

## Research Article

# Contribution of Ternary Reaction to Pd Sorption on MX-80 in Na-Ca-Cl Solution at High Ionic Strength

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In this study, we first examined the sorption of Pd on MX-80 in Na-Ca-ClO<sub>4</sub> solution as a function of pH<sub>c</sub> (3–9) and ionic strength (0.1 M–4 M) and confirmed that the experimentally derived  $K_d$  values could be fitted by a 2-site protolysis nonelectrostatic surface complexation and cation exchange (2SPNE SC/CE) model using three binary surface complexation constants previously estimated. Then, we investigated the sorption of Pd on MX-80 in Na-Ca-Cl-ClO<sub>4</sub> solution as a function of pH<sub>c</sub> (3–9) and Cl<sup>−</sup>/ClO<sub>4</sub><sup>−</sup> molar concentration ratio (0–∞) at the ionic strength = 4 M. We found that the sorption of Pd on MX-80 in Na-Ca-Cl-ClO<sub>4</sub> solution could be simulated only by the three binary and one ternary surface complexations (S-OH + Pd<sup>2+</sup> + 4Cl<sup>−</sup> ↔ S-OPdCl<sub>4</sub><sup>3−</sup> + H<sup>+</sup>). This suggests that the contribution of other ternary surface complexations such as ≡S-OH + Pd<sup>2+</sup> + xCl<sup>−</sup> ↔ ≡S-OPdCl<sub>x</sub><sup>(x−1)−</sup> + H<sup>+</sup> (x = 1, 2 and 3) to Pd sorption in Na-Ca-Cl-ClO<sub>4</sub> solution with ionic strength = 4 M was negligibly small.

## 1. Introduction

Canadian sedimentary rocks are being considered as potential host rocks for a deep geologic repository (DGR) for used nuclear fuel. Some of these rocks in Canada (for example, Southern Ontario, Michigan Basin [1]) contain Na-Ca-Cl type brine solutions with total dissolved solids (TDS) concentration up to 350 g/L or with the ionic strength (*I*) as high as 7.2 M. Sorption of radionuclides onto host rocks surrounding a DGR and onto materials comprising the engineered barrier system is considered an important mechanism for retarding their subsurface transport from the repository to the biosphere [2–6]. Therefore, it is important to elucidate the sorption behaviour of radionuclides not only on host rocks, but also on engineered barrier materials such as bentonite.

The Nuclear Waste Management Organization of Canada (NWMO) has been maintaining a database of sorption distribution coefficients,  $K_d$ , for Canadian sedimentary rocks and bentonite [2]. Palladium is selected as an element of interest by the NWMO, but the only existing relevant sorption data for Pd on bentonite had been measured in 0.01 and 0.1 M NaCl solutions [7]. Hence, sorption of Pd onto Queenston shale,

illite (the major mineral constituent of Queenston shale), and MX-80 bentonite (the candidate material for engineered barrier in Canada) in Na-Ca-Cl solutions with pH<sub>c</sub> ranging from 3 to 9 and *I* ranging from 0.01 M to 6 M was studied in our previous paper [8]. The 2-site protolysis nonelectrostatic surface complexation and cation exchange (2SPNE SC/CE) model [9, 10] with SIT parameters was applied to the pH<sub>c</sub> dependence of  $K_d$  values for illite and MX-80 (*I* ≤ 4 M), and the optimized surface complexation and cation exchange constants were estimated [8]. Since Pitzer parameters for Pd in Na-Ca-Cl solution are not completely compiled, we did not apply the 2SPNE SC/CE model to the  $K_d$  values at *I* = 6 M. We found that Pd sorption could largely be accounted for with the formation of the ≡S-OPdOH, ≡S-OPd(OH)<sub>2</sub><sup>−</sup>, ≡S-OPdCl<sub>4</sub><sup>3−</sup> surface species, and the ≡S-O<sub>2</sub>Pd exchange species with 2Na<sup>+</sup> for both sorbents, with the additional ≡S-OPd<sup>+</sup> surface species for MX-80. We included four possible ternary surface complexations (≡S-OH + Pd<sup>2+</sup> + xCl<sup>−</sup> ↔ ≡S-OPdCl<sub>x</sub><sup>(x−1)−</sup> + H<sup>+</sup>; x = 1–4) in the fitting by 2SPNE SC/CE model, but only one reaction (≡S-OH + Pd<sup>2+</sup> + 4Cl<sup>−</sup> ↔ ≡S-OPdCl<sub>4</sub><sup>3−</sup> + H<sup>+</sup>) was found to contribute to the sorption in Na-Ca-Cl solutions with high *I*.

In this work, we first measured the sorption of Pd on MX-80 in Na-Ca-ClO<sub>4</sub> solutions as a function of pH<sub>c</sub> and *I* and studied whether the experimentally derived *K<sub>d</sub>* values in the absence of Cl<sup>-</sup> can be simulated by using our previously optimized constants. Then, we measured the sorption of Pd on MX-80 in Na-Ca-Cl-ClO<sub>4</sub> solutions as a function of pH<sub>c</sub> and Cl<sup>-</sup>/ClO<sub>4</sub><sup>-</sup> molar concentration ratio (0–∞) at *I* = 4 M and investigated the contribution of ternary surface complexation to the Pd sorption on MX-80 at *I* = 4 M.

## 2. Materials and Methods

**2.1. Chemicals, Solids, and Solutions.** All chemicals used were reagent grade and were supplied from Fisher Scientific. Deionized water was prepared using a Milli-Q Direct 8 (18.2 MΩ·cm). The MX-80 bentonite sample was supplied by the American Colloid Company and was used as received. Pd used in experiments was derived from a 1000 ± 1 μg/mL standard solution with a natural isotopic abundance supplied by Agilent Technology. A Precise Controlled Atmosphere Glove Box (GB) supplied by Labconco was filled with N<sub>2</sub> gas (>99.999 %). The concentration of O<sub>2</sub> in the GB was smaller than 2 ppm.

The reference brine solution in Southern Ontario, SR-270-PW, is proposed by the NWMO [2]. It has a Na/Ca molar concentration ratio of 2.7. In this study, Na-Ca-ClO<sub>4</sub> solutions (Na/Ca molar concentration ratio = 2.7) with *I* = 0.1, 1, 2, 4 M were prepared by NaClO<sub>4</sub>·H<sub>2</sub>O and Ca(ClO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, and Na-Ca-Cl-ClO<sub>4</sub> solutions (Na/Ca ratio = 2.7; Cl<sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio = 0.01, 0.1, 1, 10, 100, ∞) with *I* = 4 M were prepared by NaCl, CaCl<sub>2</sub>·2H<sub>2</sub>O, and NaClO<sub>4</sub>·H<sub>2</sub>O. Na-Ca-ClO<sub>4</sub> solution with *I* = 4 M was considered a case of Cl<sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio = 0.

The pH values indicated on the pH meter (pH<sub>measure</sub>) should be considered as operational values at high ionic strength (*I* ≥ 0.1 M) [11]. The relationships between the operational pH<sub>measure</sub> and the molar H<sup>+</sup> concentrations (pH<sub>c</sub> = -log c<sub>H<sup>+</sup></sub>) or the molal H<sup>+</sup> concentration (pH<sub>m</sub> = -log m<sub>H<sup>+</sup></sub>) were discussed in detail by Altmaier et al. [12, 13]. In this study, the relationships between pH<sub>measure</sub> (Fisher Scientific Accumet AB 150/micro accupHast pH combination electrode) and pH<sub>c</sub> in solutions were determined by titration (Metrohm Ti-Touch 916), and the pH<sub>measure</sub> values were converted to the pH<sub>c</sub> values.

**2.2. Sorption Experiments.** All sorption experiments were carried out in triplicate at 25°C. In preliminary tests, the sorption of Pd on the wall of a polycarbonate reaction vessel was found to be negligible. Initial concentration of Pd for all sorption tests was 1.0 × 10<sup>-7</sup> M and was confirmed to be smaller than solubility of Pd [8]. The liquid/solid ratio was set to be 0.5 m<sup>3</sup>/kg.

We followed the sorption experimental procedure we conducted in Np(V) and Np(IV) sorption previously [14–16]. In the GB, MX-80 was added into a polycarbonate reaction vessel and Na-Ca-ClO<sub>4</sub> or Na-Ca-Cl-ClO<sub>4</sub> solution was added into the reaction vessel. The suspensions were kept in the GB for 3 to 4 days for preequilibration (the pH<sub>c</sub> of solutions in contact with MX-80 was confirmed to be

stabilized within 1 day in the preliminary tests). The reaction vessels were removed from the GB and the liquid and solid were separated by centrifugation for 120 min at 18,000 rpm (Beckman Coulter, Allegra X-30R). The reactions vessels were then transferred back into the GB and the liquid was removed by pipette. Na-Ca-ClO<sub>4</sub> or Na-Ca-Cl-ClO<sub>4</sub> solution was then added into the reaction vessel again, and a portion of the Pd standard solution was spiked into the reaction vessel. The pH<sub>c</sub> of the solution was adjusted to the predecided values at 3 ≤ pH<sub>c</sub> ≤ 9 by addition of 0.01 M HClO<sub>4</sub>, 0.01 M HCl, or 0.01 M NaOH solution in the GB, and the reaction vessel was tightly sealed. Change in *I* and Cl<sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio by addition of HClO<sub>4</sub>, HCl, or NaOH could be neglected.

The reaction vessels were transferred from the GB to an incubator at 25°C (Infors HT Ectron) and were shaken for 14 days. Fourteen days were enough to reach to the sorption equilibrium [8]. The pH<sub>c</sub> of the solution was measured once a day in the GB and readjusted to the original pH<sub>c</sub> value if the pH<sub>c</sub> changed by more than ± 0.3 from the original value. After 14 days, the liquid was separated from the solid by centrifugation for 120 minutes at 18,000 rpm at 25°C. We previously confirmed that the liquid phase was sufficiently separated from the solid phase by this method [14]. The pH<sub>c</sub> of the liquid was measured in the GB, and an aliquot was sampled from the liquid phase of each reaction vessel. The concentration of Pd in the aliquot was measured by ICP-MS (Agilent ICP-MS 8800).

The *K<sub>d</sub>* value (m<sup>3</sup>/kg) is calculated according to Equation (1), where *C<sub>i</sub>* is the initial concentration of Pd in solution (1.0 × 10<sup>-7</sup> M), *C<sub>eq</sub>* the concentration at sorption equilibrium (M), *L* the volume of liquid used in the sample (m<sup>3</sup>), and *M* the mass of solid used (kg). In this paper, the sorption of Pd on MX-80 is described by *K<sub>d</sub>* values.

$$K_d = \frac{C_i - C_{eq}}{C_{eq}} \times \frac{L}{M} \quad (1)$$

**2.3. Sorption Modelling.** The pH<sub>c</sub>, *I*, and Cl<sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio dependence of *K<sub>d</sub>* values for MX-80 was fitted using the 2SPNE SC/CE model with the program PHREEQC [17]. The specific-ion interaction theory (SIT) was used for the computational method, as it accounts for the electrostatic interactions of all other ions in solution with the one ion of interest. This is necessary for accuracy when computing activity coefficients in solutions of high *I*. The Pitzer computational method can be more accurate in higher *I* solutions; however, Pitzer parameters for Pd were not completely known at the present. SIT is known to be inaccurate at *I* > 4.0 M and, therefore, sorption was modelled at *I* ≤ 4.0 M in this study [18].

The Japan Atomic Energy Agency (JAEA) thermodynamic database (TDB) was chosen as the reference database since it contains the necessary thermodynamic data for Pd [19]. However, no thermodynamic data for PdOH<sup>+</sup> and Pd(OH)<sub>4</sub><sup>2-</sup> are available in JAEA TDB, so the values contained in the SIT database (v9a) included in the PHREEQC [20] were added to the JAEA TDB. The hydrolysis and

TABLE 1: Thermodynamic data of Pd(II) species used in this work [19, 20].

Hydrolysis and complexation reaction	log $K$	Reference
$\text{Pd}^{2+} + \text{H}_2\text{O} - \text{H}^+ \longleftrightarrow \text{PdOH}^+$	1.86	[18]
$\text{Pd}^{2+} + 2\text{H}_2\text{O} - 2\text{H}^+ \longleftrightarrow \text{Pd}(\text{OH})_2$	-3.49	[17]
$\text{Pd}^{2+} + 3\text{H}_2\text{O} - 3\text{H}^+ \longleftrightarrow \text{Pd}(\text{OH})_3^-$	-15.48	[17]
$\text{Pd}^{2+} + 4\text{H}_2\text{O} - 4\text{H}^+ \longleftrightarrow \text{Pd}(\text{OH})_4^{2-}$	-29.36	[18]
$\text{Pd}^{2+} + \text{Cl}^- \longleftrightarrow \text{PdCl}^+$	5.00	[17]
$\text{Pd}^{2+} + 2\text{Cl}^- \longleftrightarrow \text{PdCl}_2$	8.42	[17]
$\text{Pd}^{2+} + 3\text{Cl}^- \longleftrightarrow \text{PdCl}_3^-$	10.93	[17]
$\text{Pd}^{2+} + 4\text{Cl}^- \longleftrightarrow \text{PdCl}_4^{2-}$	13.05	[17]
$\text{Pd}^{2+} + 3\text{Cl}^- + \text{H}_2\text{O} - \text{H}^+ \longleftrightarrow \text{PdCl}_3\text{OH}^{2-}$	3.77	[17]

TABLE 2: Optimized surface complexation and cation exchange constants [8].

Sorption reaction	log $K$
Binary surface complexation:	
$\equiv\text{S-OH} + \text{Pd}^{2+} \longleftrightarrow \equiv\text{S-OPd}^+ + \text{H}^+$	$8.2 \pm 0.2$
$\equiv\text{S-OH} + \text{Pd}^{2+} + \text{H}_2\text{O} \longleftrightarrow \equiv\text{S-OPdOH} + 2\text{H}^+$	$2.3 \pm 0.2$
$\equiv\text{S-OH} + \text{Pd}^{2+} + 2\text{H}_2\text{O} \longleftrightarrow \equiv\text{S-OPd}(\text{OH})_2^- + 3\text{H}^+$	$-5.5 \pm 0.2$
Ternary surface complexation:	
$\equiv\text{S-OH} + \text{Pd}^{2+} + 4\text{Cl}^- \longleftrightarrow \equiv\text{S-OPdCl}_4^{3-} + \text{H}^+$	$13.05 \pm 0.2$
Cation exchange:	
$2\equiv\text{S-ONa} + \text{Pd}^{2+} \longleftrightarrow (\equiv\text{S-O})_2\text{Pd} + 2\text{Na}^+$	$5.90 \pm 0.2$

complexation constants used in this work are summarized in Table 1.

The specific surface area and the cation exchange capacity of MX-80 were 26.2 m<sup>2</sup>/g [21] and 102.1 meq/100g [22], respectively. However, the sorption site capacity was not measured. Hence, we assumed that the sorption site capacity is proportional to the specific surface area [14]. As shown in Supplementary Materials, the contribution of cation exchange reaction to the sorption of Pd on MX-80 was negligibly small. Therefore, the slight difference in the value of the cation exchange capacity did not affect the calculation results. Since the concentration of Pd in the solution was much smaller than the total sorption site number in the MX-80 used, the slight difference in the value of the specific surface area also did not influence the calculation results.

In the 2SPNE SC/CE model, Bradbury and Baeyens considered both strong and weak surface sites [9, 10]. In our previous work [8], we could simulate the Pd sorption on MX-80 in Na-Ca-Cl solution by considering the strong site only and estimate the optimized surface complexation and cation exchange constants at  $I = 0$  M, as shown in Table 2.

For the Pd sorption in Na-Ca-ClO<sub>4</sub> solutions, the 2SPNE SC/CE model calculation was conducted using the binary surface complexation and cation exchange constants illustrated in Table 2.

For the Pd sorption in Na-Ca-Cl-ClO<sub>4</sub> solutions, we included the additional three ternary surface complexations ( $\equiv\text{S-OH} + \text{Pd}^{2+} + x\text{Cl}^- \longleftrightarrow \equiv\text{S-OPdCl}_x^{(x-1)-} + \text{H}^+$ ;  $x = 1 - 3$ ) in the modelling. Bradbury and Baeyens proposed the linear free energy relationships (LFER) between the surface complexation constants for montmorillonite and the

hydrolysis constants [9]. In the fitting of the 2SPNE SC/CE model to the  $K_d$  values experimentally derived, we set the initial values for additional ternary surface complexation constants, by assuming that the proposed LFER equation for montmorillonite can be used for the surface complexation constants and the  $\text{PdCl}_x^{(x-2)-}$  complexation constants ( $x = 1 - 3$ ). The initial value of ternary surface complexation constant for  $\equiv\text{S-OH} + \text{Pd}^{2+} + 4\text{Cl}^- \longleftrightarrow \equiv\text{S-OPdCl}_4^{3-} + \text{H}^+$  was set as 13.05. In the fitting, the values of four ternary sorption reaction constants were used as the fitting parameters to obtain the best optimized fitting, and other values were fixed.

### 3. Results and Discussion

**3.1. Sorption in Na-Ca-ClO<sub>4</sub> Solution.** The pH<sub>c</sub> and  $I$  dependence of  $K_d$  values for MX-80 is plotted in Figure 1. It was found that the  $K_d$  values decreased with pH<sub>c</sub> (3–7) and then became constant against pH<sub>c</sub> (7–10). Little dependence of  $K_d$  values on  $I$  was also observed. These tendencies are consistent with the previous study by Tachi et al. [7].

The 2SPNE SC/CE model with the binary surface complexation and cation exchange constants previously estimated in the Na-Ca-Cl solutions [8] was applied to the pH<sub>c</sub> and  $I$  dependence of  $K_d$  values in the Na-Ca-ClO<sub>4</sub> solutions. The model calculation results are also illustrated in Figure 1. We could find the consistency between the experimental and calculation results.

In the pH region of 3 – 10, Pd(OH)<sub>2</sub> is a dominant species in the solution (Pd speciation in Na-Ca-ClO<sub>4</sub> solution at  $I = 4$  M is shown in Figure S-1. Pd speciation at  $I < 4$  M is not shown here). As shown in Figure S-8, the binary

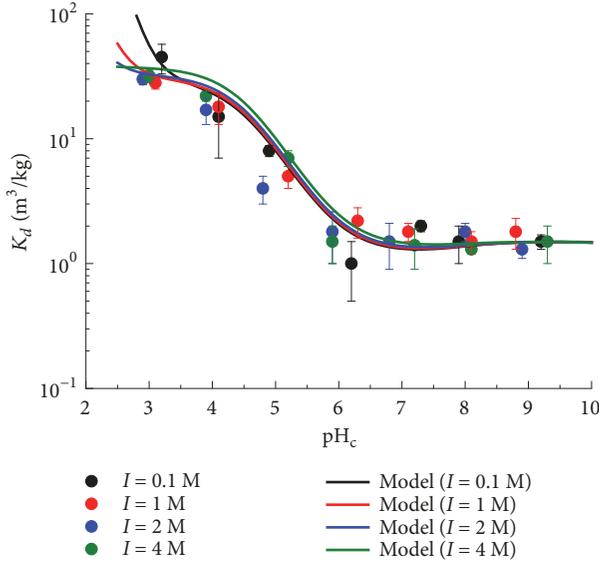


FIGURE 1:  $\text{pH}_c$  and  $I$  dependence of  $K_d$  in Na-Ca- $\text{ClO}_4$  solutions. Plots are the experimentally measured  $K_d$  values. The solid lines are the 2SPNE SC/CE model calculation results. The error bars represent the standard deviation of triplicate measurements.

surface complexations  $\equiv\text{S-OH} + \text{Pd}^{2+} \longleftrightarrow \equiv\text{S-OPd}^+ + \text{H}^+$ ,  $\equiv\text{S-OH} + \text{Pd}^{2+} + \text{H}_2\text{O} \longleftrightarrow \equiv\text{S-OPdOH} + 2\text{H}^+$ , and  $\equiv\text{S-OH} + \text{Pd}^{2+} + 2\text{H}_2\text{O} \longleftrightarrow \equiv\text{S-OPd(OH)}_2^- + 3\text{H}^+$  dominate the sorption at  $\text{pH} = 3-6$ ,  $6-8$ , and  $8-10$ , respectively. This indicates that Pd sorbs on MX-80 markedly in the acidic pH region through the  $\equiv\text{S-OH} + \text{Pd}^{2+} \longleftrightarrow \equiv\text{S-OPd}^+ + \text{H}^+$  surface complexation in the absence of  $\text{Cl}^-$ . From Figure S-8, the contribution of cation exchange reaction was also found to be negligibly small. These demonstrate that the binary surface complexation constants we previously estimated [8] can be used to simulate the sorption of Pd on MX-80 in the Na-Ca- $\text{ClO}_4$  solutions quantitatively.

**3.2. Sorption in Na-Ca-Cl- $\text{ClO}_4$  Solutions.** Figure 2 illustrates the  $\text{pH}_c$  and  $\text{Cl}^-/\text{ClO}_4^-$  ratio dependence of  $K_d$  values for MX-80. We found that the  $K_d$  values at  $\text{pH}_c < 7$  decreased as the  $\text{Cl}^-/\text{ClO}_4^-$  ratio increased. Particularly, the  $K_d$  values at  $\text{pH}_c < 6$  for MX-80 were drastically suppressed in the presence of  $\text{Cl}^-$  even at  $\text{Cl}^-/\text{ClO}_4^-$  ratio = 0.01, compared to the  $K_d$  values in the absence of  $\text{Cl}^-$  (Figure 1). On the other hand, the  $K_d$  values at  $\text{pH}_c = 7-9$  slightly increased with  $\text{Cl}^-/\text{ClO}_4^-$  ratio up to 1 and did not change any more at  $\text{Cl}^-/\text{ClO}_4^-$  ratio  $\geq 10$ .

The Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solutions at  $I = 4$  M at  $\text{Cl}^-/\text{ClO}_4^-$  ratio = 0.01, 0.1, 1, 10, 100 and infinity are shown in Figures S-2-S-7, respectively. It was found that the pH region of  $\text{PdCl}_4^{2-}$  dominance expanded with  $\text{Cl}^-/\text{ClO}_4^-$  ratio, while that of  $\text{Pd(OH)}_2$  dominance shrank. Figure 2 suggests that the formation of  $\text{PdCl}_4^{2-}$  complex strongly suppressed the Pd sorption, especially the surface complexation  $\equiv\text{S-OH} + \text{Pd}^{2+} \longleftrightarrow \equiv\text{S-OPd}^+ + \text{H}^+$ , on MX-80 at  $\text{pH}_c < 7$ .

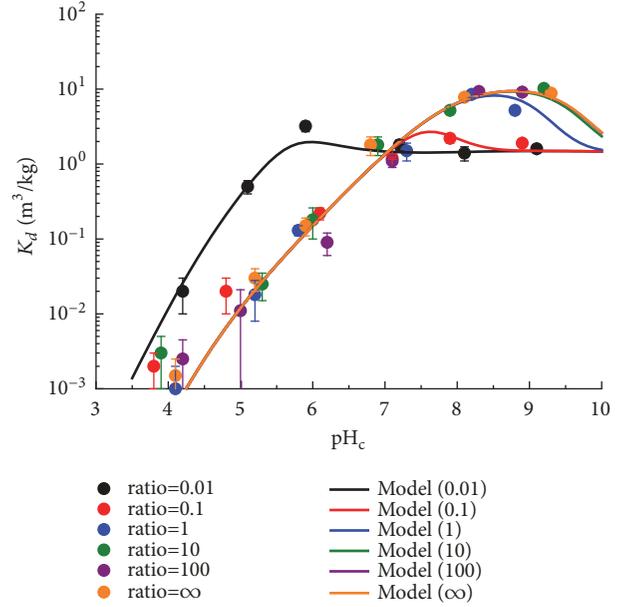


FIGURE 2:  $\text{pH}_c$  and  $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio dependence of  $K_d$  in Na-Ca-Cl- $\text{ClO}_4$  solutions at  $I = 4$  M. Plots are the experimentally measured  $K_d$  values. The solid lines are the 2SPNE SC/CE model calculation results. The error bars represent the standard deviation of triplicate measurements.

The fitting results of the 2SPNE SC/CE model to the experimentally measured  $K_d$  values using three binary and four ternary surface complexations and cation exchange reaction are also drawn in Figure 2. It was shown that the  $\text{pH}_c$  dependence of  $K_d$  values in the wide range of  $\text{Cl}^-/\text{ClO}_4^-$  ratio could be also quantitatively fitted by the 2SPNE SC/CE model. It was found that the fitting results could be obtained only with three binary and one ternary surface complexations as we studied in Na-Ca-Cl solutions [8]. Namely, only the ternary surface complexation,  $\equiv\text{S-OH} + \text{Pd}^{2+} + 4\text{Cl}^- \longleftrightarrow \equiv\text{S-OPdCl}_4^{3-} + \text{H}^+$ , among the four complexations considered in the modelling contributed to the Pd sorption on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solutions. The contribution of other three ternary surface complexations was negligible. The surface complexation constant for this ternary sorption reaction was estimated as  $13.3 \pm 0.3$ . This value is consistent with  $13.05 \pm 0.2$  which was previously estimated [8].

The pH dependence of surface complexation and cation exchange reaction at  $\text{Cl}^-/\text{ClO}_4^-$  ratio = 0, 0.01, 0.1, 1, 10, 100 and infinity is shown in Figures S-8-S-14, respectively. Three binary surface complexations dominated the sorption at  $\text{Cl}^-/\text{ClO}_4^-$  ratio = 0. In the presence of  $\text{Cl}^-$ , the surface complexation,  $\equiv\text{S-OH} + \text{Pd}^{2+} \longleftrightarrow \equiv\text{S-OPd}^+ + \text{H}^+$ , was drastically suppressed even at  $\text{Cl}^-/\text{ClO}_4^-$  ratio = 0.01. As the  $\text{Cl}^-/\text{ClO}_4^-$  ratio increased, the contribution of surface complexations,  $\equiv\text{S-OH} + \text{Pd}^{2+} \longleftrightarrow \equiv\text{S-OPd}^+ + \text{H}^+$  and  $\equiv\text{S-OH} + \text{Pd}^{2+} + \text{H}_2\text{O} \longleftrightarrow \equiv\text{S-OPdOH} + 2\text{H}^+$ , became small and was finally zero. This led to the decrease in the measured  $K_d$  values at  $\text{pH}_c < 7$ . On the other hand, the contribution of ternary surface complexation,  $\equiv\text{S-OH} + \text{Pd}^{2+} + 4\text{Cl}^- \longleftrightarrow$

$\equiv\text{S-OPdCl}_4^{3-} + \text{H}^+$ , became large at  $\text{Cl}^-/\text{ClO}_4^-$  ratio = 0.1 and was significant and dominated the sorption at  $\text{Cl}^-/\text{ClO}_4^-$  ratio  $\geq 1$ . The increase in the measured  $K_d$  values at  $\text{pH}_c$  7–9 was attributed to this ternary surface complexation.

The complexation constant for  $\text{Pd}^{2+} + 3\text{Cl}^- + \text{H}_2\text{O} - \text{H}^+ \longleftrightarrow \text{PdCl}_3\text{OH}^{2-}$  is compiled in the JAEA TDB (Table 1). Although  $\text{PdCl}_3\text{OH}^{2-}$  did not appear in Na-Ca-Cl- $\text{ClO}_4$  solutions at  $I = 4$  M (Figures S-1–S-7), the 2SPNE SC/CE model including the ternary surface complexation  $\equiv\text{S-OH} + \text{Pd}^{2+} + 3\text{Cl}^- + \text{H}_2\text{O} \longleftrightarrow \equiv\text{S-OPdCl}_3\text{OH}^{3-} + 2\text{H}^+$  was also applied to the measured  $K_d$  values to make sure of the contribution of ternary surface complexation in the Pd sorption on MX-80. However, it was found that this ternary surface complexation could be negligible.

#### 4. Conclusions

The  $K_d$  values of Pd for MX-80 were systematically measured as a function of  $\text{pH}_c$ ,  $I$ , and  $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio in Na-Ca- $\text{ClO}_4$  ( $3 \leq \text{pH}_c \leq 9$  and  $0.1 \text{ M} \leq I \leq 4 \text{ M}$ ) and Na-Ca-Cl- $\text{ClO}_4$  ( $3 \leq \text{pH}_c \leq 9$  and  $0 \leq \text{Cl}^-/\text{ClO}_4^-$  ratio  $\leq \infty$ ;  $I = 4$  M) solutions.

It was found that the  $\text{pH}_c$ ,  $I$ , and  $\text{Cl}^-/\text{ClO}_4^-$  ratio dependence of  $K_d$  values was quantitatively fitted by the 2SPNE SC/CE model. The model calculation indicated that, in the presence of  $\text{Cl}^-$ , the contributions of binary surface complexations were suppressed while that of the ternary surface complexation dominated the sorption as the  $\text{Cl}^-/\text{ClO}_4^-$  ratio increased.

It was also found that the  $\text{pH}_c$  dependence of  $K_d$  values for MX-80 in the Na-Ca-Cl- $\text{ClO}_4$  solutions at  $I = 4$  M could be simulated by considering only one ternary surface complexation reaction ( $\equiv\text{S-OH} + \text{Pd}^{2+} + 4\text{Cl}^- \longleftrightarrow \equiv\text{S-OPdCl}_4^{3-} + \text{H}^+$ ) besides the binary surface complexation reactions in all range of  $\text{Cl}^-/\text{ClO}_4^-$  ratio (0– $\infty$ ).

#### Data Availability

The sorption data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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#### Supplementary Materials

Figure S-1: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 0) at  $I = 4$  M. Figure S-2: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 0.01) at  $I = 4$  M. Figure S-3: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 0.1) at  $I = 4$  M. Figure S-4: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 1) at  $I = 4$  M. Figure S-5: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 10) at  $I = 4$  M. Figure S-6: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 100) at  $I = 4$  M. Figure S-7: Pd speciation in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio =  $\infty$ ) at  $I = 4$  M. Figure S-8: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 0) at  $I = 4$  M. Figure S-9: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 0.01) at  $I = 4$  M. Figure S-10: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 0.1) at  $I = 4$  M. Figure S-11: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 1) at  $I = 4$  M. Figure S-12: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 10) at  $I = 4$  M. Figure S-13: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio = 100) at  $I = 4$  M. Figure S-14: Pd sorption reaction on MX-80 in Na-Ca-Cl- $\text{ClO}_4$  solution ( $\text{Cl}^-/\text{ClO}_4^-$  molar concentration ratio =  $\infty$ ) at  $I = 4$  M. (*Supplementary Materials*)

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