Invited Paper

Sorption of Np(IV) on MX-80 in Ca-Na-Cl Type Reference Water of Crystalline Rock

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The pH dependence of sorption distribution coefficient ($K_d$) of Np(IV) on MX-80 in Ca-Na-Cl type solution with the ionic strength of 0.3 M, which was similar to one of the reference groundwaters in crystalline rock, was experimentally investigated under the reducing conditions. The overall trend of $K_d$ on MX-80 was independent of pH at 5 ≤ pH ≤ 10 but increased as pH increased at pH ≤ 5. The 2-site protolysis non-electrostatic surface complexation and cation exchange model was applied to the experimentally measured pH dependence of $K_d$ and the optimized surface complexation constants of Np(IV) sorption on MX-80 were estimated. The values of surface complexation constants in this work agreed relatively well with those in the Na-Ca-Cl solution previously evaluated, suggesting that compared to Na⁺, the competition of Ca²⁺ with Np(IV) for surface complexation on MX-80 was not much strong in Ca-Na-Cl solution. The sorption model well predicted the pH dependence of $K_d$ values but slightly overestimated the sorption at the low pH region.

Keywords: Np(IV), MX-80, Sorption, pH dependence, Sorption distribution coefficient, 2 SPNE SC/CE model

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1. Introduction

The Nuclear Waste Management Organization (NWMO) has a responsibility to implement the Adaptive Phased Management (APM) which was approved by the Canadian federal government for a long-term management plan of used nuclear fuel in Canada [1]. Under the APM plan, used nuclear fuel will be placed within a deep geological repository (DGR) in a suitable rock formation. Crystalline rocks in Canada are being as potential host rocks for a DGR [1].

The NWMO proposes a reference groundwater composition to represent the saline groundwater conditions at the depth of the hypothetical repository (CR-10) [1]. CR-10 is Ca-Na-Cl type water with an ionic strength ($I$) of about 0.26 M and is under reducing conditions. It was defined by groundwater chemistry at this depth in the crystalline rock under reducing conditions in Canada.

Sorption of radionuclides, including actinides and their daughter products 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 behavior of radionuclides not only on host rocks but also on engineered barrier materials such as MX-80 bentonite which is one of the candidate buffer materials in the DGR project.

$^{237}$Np is one of the key elements to dominate a long-term radiological risk of used nuclear fuel and high-level radioactive waste disposal. Np exists as Np(IV) under reducing conditions. For Np(IV) sorption on bentonite and other clay minerals, some investigations have been carried out [7-14]. However, only three papers studied the Np(IV) sorption at $I > 0.1$ M. Kitamura and Tomura [11] and Ashida et al. [12] studied the effect of carbonate ions on sorption of Np(IV) on smectite at $I = 1.0$ M. Nagasaki et al. [14] studied the sorption of Np(IV) on illite, shale and MX-80 in Na-Ca-Cl type solution with $I = 0.1$ M to 6 M, and showed that $K_d$ (sorption distribution coefficient [15]) values for illite, shale and MX-80 were independent of the ionic strength at $I \geq 1$ M, but dependent on it at $0.1$ M $\leq I \leq 1$ M. However, there is no $K_d$ data of Np(IV) on bentonite like MX-80 in Ca-Na-Cl type solution with $I > 0.1$ M such as CR-10. Both Ca-Na-Cl and Na-Ca-Cl type solutions contain Ca, Na and Cl, but in the former, Ca is richer than Na and, in the latter, vice versa. Although the ionic strength is the same as each other, the sorption competition between Np(IV) and Ca$^{2+}$ may be enhanced in Ca-Na-Cl type solution.

Sorption modelling improves the understanding of sorption processes. The 2-site protolysis non-electrostatic surface complexation and cation exchange model (2 SPNE SC/CE model) has been successfully applied to simulate the sorption of tetravalent actinides such as Th(IV), Np(IV), and Pu(IV) on illite and montmorillonite [16, 17].

In this study, the sorption of Np(IV) on MX-80 in Ca-Na-Cl type solution with $I = 0.3$ M was studied as a function of pH, and the 2 SPNE SC/CE model was applied and the surface complexation constants were estimated and compared to the constants obtained from the Np(IV) sorption in Na-Ca-Cl type solution on MX-80.

2. Experimental

2.1 Materials

All chemicals used were reagent grade and supplied from Fisher Scientific. Deionized water from a Milli-Q Direct 8 was used after being contacted with 10% H$_2$ + 90% N$_2$ gas in the presence of iron (electrolytic powder) for three days. After the iron powder was removed by centrifugation, $1 \times 10^{-3}$ M Na$_2$S$_2$O$_4$ was added to the deionized water, and that was then stored in a glove box (GB). Eh value of the water was confirmed to be stable in the range of $-250$ mV to $-170$ mV (vs. SHE) for 30 days. Just before use, the water was treated with 10% H$_2$ + 90% N$_2$ gas again for several hours without iron powder addition. The concentration of Fe in the solution was smaller than the detection limit of
ICP-MS (Agilent ICP-MS 8800). Hence, it was considered that the iron dissolved in the water did not affect the sorption behaviour of Np(IV).

The solid used was MX-80. The specific surface area was 26.2 m²·Rg⁻¹ [13]. Other information including their mineralogy is described elsewhere [2, 13, 15]. A Precise Controlled Atmosphere GB supplied by Labconco was filled with N₂ gas (> 99.999 %) to exclude CO₂, and the N₂ gas was left running through the GB. The concentration of O₂ in the running N₂ gas was confirmed to be less than 2 ppm by an oxygen sensor.

The ²³⁷Np solution was purchased from Stuart Hunt & Associates Ltd. Np(IV) solution was prepared using the established procedures [18-21]. The tetravalent oxidation state of the prepared Np solution was confirmed by UV-VIS spectroscopy (Agilent 8453 UV-Vis spectrometer) and 0.1 M TTA-xylene extraction. The oxidation of Np(IV) to Np(V) was also confirmed to be negligibly small at least for 30 days after the Np(IV) stock solution was prepared. Np(IV) stock solution was prepared for use just before sorption experiments. The concentration of the Np(IV) stock solution was 1.0×10⁻⁷ M in 0.01 M HClO₄ solution.

2.2 Sorption experiment

The CR-10 reference groundwater contains 1,900 mg·L⁻¹ of Na and 2,130 mg·L⁻¹ of Ca (Na/Ca molar ratio = 0.64) [1]. Therefore, in this study, Ca-Na-Cl solutions with Na/Ca molar ratio = 0.64 and I = 0.3 M was prepared by using NaCl and CaCl₂·2H₂O.

When I is higher than 0.1 M, the molar H⁺ concentrations (pH = −log cH⁺) or the molal H⁺ concentration (pH = −log mH⁺) should be used instead of the pH values indicated on the pH meter (pHwater). However, since the difference between pH and pHwater was confirmed to be small at I = 0.3 M, the pH values indicated on the pH meter were used in this study.

All sorption experiments were carried out at 25°C in triplicate. The basic procedures of sorption experiments were the same as those we used in the sorption experiments of Np(IV) in Na-Ca-Cl solutions [14]. In this study, the sorption results were expressed as

\[ K_d = \frac{(C_0 - C_e)}{C_e} \frac{V}{W} \]

where \( C_0 \) (M) is the initial concentration of Np(IV) in the liquid phase, \( C_e \) [M] the equilibrium concentration of Np(IV) in the liquid phase, \( V \) [m³] the volume of the liquid phase, and \( W \) [kg] the mass of the solid phase.

In this study, assuming that the time required for sorption equilibrium was the same as that in the Na-Ca-Cl solution case (3~7 days) [14], the sorption test period was set 14 days. The pH dependence of the \( K_d \) value of Np(IV) sorption for MX-80 in Ca-Na-Cl solutions (I = 0.3 M) was measured. During the solid/liquid (MX-80/Ca-Na-Cl solutions (I = 0.3 M)) pre-equilibration period of 3 to 4 days, 10% H₂ + 90% N₂ gas passed through the solid/liquid mixture for 30 minutes once a day. The solid/liquid mixture was then removed from the GB, and the liquid and solid were separated by centrifugation for 30 minutes at 12,000 rpm. pH and Eh of the solution were measured in the GB to confirm the low Eh values (smaller than −100 mV (vs. SHE)).

Ca-Na-Cl solution (I = 0.3 M) was added again to the pre-equilibrated solid in the polycarbonate reaction vessel in the GB. A portion of the Np(IV) stock solution was spiked into the reaction vessel in the GB. The pH of the solution was adjusted to the pre-decided values between about 3 and about 10 by the addition of 0.01 M HCl, 0.1 M HCl, 0.1 M NaOH, or 0.01 M NaOH solution in the GB. The reaction vessels were tightly sealed in the GB, transferred from the GB to an incubator at 25°C (Infors HT Ecotron), and were gently shaken for a pre-decided period of time. The pH of the solution was measured once a day in the GB and re-adjusted to the original pH value if the pH changed by more than ± 0.3 from the original value. Then, the reaction vessels were returned to the incubator. The ini-
Initial Np(IV) concentrations were $1.0 \times 10^{-11}$ M. The solid/liquid ratio was 0.2 g·L$^{-1}$ ($2 \times 10^{-4}$ kg·m$^{-3}$). The liquid was separated from the solid by centrifugation (Nalgene Oak Ridge tubes for 120 minutes at 18,000 rpm at 25°C). The concentration of Np in the liquid was measured by ICP-MS.

### 3. Results and discussion

The pH dependence of $K_d$ value of Np(IV) sorption in Ca-Na-Cl solution is illustrated in Fig. 1. The details of Np(IV) concentration in liquid at sorption equilibrium and the $K_d$ values are summarized in Supplementary Material. Fig. 1 shows that the $K_d$ values of Np(IV) for MX-80 increased with pH from 3 to 5 and were not dependent on pH between 5 and 10. This trend was identical to that measured in Na-Ca-Cl solution at $I = 0.1$ M to 6 M. The absolute values of $K_d$ in Ca-Na-Cl were also close those in Na-Ca-Cl solution. These suggest that the trend of Np(IV) sorption behavior on MX-80 toward pH is similar both in Ca-Na-Cl solution ($I = 0.3$ M) and in Na-Ca-Cl solution ($0.1 \leq I \leq 6$ M).

The 2 SPNE SC/CE model was applied to simulate the pH dependence of $K_d$ values of Np(IV) on MX-80. The specific ion interaction theory (SIT [22]) was used to calculate the activity coefficients of aqueous species. Thermodynamic constants for Np(IV) aqueous species were taken from the NEA thermodynamic database [23]. When the SIT parameters required for the calculation were not reported in the NEA thermodynamic database, the parameters in the SIT database provided with PHREEQC [24] were used. The surface complexation constants estimated for Np(IV) on MX-80 in Na-Ca-Cl solution were used as initial values for fitting. Other parameters for fitting such as protolysis constants were cited from the values used by Bradbury and Baeyens [16, 17] because Np(IV) sorption on MX-80 in Na-Ca-Cl solution was successfully simulated by using those values [14].

The fitting result was also shown in Fig. 1. It was found

**Table 1. Surface complexation constants for MX-80 estimated in this work and estimated in Na-Ca-Cl solution at $I = 0.1$ to 4 M [14]**

| Surface species | log $K$ ($I = 0$ M) on strong site in Na-Ca-Cl solution (this work) | log $K$ ($I = 0$ M) on strong site in Na-Ca-Cl solution [14] |
|----------------|-------------------------------------------------|-------------------------------------------------|
| $\equiv S\text{ONp}^{3+}$ | nd | nd |
| $\equiv S\text{ONpOH}^{+}$ | $12 \pm 0.3$ | $10 \pm 0.3$ |
| $\equiv S\text{ONp(OH)}_{2}^{+}$ | $5.8 \pm 0.3$ | $5.7 \pm 0.2$ |
| $\equiv S\text{ONp(OH)}_{3}^{n}$ | $0.15 \pm 0.2$ | $0.10 \pm 0.1$ |
| $\equiv S\text{ONp(OH)}_{4}^{-}$ | $-7.6 \pm 0.4$ | $-7.8 \pm 0.3$ |

*"nd" referes to value that could not be determined.*

Fig. 1. pH dependence of the $K_d$ values in Ca-Na-Cl solution ($I = 0.3$ M). Solid line is the simulation results using 2 SPNE SC/CE model.
that the fitting result was quantitatively consistent with the experimental $K_d$ values at pH ≥ 5, but slightly overestimated the experimental data at pH ≤ 4. The surface complexation constants obtained are summarized in Table 1 together with those in Na-Ca-Cl solution with $I = 0.1$ to 4 M [14]. The values of surface complexation constants in this work agreed relatively well with those in the Na-Ca-Cl solution. This may suggest that compared to Na$^+$, the competition of Ca$^{2+}$ with Np(IV) for surface complexation on MX-80 was not much strong in the Ca-Na-Cl solution.

In this estimation, we neglected the surface complexation reactions on weak sites, because the concentration of Np(IV) was very small and the reactions "≡ S$^s$OH + Np$^{4+}$ ↔ ≡ S$^s$ONp$^{3+}$ + H$^+$" and "≡ S$^w$OH + Np$^{4+}$ ↔ ≡ S$^w$ONp$^{3+}$ + H$^+$" did not contribute to the simulation practically. The sorption capacity of the strong site was set 2.0×10$^{-3}$ mol·kg$^{-1}$ for Na-montmorillonite [16]. This meant 4.0×10$^{-7}$ mol on 0.2 g MX-80. Compared to the initial Np(IV) concentration (1×10$^{-11}$ M), it was much large. In such a situation, the contribution of weak sites frequently could be negligible [16, 17]. The result in this study is consistent with the previous works [16, 17].

In the 2 SPNE SC/CE model, cation exchange reaction as well as surface complexation reaction is considered. From the simulation, it was found that the fitting result agreed well with the experimental results only by the surface complexation. However, as we pointed out in our previous studies [14, 25], a non-electrostatic model like the 2 SPNE SC/CE model may not be sufficient when electrostatic effects could play an important role in the cation exchange. This might be related to the overestimation of fitting at pH ≤ 4. This will be left for the challenge to be solved in the future.

The surface complexation constants for surface species "≡ S'ONp(OH)$_2$" and "≡ S'ONp(OH)$_3$" were well consistent with those estimated by the linear free energy relationship (LFER) [16, 17]. On the other hand, the surface complexation constant for surface species "≡ S'ONpOH$_2$" estimated in this work was larger than that by LFER. These consistency and discrepancy were also observed in the Na-Ca-Cl study [14]. Hence, this might suggest a necessity of review of hydrolysis constants of Np(IV). However, in this study, we used the parameter values such as protolysis constants which Bradbury and Baeyens reported. So, we need more investigations.

4. Conclusions

The $K_d$ values of Np(IV) on MX-80 in Ca-Na-Cl solution with $I = 0.3$ M were measured as a function of pH. The overall trend of pH dependence of Np(IV) on MX-80 was that the $K_d$ values increased with pH at pH ≤ 5 and were independent of pH at 5 ≤ pH ≤ 10. The trend and the $K_d$ values were almost the same as those observed in the Na-Ca-Cl solution with $I = 0.1$ to 6 M.
The pH dependence of $K_d$ values was simulated by the 2 SPNE SC/CE model well. The surface complexation constants for Np(IV) sorption on MX-80 were estimated by fitting the 2 SPNE SC/CE.

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Appendix

In this study, the triplicate measurements were conducted at each pH. $K_d$ value was determined by average of three measurements. Error of $K_d$ was the maximum deviation between measurement values and average value. Initial concentration of Np(IV) was $1.0 \times 10^{-11}$ M.

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