value of the solution ranged from 470 to 500mV. The data from sorption experimentswere used to validate surface complexation models developed in PHREEQC with the JAEA thermodynamic database (TDB). The sorption of Pd on bentonite, shale and illite all showed strong dependence on *I*. Palladium sorption on all solids decreased with increasing *I*, however the rate of decrease was greatly reduced beyond an *I* of 2M. The surface complexation models for montmorillonite (the major constituent clay mineral of sodium bentonite), and illite (the major constituent clay mineral of shale) also predicted a strong dependence on *I*. In the experiments, the sorption of Pd on bentonite, shale and illite showed a dependence on pH. Between*I* of 0.1M and 1M,sorption was observed to decrease with increasing pH. At *I* of 4M, sorption appears to peak around a pH of 7.The speciation of Pd was also evaluatedusing PHREEQC with the JAEA TDB. At low *I* (0.1 M), when pH is less than 6, negatively charged $PdCl_2^-$ is predicted to be the dominant species and when pH is greater than 6 neutral $Pd(OH)_2$ is dominant. As *I* increases, the pH value of the transition point from $PdCl_2^-$ dominance to $Pd(OH)_2$ dominance increases.

1. Introduction

Both crystalline and sedimentary rocks are being considered as potential host rocks for a deep geological repository (DGR) in Canada. The two sedimentary rock types of particular interest are argillaceous limestone (as host rock) and shale (as natural barriers). The engineered barriers, or seal materials are bentonite, and bentonite-sand mixtures [1]. Deep-seated sedimentary rocks in the Michigan Basin, Ontario, Canada contain highly saline ground and porewaters, the relatively high ionic strength (*I*) of which may influence speciation and rock matrix sorption properties.

Sorption datahas been complied for several elements by Vilks (2011) [2], however data gaps still exist between sorption data and various experimental conditions, such as high *I.*Palladium (Pd) is of interest because isotopes of Pd are present in high-level radioactive waste [2], specifically Pd-107, which has a half-life of 6.5×10^6 years [3]. The aim of this paper is to investigate the effects of ionic strength, pH and speciation on the sorption of Pd in highly saline Na-Ca-Cl solutions.

Laboratory sorption experiments with Pdwere recently conducted on sodium bentonite, illite and Ordovician age shale as a function of pH and solution *I*.pH values in the range of 5 to 9 were considered as well as *I* values of 0.1M, 0.5 M, 1M, 2 M, 3 M and 4 M. The initial concentration of palladium was 1×10^{-7} M, which was confirmed with experiments to be below the solubility limit. The

experiments were carried out under aerobic conditions at 25˚C. In aqueous solution, Pd only occurs in a single redox state, Pd(II), so reducing conditions were not considered [2]. The Eh value of the solutions ranged from 470to 500mV as SHE.

The sorption data obtained from the experiments were used to validate surface complexation models incorporated in PHREEQC with the Japan Atomic Energy Association (JAEA) thermodynamic database (TDB). Speciation models for the aqueous speciation of Pd as well as the speciation of surface sites on montmorillonite and illite were developed using PHREEQC with the JAEA TDB. The speciation calculations are used to explain sorption behaviour with regard to pH and ionic strength dependence.

2. Theory

2.1 Calculation of K_dValues

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

$$K_d = \frac{C_b - C_t}{C_t} \times \frac{L}{S} \quad (1)$$

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) [3], Pd sorption onto the wall of the experimental vessel is only significant in blank solutions, and only a small amount of 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):

$$K_d = \frac{C_i - C_t}{C_t} \times \frac{L}{S} \quad (2)$$

2.2 Speciation

Version 3.2.2 of the geochemical code PHREEQC was used to calculate the speciation of Pd in solution as a function of pH and solution *I*. The thermodynamic data for all Pd species considered in the calculation are given in Table 1[4]. The JAEA TDB includes specific ion interaction theory (SIT) parameters for calculating single ion activity coefficients. SIT theory has been proven adequate for solutions with ionic strengths up to 3-4 mol/L [5]. The Debye-Hückel approach was used to correct activity coefficients for species in the database for which no SIT parameter is specified.A list of species with SIT parameters can be found in Table 2[4,6].

Table 1: Thermodynamic Data of Pd(II) from the JAEA-TDB [4]

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

Table 2: SIT parameters for select species of Pd(II) Taken from JAEA-TDB [4][6]

Cation Species	*Anion*	*SIT Parameter*	*Error*
$PdCl_3^-$	Na^+	0.03	0.01
$PdCl_4^{2-}$	Na^+	-0.044	
$Pd(OH)_3^-$	Na^+	-0.11	
$PdCl_3OH^{2-}$	Na^+	-0.044	

2.3 Surface Complexation Modelling

Surface complexation modelling (SCM) was used to model the sorption behaviour of Pd onto montmorillonite (constituent clay responsible for sorption in bentonite) and illite (constituent clay responsible for sorption in shale). A generalized two layer model was developed in PHREEQC using SCM reactions listed in Table 3. The first two reactions are protonation and deprotonation of the neutral surface hydroxyl site ($\boldsymbol{S \equiv OH}$) into the charged surface sites $\boldsymbol{S \equiv O^-}$ and $\boldsymbol{S \equiv OH_2^+}$. The last three reactions represent the formation of surface bound Pd species. The SCM reactions were taken from Vilks (2011) [2]. The log *K* values shown in Table 3 were calculated using correlation between log *K* and log ${}^{OH}K$ from Bradbury and Baeyens [7, 8].The correlation is shown in equation (3) for montmorillonite [7] and equation (4) for illite [8]:

$$\log K = 8.1 \pm 0.3 + (0.90 \pm 0.02) \log {}^{OH}K \quad (3)$$

$$\log K = 7.9 \pm 0.4 + (0.83 \pm 0.02) \log {}^{OH}K \quad (4)$$

The surface site density was also obtained from Vilks (2011) [2] and the specific surface areas of montmorillonite and illite were obtained from Macht [9].

Table 3: Surface complexation reactions for Pd(II)

Surface Complexation Reaction	$log\ {}^{OH}K$	$log\ K$ *Montmorillonite*	$log\ K$ *Illite*
$S \equiv OH + H^+ \Leftrightarrow S \equiv OH_2^+$		4.0	4.5
$S \equiv OH \Leftrightarrow S \equiv O^- + H^+$		-6.2	-7.9
$S \equiv OH + Pd^{+2} \Leftrightarrow S \equiv OPd^+ + H^+$		6.4	6.4
$S \equiv OH + Pd^{+2} + H_2O \Leftrightarrow S \equiv OPdOH + 2H^+$	-4.0	4.5	4.6
$S \equiv OH + Pd^{+2} + 2H_2O \Leftrightarrow S \equiv OPd(OH)_2^- + 3H^+$	-15.5	-5.9	-5.0

3. Experimental Procedures

3.1 Material

Bentonite used in the experiment was bentonite MX-80, a sodium rich bentonite clay found in Wyoming that is passed through an 80 mesh sieve [2]. The bentonite MX-80 was acquired from the American Colloid Company (ACC). The shale, a sample of Queenston shale, was provided by the Nuclear Waste Management Organization (NWMO) and was crushed to a particle size of 150 to 300μm. The illite sample was purchased from the Clay Mineral Society (CMS) and was IMt-2 (50 grm/unit) Illite from Silver Hill, Mont. Certified ACS calcium chloride ($CaCl_2$) dehydrate and sodium chloride (NaCl) were acquired from Fischer Scientific and used to make a 4M Na-Ca-Cl stock solution.The mass ratio of NaCl:$CaCl_2$ is 50:32, in accordance with the SR-270-PW synthetic reference brine solution [2].0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH) acquired from ACP were used to control the pH of solutions. A palladium stock solution of concentration 1000μg/mL in 5% HNO_3 was purchased from Agilent Technologies and diluted to make ICP-MS calibration solutions and the 1μg/mL (approximately 1×10^{-5} M) stock solution used in experiments. The calibration solutions have Pd concentrations of 1×10^{-8} M, 5×10^{-8} M, 1×10^{-7} M, 2.5×10^{-7} M and 5×10^{-7} M.

3.2 Solubility Experiment

A solubility experiment was conducted to ensure that the Pd concentration used during the sorption experiments was below the solubility limit and to determine how long Pd takes to reach a steady dissolved state when added to a Na-Ca-Cl solution. Na-Ca-Cl solutions with *I* of 0.1M, 1M and 4M were used. Pd wasadded to the solutions such that the initial concentration of Pd in solution was 1×10^{-7} M. Measurements of Pd concentration were taken after 1 hour, 1 day, 2 days, 5 days, 1 week, 9 days, and 2 weeks, using the procedure outlined in section 3.3.1.

3.3 Sorption Experiment

Batch sorption experiments were carried out under aerobic conditions at 25˚C. Triplicate samples were used for each experimental condition to ensure experimental accuracy. The figure below shows the procedure used for the experiments.

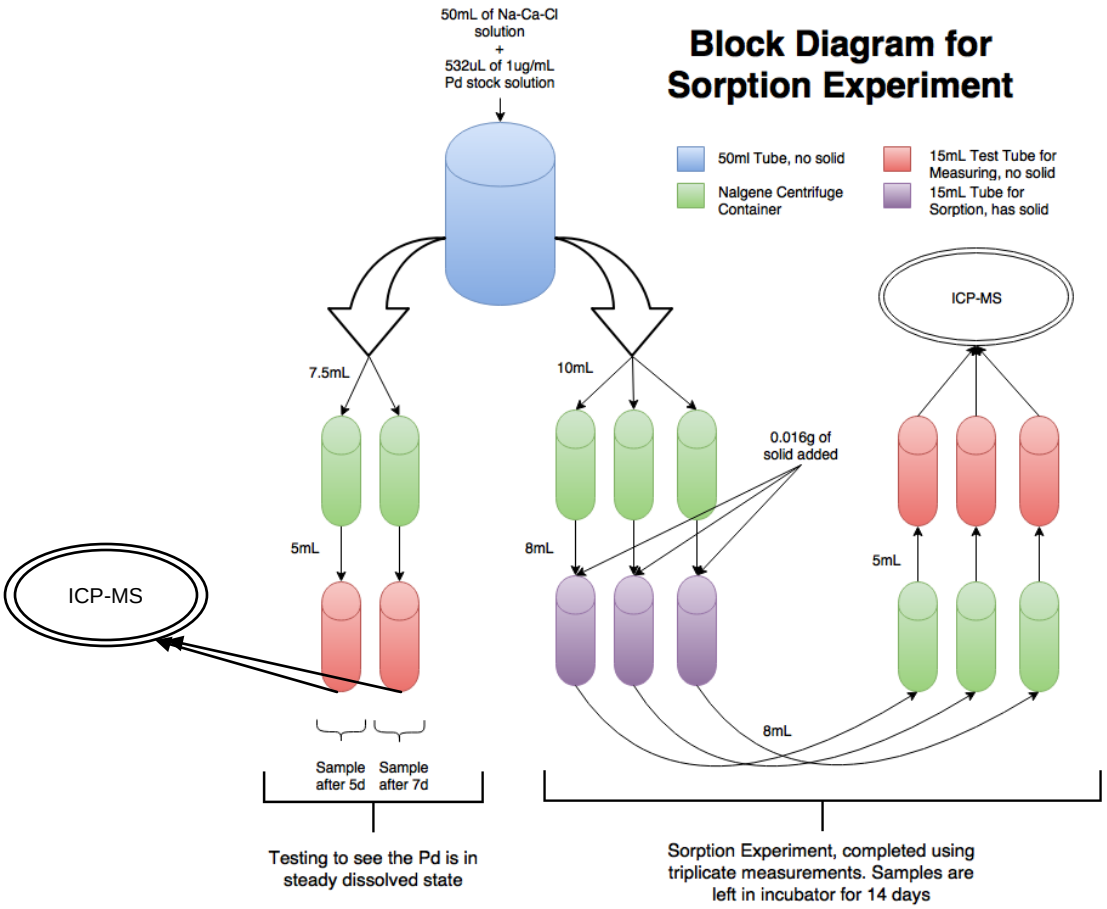

Figure 1: Block diagram showing experimental procedure.

3.3.1 Separation and Measurement Procedure

When a sorption measurement was taken, a volume of solution was removed and placed in a Nalgene centrifuge container and centrifuged for 30min at 18000rpm. The volume removed depends on the measurement type (see Table 4). After centrifuging, a smaller volume of solution was removed (Table 4) and placed into a new polypropylene test tube. A smaller volume was used after centrifuging to ensure that any Pd precipitate or solids separated during centrifuging was not transferred to the new vessels. Solutions with *I* of 1M were diluted by a factor of two, 2M solutions by a factor of 2.5, 3M solutions by a factor of four and 4M solutions by a factor of five. This was done to ensure the *I* of solutions being measured by ICP-MS was below 1 M, a limit of the machine. The concentration of Pd in the polypropylene test tube was then measured by ICP-MS.

Table 4: Volume used for centrifuging by measurement type

Measurement	***Volume Removed before Centrifuge (ml)***	***Volume Removed after Centrifuge (ml)***
Initial conc. of Pd	7.5	5
Contacting solid	10	8
Equilibrium conc. of Pd	~8	5

3.3.2 Kinetics Experiment

A kinetics experiment was conducted in order to determine the amount of time required for Pd sorption to reach equilibrium. The two different solid samples, bentonite MX-80 and shale, were added to 8ml of Na-Ca-Cl solutions of *I of* 0.1M, 1M and 4M in polyethylene vials. A liquid to solid ratio of 2.0 g/L was used for both the MX-80 and shale. A 1μg/mL Pd solution was added to the solutions such that the final concentration of Pd in the samples was 1×10^{-7} M. The samples were stored in an incubator at 20 rpm and 25˚C up until it was time to take measurements. The concentration of Pd was measured after 1 hour, 1 day, 2 days, 5 days, 1 week, 9 days and 2 weeks, using the procedure outlined in section 3.3.1.

3.3.3 Ionic Strength Dependence

50ml solutions of *I*of0.1M, 0.5M, 1M, 2M, 3M and 4M were placed in polypropylene test tubes, Pd was added to the solutions such that the initial concentration of Pd in solution was 1×10^{-7} M.The samples were stored in an incubator at 20 rpm and 25˚C for 1 week, as determined by the solubility and stability experiment. The solution was sampled, according to the procedure outline in section 3.3.1, after 5 days and 7 days in order to verify that the concentration of Pd in solution had reached a steady dissolved state. After which 0.016g of bentonite MX-80, shale and illite were added to 8mL of the solutions. A liquid to solid ratio of 2.0 g/L was used for all solids. The samples were then returned to the incubator for 2 weeks, as determined by the kinetics experiment, to reach sorption equilibrium. After 2 weeks, measurements were taken according to the procedure outlined in section 3.3.1.

3.3.4 pH Dependence

50ml solutions of *I*of0.1M, 1M and 4M were placed in polypropylene test tubes and Pd was added to the solutions such that the initial concentration of Pd in solution was 1×10^{-7} M. The pH was then adjusted to either 5 or 9 using 0.1N HCl or NaOH. The samples were stored in an incubator at 20rpm and 25˚C for 1 week during which he pH was adjusted daily (to within ±0.1 of the desired value). The solution was sampled, according to the procedure outline in section 3.3.1, after 5 days and 7 days in order to verify that the concentration of Pd in solution had reached a steady dissolved state. After which 0.016g of bentonite MX-80, shale and illite were added to 8ml of solution. A liquid to solid ratio of 2.0 g/L was used for all solids. The samples were then returned to the incubator for 2 weeks, during which time the pH continued to be adjusted daily (to within ±0.1 of the desired value). After 2 weeks, measurements were taken according to the procedure outlined in section 3.3.1.

3.4 Titration Experiment

When the *I* is greater than 0.1M, the pH indicated by the pH meter ($pH_{measured}$) is not correct and therefore $pH_{measured}$ values are only considered operational values. A relationship between $pH_{measured}$ and pH_c was obtained by titration in order to convert $pH_{measured}$ values to the proton concentration. The titration experiments were carried out under aerobic conditions at room temperature. 100mL solutions were prepared at the ionic strengths of 0.5M, 1M, 2M, 3M and 4M and contained 0.001 moles of 0.1N HCl in order to adjust the $pH_{measured}$to less than 3. The solution was then placed in the titrator, where the $pH_{measured}$ was measured continuously as a function of 0.1N NaOH added until the pH reached a value of 12. The experiment was then repeated in the opposite direction; $pH_{measured}$ was measured continuously as a function of 0.1N HCl added until the $pH_{measured}$ reached 3. Throughout the

experiment, a stirrer was used to ensure that the acid/base added was mixed evenly, and the pH readings were accurate.

4. Results and Discussion

4.1 Solubility

The Pd stability experiment showed that there were minor fluctuations in Pd concentration initially, however after approximately 5 days it remained constant. When the concentration in solution remained at 1×10^{-7} M, no Pd was removed during centrifuging, which means no precipitate was present and the concentration of Pd in solution was below the solubility limit. In all experiments, the concentration of Pd in solution was measured after 5days and 7 days before adding the solid. In all cases, the Pd was found to be in a steady dissolved state as the concentration of Pd was constant between 5 and 7days. Additionally, since the measured concentration was always comparable to the calculated concentration (based on the amount of Pd stock solution added), we can assume that there was no precipitate present and that the concentration of Pd in solution was below the solubility limit.

The solubility limit of Pd was also confirmed using a PHREEQC calculation. The results are shown in Figure 3(b). The solubility is heavily dependent on ionic strength and on pH. In our experiment we are concerned with the $pH_{measured}$range from 5 to 9 and ionic strengths from 0.1M to 4 M. Only the case of I =0.1M is close to the solubility limit of Pd, however as described above, no precipitate was detected.

4.2 pH Correction

The results of the bi-directional acid base titrations for 0.1M, 1M and 4M I are shown in Figure 2. The slope, or correction factor, for each titration was determined by linear regression and is shown in the legend; the intercept is not shown because it was insignificant.

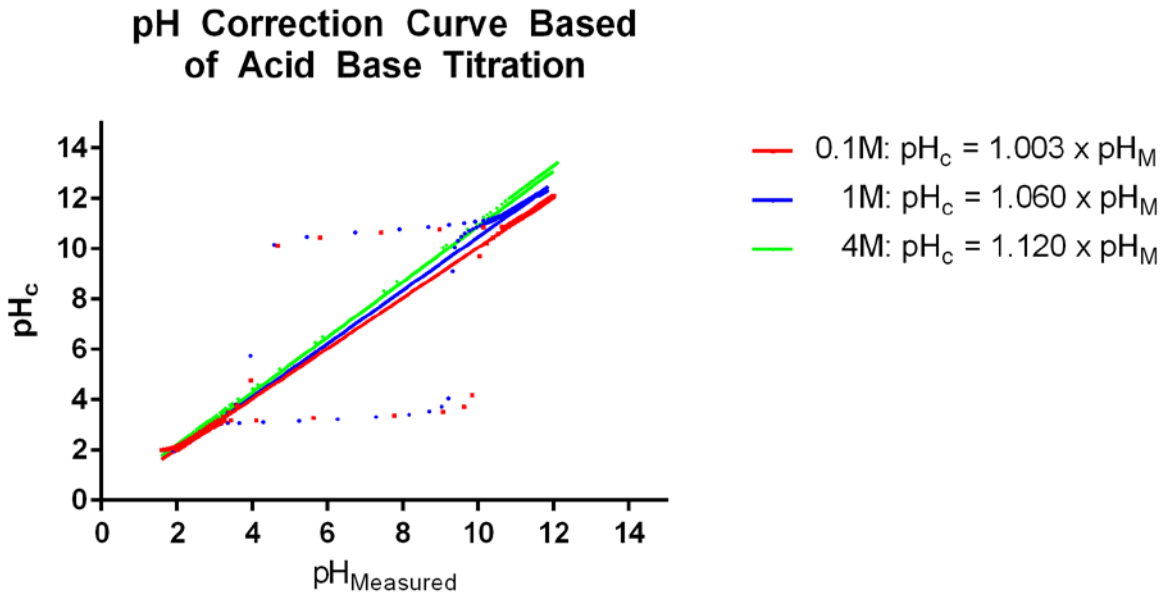

Figure 2: Results of acid base titration for solution of *I* of 0.1M, 1M and 4M.The legend shows the correction factors used to determine pH_c from $pH_{measured}$

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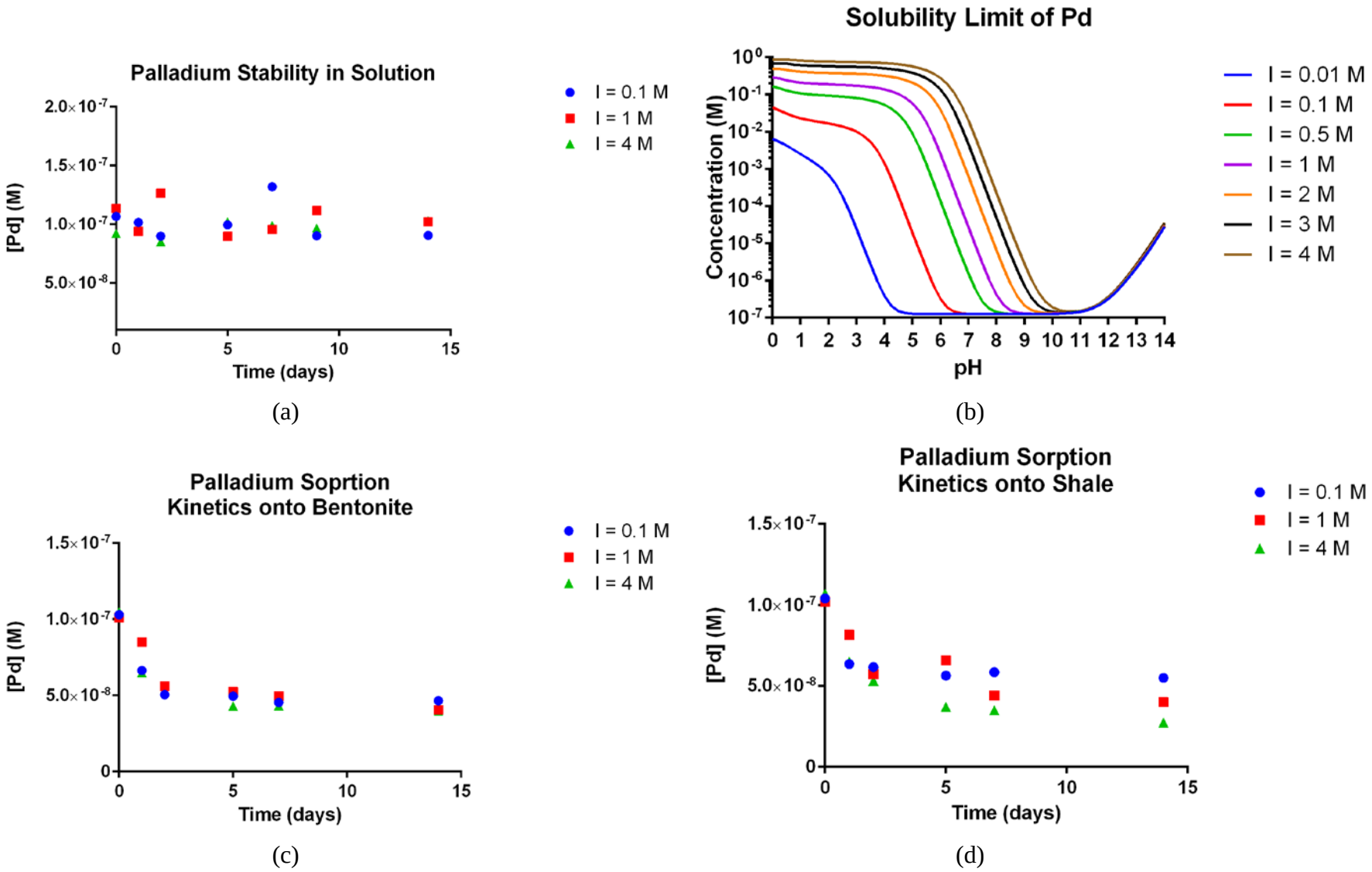


Figure 3: (a) The stability of Pd in Na-Ca-Cl solutions with different *I*as a function of time over the course of two weeks. (b) The PHREEQC solubility calculation in Na-Ca-Cl solutions with different *I*. (c) and (d) The sorption kinetics experiments for sorption onto bentonite and shale respectively in Na-Ca-Cl solutions with different *I*.

4.3 Sorption Kinetics

Both bentonite and shale throughout the range of *I* reached sorption equilibrium after 5 to7 days. In order to ensure that equilibrium was reached during the sorption experiments, the samples were left for approximately twice this time (14 days).

4.4 Ionic Strength Dependence of K_d

The sorption of Pd onto shale, bentonite and illite were strongly dependant on *I* (Figure 4(a)). As *I* increased, sorption decreased. The rate of decrease is largest at low ionic strength, and the rate of decrease becomes very small above an*I* of 2M.

4.5 pH_c Dependence of K_d

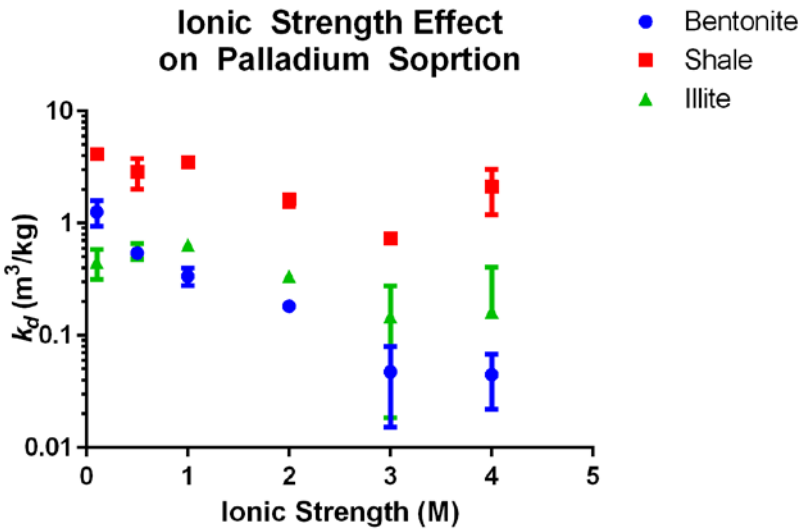
Figures 4 (b) – (d) show the pH_c dependence of K_d onto bentonite, shale and illite respectively. At *I* =0.1M, the relationship between K_d and pH_c is simple in that as pH_c increases, K_d decreases. However, as *I* increases, the relationship between $K_d$and pH_c becomes more complicated. For bentonite at *I* = 1M, the K_d decreases initially with increasing pH_c, however at pH_c 9 the $K_d$is larger than it was at pH_c 5. The same relationship is seen for bentonite at *I* = 4M. For illite and shale, at *I* =1M there is an initial decrease in K_d(for illite) however as pH_c increases further we find that $K_d$reaches a maximum around pH_c 7 (for shale) and then decreases to a value lower than pH_c5 (for both illite and shale). At *I* = 4M we see an identical trend for both solids, the value $K_d$is approximately equal at pH_c 5 and 9, and the $K_d$appears to peak around pH_c 7. In the limited areas where our experimental data overlaps with Tachi et. al. (1999), *e.g.* sorption onto bentonite in 0.1M solution, our data fits well with the lower range of their reported values for pH_c 8 and 11.

4.6 Palladium Speciation in Na-Ca-Cl Solution

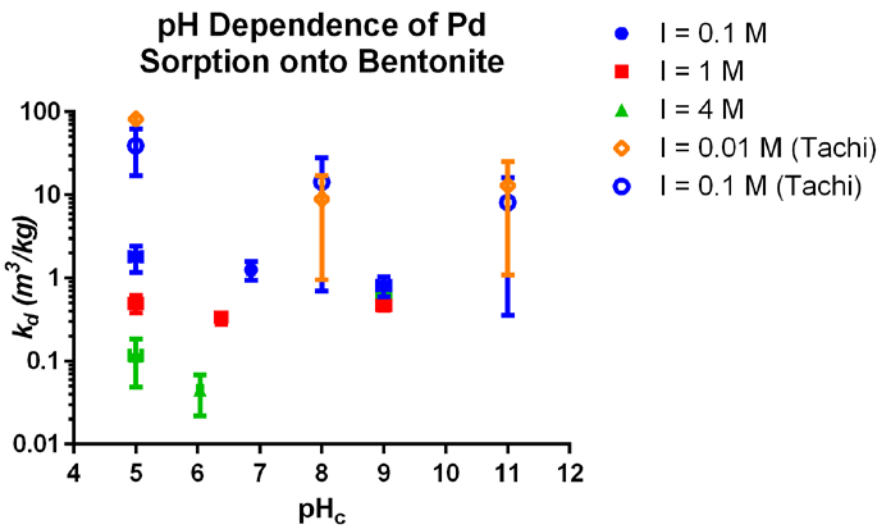
Both the surface site speciation and the speciation of Pd were modelled using PHREEQC with the JAEA TDB. At low *I* (0.1 M), when pH is less than 6, negatively charged $PdCl_4^{-2}$ is predicted to be the dominant species, and when pH is greater than 6 neutral $Pd(OH)_2$ is dominant. As *I* increases, the pH value of the transition point from $PdCl_4^{-2}$ dominance to $Pd(OH)_2$ dominance increases. At *I* of 1M the transition point is around pH 8 and at *I* of 4M it is around pH 9.5 (Figures 5 (b) – (d)). Surface site speciation was predicted to be independent of ionic strength, this is not shown in 5(a) as data for *I* of 0.1M, 1M and 4M overlapped, however it did vary strongly with pH. Both montmorillonite and illite showed the same trends; at low pH the positive $\boldsymbol{S \equiv OH_2^+}$ is dominant, at high pH negative $\boldsymbol{S \equiv O^-}$ is dominant and in between neutral $\boldsymbol{S \equiv OH}$ is dominant. The transition point between dominant species varies between montmorillonite and illite; transitions occur at lower pHfor montmorillonite.

4.7 Surface Complexation Modelling Using PHREEQC

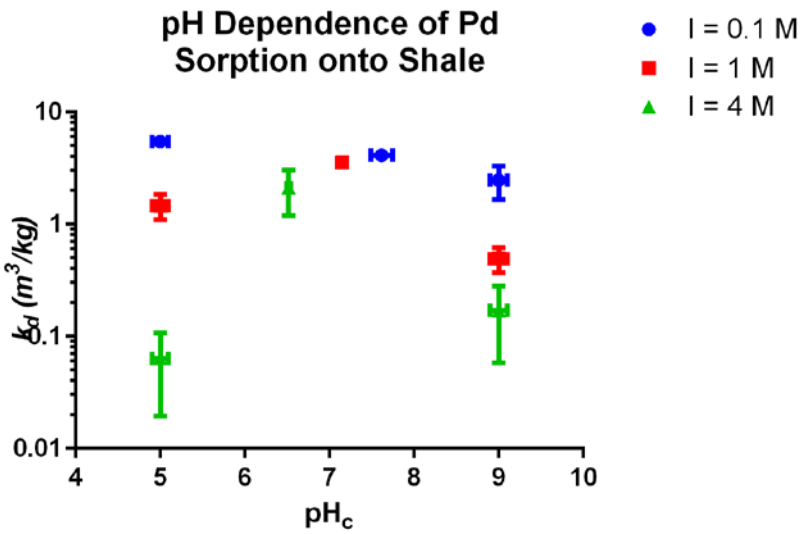
The results of the sorption experiments and of the PHREEQC SCM are shown in figures 6 (a) and (b) for montmorillonite and illite respectively. For montmorillonite at pH 5 and 9, the 0.1M data points fit the curve, however the other data (from the neutral pH range and other *I*) do not fit the sorption model. For illite at pH 5 for 0.1M and pH 9 for 1M, the sorption model fits the experimental data, however the sorption model does not fit all the other data.The fit maybe poor because the log *K* values in the database used for the surface complexation reactions were optimized at low (<0.1M) *I*. In order to improve the fit, we should continue to measure K_d over a wider range of *I* and pH and optimize log *K* with actual experimental data.

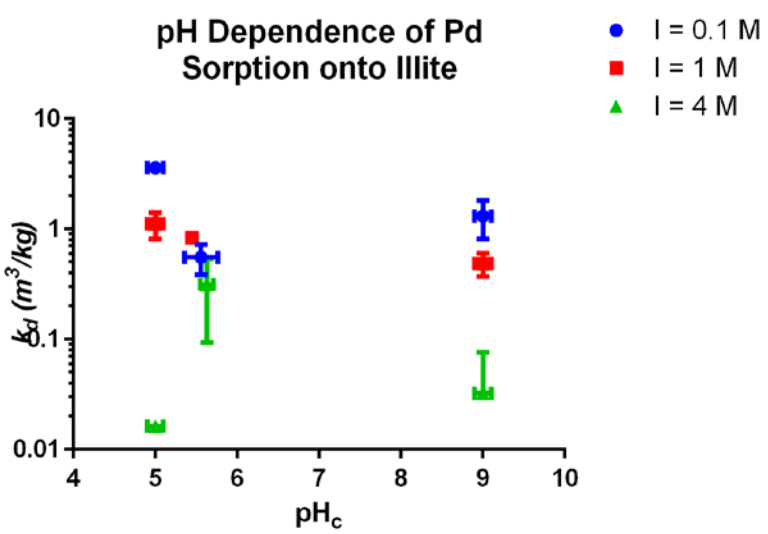


(a)



(b)





(c)(d)

Figure 4: (a) Results of ionic strength dependence sorption experiments. (b)-(d) Results for the pH_c dependence experiments for sorption onto bentonite, shale and illite respectively. 'Error' bars for Tachi et al. data (hollow points) represent the range of values reported.

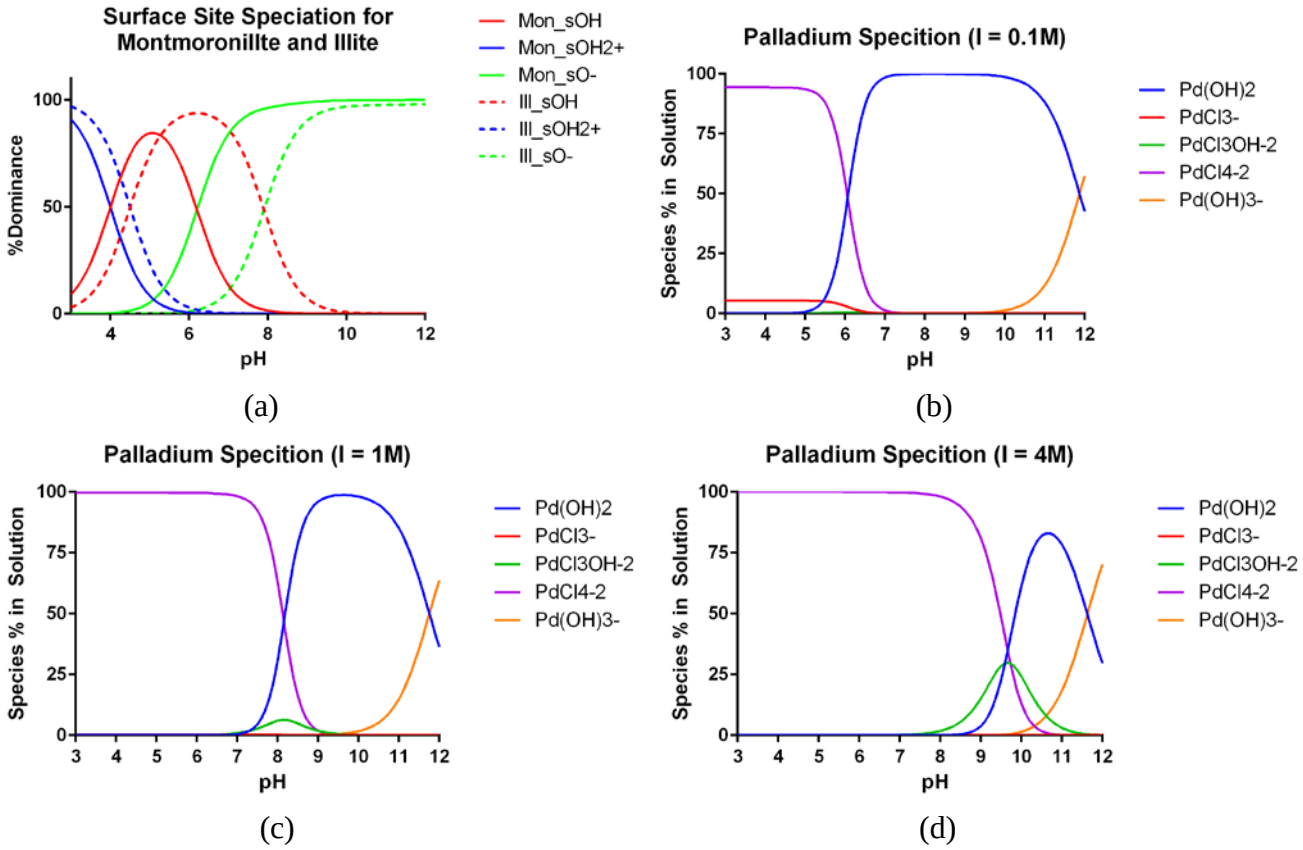


Figure 5: (a) The surface site speciation for montmorillonite (solid line) and illite (dashed line). (b)-(d) PHREEQC speciation calculation for 0.1M, 1M and 4M solutions respectively.

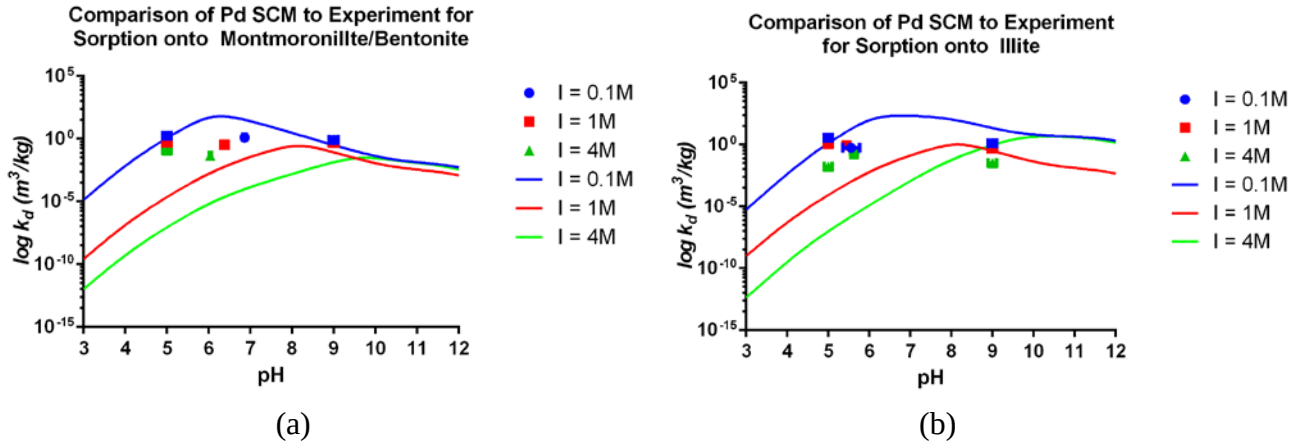


Figure 6: Results of surface complexation modelling using values taken from Bradbury and Baeyens (2005, 2009). Experimental data from this study are also shown.

5. Conclusions

This study first investigated the relationship between K_d and I for sorption of Pd onto bentonite, shale and illite. The K_d decreases with increasing I, however the rate of decrease slows around 2M. Additionally we began to determine the relationship between K_d and pH_c for sorption of Pd onto bentonite, shale and illite, however more data is required in the pH range of 6 – 8, in order to clearly

understand the relationship. A SCM has been developed for modelling the sorption of Pd onto montmorillonite and illite, and in future research we hope to improve the reliability of the model by optimizing fit parameters to experimental data.

6. References

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

[2] P. Vilks, "Sorption of Selected Radionuclides on Sedimentary Rocks in Saline Conditions – Literature Review",NWMO Technical Report NWMO TR-2011-12, Toronto, Canada, 2011.

[3] 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.

[4] 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

[5] Grenthe, I. and Plyasunov, A.V., "On the Use of Semiempirical Electrolyte Theories for the Modeling of Solution Chemical Data", Pure and Applied Chemistry, Vol. 69 No. 5, pp. 951-958, 1997.

[6] Kitamura, A. et al, "Thermodynamic model for amorphous $Pd(OH)_2$ solubility in the aqueous Na+-K+-H+-OH--Cl--ClO4--H2O system at 25˚C: A critical review", J. Solution Chem., Vol. 41, pp. 1965-1985, 2012.

[7] Bradbury, M. H. and Baeyens, B., "Modelling the sorption of Mn(II), Co(II), Ni(II), Cd(II)), Eu(II), Am(III), Sn(IV), Th(IV) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface bindings constants for some slected heavy metals and actinides", Geochimica et Cosmochimica Acta, Vol. 69 No. 4 pp. 865-892, 2005.

[8] Bradbury, M. H. and Baeyens, B., "Sorption modelling on illite. Part II: Actinide sorption and linear free energy relationships", Geochimica et Cosmochimica Acta, Vol. 73 No. 4 pp. 1004-1013, 2009.

[9] Macht, F., et al, "Specific surface area of clay minerals: Comparison between atomic force microscopy measurements and bulk-gas (N_2) and –liquid (EGME) adsorption methods" Applied Clay Science, Vol. 53 pp. 20-26, 2011.

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