Sorption Properties of Np on Shale, Illite and Bentonite Under Saline, Oxidizing and Reducing Conditions

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ABSTRACT

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Abstract

Sorption experimental measurements of Np(V) and Np(IV) on illite (Silver Hill, USA), Queenston shale and bentonite (MX-80) under oxidizing and reducing conditions were carried out by batch tests in three types of solutions: (i) SR-270-PW reference brine solution with an ionic strength (*I*) of 6.0 M; (ii) $NaCl-CaCl_2$ aqueous solutions with different ionic strength up to a maximum of 4.6 M; and (iii) $NaCl-CaCl_2-NaClO_4$ solution with *I* = 6 M.

The Np(V) sorption kinetics and the effect of the solid/liquid ratio on Np(V) sorption were investigated under oxidizing conditions. The K_d (sorption distribution coefficient) values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 were determined in the SR-270-PW reference brine and the $NaCl-CaCl_2$ solution with *I* = 4.6 M. The effects of pH_c, ionic strength, Na/Ca ratio and Np(V) initial concentration on K_d value of Np(V) on illite (Silver Hill), Queenston shale and MX-80 were also studied in $NaCl-CaCl_2$ solutions.

The sorption equilibrium of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine and $NaCl-CaCl_2$ solutions was achieved in 3 days and was independent of the studied solution compositions, solid types and the solid/liquid ratios used in this study. It was found that the K_d value of Np(V) increases with increasing pH_c and Na/Ca ratio in $NaCl-CaCl_2$ solutions, and Np(V) sorption is not dependent on the ionic strength of $NaCl-CaCl_2$ solutions when the ionic strength is over 1 M. In the SR-270-PW reference brine and $NaCl-CaCl_2$ (*I* = 4.6 M) solutions, the measured isotherms were found to be linear on log-log plots with slopes of approximately 1 at a Np(V) equilibrium concentration in the liquid less than 2×10^{-6} mol/L .

Sorption of Np(IV) on illite (Silver Hill), Queenston shale, and MX-80 under reducing conditions was also studied in the SR-270-PW reference brine, $NaCl-CaCl_2$ ($0.1 \text{ M} \leq I \leq 4 \text{ M}$) and $NaCl-CaCl_2-NaClO_4$ (*I* = 6 M) solutions. The sorption kinetics was examined, and the dependence of Np(IV) sorption was investigated as a function of pH_c, ionic strength and Na/Ca ratio.

The sorption equilibrium of Np(IV) on illite (Silver Hill), Queenstone shale and MX-80 in $NaCl-CaCl_2-NaClO_4$ (*I* = 6 M) solution was achieved within 3 to 7 days. The K_d values of Np(IV) for illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine (*I* = 6 M) were determined as $(9.2\pm1.5)\times10^4$ cm^3/g, $(9.8\pm0.93)\times10^4$ cm^3/g, and $(1.3\pm0.31)\times10^5$ cm^3/g, respectively. The overall trends of Np(IV) K_d values on illite (Silver Hill), Queenstone shale and MX-80 were independent of pH_c at $5 \leq pH_c \leq 10$ and ionic strength at $0.5 \text{ M} \leq I \leq 6 \text{ M}$. The K_d values on these solids were all observed to increase with the Na/Ca ratio. The surface complexation constants of Np(IV) sorption on illite (Silver Hill) and MX-80 were estimated by the 2 SPNE SC/CE model. The sorption model well predicted the pH_c dependence of K_d, but could not completely describe the ionic strength dependence (i.e. the decrease in the K_d values from 0.1 M to 0.5 M).

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1. INTRODUCTION

Sedimentary rocks in Canada are being considered as potential host rocks for a deep geologic repository (DGR) for radioactive waste. Some of these rocks in Canada (for example, Southern Ontario, Michigan Basin) contain Na-Ca-Cl brine solution with total dissolved solids (TDS) concentration up to 350 g/L (Hobbs et al. 2011).

Sorption of radionuclides, including actinides and their daughter products onto host rock 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 (Geckeis et al. 2013, Zavarin et al. 2012, Chapman et al. 2012, Vilks 2011, National Academy of Science 1983). Therefore, it is important to elucidate the sorption behaviours of radionuclides both on host rocks and on engineered barrier materials such as MX-80 bentonite.

The Nuclear Waste Management Organization (NWMO) has been developing a sorption database of sorption coefficient values for Canadian sedimentary rocks (shale and limestone) and bentonite (Vilks 2011). The principal objective of this study is to investigate the sorption behavior of Np(V) and Np(IV) in highly saline solutions. The sorption data obtained from this study will be used to update the NWMO's database of sorption values for Canadian sedimentary rocks and bentonite in highly saline solutions.

Under anaerobic conditions, such as in the deep groundwater systems, tetravalent Np(IV) (e.g. Np^{4+}) is the dominant oxidation state. Under aerobic conditions, such as in the shallow groundwaters, pentavalent Np(V) (e.g. NpO_2^+) is the dominant oxidation state. In general, the solubility of Np(IV) is very low (e.g. approximately 10^{-10} mol/L in a diluted neutral pH solution (Neck and Kim 2001)) and its interaction with bentonite and rocks is strong (Geckeis et al. 2013, Choppin 2006, Japan Atomic Energy Agency 2000). On the other hand, Np(V) is more soluble (e.g. the solubility of Np(V) is approximately 10^{-4} mol/L in a diluted neutral pH solution (Itagaki et al. 1992)) and has moderate interaction with bentonite and rocks (Geckeis et al. 2013, Choppin 2006, Japan Atomic Energy Agency 2000, Nagasaki et al. 1998a). This indicates that due to the different chemical behaviors of Np under oxidizing and reducing conditions, the sorption of Np must be studied by strictly controlling its oxidation state. Marsac et al. (2015) found the partial reduction of Np(V) to Np(IV) on the illite surface although the measurement of redox potentials suggests the predominance of Np(V) in the aqueous phase. This indicates that the redox reaction of Np on the solid/liquid interface is critical in the sorption behavior of Np for some minerals.

Recently, several extensive reviews on the aqueous chemistry of actinides have been published (Geckeis et al. 2013, Altmaier et al. 2013, Knope and Soderholm 2013, Walther and Denecke 2013, Yoshida et al. 2010, Choppin and Jensen 2010, Wolfgang and Neu 2010). Many studies have been conducted to investigate the influence of salinity on the sorption of radionuclides, mainly in the ionic strength range from dilute to saline waters (Marsac et al. 2015, Geckeis et al. 2013, Kar et al. 2012, Zhu et al. 2012, Tertre et al. 2011, Amayri et al. 2011, Schmeide and Bernhard 2010, Schlegel and Descostes 2009, Kitamura and Tomura 2003, Ashida et al. 1999, Nagasaki et al. 1999, Tanaka et al. 1998, Baston et al. 1997). Some sorption experiments have been carried out in solutions with higher ionic strengths (Bertetti 2016, Schnurr et al. 2015, Vilks and Miller 2014, U.S. Environmental Protection Agency 1998, Warnecke et al. 1994, Lieser and Muhlenweg 1988, Laul et al. 1985, Mucciardi et al. 1978). Recently, Bertetti (2016) investigated the sorption of Se, As, Tc, U, Pu and Np on Canadian sedimentary rocks (shale and limestone) and MX-80 in brine (ionic strength (*I*) = 6.0 mol/kgw (M)) and dilute (*I* = 0.01 M) solutions under low O_2, reducing conditions. It was discussed that with the exception of Np, it was likely that the experiments adequately evaluated the sorption of target valence state for the radioelements tested (Se(−II), As(III), Tc(IV), U(IV) and Pu(III/IV)) (Bertetti 2016). Further study is required to investigate the sorption behavior of Np(IV) in high ionic strength solutions under strictly controlled reducing conditions. There are no published sorption measurements of Np(V) on Canadian sedimentary rocks and MX-80 in brine solutions.

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) (Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005) has been successfully applied to simulate the sorption of tetravalent actinides such as Th(IV), Np(IV) and Pu(IV) on illite and montmorillonite (Marsac et al. 2017, Marsac et al. 2015, Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005). The simulated K_d values contributed to explaining and extrapolating the K_d values measured experimentally. To my knowledge, however, only Marsac et al. (2015) estimated the surface complexation constants for Np(IV) sorption on illite (Illite du Puy) and demonstrated the reliability of the 2 SPNE SC/CE model in prediction of K_d values in 0.1 M NaCl solution. It is important to confirm whether the surface complexation constants estimated by Marsac et al. (2015) are also appropriate for Np(IV) sorption on illite in the high ionic strength solutions. The surface complexation constants for Np(IV) sorption on illite and montmorillonite were estimated by the linear free energy relationship (LFER) (Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005). However, the reliability of such estimates has not yet been demonstrated by directly applying the 2 SPNE SC/CE model to the real sorption data of Np(IV) on these solids. LFER assumes a linear correlation between the surface complexation constants on amphoteric surface hydroxyl sorption sites and the hydrolysis constants for a list of metals. Using this relationship one can estimate surface complexation constants for metals for which there are no measured data based on their aqueous hydrolysis constants.

This report presents the results of a study of the sorption behaviors of Np(V) and Np(IV) on illite (Silver Hill), Queenston shale and MX-80 bentonite in brine solutions by batch sorption tests and sorption modelling.

The following batch sorption tests have been conducted for Np(V) under oxidizing conditions:

- measurement of the sorption distribution coefficient (K_d) of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine solution (Na-Ca-Cl type; *I* = 6 M; Bertetti 2016 (see Table 1)) and the NaCl-$CaCl_2$ solution (*I* = 4.6 M);
- investigation of the dependence of pH_c (= $-\log c_{H^+}$, the molar H^+ concentration) on Np(V) sorption at $6 \leq pH_c \leq 10$ (in NaCl-$CaCl_2$ solutions with *I* = 4.6 M);
- investigation of the dependence of Np(V) sorption on ionic strength at $0.10 \text{ M} \leq I \leq 4.6 \text{ M}$;
- investigation of the dependence of Np(V) sorption on Na/Ca molar concentration ratio (using pure $CaCl_2$ solution, NaCl-$CaCl_2$ solutions, and pure NaCl solution); and
- measurement of the Np(V) sorption isotherm with initial Np(V) concentration ranging from 1.0×10^{-4} mol/L to 1.0×10^{-8} mol/L.

The following batch sorption tests and sorption modelling have been conducted for Np(IV) under reducing conditions:

- measurement of the K_d value of Np(IV) for illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine solution;
- investigation of the dependence of Np(IV) sorption on pH_c at $3 \le pH_c \le 10$ (in NaCl-$CaCl_2$ solutions with I = 0.1 M and 4 M, and NaCl-$CaCl_2$-$NaClO_4$ solution with I = 6 M);
- investigation of the dependence of Np(IV) sorption on ionic strength at 0.1 M ≤ I ≤ 6 M (NaCl-$CaCl_2$ solutions with I ≤ 4 M, and NaCl-$CaCl_2$-$NaClO_4$ solution with I = 6 M);
- investigation of the dependence of Np(IV) sorption on Na/Ca molar concentration ratio (using pure $CaCl_2$ solution, Ca-Na-Cl solutions, Na-Ca-Cl solutions, and pure NaCl solution); and
- sorption modelling of the pH_c and ion strength dependences of Np(IV) K_d values on illite (Silver Hill) and MX-80 by 2 SPNE SC/CE model and estimation of the surface complexation constants for Np(IV) sorption on these solids.

2. EXPERIMENTAL METHODS

This section describes the experimental methods for performing Np(V) sorption under oxidizing conditions and Np(IV) sorption under reducing conditions. Sorption measurements were carried out by batch tests.

For Np(V) sorption tests, two types of solutions were used: (i) SR-270-PW reference brine solution (Eh = 300 – 370 mV vs. SHE); and (ii) aqueous solutions with a $NaCl\text{-}CaCl_2$ type composition ($NaCl\text{-}CaCl_2$ solutions; oxidizing conditions (Eh = 233 – 448 mV vs. SHE)). The $NaCl\text{-}CaCl_2$ solutions were used for sorption tests to investigate the effects of pH_c, ionic strength, and Na/Ca ratio on the K_d values of Np(V). Both types of solutions were used to measure the sorption isotherm of Np(V).

For Np(IV) sorption tests, three types of solutions were used: (i) SR-270-PW reference brine solution (Eh ≤ -80 mV); (ii) aqueous solutions with a $NaCl\text{-}CaCl_2$ type composition ($NaCl\text{-}CaCl_2$ solution; reducing conditions); and (iii) aqueous solutions with a $NaCl\text{-}CaCl_2\text{-}NaClO_4$ type composition ($NaCl\text{-}CaCl_2\text{-}NaClO_4$ solutions; reducing conditions (Eh = -200 – -100 mV vs. SHE)). The $NaCl\text{-}CaCl_2$ and $NaCl\text{-}CaCl_2\text{-}NaClO_4$ solutions were used for sorption tests to investigate the effects of pH_c, ionic strength and Na/Ca ratio on the K_d values of Np(IV). Because of solubility limits of NaCl and $CaCl_2{\bullet}2H_2O$ compounds which are used to make $NaCl\text{-}CaCl_2$ solutions, $NaCl\text{-}CaCl_2$ solutions were used for the experiments at $I \leq 4$ M and $NaCl\text{-}CaCl_2\text{-}NaClO_4$ solution was used for the experiments at $I = 6$ M.

Sorption results were expressed as K_d (cm^3/g), which are calculated as follows:

$$K_d = \frac{(C_0 - C_e)}{C_e}\frac{V}{W} \qquad (1)$$

where C_0 is the molar concentration of Np initially added to the liquid phase (mol/L), C_e the equilibrium molar concentration of Np in the liquid phase (mol/L), V the volume of liquid phase (cm^3), and W the mass of solid phase (g).

The percent of sorbed Np is defined as

$$\text{Percent sorbed} = \frac{\text{Np removed from solution}}{\text{total Np available for sorption}} \qquad (2)$$

2.1 MATERIALS

The Np solution was purchased from Stuart Hunt & Associates Ltd. All chemicals used were reagent grade. Deionized water was prepared using a Milli-Q Ultra-pure water system to achieve a resistance of 18.2 MΩ/cm. Illite was purchased from the Clay Minerals Society, USA (Silver Hill, Montana, USA). Shale core sample was provided by the NWMO from the Queenston formation of the Michigan Basin at the Bruce nuclear site (sample DGR5-548.02). The mineralogy of the Queenston shale was described elsewhere (Bertetti 2016, Vilks and Miller 2014). Illite and shale samples were crushed using the super hard cylinder of Nichika, which is made of WC (tungsten carbide). Crushed illite and shale samples were sieved by stainless steal sieves, and the samples of size between 150 μm and 75 μm were collected and used for sorption tests. The MX-80 bentonite sample was supplied by the American Colloid Company, and was used as received. According to the American Colloid Company, the size of MX-80 is such that a maximum of 20% is retained on 40 mesh and a maximum of 12% passes through 200 mesh. The specific surface area of illite (Silver Hill), Queenston shale and MX-80 are 70 m^2/g, 10.3 m^2/g and 26.2 m^2/g, respectively (Bertetti 2016, Pivovarov 2006). Other information including their mineralogy are described elsewhere (Bertetti 2016, Nagasaki et al. 2016, Vilks 2011, Hower and Mowatt 1966).

2.2 PH$_c$ EVALUATION AND EH MEASUREMENT

The pH values indicated on the pH meter ($pH_{measure}$) in the solutions with $I \geq 0.1$ M should be considered as operational values (Fanghänel et al. 1996). The relationship between the operational $pH_{measure}$ and pH_c ($pH_c = -\log c_{H^+}$, the molar H^+ concentration) or pH_m ($pH_m = -\log m_{H^+}$, the molal H^+ concentration) were discussed in detail by Altmaier et al. (2008, 2003). In this study, a series of aqueous solutions with given salt compositions (Na^+, Ca^{2+} and Cl^-) were prepared, the pH value of each solution was measured by pH electrode ($pH_{measure}$), the pH_c value of the solution was also measured by titration (Metrohm Ti-Touch 916), and then the relationship between $pH_{measure}$ and pH_c in solutions was determined for a given salt composition of the aqueous phase. The $pH_{measure}$ values were then converted to the pH_c values.

The redox potentials in the solutions were measured using a Pt combined electrode with Ag/AgCl reference electrode (Fisher Scientific Accumet AB 150/Accumet ORP electrode), and converted into Eh versus SHE (Standard Hydrogen Electrode). As noted by Marsac et al. (2017), there was no reported ionic strength dependent correction to apply to the experimental Eh values. Therefore, in this work, any ionic strength dependent correction was not considered to the Eh values experimentally measured. A commercial redox buffer (+220 mV vs. SHE) was used for calibration. An equilibrium time of 15 to 20 minutes was allowed for all Eh measurements. According to the calibration results and Marsac et al. (2017) and Altmaier et al. (2010), the uncertainties of Eh measurements in this study were considered to be ±50 mV.

2.3 EXPERIMENTAL METHODS OF NP(V) SORPTION

2.3.1 Preparation of Np(V) Stock Solution

Purchased Np in HNO_3 solution may contain Np(IV), Np(V) and Np(VI). Pure Np(V) in $HClO_4$ solution was prepared by the following procedures (Kirishima et al. 2003, Kirishima 2014):

1) Np in HNO_3 solution was fed to an evaporation glass plate.
2) Np solution was evaporated and dried in the evaporation glass plate.
3) The Np dried in Step 2 was dissolved in a mixture of concentrated HNO_3 and concentrated $HClO_4$ solutions (HNO_3 : $HClO_4$ = 2 : 1 by volume ratio).
4) The Np solution prepared in Step 3 was evaporated and dried.
5) The dry Np prepared in Step 4 was dissolved in a mixture of concentrated HNO_3 and concentrated $HClO_4$ solutions (HNO_3 : $HClO_4$ = 2 : 1 by volume ratio).

6) The Np solution prepared in Step 5 was evaporated and dried.

7) The dry Np prepared in Step 6 was dissolved in 0.01 mol/L $HClO_4$ solution.

8) $HONH_3Cl$ was added to the Np solution prepared in Step 7 to stabilize the pentavalent oxidation state.

9) The oxidation state of Np prepared in Step 8 was confirmed to be pentavalent by the UV-VIS spectroscopic method.

10) The concentration of the Np(V) solution was adjusted to 1.0×10^{-3} mol/L.

The Np(V) stock solution was stored in a precise Controlled Atmosphere Glove Box supplied by Labconco which was filled with N_2 gas (> 99.999 %) (GB). Low concentration Np(V) solutions were prepared by diluting Np(V) stock solution with deionized water.

2.3.2 Preparation of Aqueous Solutions

2.3.2.1 SR-270-PW Reference Brine Solution

SR-270-PW reference brine solution used for sorption tests under oxidizing conditions was prepared by the following procedures, based on the chemical compounds developed by Bertetti (2016) (Table 1):

1) Each salt was weighed out, according to the given mass shown in Table 1.

2) Each salt was transferred to a 1 L volumetric flask.

3) Deionized water was added to the flask to bring the final volume to 1 L.

4) The flask was stirred, and the solution was transferred to a 1 (L) polypropylene bottle.

5) It was verified that the solution was stable and no precipitates/residues had settled to the bottom of the bottle.

6) pH_c and Eh of solution were measured.

7) The reference brine solution was decanted and centrifuged before use.

8) The reference brine solution was stored in a glove box filled with N_2 gas (99.999%).

Note that no attempt was made to achieve low Eh value for SR-270-PW reference brine solution as this is for Np(V) sorption tests under oxidization conditions.

Table 1: Preparation of 1 Liter of SR-270-PW Reference Brine Solution

Compound	Mass (g) of Compound
KCl	2.22×10^{1}
NaCl	1.27×10^{2}
$CaCl_2 \bullet 2H_2O$	1.17×10^{2}
$MgCl_2 \bullet 6H_2O$	6.86×10^{1}
$SrCl_2 \bullet 6H_2O$	3.65
$NaHCO_3$	1.51×10^{-1}
Na_2SO_4	6.51×10^{-1}
KBr	2.53

The prepared reference brine solution had an ionic strength of 6 M, and was decanted and centrifuged before use in order to ensure that no precipitates were present. The SR-270-PW reference brine solution was stored in the GB.

2.3.2.2 NaCl-$CaCl_2$ (I = 4.6 M) Solution

A NaCl-$CaCl_2$ solution was prepared using the same weights of NaCl and $CaCl_2 \bullet 2H_2O$ compounds as for the development of 1 L of SR-270-PW reference brine solution (Table 2), and was stored in the GB. The prepared NaCl-$CaCl_2$ solution has an ionic strength of 4.6 M and a Na/Ca molar concentration ratio of 2.7 which is the same as SR-270-PW reference brine solution. This established NaCl-$CaCl_2$ solution is referred to as NaCl-$CaCl_2$ (I = 4.6 M) solution in this report. No precipitate was observed in the prepared NaCl-$CaCl_2$ (I = 4.6 M) solution.

Table 2: Preparation of 1 Liter of NaCl-$CaCl_2$ (I = 4.6 M) Solution

Compound	Mass (g) of Compound
NaCl	1.27×10^{2}
$CaCl_2 \bullet 2H_2O$	1.17×10^{2}

2.3.2.3 NaCl-$CaCl_2$ Solutions with Various Ionic Strengths

Six NaCl-$CaCl_2$ solutions with the same Na/Ca molar concentration ratio of 2.7 were prepared to study the ionic strength effect on the Np(V) sorption. The weights of NaCl and $CaCl_2 \bullet 2H_2O$ for preparation of 1 L of the six NaCl-$CaCl_2$ solutions are shown in Table 3. These solutions were stored in the GB. No precipitate was observed in the prepared NaCl-$CaCl_2$ solutions.

Table 3: Preparation of 1 Liter of NaCl-$CaCl_2$ Solutions with Various Ionic Strengths

Ionic strength (M)	NaCl (g)	$CaCl_2 \bullet 2H_2O$ (g)
0.1	2.78	2.57
0.5	1.39×10^1	1.29×10^1
1	2.78×10^1	2.57×10^1
2	5.55×10^1	5.14×10^1
3	8.33×10^1	7.72×10^1
4	1.11×10^2	1.03×10^2

2.3.2.4 NaCl-$CaCl_2$ Solutions (*I* = 4.6 M) with Various Na/Ca Ratios

Four NaCl-$CaCl_2$ solutions with the constant ionic strength of 4.6 M but with different Na/Ca molar concentration ratios, as well as one pure $CaCl_2$ solution and one pure NaCl solution with the ionic strength of 4.6 M were prepared. The weights of NaCl and $CaCl_2 \bullet 2H_2O$ for preparation of 1 L of solutions are shown in Table 4. These solutions were stored in the GB. No precipitate was observed in the prepared NaCl-$CaCl_2$ solutions.

Table 4: Preparation of 1 Liter of $CaCl_2$ Solution, NaCl Solution and NaCl-$CaCl_2$Solutions (*I* = 4.6 M) with Various Na/Ca Ratio

Solution	Na/Ca ratio	NaCl (g)	$CaCl_2 \bullet 2H_2O$ (g)
$CaCl_2$	0	0	2.24×10^2
NaCl-$CaCl_2$	0.1	8.60	2.16×10^2
NaCl-$CaCl_2$	1	6.67×10^1	1.68×10^2
NaCl-$CaCl_2$	5	1.67×10^2	8.39×10^1
NaCl-$CaCl_2$	10	2.05×10^2	5.16×10^1
NaCl	∞	2.67×10^2	0

2.3.3 Np(V) Sorption Experimental Procedures

All sorption experiments were carried out in triplicate at 25 ^oC. During the Np(V) sorption tests, the GB was used to exclude CO_2. The pH_c and Eh (vs. SHE) values in each measurement are summarized in APPENDIX A.

2.3.3.1 Kinetics of Np(V) Sorption

Sorption kinetics of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine solution and the NaCl-$CaCl_2$ (I = 4.6 M) solution were measured to determine the sorption time to achieve the sorption equilibrium. The sorption kinetic measurements were conducted at two solid/liquid (*S*/*L*) ratios of 0.5 g/5.0 mL and 0.1 g/5.0 mL. The procedures for conducting sorption kinetics experiments are described below.

0.5 g or 0.1 g of illite (Silver Hill), Queenston shale or MX-80 was added into a polycarbonate reaction vessel. 5.0 mL of SR-270-PW reference brine or NaCl-$CaCl_2$ (I = 4.6 M) solution was added into the reaction vessel in the N_2 gas filled GB. The suspensions were kept in the GB for 3 to 4 days for pre-equilibration (the pH_c and Eh of solutions which contacted with illite (Silver Hill) (e.g. pH_c = 7.9, Eh = 390 mV), Queenston shale (e.g. pH_c = 8.3, Eh = 400 mV) and MX-80 (e.g. pH_c = 9.2, Eh = 380 mV) were found to become steady within 1 day in the preliminary test). The liquid was separated from the solid by centrifugation for 30 min at 12,000 rpm (Beckman Coulter, Allegra X-30R). The liquid was removed by a pipette in the GB. Then volume of SR-270-PW reference brine or the NaCl-$CaCl_2$ (I = 4.6 M) solution was added into the reaction vessel in the GB again. A portion of the Np(V) stock solution was spiked in the reaction vessel in the GB. The initial Np(V) concentration in the liquid of the reaction vessel was set to 1.0×10^{-5} mol/L. The final volume of the liquid was 5.0 mL. After one day, the pH_c and Eh of the liquid in the reaction vessel were measured in the GB. The reaction vessel was tightly sealed in the GB.

The reaction vessels were transferred to an incubator at 25 ^oC (Infors HT Ectron) and were shaken for pre-determined periods (1 day, 2 days, 3 days, 1 week and 3 weeks). After each pre-determined period, the liquid was separated from the solid by centrifugation for 30 minutes at 12000 rpm at 25 ^oC. The pH_c and Eh values of the liquid were measured in the GB.

An aliquot (1 mL) was sampled from the liquid phase of each reaction vessel. The concentration of Np in the aliquot was measured using a HPGe (High Purity Germanium) spectrometer. The concentration of Np sorbed on the solid was evaluated, and the percent sorption of Np(V) was calculated.

As discussed in Section 3.1.2, the sorption equilibrium for Np(V) on illite (Silver Hill), Queenston shale and MX-80 was found to be achieved within 3 days. Hence, the sorption reaction time for Np(V) was set to one week or longer in the subsequent sorption tests of Np(V).

2.3.3.2 Effect of the Solid/Liquid (*S*/*L*) Ratio on Np(V) Sorption

The *S*/*L* ratio dependence of the Np(V) sorption onto illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine and the NaCl-$CaCl_2$ (I = 4.6 M) solutions was measured at *S*/*L* ratios of 0.2 g/5.0 mL, 0.3 g/5.0 mL, and 0.4 g/5.0 mL. The sorption experimental procedures are the same as that described in Section 2.3.3.1.

As discussed in Section 3.1.3, the K_d values were independent of the *S*/*L* ratio as the *S/L* ratio was above 0.30 g/5.0 mL. Hence, the *S*/*L* ratio was set to 0.50 g/5.0 mL in the subsequent sorption tests of Np(V).

2.3.3.3 Np(V) K_d Measurement in SR-270-PW brine and NaCl-$CaCl_2$ Solutions

The K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine and the NaCl-$CaCl_2$ (I = 4.6 M) solutions were measured following the same experimental procedures as described in Section 2.3.3.1.

2.3.3.4 Effect of pH_c on Np(V) K_d Values

The pH_c dependence of the K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the NaCl-$CaCl_2$ (I = 4.6 M) solution was measured. The pH_c of the liquid in reaction vessels was adjusted to from 6 to 10 by addition of 0.01 mol/L $HClO_4$ or 0.01 mol/L NaOH solution in the GB. The pH_c of the liquid in the reaction vessel was measured twice per day, and the pH_c was readjusted to the original pH_c value by addition of 0.01 mol/L $HClO_4$ or 0.01 mol/L NaOH solution if pH_c of the liquid changed by more than ±0.3 unit. In this experiment, the sorption reaction time was set to two weeks. The sorption experimental procedures were the same as that described in Section 2.3.3.1.

2.3.3.5 Effect of the Ionic Strength on Np(V) K_d Values

The ionic strength dependence of the Np(V) K_d values on illite (Silver Hill), Queenston shale and MX-80 in the NaCl-$CaCl_2$ solutions with various ionic strengths was measured, following the same experimental procedures as that described in Section 2.3.3.1.

2.3.3.6 Effect of the Na/Ca Ratio on Np(V) K_d Values

The Na/Ca ratio dependence of the K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in NaCl-$CaCl_2$ solutions with various Na/Ca ratios was investigated, following the same experimental procedures as that described in Section 2.3.3.1.

2.3.3.7 Np(V) Sorption Isotherms

The sorption isotherms of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine and the NaCl-$CaCl_2$ (I = 4.6 M) solutions were measured. The initial Np(V) concentrations ranged from 1.0×10^{-8} mol/L to 1.0×10^{-4} mol/L. The concentration of Np(V) in the liquid phase after centrifugation was measured by Ge detector. The experimental procedures were the same as that described in Section 2.3.3.1.

2.4 EXPERIMENTAL METHODS OF NP(IV) SORPTION

2.4.1 Preparation of Np(IV) Stock Solution

Pure Np(IV) stock solution in 0.01 mol/L $HClO_4$ solution was prepared by the following procedures (Kirishima 2014, Kirishima et al. 2003, Inoue et al. 1980):

1) Np(V) in 0.1 mol/L $HClO_4$ solution was prepared, according to the procedures described in Section 2.3.1. However, 0.1 mol/L $HClO_4$ was used instead of 0.01 mol/L $HClO_4$ (step 7), and $HONH_3Cl$ was not added (step 8).
2) 10% H_2 + 90% N_2 gas was flown through the Np(V) solution with Pt(Pt) catalyst in the fume hood for 12 hours (6 hours in the first day and 6 hours in the second day).
3) The oxidation state of Np was spectroscopically measured. Confirm that Np was reduced to Np(IV) or Np(III)+Np(IV) and that Np(V) was not detected.
4) Contact the Np solution with air in the fume hood for 30 min to oxide any Np(III) to Np(IV).
5) The oxidation state of Np was spectroscopically measured. Confirm that Np(IV) was prepared.
6) Np(IV) was purified and Np(V) was removed by 0.1 mol/L TTA-xylene extraction and 0.01 mol/L $HClO_4$ back-extraction (Fujiwara and Kohara, 2008).
7) The Np(IV) solution was stored in a N_2 (99.999 %) filled glove box.
8) The concentration of the Np(IV) solution in 0.01 mol/L $HClO_4$ was adjusted to 1.0×10^{-7} mol/L. This was the Np(IV) stock solution used in this work.

The Np(IV) stock solution was stored in the GB. Low concentration Np(IV) solutions were prepared by diluting Np(IV) stock solution with deionized water with low Eh value prepared as described in Section 2.4.2.1.

2.4.2 Preparation of Aqueous Solutions

The experimental SR-270-PW reference brine and NaCl-$CaCl_2$ solutions were prepared using the same chemical components as prepared for Np(V) sorption tests. The chemical compounds were dissolved using deionized water with low Eh value.

2.4.2.1 Deionized Water with Low Eh Value

The deionized water with low Eh value, which was used for Np(IV) sorption experiments, was prepared by the following procedures:

1) 10% H_2 + 90% N_2 gas was flown through the distilled water supplied by Milli-Q water system for 3 days in the fume hood in the presence of electrolyte Fe powder.
2) After Fe powder was removed, the pH and Eh of solution were measured. The measured pH and Eh were summarized in APPENDIX (A.1) (i.e., pH of 7.1~7.3, Eh of -450 ~ -500 mV vs Ag/AgCl).

3) After 1 x 10^{-2} mol/L $Na_2S_2O_4$ was added, the pH and Eh were measured and the solution was stored in GB. The measured pH and Eh were summarized in APPENDIX (A.1) (i.e., pH of 6.1~6.5, Eh of -450 ~ -500 mV vs Ag/AgCl).

It was found that the deionized water with sufficiently low Eh values (-250 ~ -300 mV vs SHE) could be prepared, and that the low Eh was maintained for 30 days (See APPENDIX (A.1)). This low Eh deionized water was used to prepare all the experimental solutions for Np(IV) sorption tests.

2.4.2.2 SR-270-PW Reference Brine Solution

The chemical compounds used to prepare 1 L of SR-270-PW reference brine solution for Np(IV) sorption tests is described Table 1. Bertetti (2016) successfully established a recipe for the SR-270-PW reference brine solution with low Eh (smaller than –100 mV (vs. SHE)). In this work, the deionized water with low Eh value prepared in Section 2.4.2.1 was used to achieve the low Eh conditions, followed the established procedures (Bertetti 2016) to prepare the SR-270-PW reference brine solution, and stored it in the GB. The prepared SR-270-PW reference brine solution was decanted and centrifuged before use in order to ensure that no precipitates were present.

2.4.2.3 NaCl-$CaCl_2$ Solutions with Various Ionic Stength ($I \leq 4$ M)

The weights of NaCl and $CaCl_2{\bullet}2H_2O$ compounds used to make 1 L of NaCl-$CaCl_2$ solutions with different ionic strengths (I = 0.1, 0.5, 1, 2, 3, 4 M) were summarized in Table 3. NaCl-$CaCl_2$ solutions were prepared using the low Eh deionized water and stored in the GB. No precipitate was observed in the prepared NaCl-$CaCl_2$ solutions.

2.4.2.4 NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) Solution

An ionic strenght of 6 M NaCl-$CaCl_2$-$NaClO_4$ brine solution was prepared using NaCl, $CaCl_2{\bullet}2H_2O$ and $NaClO_4{\bullet}H_2O$ compounds. $NaClO_4{\bullet}H_2O$ compound was used because of the solubility limit of NaCl and $CaCl_2{\bullet}2H_2O$. The weights of NaCl, $CaCl_2{\bullet}2H_2O$ and $NaClO_4{\bullet}H_2O$ compounds for preparing 1 L NaCl-$CaCl_2$-$NaClO_4$ solution were summarized in Table 5. The NaCl-$CaCl_2$-$NaClO_4$ solution was prepared using the low Eh deionized water. The measured pH_c and Eh values were summarized in APPENDIX (A.1). NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) solution was stored in the GB. No precipitate was observed.

Table 5: Preparation of 1 Liter of NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) Solution

Compound	Mass (g) of Compound
NaCl	1.27×10^{2}
$CaCl_2{\bullet}2H_2O$	1.55×10^{2}
$NaClO_4{\bullet}H_2O$	9.30×10^{1}

2.4.2.5 NaCl-$CaCl_2$-$NaClO_4$ Solutions (I = 6 M) with Various Na/Ca Ratios

Four NaCl-$CaCl_2$-$NaClO_4$ solutions with the constant ionic strength of 6 M but with different Na/Ca molar concentration ratios, as well as one pure $CaCl_2$ solution and one pure NaCl solution with I = 6 M were prepared using the low Eh deionized water. The weights of NaCl, $CaCl_2$•$2H_2O$ and $NaClO_4$•H_2O compounds for preparation of 1 L of NaCl-$CaCl_2$-$NaClO_4$ solutions are shown in Table 6. These solutions were stored in the GB. No precipitate was observed in the prepared NaCl-$CaCl_2$-$NaClO_4$ solutions.

Table 6: Preparation of 1 Litre of NaCl-$CaCl_2$-$NaClO_4$ Solution (I = 6 M) with Various Na/Ca Ratio

Solutions	Na/Ca ratio	NaCl (g)	$CaCl_2$•$2H_2O$ (g)	$NaClO_4$•H_2O (g)
$CaCl_2$	0	0	2.94×10^2	0
NaCl-$CaCl_2$-$NaClO_4$	0.1	1.00×10^1	2.85×10^2	3.20
NaCl-$CaCl_2$-$NaClO_4$	1	8.50×10^1	2.20×10^2	6.30
NaCl-$CaCl_2$-$NaClO_4$	5	2.00×10^2	1.10×10^2	4.69×10^1
NaCl-$CaCl_2$-$NaClO_4$	1×10^1	2.50×10^2	6.78×10^1	4.71×10^1
NaCl	∞	2.63×10^2	0	2.09×10^2

2.4.3 Np(IV) Sorption Experimental Procedures

All Np(IV) sorption experiments were conducted under strictly controlled reducing conditions. All sorption experiments were carried out in triplicate at 25 ^oC. The GB was filled with N_2 gas (> 99.999 %) to exclude CO_2, and the N_2 gas was left running through the GB. The concentration of O_2 in the running N_2 gas was confirmed to be less than 2 ppm by oxygen sensor (Inert Technology). The pH_c and Eh (vs. SHE) values in each measurement are summarized in APPENDIX A.

The basic procedures of Np(IV) sorption experiments were the same as those described in Section 2.3.3 for Np(V) sorption. Only the differences in the experimental procedures and conditions from the previous Np(V) sorption tests are described here.

In the Np(IV) sorption tests, the liquid was separated from the solid by filtration (Vivaspin 6 (3000 MWCO) for 120 minutes at 10,000 rpm and 25 ^oC; Beckman Coulter, Allegra X-30R) or centrifugation (Nalgene Oak Ridge tubes for 120 minutes at 18,000 rpm and 25 ^oC). Nitsche (1991) described the procedures to minimize the effect of sorption of metals on filter. In this study, Nitsche's procedure (Nitsche 1991) was applied in the filtration. The filter was pre-conditioned by washing it with Np(IV) solution with the same pH_c and Eh as those of the sample for solid/liquid separation. It was confirmed that the sorption of Np(IV) on the filter was negligible at I = 1 M to 6 M solutions, but 0% to 5% of Np(IV) added was found to be sorbed on the filter at I = 0.1 M and 0.5 M solutions. Therefore, the liquid was separated from the solid by centrifugation for I = 0.1 M and 0.5 M solution and by filtration for I = 1 M to 6 M solution systems. In the preliminary test, by comparing the solid/liquid separation by centrifugation with that by filtration, it is confirmed that the liquid can be successfully separated from the solid by centrifugation.

2.4.3.1 Kinetics of Np(IV) Sorption

Sorption kinetics of Np(IV) for illite (Silver Hill), shale, and MX-80 were measured in the NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) solution with the solid/liquid (S/L) ratio of 0.2 g/1 L and 0.1 g/1 L. The S/L ratio was set to 0.2 g/1 L or 0.1 g/1 L for all the sorption experiments.

During the solid/liquid pre-equilibration period of 3 to 4 days, 10% H_2 + 90% N_2 gas passed through the solid/liquid mixture for 30 minutes once a day. The solid/liquid mixture was then removed from the GB, the liquid and solid were separated by centrifugation for 30 minutes at 12,000 rpm. pH_c and Eh values of the solution were measured in the GB to confirm the low Eh values (smaller than –100 mV (vs. SHE)). The NaCl-$CaCl_2$-$NaClO_4$ solution (I = 6 M) was added to the pre-equilibrated solid in the polycarbonate reaction vessel in the GB and the reaction vessel was fully shaken. The solid/liquid mixture was then quantitatively transferred to different reaction vessels for the kinetics sorption experiments, and a portion of the Np(IV) stock solution was spiked into the reaction vessels in the GB. The initial Np(IV) concentrations in the vessels were 1.0×10^{-11} mol/L.

The reaction vessels were tightly sealed in the GB, transferred from the GB to an incubator at 25 ^{o}C (Infors HT Ectron), and were gently shaken for pre-determined period of time (1 day, 2 days, 3 days, 1 week, 2 weeks and 4 weeks). Once a day, all reaction vessels were transferred to the GB and 10% H_2 + 90% N_2 gas passed through the vessels for 30 minutes to 1 hour to keep the low Eh condition, and then returned to the incubator. After each pre-determined period of time, the pH_c and Eh of the solution were measured in the GB. A portion of the mixture (1 mL) was sampled from the reaction vessel, and the liquid was separated from the solid by filtration. The concentration of Np in the liquid was measured using the ICP-MS (Agilent ICP-MS 8800).

As discussed in the Results and Discussion (see Section 3.2.2), the sorption equilibrium of Np(IV) on illite (Silver Hill), shale, and MX-80 in the NaCl-$CaCl_2$-$NaClO_4$ solution (I = 6 M) was achieved within 3 to 7 days for both S/L ratios. In the previous study (Nagasaki et al. 1999), the sorption equilibrium of Np(IV) on bentonite in 0.01 mol/L $NaClO_4$ solution was confirmed to be achieved within 7 to 10 days. Hence, the sorption reaction time was set to 7 to 10 days in the subsequent experiments.

2.4.3.2 Np(IV) K_d Measurements in the SR-270-PW Reference Brine Solution

The K_d values of Np(IV) sorption on illite (Silver Hill), shale, and MX-80 in the SR-270-PW reference brine solution were measured. The initial Np(IV) concentration in the sorption samples was 1.0×10^{-11} mol/L. The S/L ratio was 0.1 g/1 L.

2.4.3.3 Effect of pH_c on Np(IV) K_d Values

The pH_c dependence of the K_d values of Np(IV) sorption on illite (Silver Hill), shale, and MX-80 in the NaCl-$CaCl_2$ solution (I = 4 M) and the NaCl-$CaCl_2$-$NaClO_4$ solution (I = 6 M) was measured. The pH_c of the solution was adjusted to the pre-determined values between $3 \leq pH_c$

≤ 10 by addition of 0.01 mol/L HCl, 0.1 mol/L HCl, 0.1 mol/L NaOH or 0.01 mol/L NaOH solution in the GB. For illite (Silver Hill) and MX-80, the sorption of Np(IV) at $I = 0.1$ M was also measured at $3 \leq \mathrm{pH_c} \leq 10$. The $\mathrm{pH_c}$ of the solution was measured once a day in the GB and re-adjusted to the original $\mathrm{pH_c}$ value if the $\mathrm{pH_c}$ changed by more than ±0.3 from the original value. The initial Np(IV) concentration in the mixtures was 1.0×10^{-11} mol/L. The S/L ratio was 0.2 g/1 L.

2.4.3.4 Effect of the Ionic Strength on Np(IV) K_d Values

The ionic strength dependence of the K_d values of Np(IV) sorption on illite, shale, and MX-80 in the NaCl-$CaCl_2$ solutions with $I = 0.1$ M to 4 M and in the NaCl-$CaCl_2$-$NaClO_4$ solution with $I =$ 6 M was investigated. During the sorption experiments, the $\mathrm{pH_c}$ of the solution was measured once a day, and adjusted to 8.0±0.3 (illite (Silver Hill)), 8.2±0.3 (Queenston shale) and 8.8±0.3 (MX-80) if $\mathrm{pH_c}$ changed. The values of 8.0, 8.2, and 8.8 were the equilibrium $\mathrm{pH_c}$ values of the illite-, shale- and MX 80-equilibrated NaCl-$CaCl_2$-$NaClO_4$ solutions ($I = 6$ M), respectively, which were measured in the preliminary tests. In this work, Np(IV) sorption tests were conducted at the ionic strength of 0.1, 0.5, 1, 2, 3, 4 and 6 M. The experiments at $I = 0.1$, 2, 3, 4 and 6 M were carried out twice to confirm the reproducibility. The initial Np(IV) concentration in the sorption samples was 1.0×10^{-11} mol/L. The S/L ratio was 0.1 g/1 L for MX-80 at $I = 0.1$ M and 0.5 M. It was 0.2 g/1 L for other experimental conditions.

2.4.3.5 Effect of the Na/Ca Ratio on Np(IV) K_d Values

The Na/Ca ratio dependence of the K_d values of Np(IV) on illite (Silver Hill), Queenston shale and MX-80 in NaCl-$CaCl_2$-$NaClO_4$ solution ($I = 6$ M) with various Na/Ca ratio was investigated. During the sorption experiments, the $\mathrm{pH_c}$ of solution was measured and adjusted to 8.0±0.3 (iilite (Silver Hill)), 8.2±0.3 (Queenston shale) and 8.8±0.3 (MX-80). The initial Np(IV) concentration in the sorption samples was 1.0×10^{-11} mol/L. The S/L ratio was 0.2 g/1 L.

3. RESULTS AND DISCUSSION

3.1 NP(V) SORPTION

3.1.1 Preparation of Np(V) Solution

The established procedures by Kirishima (2014) and Kirishima et al. (2003) were used to prepare Np(V) stock solution. The absorbance of the prepared Np(V) solution, which was diluted by 10 fold (i.e., 1.0 x 10^{-4} mol/L) with 0.01 mol/L $HClO_4$ solution, is illustrated in Figure 1. The intense absorption peak at 981 nm indicates the presence of Np(V) in the solution. There are no absorption peaks at 727 nm and 960 nm, indicating no Np(IV) is present in this solution. Using the molar absorption coefficient of Np(V) at 981 nm, ε = 385 L/mol⋅cm (Kirishima 2014), the concentration of Np(V) was calculated to be 1.0 x 10^{-4} M. It was considered that no Np(IV) or Np(VI) were present in the prepared Np(V) stock solution.

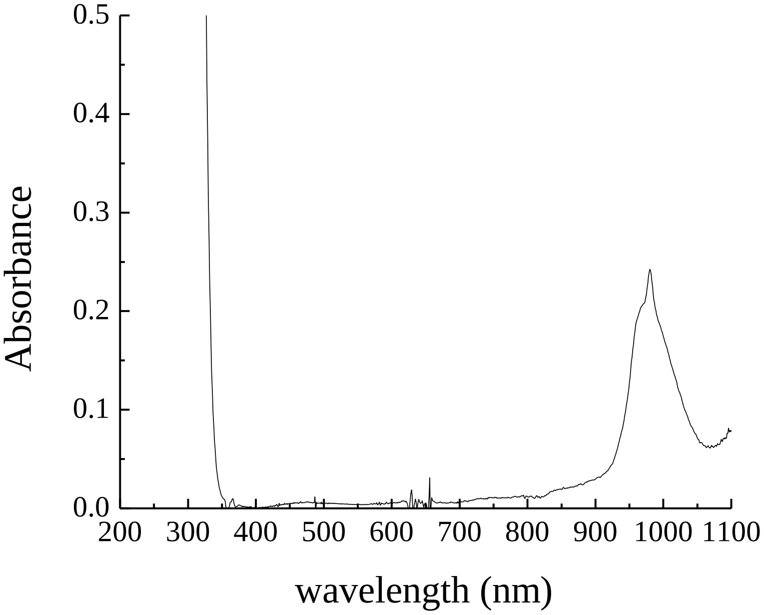


Figure 1: Absorbance of Np(V) in the Prepared Np(V) Solution

3.1.2 Kinetics of Np(V) Sorption

The percent sorption of Np(V) measured on illite (Silver Hill), Queenston shale and MX-80 at the *S/L* ratio of 0.1 g/5.0 mL and 0.5 g/5.0 mL in the SR-270-PW reference brine and the NaCl-$CaCl_2$ solution (*I* = 4.6 M) is shown in Figures 2 and 3, respectively. The values of pH_c, Eh and sorption percent at the sorption equilibrium are shown in APPENDIX (A.2). These results illustrate that sorption equilibrium for Np(V) on illite (Silver Hill), Queenston shale and MX-80 was achieved within 3 days. The time to attain the sorption equilibrium was independent of the studied solution compositions, solid types and the solid/liquid ratios.

Nagasaki et al. (1998b) measured the sorption kinetics of Np(V) on poorly crystallized ferric oxide at pH = 4 – 8 in 0.01 mol/L $NaNO_3$ solution and found that sorption equilibrium was achieved in 1 hour. Snow et al. (2013) found that no significant changes were observed in the Np(V) sorption on goethite at pH = 8 in 5 mmol/L NaCl and 0.7 mmol/L $NaHCO_3$ solution from 1 to 8 days, suggesting that the sorption equilibrium was achieved in 1 day.

On the other hand, Nagasaki and Tanaka (1998, 2000) measured the sorption kinetics of Np(V) on illite and Na-montmorillonite in 0.01 mol/L $NaNO_3$ solution at pH = 6, and found that more than 1 day was required to reach sorption equilibrium. This difference in the sorption equilibration times may be due to the difference in structures between clay minerals and Fe(III) oxides. The solid structures of illite (Silver Hill), Queenston shale and MX-80 and the brine conditions considered in the current study may contribute to the slightly longer time required to reach sorption equilibrium.

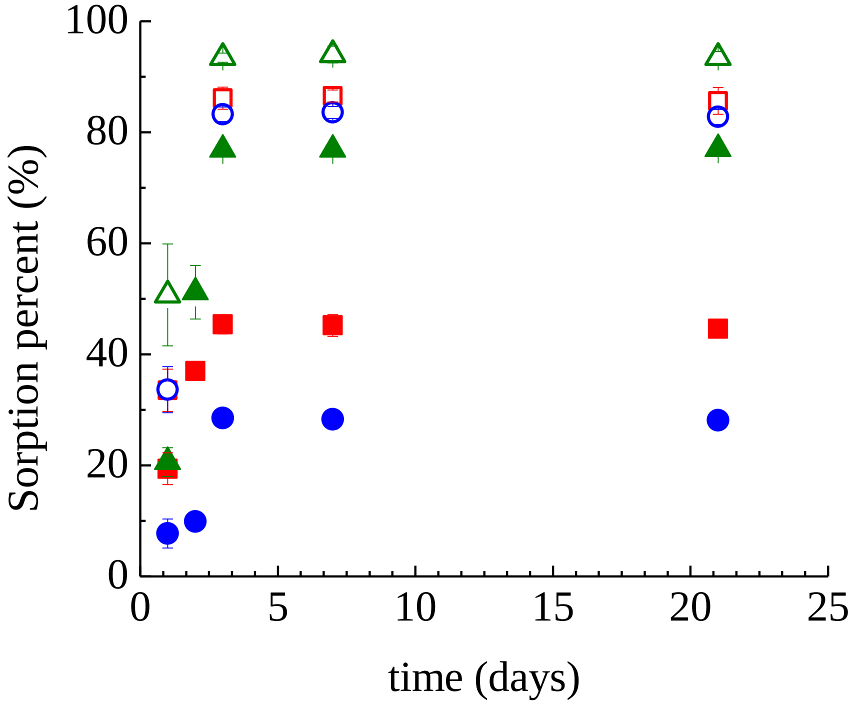


Figure 2: Sorption Kinetics of Np(V) in the SR-270-PW Reference Brine Solution at *S/L* of 0.1 g/5.0 mL(■: Illite (Silver Hill); ●: Queenston Shale; ▲: MX-80) and 0.5 g/5.0 mL (□: Illite (Silver Hill); ○: Queenston Shale; △: MX-80). The Initial Concentration of Np(V) was 1.0×10^{-5} mol/L

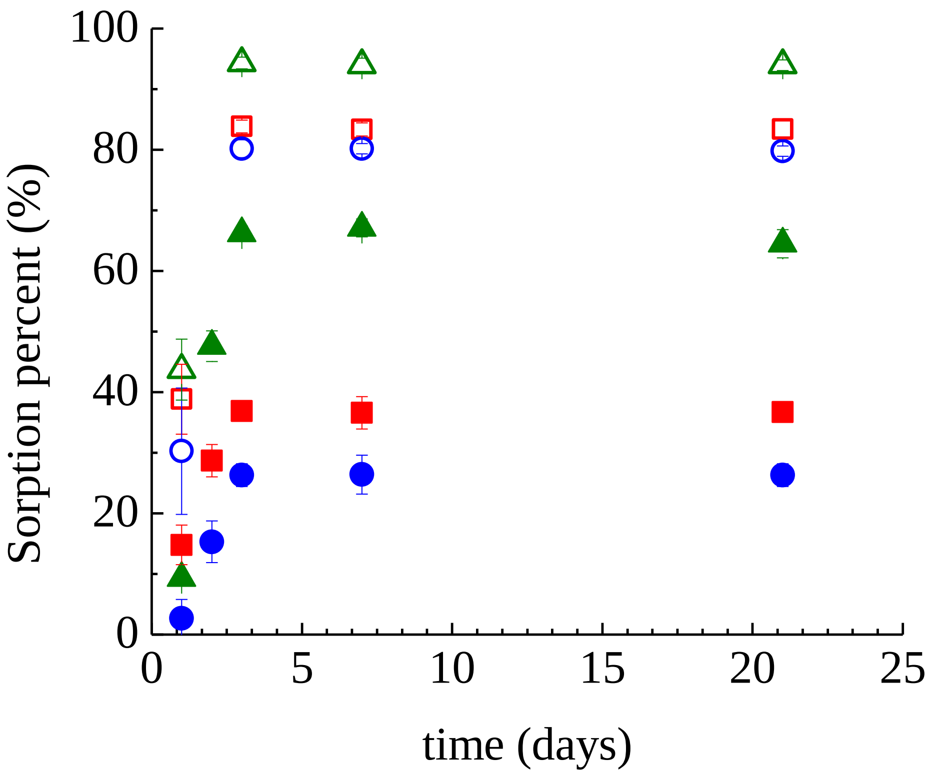


Figure 3: Sorption Kinetics of Np(V) in the NaCl-CaCl$_2$ (*I* = 4.6 M) Solution at *S/L* of 0.1 g/5.0 mL(■: Illite (Silver Hill); ●: Queenston Shale; ▲: MX-80) and 0.5 g/5.0 mL (□ : Illite (Silver Hill); ○: Queenston Shale; △: MX-80). The Initial Concentration of Np(V) was 1.0×10^{-5} mol/L

3.1.3 Effect of Solid/Liquid (*S*/*L*) Ratio on Np(V) Sorption

The dependence of the K_d values of Np(V) sorption on the solid/liquid (*S*/*L*) ratio in the SR-270-PW reference brine and the NaCl-CaCl$_2$ (*I* = 4.6 M) solution is illustrated in Figure 4. The data at the *S/L* ratio of 0.1 g/5.0 mL and 0.5 g/5.0 mL in Figure 4 were taken from the results of sorption kinetics. The pH$_c$, Eh and K_d values of solutions at sorption equilibrium are summarized in APPENDIX (A.3). It was found that the pH$_c$ value was dependent on the solid, but was independent of the *S*/*L* ratio.

With the exception of MX-80 in the SR-270-PW reference brine solution, it was found that K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 increased as the *S*/*L* ratio increased from 0.1 g/5.0 mL to 0.2 g/5.0 mL, and reached plateaus at the *S*/*L* ratios above 0.3 g/5.0 mL. For MX-80 in the SR-270-PW, the K_d values were independent of the *S*/*L* ratios considered in this study. Figure 4 illustrates that the ideal sorption range under the selected experimental conditions is reached at *S*/*L* ≧ 0.3 g/5.0 mL.

Several researchers have reported a decrease of the K_d value with the *S*/*L* ratio for some elements (e.g. Tachi et al. 1999); whereas, others reported that the K_d value was independent of the *S*/*L* ratio (e.g. Wang et al. 2004). An increase of the K_d value with the *S*/*L* ratio as observed in this study was also reported in the studies of Th sorption on graphene oxide (Li et al. 2014) and on attapulgite (Wu et al. 2007). It was discussed that with increasing solid content in the suspension, the number of sites on the solids which participated in the sorption of Th increased and thereby the removal of Th increased (Li et al. 2014, Wu et al. 2007).

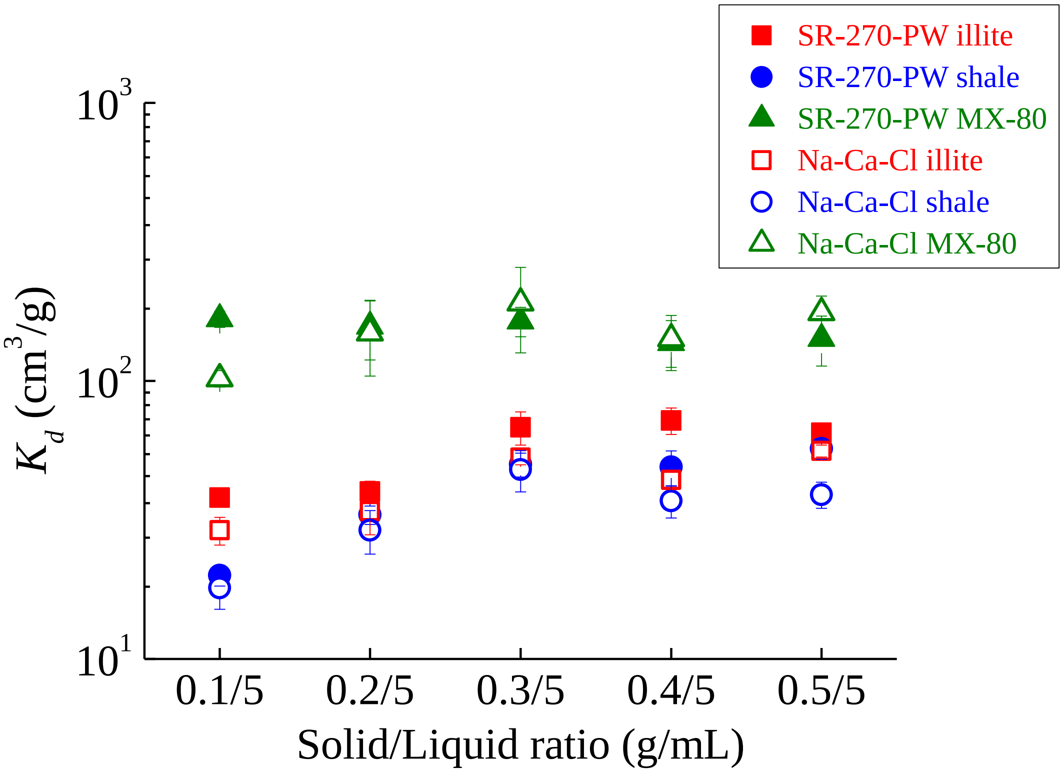


Figure 4: Dependence of K_d Values of Np(V) on the *S*/*L* ratio for Illite (Silver Hill), Queenston Shale and MX-80 in SR-270-PW Reference Brine and NaCl-CaCl$_2$ (*I* = 4.6 M) Solution. The Initial Concentration of Np(V) was 1.0×10^{-5} mol/L

3.1.4 Np(V) K_d Values in the SR-270-PW and the NaCl-CaCl$_2$ (*I* = 4.6 M) Solutions

The measured K_d values of Np(V) on illite (Silver Hill), Queenston shale, and MX-80 in the SR-270-PW reference brine and the NaCl-CaCl$_2$ (*I* = 4.6 M) solution are summarized in Table 7. Table 7 also lists the K_d values calculated from the kinetics experiment conducted at a *S*/*L* ratio of 0.5 g/5.0 mL.

The average K_d values on illite (Silver Hill) in the SR-270-PW reference brine solution are slightly larger than those in the NaCl-CaCl$_2$ (*I* = 4.6 M) solution. The average K_d values on MX-

80 in the SR-270-PW reference brine solution are slightly smaller than those in the NaCl-CaCl$_2$ (I = 4.6 M) solution. However, considering the experimental errors in the K_d values and the difference of pH$_c$, there may be no marked differences in the K_d values on illite (Silver Hill) and MX-80 between these two solutions. On the other hand, the K_d value on Queenston shale in the SR-270-PW reference brine solution is appreciably larger than those in the NaCl-CaCl$_2$ (I = 4.6 M) solution, even when the experimental errors in the K_d values and the difference of pH$_c$ are taken into account.

Table 7: K_d Values of Np(V) for Illite (Silver Hill), Queenston Shale and MX-80 Measured in the SR-270-PW Reference Brine and NaCl-CaCl$_2$ (I = 4.6 M) Solutions. The Initial Np(V) Concentration was 1.0×10^{-5} mol/L

Solution		**SR-270-PW**	
Solid	**Illite (Silver Hill)**	**Queenston shale**	**MX-80**
K_d (cm^3/g) Sorption experiment	$(6.5\pm0.44)\times10^{1}$ (pH$_c$ = 7.6) (Eh = 347 mV)	$(5.7\pm0.47)\times10^{1}$ (pH$_c$ = 7.4) (Eh = 354 mV)	$(1.42\pm0.29)\times10^{2}$ (pH$_c$ = 8.1) (Eh = 356 mV)
K_d (cm^3/g) Kinetics experiment	$(6.5\pm0.79)\times10^{1}$ (pH$_c$ = 7.6) (Eh = 349 mV)	$(5.1\pm0.41)\times10^{1}$ (pH$_c$ = 7.4) (Eh = 353 mV)	$(1.61\pm0.38)\times10^{2}$ (pH$_c$ = 8.1) (Eh = 354 mV)

Solution		**NaCl-CaCl$_2$ (I = 4.6 M)**	
Solid	**Illite (Silver Hill)**	**Queenston shale**	**MX-80**
K_d (cm^3/g) Sorption experiment	$(5.6\pm0.28)\times10^{1}$ (pH$_c$ = 7.7) (Eh = 349 mV)	$(3.9\pm0.42)\times10^{1}$ (pH$_c$ = 7.9) (Eh = 364 mV)	$(1.76\pm0.26)\times10^{2}$ (pH$_c$ = 9.0) (Eh = 310 mV)
K_d (cm^3/g) Kinetics experiment	$(5.0\pm0.39)\times10^{1}$ (pH$_c$ = 7.8) (Eh =343 mV)	$(4.0\pm0.21)\times10^{1}$ (pH$_c$ = 8.0) (Eh = 362 mV)	$(1.60\pm0.35)\times10^{2}$ (pH$_c$ = 9.1) (Eh = 311 mV)

Note: Eh represents the redox potential vs. SHE. pH$_c$ and Eh are the values at sorption equilibrium. K_d values are averaged values over the triplicate measurements.

The K_d value for illite is sometimes used as an approximation for shale when its K_d value is not available. For example, the K_d values of some elements for shale were estimated by using 60% of K_d values for illite, assuming that illite dominates the sorption for shale (Vilks 2011). In the present work, it was found that the K_d values of Np(V) for Queenston shale were similar to (i.e. greater than 60% of) those for illite (Silver Hill). The specific surface areas of illite (Silver Hill) and Queenston shale used are 70 m^2 g^{-1} and 10.3 m^2 g^{-1}, respectively (Bertetti 2016; Pivovarov 2006). This suggests that Np(V) also sorbed onto other minerals in shale (e.g. chlorite, calcite and dolomite) in the SR-270-PW brine and NaCl-CaCl$_2$ (I = 4.6 M) solution with high ionic strength.

Marsac et al. (2015) found the reduction of Np(V) on the purified illite surface in 0.1 mol/L NaCl solution under Ar atmosphere. In this work, whether Np(V) was reduced to Np(IV) was not measured. However, because measured K_d values of Np(V) on the illite (Silver Hill) are similar to those reported in the previous researches (Gorgeon 1994, Torstenfelt et al. 1988, Mucciardi et al. 1978) as discussed later, and because the measured K_d values are much smaller than those by Marsac et al.(2015), the possibility of reduction of Np(V) to Np(IV) is considered to be very small in this work.

3.1.5 Effect of pH$_c$ on Np(V) K_d Values

The pH$_c$ dependence of K_d values of Np(V) in the NaCl-CaCl$_2$ (I = 4.6 M) solution is illustrated in Figure 5. The values of pH$_c$, Eh and K_d at the sorption equilibrium are shown in APPENDIX (A.4). Figure 5 shows that the K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 increase with pH$_c$. This tendency is consistent with the results of the previous studies (Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005, Kitamura and Tomura 2003, Gorgeon 1994, Stammose et al. 1992, Mucciardi et al. 1978), although many of those K_d data were not measured under brine conditions. It was also found that the slope of K_d value vs. pH$_c$ for illite (Silver Hill) was similar to that for Queenston shale, and slightly smaller than that for MX-80.

In April 2014, the Japan Atomic Energy Agency (JAEA) updated their Thermodynamic Database and the SIT (Specific Ion Interaction Theory) (Ciavatta 1980) model parameters (Kitamura et al. 2014). Using the geochemical code PHREEQC (version 3.1.2) (Parkhurst and Appelo 1999) and JAEA's SIT thermodynamic database for NaCl-CaCl$_2$ solutions with ionic strengths of less than 4 M, it was predicted that NpO_2^+ is the dominant species at pH values from 6 to 10. If NpO_2^+ is the dominant species in both the SR-270-PW reference brine and the NaCl-CaCl$_2$ (I = 4.6 M) solution, this pH$_c$ dependence of the K_d values can be explained by deprotonation of the surface complexation sites and then formation of surface complexes with NpO_2^+ as pH$_c$ increases. This pH$_c$ dependence is also predicted by the stoichiometry of sorption equations which were formulated by Bradbury and Baeyens (2009b, 2005).

Mucciardi et al. (1978) measured the sorption of Np(V) on illite in NaCl solution (I = 5.1 M) at pH around 7, and reported K_d values of 9.8 – 1.39×10^2 cm^3/g. Gorgeon (1994) reported K_d values of 6.0×10^1 – 1.95×10^2 cm^3/g on illite in NaClO$_4$ solution (I = 1.0 M) at pH 6 – 7. There are some K_d values measured under low ionic strength conditions. Torstenfelt et al. (1988) observed K_d values of 8.0×10^1 – 9.0×10^1 cm^3/g in Na-Ca-HCO$_3$-SO$_4$ solution (I = 0.004 M) at pH 8.5. Mucciardi et al. (1978) also reported K_d values of 1.5×10^2 – 4.6×10^2 cm^3/g in NaHCO$_3$ solution (I = 0.03 M) at pH 8.7 – 9.2, 1.2×10^1 – 7.3×10^1 cm^3/g in NaCl solution (I = 0.03 M) at pH 6 – 7, and 1.3×10^1 – 4.4×10^1 cm^3/g in CaCl$_2$ solution (I = 0.03 M) at pH 6-7. Considering that the K_d value of Np(V) on illite is independent of ionic strength as discussed below, the K_d values obtained in this work agreed with these previous researches.

Mucciardi et al. (1978) also studied the sorption of Np(V) on montmorillonite, and reported K_d values of 8.0×10^1 – 1.6×10^2 cm^3/g in NaCl solution (I = 5.1 M) at pH of 7.7 – 9.3. Gorgeon (1994) reported K_d values of 2.5×10^1 – 1.3×10^2 cm^3/g on smectite in NaClO$_4$ solution (I = 1.0 M) at pH 6 – 7. Kitamura and Tomura (2003) measured the K_d values of 2 – 2.1×10^1 cm^3/g on smectite in NaCl solution (I = 1 M) at pH 8 – 9. Considering that the K_d value of Np(V) on MX-80 is not dependent on the ionic strength when the ionic strength is over 1 M as discussed below, the K_d values obtained in this work were consistent with the study of Gorgeon (1994), but were larger than the the K_d values by Mucciardi et al. (1978) and Kitamura and Tomura (2003).

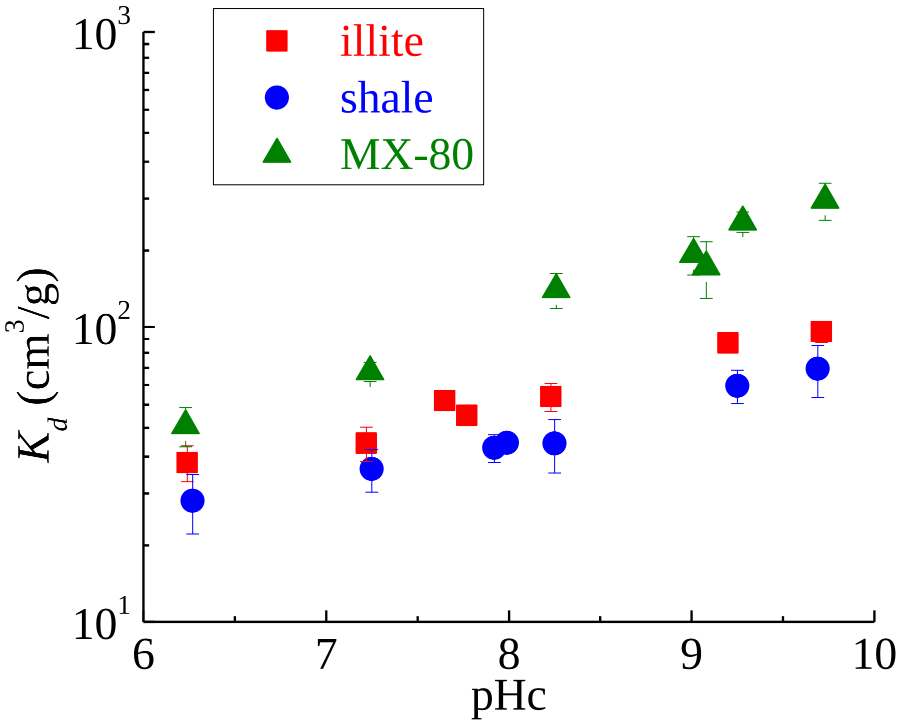


Figure 5: pH$_c$ Dependence of the K_d Values of Np(V) in the NaCl-CaCl$_2$ (I = 4.6 M) Solution. The Initial Concentration of Np(V) was 1.0×10^{-5} mol/L

3.1.6 Effect of the Ionic Strength on Np(V) K_d Values

The ionic strength dependence of the K_d values of Np(V) in NaCl-CaCl$_2$ solutions is illustrated in Figure 6. The pH$_c$, Eh and K_d values at sorption equilibrium are summarized in APPENDIX (A.5).

The pH$_c$ value changed slightly over a series of sorption experiments on illite (Silver Hill) (pH$_c$ = 7.1 – 7.8), Queenston shale (pH$_c$ = 7.6 – 8.1) and MX-80 (pH$_c$ = 8.5 – 9.1). Considering the variation of pH$_c$ of the NaCl-CaCl$_2$ solutions with different ionic strengths and the pH$_c$ dependence of K_d values (Figure 5), the K_d values on illite (Silver Hill) and Queenston shale can be considered to be independent of the ionic strength in the range of 0.10 – 4.6 M being investigated. On the other hand, the K_d value on MX-80 decreased with increasing the ionic strength from 0.1 M to 1.0 M, but was independent of the ionic strength when the ionic strength was over 1 M. The difference in the sorption on illite (Silver Hill) and MX-80 may be explained by (i) the difference in the structures of interlayer of illite (Silver Hill) and MX-80, and (ii) sorption by ionic exchange reactions at ionic strengths below 1 M for MX-80. Furthermore, as Schnurr et al. (2015) pointed out, the coagulation effects of MX-80 might also be a possibility for the decrease in sorption with increasing ionic strength, although the coagulation effects are marked at relatively low salt concentration such as 0.01 – 0.1 M.

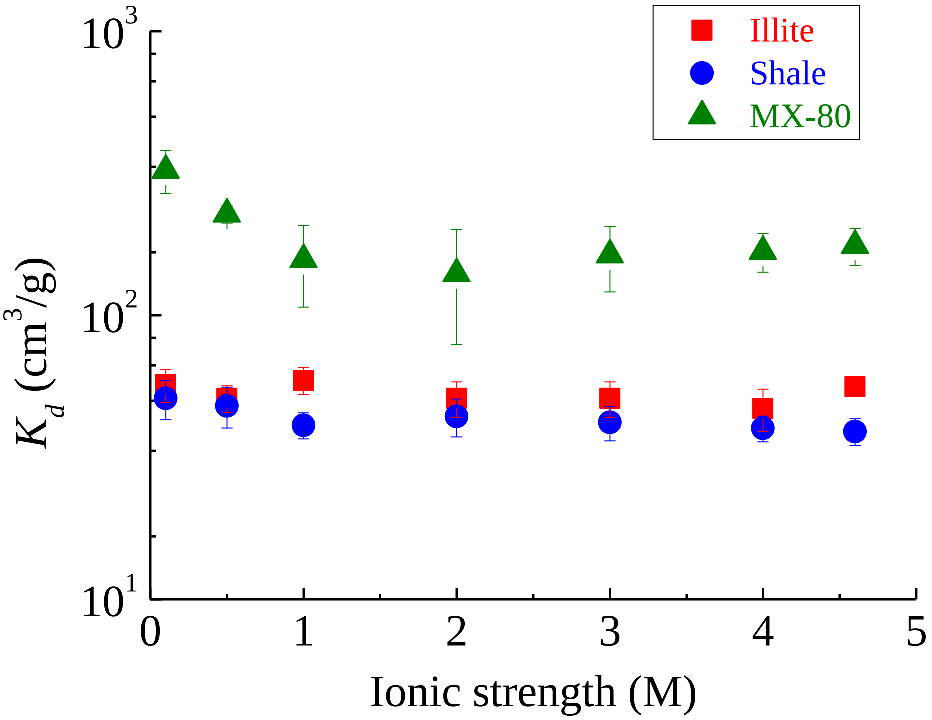


Figure 6: Ionic Strength Dependence of the K_d Values of Np(V) in the NaCl-CaCl$_2$ Solutions. The Initial Concentration of Np(V) was 1.0×10^{-5} mol/L

Gorgeon (1994) measured the sorption of Np(V) on Na-smectite in 0.025 mol/L and 0.1 mol/L NaClO$_4$ solutions and reported K_d values of 6.0×10^1 – 1.6×10^2 cm^3/g at pH 7 – 9. Turner et al. (1998) reported K_d values of 5.0×10^1 – 2.0×10^2 cm^3/g on Na-montmorillonite in 0.1 mol/L NaNO$_3$ solution at pH 7.5 – 9. Sakamoto et al. (1990) reported K_d value of 1.5×10^1 – 4.4×10^1 cm^3/g on bentonite in 0.01 mol/L NaClO$_4$ solution. Higgo et al. (1983) reported K_d values of 1.1×10^3 – 1.24×10^4 cm^3/g on smectite in sea water. Morgan et al. (1988) studied the sorption of Np(V) on bentonite in deionized water and reported the K_d value of 1.1×10^2 – 4×10^3 cm^3/g. The K_d values on illite (Silver Hill) and Queenston shale (I = 0.10 – 4.6 M) and those on MX-80 ($I \geq 1.0$ M) obtained in this work are consistent with the studies by Gorgeon (1994), Turner et al. (1998) and Sakamoto et al. (1990). However, the K_d values on MX-80 (I = 0.1 M and 0.5 M) are higher than those by Gorgeon (1994), Turner et al. (1998) and Sakamoto et al. (1990), but much smaller than those by Higgo et al. (1983), and Morgan et al. (1988). The reproducibility of the solid/liquid separation by centrifugation for 30 minutes at 12,000 rpm was confirmed. However, there is a possibility that colloids might be formed from bentonite and present in the separated solutions in MX-80 series in I = 0.10 M and 0.50 M solutions. If colloids are not sufficiently separated from liquid phase by centrifuge, K_d values are underestimated.

3.1.7 Effect of the Na/Ca Ratio on Np(V) K_d Values

The effect of the Na/Ca molar concentration ratio on the K_d value of Np(V) in $CaCl_2$, Ca-Na-Cl, Na-Ca-Cl, and NaCl solutions with an ionic strength of 4.6 M is summarized in Table 8. The pH_c and Eh values of the solutions at the sorption equilibrium are shown in APPENDIX (A.6).

Although the pH_c value of the solutions varied over a series of sorption experiments on illite (Silver Hill) (pH_c = 6.9 – 8.6), Queenston shale (pH_c = 7.4 – 9.2) and MX-80 (pH_c = 8.5 – 10.2), the K_d value seemed to increase as the Na/Ca ratio increased for all three solids, suggesting that the presence of Ca^{+2} in solution reduces the sorption of Np(V) on illite (Silver Hill), Queenston shale and MX-80. Possible explanations may be the competition of Ca^{+2} with Np(V) for sorption sites, or the change in the aqueous speciation of Np(V) induced by high concentration of Ca^{+2}. However, these cannot explain the ionic strength dependence and the Na/Ca ratio dependence simultaneously.

Table 8: Na/Ca Ratio Dependence of K_d Values of Np(V) Measured in $CaCl_2$, $NaCl\text{-}CaCl_2$, and NaCl Solutions with the Ionic Strength of 4.6 M. The Initial Concentration of Np(V) was 1.0×10^{-5} mol/L

Solution		$CaCl_2$ solution	$NaCl\text{-}CaCl_2$ solution				NaCl solution
Na/Ca ratio		0	0.10	1.0	5.0	10	∞
K_d (cm^3/g)	Illite (Silver Hill)	9.9 ± 1.3	$(1.8\pm0.22)\times10^{1}$	$(5.8\pm0.62)\times10^{1}$	$(6.0\pm0.68)\times10^{1}$	$(1.02\pm0.14)\times10^{2}$	$(1.89\pm0.24)\times10^{2}$
	Queenston shale	9.0 ± 0.39	$(1.7\pm0.12)\times10^{1}$	$(4.0\pm0.51)\times10^{1}$	$(4.2\pm0.42)\times10^{1}$	$(8.8\pm0.93)\times10^{1}$	$(1.22\pm0.18)\times10^{2}$
	MX-80	$(3.2\pm0.27)\times10^{1}$	$(7.1\pm0.38)\times10^{1}$	$(1.35\pm0.04)\times10^{2}$	$(1.39\pm0.09)\times10^{2}$	$(2.82\pm0.37)\times10^{2}$	$(5.12\pm0.52)\times10^{2}$

Schnurr et al. (2015) observed the similar effect in the Eu sorption on illite and smectite, but they considered that the competition of Ca^{2+} for the same sorption sites might not be a sufficient explanation. Bradbury and Baeyens (2005) found that the K_d value of Eu(III) on smectite in 0.1 mol/L $NaClO_4$ solution is more than one order of magnitude higher than that in 0.066 mol/L $Ca(NO_3)_2$ solution. Activity coeffcients in the solution containing Ca^{+2} might be different from those in the solution containing Na^+. The effect of Na/Ca ratio on Np(V) sorption has not yet been understood.

3.1.8 Np(V) Sorption Isotherms

Sorption isotherms of Np for the initial concentration from 10^{-9} to 10^{-4} mol/L conducted in the SR-270-PW reference brine and the NaCl-$CaCl_2$ (I = 4.6 M) solutions are illustrated in Figures 7 and 8, respectively. The data at the initial concentration of 1.0×10^{-5} mol/L were plotted from the experimental results of K_d measurements in the SR-270-PW reference brine and NaCl-$CaCl_2$ (I = 4.6 M) solutions (see Section 3.1.4). The pH_c and Eh values of the solutions at the sorption equilibrium are shown in APPENDIX (A.7). The pH_c of solution was adjusted to the same value for each solid (i.e. pH_c of 7.6 for illite, 7.5 for shale and 8.0 for MX-80 in the SR-270-PW brine).

In both solutions, the measured Np(V) sorption isotherms are observed to be linear on log-log plots with slopes of approximately 1 at a Np(V) equilibrium concentration in the liquid less than 2×10^{-6} mol/L (the initial Np(V) concentration was 1.0×10^{-5} mol/L). The data points at Np(V) equilibrium concentrations of 1×10^{-5} to 2×10^{-5} mol/L in the liquid (the initial Np(V) concentration was 1.0×10^{-4} mol/L) slightly deviate from a linear relationship (Figures 7 and 8). Figures 7 and 8 illustrate that the ideal sorption range under the selected experimental conditions is reached at the Np(V) concentration in the liquid less than 2×10^{-6} mol/L.

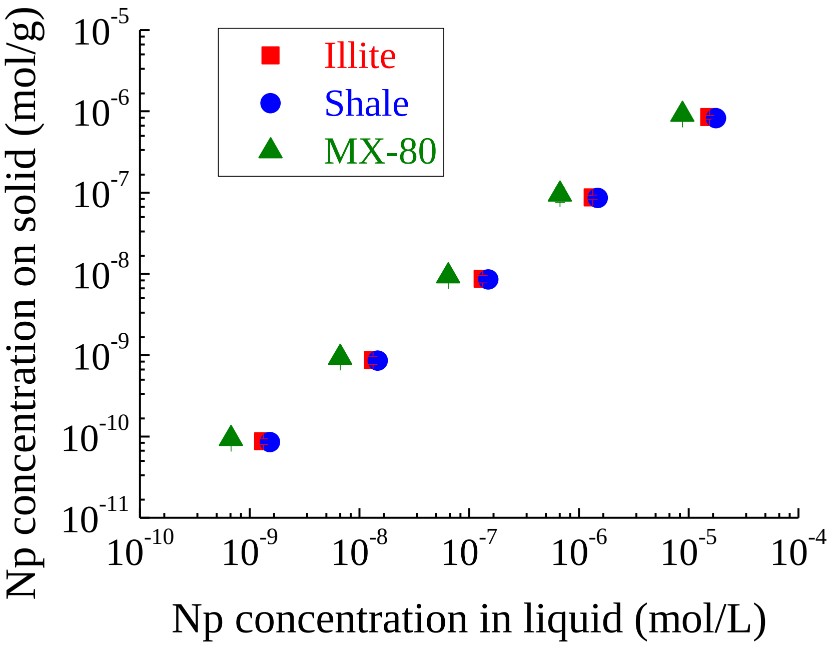


Figure 7: Sorption Isotherms of Np(V) in the SR-270-PW Reference Brine Solution. The Data at the Initial Concentration of 1.0×10^{-5} mol/L was Plotted from the K_d Value Measurement in the SR-270-PW Brine

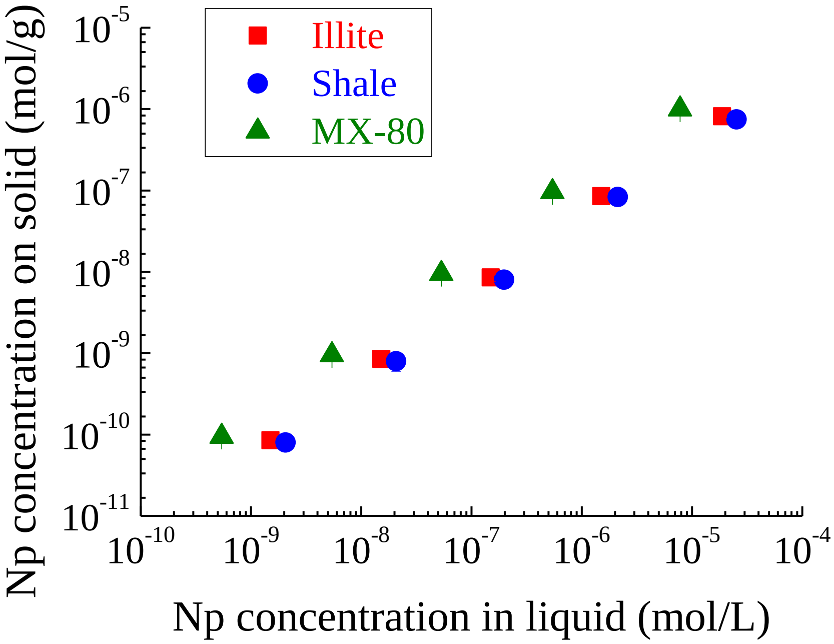


Figure 8: Sorption Isotherms of Np(V) in the NaCl-CaCl$_2$ (I = 4.6 M) Solution. The Data at the Initial Concentration of 1.0×10^{-5} mol/L was Plotted from the K_d Value Measurement in the NaCl-CaCl$_2$ (I = 4.6 M) Solution

3.2 NP(IV) SORPTION

3.2.1 Preparation of Np(IV) Solution

The established procedures by Kirishima (2014) and Kirishima et al. (2003) were followed to prepare Np(IV) solution. The absorbance spectrum of the Np(IV) solution before and after it contacted to air is shown in Figure 9. In these spectra, the presence of Np(V) was not observed because the intense absorption peak at 981 nm by Np(V) was not measured. Furthermore, the presence of Np(V) was not detected by 0.1 mol/L TTA-xylene extraction. It was considered that Np(IV) stock solution was well prepared.

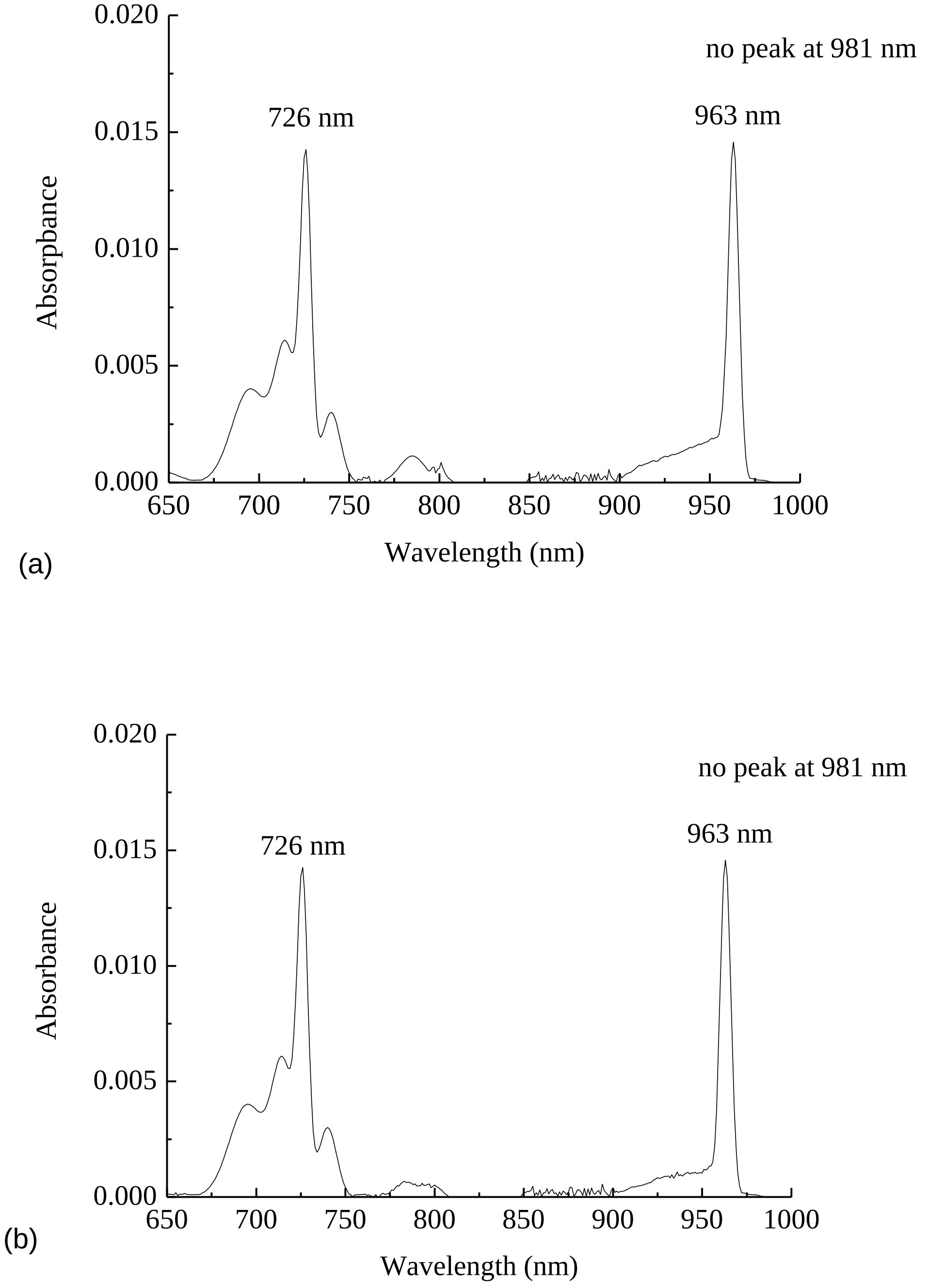


Figure 9: Absorbance of Np Solution After Reduction with 10% H_2 + 90% N_2 Gas under Pt(Pt) Catalyst. (a): Before Air Contact; (b): After Air Contact

3.2.2 Kinetics of Np(IV) Sorption

The results of the sorption kinetics of Np(IV) for illite (Silver Hill), Queenston shale, and MX-80 in NaCl-$CaCl_2$-$NaClO_4$ solution (I = 6 M) at S/L = 0.2 g/1 L and 0.1 g/1 L are illustrated in Figure 10. The values of pH_c and Eh of solutions and K_d are shown in APPENDIX (A.8). These results illustrated that sorption equilibrium of Np(IV) for three solids were achieved within 3 to 7 days for both S/L ratios. Figure 10 also shows that there was no marked difference in the K_d values of Np(IV) between S/L = 0.2 g/1 L and 0.1 g/1 L for each solid, considering the experimental uncertainties of the K_d values.

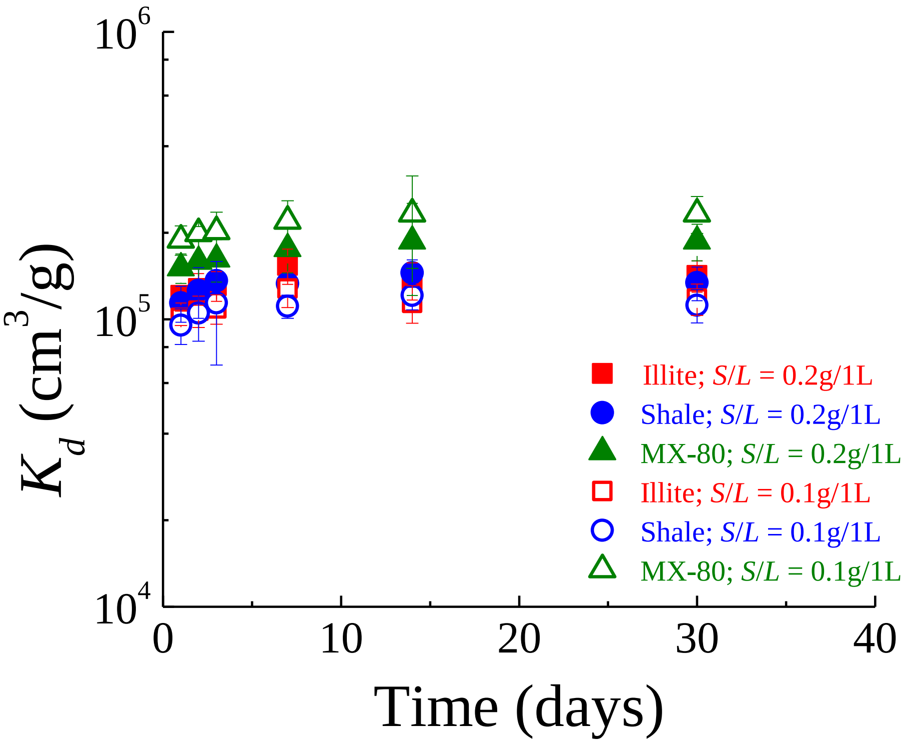


Figure 10: Sorption Kinetics of Np(IV) for Illite (Silver Hill), Queenston Shale, and MX-80 in NaCl-$CaCl_2$-$NaClO_4$ Solution (I = 6 M). The Initial Concentration of Np(IV) was 1.0×10^{-11} mol/L

3.2.3 Np(IV) K_d Measurement in the SR-270-PW Reference Brine Solution

The K_d values of Np(IV) sorption on illite (Silver Hill), Queenston shale, and MX-80 in the SR-270-PW reference brine solution are summarized in Table 9. The initial and final pH_c and Eh values of solutions are shown in APPENDIX (A.9). Compared with the K_d values of Np(V) for these solids (Table 7), those of Np(IV) were found to be three orders of magnitude larger.

The retardation factor R ($R = 1 + \rho K_d / \varepsilon$, ρ is the rock density, ε rock porosity) provides an indication of how much slower a sorbing contaminant will be transported compared to the average groundwater pore velocity (JAEA 2000). For example, Np(IV) would be transported 3×10^6 times slower than groundwater in Queenston shale ($\rho = 2.608$ g/cm, $\varepsilon = 0.0663$, Vilks et al. 2011). It indicates that Np(IV) is very strongly retarded in illite, shale and MX-80, and essentially immobile.

Table 9: K_d Values of Np(IV) for Illite (Silver Hill), Queenston Shale and MX-80 in SR-270-PW Reference Brine. The Initial Concentration of Np(IV) was 1.0×10^{-11} mol/L

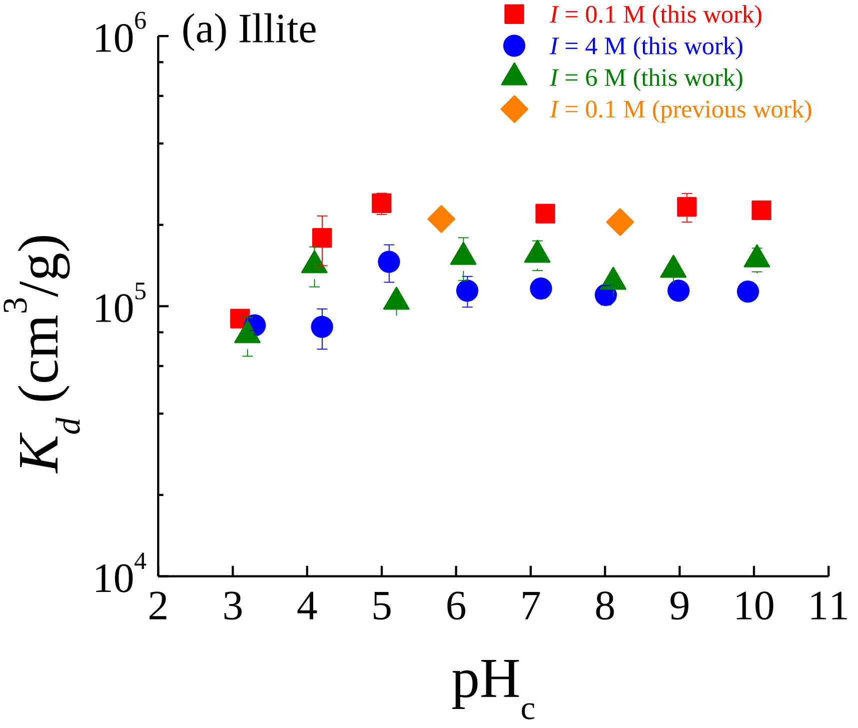
Solid	K_d (cm^3/g)
Illite (Silver Hill)	$(9.2 \pm 1.5) \times 10^4$
Queenston Shale	$(9.8 \pm 0.93) \times 10^4$
MX-80	$(1.3 \pm 0.31) \times 10^5$

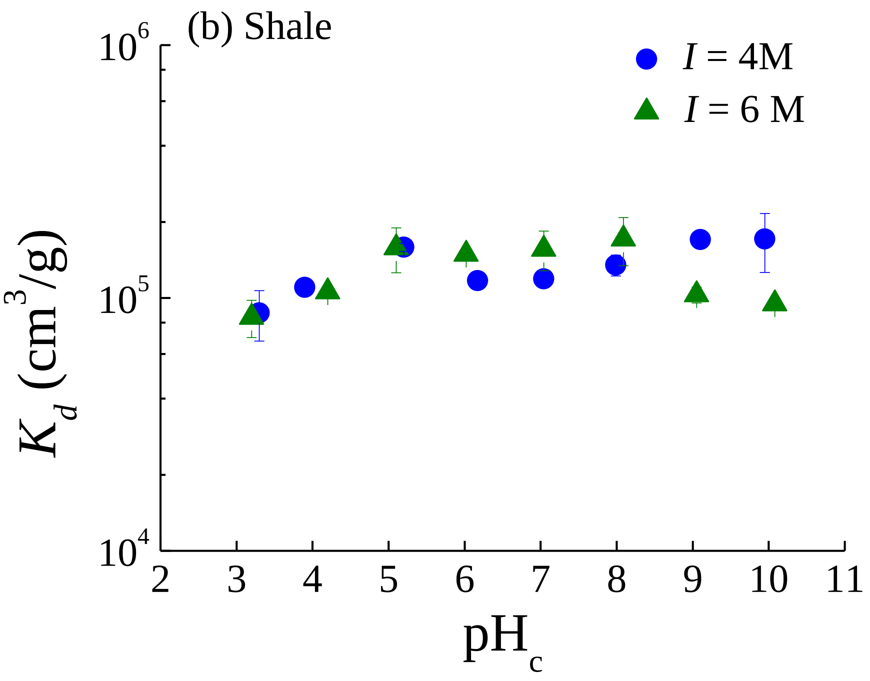
Note: K_d values are averaged values over the triplicate measurements.

3.2.4 Effect of pH$_c$ on Np(IV) K_d Values

The pH$_c$ dependence of K_d values of Np(IV) sorption in NaCl-CaCl$_2$ solutions (I = 0.1 M and 4 M) and NaCl-CaCl$_2$-NaClO$_4$ solution (I = 6 M) is illustrated in Figure 11. The K_d values of Np(IV) on illite (Rochester, USA) and montmorillonite (Tsukinuno, Japan) in 0.1 mol/L NaClO$_4$ solution estimated from the migration curves of Np(IV) which had been experimentally observed in the presence of clay (Nagasaki 1994) are also plotted (around pH 6 and 8) in Figure 11 for reference. These were found to be consistent with the K_d values measured in the present work at I = 0.1 M. The values of pH$_c$, Eh and K_d at the sorption equilibrium measured in the present work are shown in APPENDIX (A.10).

Figure 11 shows that the K_d values of Np(IV) for illite (Silver Hill) and MX-80 were independent of pH$_c$ between 5 and 10 at I = 0.1 M, 4 M and 6 M. The K_d values on Queenston shale were also independent of pH$_c$ between 5 and 10 at I = 4 M. The K_d values on the shale at pH$_c$ = 9 and 10 obtained at I = 6 M were slightly smaller than those at $5 \leq \text{pH}_c \leq 8$. It was considered that the overall trend of pH$_c$ dependence of the K_d values at I = 0.1 M, 4 M and 6 M for all three solids did not depend on pH$_c$ at $5 \leq \text{pH}_c \leq 10$. The K_d values of Np(IV) for illite (Silver Hill), Queenston shale, and MX-80 in I = 6 M solution at the same pH$_c$ as in kinetics measurements were $(1.2 \pm 0.06) \times 10^5$ cm^3/g (pH$_c$ = 8.1), $(1.7 \pm 0.37) \times 10^5$ cm^3/g (pH$_c$ = 8.1) and $(1.7 \pm 0.07) \times 10^5$ cm^3/g (pH$_c$ = 9.1), respectively (Figure 11). The K_d values of Np(IV) for illite (Silver Hill), Queenston shale, and MX-80 in I = 6 M NaCl-CaCl$_2$-NaClO$_4$ solution measured in the sorption kinetics experiments (7 days) were $(1.5 \pm 0.22) \times 10^5$ cm^3/g, $(1.3 \pm 0.12) \times 10^5$ cm^3/g and $(1.8 \pm 0.31) \times 10^5$ cm^3/g at S/L ratio = 0.2 g/1 L and $(1.3 \pm 0.18) \times 10^5$ cm^3/g, $(1.1 \pm 0.10) \times 10^5$ cm^3/g and $(2.2 \pm 0.39) \times 10^5$ cm^3/g at S/L ratio = 0.1 g/1 L, respectively (Figure 10). The K_d values were slightly smaller in the SR-270-PW reference brine (Table 9) than those in the NaCl-CaCl$_2$-NaClO$_4$ solutions. Considering the experimental uncertainties of the K_d values in both media, the variation in K_d values was considered not to be significant.


(a) Illite
I = 0.1 M (this work)
I = 4 M (this work)
I = 6 M (this work)
I = 0.1 M (previous work)
K_d (cm^3/g)
10^6
10^5
10^4
2
3
4
5
6
7
8
9
10
11
pH$_c$


(b) Shale
I = 4M
I = 6 M
K_d (cm^3/g)
10^6
10^5
10^4
2
3
4
5
6
7
8
9
10
11
pH$_c$

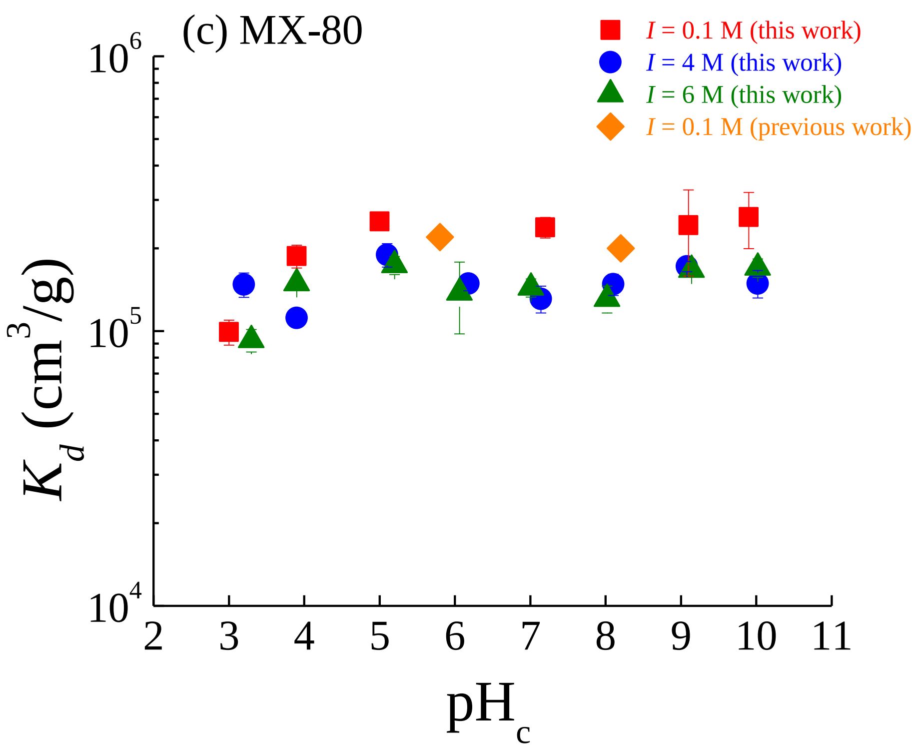


Figure 11: pH$_c$ Dependence of the K_d Values of Np(IV) in NaCl-CaCl$_2$ Solution (I = 0.1 M and 4 M) and NaCl-CaCl$_2$-NaClO$_4$ (I = 6 M) Solution: (a) Illite (Silver Hill); (b) Queenston Shale; (c) MX-80. The Initial Concentration of Np(IV) was 1.0×10^{-11} mol/L. The K_d Values on Illite (Rochester) and Montmorillonite (Tsukinuno) in 0.1 mol/L NaClO$_4$ Solution Estimated from the Previous Work (Nagasaki 1994) are also Plotted for Reference

3.2.5 Effect of the Ionic Strength on Np(IV) K_d Values

The ionic strength dependence of the K_d values of Np(IV) sorption in NaCl-CaCl$_2$ solutions (I = 0.1 – 4 M) and NaCl-CaCl$_2$-NaClO$_4$ (I = 6 M) solution is illustrated in Figure 12. The pH$_c$ and Eh values of solutions at sorption equilibrium and K_d values are summarized in APPENDIX (A.11).

The pH$_c$ of the solution was adjusted to 8.0±0.3 for illite (Silver Hill), 8.2±0.3 for Queenston shale and 8.8±0.3 for MX-80. Considering the pH$_c$ dependence of Np(IV) K_d values ($5 \leq$ pH$_c$ ≤ 10) and the uncertainties of the K_d values, the K_d values for illite (Silver Hill), Queenston shale and MX-80 were found to be independent of the ionic strength in the range of 0.5 M – 6 M. On the other hand, the K_d values on all three solids at I = 0.1 M were slightly larger than those at $I \geq 0.5$ M. As illustrated in Figure 11 (a) and (c), the K_d values on illite (Silver Hill) and MX-80 at $5 \leq$ pH$_c$ ≤ 10 at I = 0.1 M were a bit larger than at I = 4 M and 6 M.

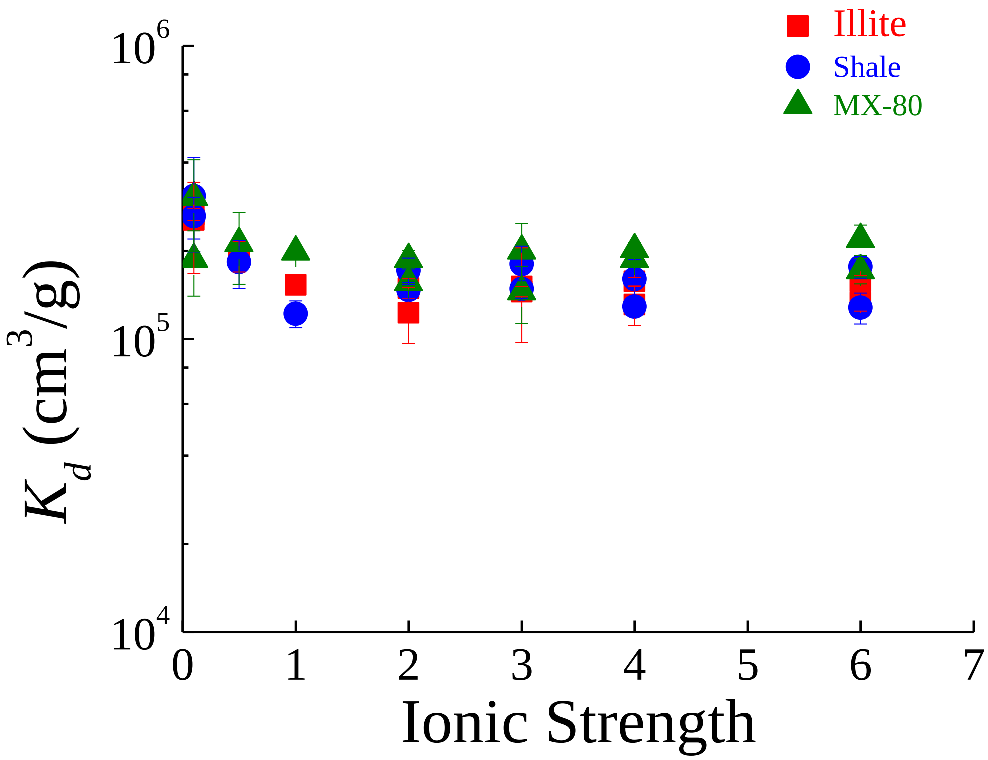


Figure 12: Ionic Strength Dependence of the K_d Values of Np(IV) in NaCl-$CaCl_2$ Solutions (I = 0.1 – 4 M) and NaCl-$CaCl_2$-$NaClO_4$ Solution (I = 6 M). The Initial Concentration of Np(IV) was 1.0×10^{-11} mol/L

3.2.6 Effect of the Na/Ca Ratio on Np(IV) K_d Values

The effect of the Na/Ca molar concentration ratio on the K_d values of Np(IV) sorption in NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) solution is summarized in Table 10. K_d values measured in pure $CaCl_2$ and NaCl solutions with ionic strenght of 6 M are also shown in the table. The pH_c and Eh values of solutions at sorption equilibrium are summarized in APPENDIX (A.12).

The pH_c of the solution was adjusted to 8.0±0.3 (iilite (Silver Hill)), 8.2±0.3 (Queenston shale) and 8.8±0.3 (MX-80). Considering that the K_d values were independent of pH_c, it was found that the K_d values of Np(IV) increased with Na/Ca ratio for all three solids. A similar Na/Ca ratio dependence was found for Np(V) sorption as shown in Table 8, suggesting that the presence of Ca in high ionic strength solutions reduces the sorption of Np(IV), as well as Np(V) on illite (Silver Hill), Queenston shale and MX-80.

Table 10: Na/Ca Ratio Dependence of K_d Values of Np(IV) Measured in $CaCl_2$, NaCl-$CaCl_2$-$NaClO_4$, and NaCl Solutions with the Ionic Strength of 6 M. The Initial Concentration of Np(IV) was 1.0×10^{-11} mol/L

Solution		**$CaCl_2$ solution**	**NaCl-$CaCl_2$-$NaClO_4$ solution**				**NaCl solution**
Na/Ca ratio		**0**	**0.1**	**1.0**	**5.0**	**10**	**∞**
K_d (cm^3/g)	Illite (Silver Hill)	$(3.0\pm0.032)\times10^4$	$(7.9\pm2.7)\times10^4$	$(1.3\pm0.12)\times10^5$	$(1.3\pm0.086)\times10^5$	$(3.1\pm0.36)\times10^5$	$(4.5\pm0.88)\times10^5$
	Queenston shale	$(2.9\pm0.067)\times10^4$	$(7.6\pm0.65)\times10^4$	$(1.3\pm0.032)\times10^5$	$(1.3\pm0.047)\times10^5$	$(3.0\pm0.22)\times10^5$	$(3.2\pm0.39)\times10^5$
	MX-80	$(3.5\pm0.26)\times10^4$	$(5.2\pm0.27)\times10^4$	$(1.1\pm0.12)\times10^5$	$(8.7\pm0.054)\times10^4$	$(1.4\pm0.10)\times10^5$	$(5.5\pm1.4)\times10^5$

3.2.7 Discussion on Np(IV) Sorption

There are several previous studies on Np(IV) sorption on clay minerals and shale (Marsac et al. 2015, Kitamura and Tomura 2003, Nagasaki et al. 1999, Asida et al. 1999). Nagasaki et al. (1999) studied Np(IV) sorption on bentonite in 0.01 mol/L $NaClO_4$ solution, and reported that the K_d values of Np(IV) were constant in the pH range of 6.3 to 8.2. Marsac et al. (2015) performed the predictive simulation of Np(IV) sorption onto illite in 0.1 mol/L NaCl solution, indicating the pH independence of K_d values in the pH range of 6 to 11. Kitamura and Tomura

(2003) investigated the pH dependence of K_d values of Np(IV) sorption on smectite in 1.0 M NaCl solution in the pH range of 7.4 to 8.5. They reported that the K_d values decreased with pH. However, in their experiments, carbonates (0.09 – 1.0 M) were included and Np(V) and Np(IV) coexisted. Ashida et al. (1999) studied the effect of carbonate on Np(IV) sorption in 1 M NaCl solution on smectite. They found that the K_d values were apparently constant ($K_d = 10^2 - 10^3$ cm^3/g) over the carbonate concentration (total carbonate concentration: 0.04 - 0.15 mol/L). The K_d values for illite (Silver Hill) at $I = 0.1$ M measured in the present work were approximately $2.3\times10^5 – 2.7\times10^5$ cm^3/g. These values were found to be comparable to those predicted by Marsac et al. (2015). Since the concentration of Ca^{2+} was very low at $I = 0.1$ M, the effect of Ca^{2+} on Np(IV) sorption could be considered small. There is no previous work studying the pH_c and ionic strength dependences of K_d values of Np(IV) sorption in high ionic strength solutions (ionic strength up to 6 M) for illite, shale, and montmorillonite like MX-80. Hence, the present work is considered to be the first systematic study of the effects of pH_c and ionic strength on Np(IV) sorption for illite, shale, and montmorillonite in high ionic strength solutions.

Vilks (2011, 2017) extensively reviewed the K_d values of Np(IV) sorption onto shale, bentonite and limestone published in scientific papers and reports, compiled the K_d values under saline conditions. It was found that the Np(IV) sorption measurements under reducing, brine conditions were scarce.

As with Np(V) sorption, it was found that the K_d values of Np(IV) for Queenston shale were similar to those for illite (Silver Hill). The specific surface areas of illite (Silver Hill) and Queenston shale used in this work are 70 m^2/g and 10.3 m^2/g, respectively (Bertetti 2016, Pivovarov 2006). This suggests that Np(IV) also sorbed onto other minerals in shale (e.g. chlorite, calcite and dolomite) in SR-270-PW reference brine and high ionic strength NaCl-$CaCl_2$ and NaCl-$CaCl_2$-$NaClO_4$ solutions.

Recently, Marsac et al. (2017) investigated Pu sorption on illite under anaerobic conditions at $3 < pH_m < 10$ and $m_{NaCl} = 1.0$ molal and 3.2 molal. They found that the overall Pu uptake at $pH_m < 6$ is mainly attributed to the presence of Pu(III) and its competition with Na^+ and that the overall Pu uptake at $pH_m > 6$ is largely insensitive to m_{NaCl} due to the prevalence of strongly adsorbing Pu(IV). The pH_c dependence of K_d value of Np(IV) on illite (Silver Hill), Queenston shale and MX-80 observed in the present work at $pH_c > 5$ was qualitatively the same as that of Pu observed by Marsac et al. (2017) at $pH_m > 6$. Furthermore, the absence of ionic strength dependence of Np(IV) sorption on illite (Silver Hill), Queenston shale and MX-80 at $I \geq 0.5$ M observed in this work also agreed well with that of Pu(IV) sorption observed by Marsac et al. (2017).

According to Marsac et al. (2017) and Banik et al. (2016), the K_d values of Pu(IV) on illite du Puy are independent of ionic strength (m_{NaCl} = 0.1, 1.0 and 3.2 molal) at $pH_m > 6$. The K_d values on illite (Silver Hill) and MX-80 at $I = 0.1$ M were slightly but clearly larger than those at $I \geq 0.5$ M in the present work (Figures 11 and 12). The K_d values of Th(IV) on montmorillonite (Na-SWy-1) experimentally measured at $I = 0.1$ M were reported to be smaller than those measured at $I = 1$ M between $3 \leq pH \leq 8$ (Bradbury and Baeyens. 2005). Zhao et al. (2008) studied the effect of pH, ionic strength and temperature on Th(IV) sorption for MX-80. They found that the sorption decreased with the concentration of KNO_3 (up to 0.3 mol/L) at pH = 1.86 ± 0.02 and concluded that cation exchange partly contributed to the sorption of Th(IV) on MX-80.

4. SORPTION MODELLING

4.1 SORPTION MODELLING APPROACH

4.1.1 Sorption Modelling for Np(IV) K_d Values

In this work, the 2-site protolysis non-electrostatic surface complexation and cation exchange model (2 SPNE SC/CE model) (Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005) was applied to simulate the pH_c dependence of K_d values of Np(IV) on illite and MX-80 at I = 0.1 M and 4 M. The SIT model (Ciavatta 1980) was used to calculate activity coefficients of aqueous species. Because Pitzer parameters for Np(IV) in NaCl-$CaCl_2$-$NaClO_4$ solution are not completely compiled, the 2 SPNE SC/CE model was not applied to the K_d values measured at I = 6 M brine. Thermodynamic constants for Np(IV) aqueous species were taken from the NEA thermodynamic database (Guillaumont et al. 2003). 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 (Parkhurst and Appelo 1999) were used.

For illite du Puy, Bradbury and Baeyens (2009a, 2009b) reported the specific surface area of 97 m^2/g, the sorption site capacity of 2.0×10^{-3} mol/kg (strong site: $\equiv S^sOH$) and 4.0×10^{-2} mol/kg (weak site: $\equiv S^{w1}OH$), and the CEC of 225±15 meq/kg. The illite (Silver Hill) used in this work has the specific surface area of 70 m^2/g and the CEC of 150 meq/kg (Pivovarov 2006), but the sorption site capacity has not been measured. Hence, assuming that the sorption site capacity is proportional to the specific surface area, the value of 1.4×10^{-3} mol/kg (strong site) was adopted. The equilibrium constants for surface protolysis reactions estimated by Bradbury and Baeyens (2009b) and the surface complexation constants estimated for Np(IV) by Marsac et al. (2015) were used. As shown later in Figure 13, the simulation using the surface complexation constants by Marsac et al. (2015) was found to overestimate the sorption of Np(IV). Hence, in the present work, the surface complexation constants which provided the best fit of simulation to the experimental K_d values were estimated. For the fitting, the surface complexation constants estimated for Pu(IV) (Banik et al. 2016) were used as the initial guesses. This was because the Np(IV) K_d values between $5 \le pH_c \le 10$ at I = 0.1 M and 4 M in the present work agreed with the simulation results of 2 SPNE SC/CE model using the surface complexation constants estimated for Pu(IV) (Marsac et al. 2017). Like Marsac et al. (2015), a weight of 1 was applied to all data (I = 0.1 M and 4 M), and the error between experimental and simulated K_d values was estimated by the root mean squared deviation.

For MX-80, the surface complexation constants which Bradbury and Baeyens (2005) estimated for Np(IV) on montmorillonite by the linear free energy relatiosnhip (LFER) were used. However, the surface complexation constant for the reaction

$$\equiv S^sOH + Np^{4+} + 4H_2O \leftrightarrow \equiv S^sONp(OH)_4^- + 5H^+ \qquad (3)$$

was not reported, although the surface complexation constant for similar reaction of Th(IV) was estimated as $\log {}^sK = -16.9$. This is because the hydrolysis constant for $Np(OH)_5^-$ is required for the estimation with LFER but it is not compiled in the NEA database (Guillaumont et al. 2003). Hence, the surface complexation constant for reaction (3) was estimated by fitting to the K_d values measured in this work. In addition, the surface complexation constants for other reactions which provided the best fit of simulation to the experimental K_d values were also estimated. For the fitting, the surface complexation constants for Np(IV) estimated by using

LFER by Bradbury and Baeyens (2005) were used as the initial guesses. For the starting value for the reaction (3), log $^{s}K = -16.9$ was used although this was estimated for Th(IV). As explained above, a weight of 1 was applied to all data (I = 0.1 M and 4 M), and the error was estimated by the root mean squared deviation.

In this work, the 2 SPNE SC/CE model (Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005) was not applied for the K_d values on shale. This was because (i) there was a possibility that Np(IV) sorbed not only on illite contained in Queenston shale but also on other minerals such as chlorite, calcite and dolomite as discussed in Section 3.2.7, and the investigation on the reliability of 2 SPNE SC/CE model for various types of solid surface was beyond the scope of the present study, (ii) the composition of minerals contained in shale significantly depends on its origin, and (iii) the LFER for shale has not yet been developed, and therefore it was not easy to discuss the validity of surface complexation constants of Np(IV) for shale.

4.1.2 Sorption Modelling for Np(V) K_d Values

The pH$_c$ dependence of Np(V) K_d values was studied at I = 4.6 M (see Section 3.1.5). The SIT thermodynamic database can be used to calculate activity coefficients of aqueous species up to approximately I = 4 M (Ciavatta 1980). Pitzer parameters for Np(V) in NaCl-CaCl$_2$ solution are not completely compiled. Hence, the speciation in aqueous solution at I = 4.6 M cannot be estimated at the present. However, as shown in Section 3.1.6, the K_d values do not depend on the ionic strength, suggesting that the pH$_c$ dependence of K_d values at I = 4 M is similar to that at I = 4.6 M. In this work, keeping the reliability limit of SIT in mind, the 2 SPNE SC/CE model (Bradbury and Baeyens 2009b, Bradbury and Baeyens 2005) was applied to the pH$_c$ dependence of Np(V) K_d values on illite (Silver Hill) and MX-80 measured at I = 4.6 M (Figure 5). The SIT database was used to calculate activity coefficients of aqueous species. Thermodynamic constants for Np(V) aqueous species were taken from the NEA thermodynamic database (Guillaumont et al. 2003). The values of specific surface area, sorption site capacity, and equilibrium constants for surface protolysis reactions for solids explained in Section 4.1.1 were adopted in the model simulation. At first, the Np(V) K_d values for illite (Silver Hill) and MX-80 were calculated using the surface complexation constants proposed by Bradbury and Baeyens (2009b, 2005). Then, the surface complexation constants which provided the best fit to the measured Np(V) K_d values for illite (Silver Hill) and MX-80 were estimated.

4.2 RESULTS AND DISCUSSION

4.2.1 Sorption Modelling for Np(IV) K_d Values

The simulation results for illite and bentonite by 2 SPNE SC/CE model are presented in Figure 13 (a) and (b). As shown in Figure 13 (a) and (b), the simulation results in the pH$_c$ range between 5 and 10 at I = 4 M was identical to that at I = 0.1 M for both solids. This trend is the same as the results shown in the previous research (Marsac et al. 2017, Bradbury and Baeyens. 2009b, Bradbury and Baeyens 2005). Furthermore, the best fits using the surface complexation constants obtained in this work (lines ① and ② in Figure 13 (a) and (b)) were significantly different from the simulation results using the reported surface complexation constants (Marsac et al. 2015, Bradbury and Baeyens. 2005) (lines ③ and ④ in Figure 13 (a) and (b)).

For illite, it was found that the K_d values simulated using the surface complexation constants of Np(IV) by Marsac et al. (2015) (lines ③ and ④ in Figure 13 (a)) were larger than the measured K_d values at $pH_c \geq 4$. The reason is not clear at the present. Banik et al. (2016) reported that the K_d values in 0.1 mol/L NaCl solution by 2 SPNE SC/CE model using the surface complexation constants of Np(IV) by Marsac et al. (2015) were larger at pH ≥ 4 and smaller at pH ≤ 4 than those using the surface complexation constants of Pu(IV) by Banik et al. (2016). The surface complexation constants of Pu(IV) were fully obtained through the sorption experiments at m_{NaCl} = 0.1, 1.0 and 3.2 molal (Marsac et al. 2017, Banik et al. 2016), while those of Np(IV) were estimated only from the sorption experiments at m_{NaCl} = 0.1 mol/L (Marsac et al. 2015). Furthermore, Marcas et al. (2015) compared the predicted Np(IV)-illite pH-edge with the experimental pH-edge of Th(IV) and Sn(IV). The predicted Np(IV) K_d values were larger than the experimental values of Th(IV) and Sn(IV) at pH ≥ 5. Hence, the model using the surface complexation constants of Np(IV) by Marsac et al. (2015) might overestimate the sorption of Np(IV) on illite (Silver Hill).

Table 11 summarizes the surface complexation constants for Np(IV) sorption on illite (Silver Hill) estimated in the present work. The estimated surface complexation constants for Np(IV) by this work agreed well with those estimated for Pu(IV) sorption on illite du Puy (Banik et al. 2016). The K_d values of Np(IV) on illite (Silver Hill) were qualitatively simulated using these estimated surface complexation constants by the 2 SPNE SC/CE model in the wide range of pH_c (lines ① and ② in Figure 13 (a)). Although there were several assumptions in the simulation as mentioned before, the Np(IV) sorption on illite (Silver Hill) was found to be explained by the surface complexation reactions that Bradbury and Baeyens considered for illite du Puy (Bradbury and Baeyens. 2009b), and the surface complexation constants estimated for Np(IV) sorption on illite (Silver Hill) followed the LFER approach proposed for illite du Puy (Bradbury and Baeyens. 2009b).

For MX-80, the surface complexation constant of the reation (3) was estimated as $\log {}^{s}K = -7.8 \pm 0.3$ (I = 0 M). Using $\log {}^{s}K = -7.8 \pm 0.3$ for reaction (3) and the surface complexation constants of Np(IV) on montmorillonite estimated by Bradbury and Baeyens (2005) for other reactions, it was found that the simulation results by 2 SPNE SC/CE model were qualitatively consistent with the experimental K_d values at $pH_c \geq 6$, but were much smaller than those at $pH_c \leq 5$ (lines ③ and ④ in Figure 13 (b)).

The values of surface complexation constants for Np(IV) on MX-80 which gave the best fit to the pH_c dependence of K_d values measured in the present work (lines ① and ② in Figure 13 (b)) were estimated, as given in Table 12. The values estimated by Bradbury and Baeyens (2005) based on the LFER are also shown in Table 12. In this estimation, the surface complexation reactions on weak sites were neglected, because the concentration of Np(IV) is very small.

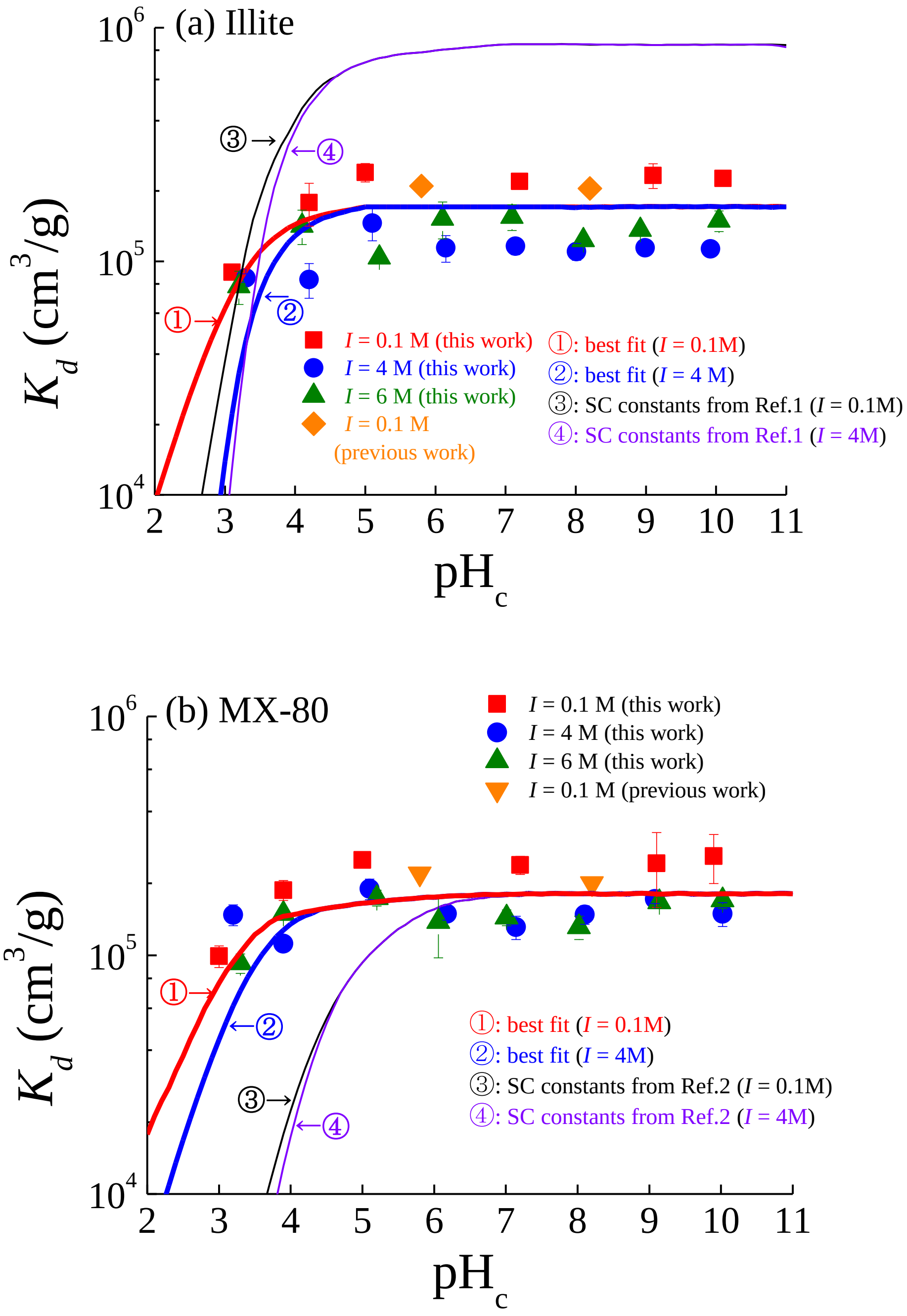


Figure 13: Simulation Results Using 2 SPNE SC/CE Model for Np(IV) Sorption on (a) Illite (Silver Hill), and (b) MX-80. “SC constant” Represents Surface Complexation Constant. Ref.1: Marcas et al. (2015). Ref.2: Bradbury and Baeyens (2005). Previous Work: Nagasaki (1994)

Table 11: Surface Complexation Constants for Illite Estimated in This Work, by Marsac et al. (2015) and by Banik et al. (2016)

Surface species	log *K* (*I* = 0 m) for Np(IV) (this work)	log *K* (*I* = 0 m) for Np(IV) (Marsac et al. 2015)	log *K* (*I* = 0 m) for Pu(IV) (Banik et al. 2016)
$\equiv S^sONp^{3+}$	nd	na	na
$\equiv S^sONpOH^{2+}$	9.9±0.1	na	9.9
$\equiv S^sONp(OH)_2^{+}$	5.9±0.2	6.4±1.2	5.9
$\equiv S^sONp(OH)_3^{0}$	0.0±0.3	0.7±1.0	0.1
$\equiv S^sONp(OH)_4^{-}$	-6.6±0.2	-5.7±1.2	-6.4

“nd” refers to value that could not be determined. “na” refers to values that are not available.

Table 12: Surface Complexation Constants for MX-80 Estimated in This Work and Estimated by Bradbury and Baeyens (2005)

Surface species	log ^sK (*I* = 0 m) on strong site (this work)	log ^sK on strong site (Bradbury and Baeyens 2005)
$\equiv S^sONp^{3+}$	nd	8.5 (8.2 – 8.9)
$\equiv S^sONpOH^{2+}$	10±0.3	8.3 (8.1 – 8.8)
$\equiv S^sONp(OH)_2^{+}$	5.7±0.2	5.5 (5.3 – 5.8)
$\equiv S^sONp(OH)_3^{0}$	0.10±0.1	0.1 (-0.032 – 0.21)
$\equiv S^sONp(OH)_4^{-}$	-7.8±0.3	–

“nd” refers to value that could not be determined. The range of log *K* on strong site calculated with a LFER equation proposed by Bradbury and Baeyens (2005) are shown in parentheses.

We found that the reactions “$\equiv S^sOH + Np^{4+} \leftrightarrow \equiv S^sONp^{3+} + H^{+}$” on MX-80 did not contribute to the simulation practically. The surface complexation constants for surface species “$\equiv S^sONp(OH)_2^{+}$” and “$\equiv S^sONp(OH)_3^{0}$”, log ^sK = 5.7±0.2 and log ^sK = 0.10±0.1, respectively, were consistent well with those estimated by LFER by Bradbury and Baeyens (2005). On the other hand, the surface complexation constant for surface species “$\equiv S^sONpOH^{2+}$” estimated in this work was larger than that by LFER.

These observations suggest that the 2 SPNE SC/CE model is a valuable tool to predict the K_d values of Np(IV) and simulate the variation of the K_d values of Np(IV) in high ionic strength solutions (0.5 M ≤ I ≤ 4 M) for illite (Silver Hill) and MX-80 in the wide range of pH_c ($3 \le pH_c \le 10$). On the other hand, it is noteworthy that because it neglects an electrostatic part of the surface complexation reaction, the 2 SPNE SC/CE model is unable to describe the ionic strength dependence. Namely the decrease in the K_d values from I = 0.1 M to 0.5 M cannot be seen in the fitting of Figure 13 (a) and (b) (at pH_c = 8 for illite and pH_c = 8.8 for MX-80), while the decrease was observed experimentally as shown in Figure 12. Furthermore, according to Bradbury and Baeyens (2005) and Marsac et al. (2017), the contribution of cation exchange reaction for Np(IV) sorption to illite (Silver Hill) and MX-80 was also neglected in the simulation. In other words, the 2 SPNE SC/CE model is not able to describe the ionic strength dependence for the sorption of tetravalent ions such as Np(IV) in principle except for that caused by the variation of the activity coefficients of relevant species. These assumptions are certainly valid for Np(IV) and Pu(IV) sorption on Illite du Puy, and reasonable for the sorption of tetravalent actinides in high ionic strength solutions (*I* ≥ 0.5 M, for example). However, the contribution of electrostatic interactions and cation exchange reactions needs to be considered for Np(IV) sorption on illite (Silver Hill) and MX-80 in low ionic strength solutions.

4.2.2 Sorption Modelling for Np(V) K_d Values

The simulation results of Np(V) sorption on illite and MX-80 using the surface complexation constants proposed by Bradbury and Baeyens (2009b, 2005) are illustrated in Figure 14. It was found that the simulation results underestimated the Np(V) K_d values both for illite (Silver Hill) and MX-80.

The best fit simulation using the 2 SPNE SC/CE model is shown in Figure 15. The surface complexation constants estimated in this study for illite and MX-80 are shown in Table 13 and Table 14, respectively. For illite (Silver Hill), the simulation results agreed well with the measured Np(V) K_d values. For MX-80, there was still a small discrepancy between the simulation results and the measured K_d values. Considering the simulation of Np(V) K_d values on Na-smectite (Bradbury and Baeyens 2005) and the uncertainties of K_d values, the simulation results for Np(V) on MX-80 in this work could be considered to agree with the measured K_d values.

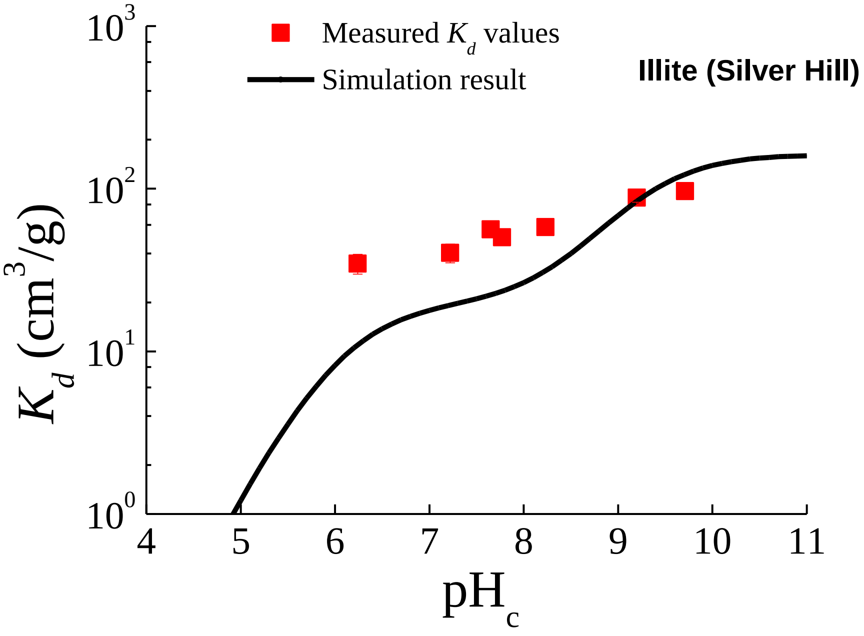
Table 13: Np(V) Surface Complexation Constants for Illite (Silver Hill) Estimated in This Work and Estimated by Bradbury and Baeyens (2009b, 2005)

Surface species	log ^sK (I = 0 M) on strong site (this work)	log ^sK on strong site (Bradbury and Baeyens 2009b)
$\equiv S^sONpO_2^0$	-2.1	-2.0
$\equiv S^sONpO_2OH^-$	-13.1	-10.3

Table 14: Np(V) Surface Complexation Constants for MX-80 Estimated in This Work and Estimated by Bradbury and Baeyens (2005)

Surface species	log ^sK (I = 0 M) on strong site (this work)	log ^sK on strong site (Bradbury and Baeyens 2005)
$\equiv S^sONpO_2^0$	-2.1	-2.9
$\equiv S^sONpO_2OH^-$	-12.0	-12.7

Note that because the SIT database cannot be applied to the aqueous solution with *I* = 4.6 M in principle, the reliability of simulation results should be further discussed when the Pitzer parameters for Np in brine solutions are available.



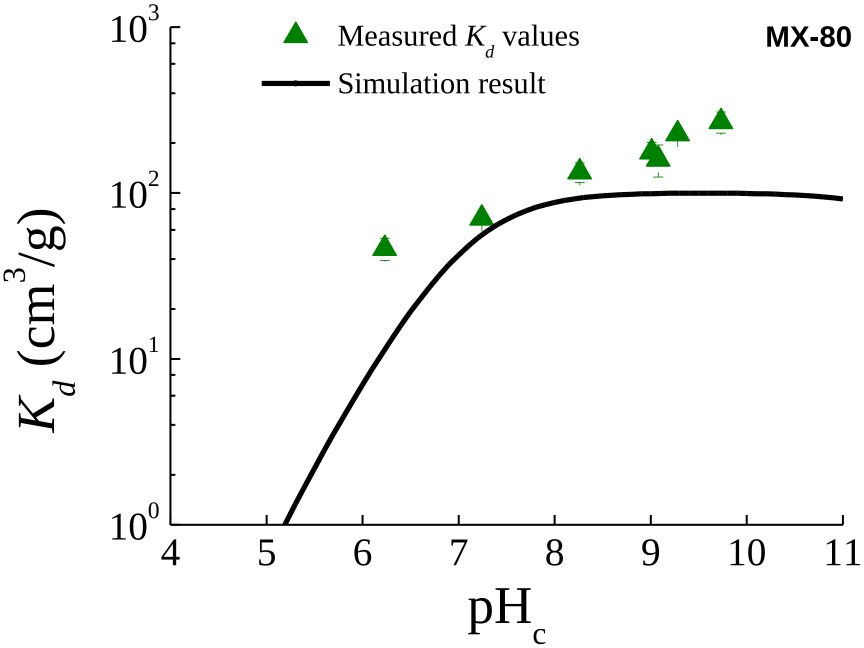


Figure 14: Simulation Results Using 2 SPNE SC/CE Model for Np(V) Sorption on Illite and MX-80 Using the the Surface Complexation Constants by Bradbury and Baeyens (2009b, 2005)

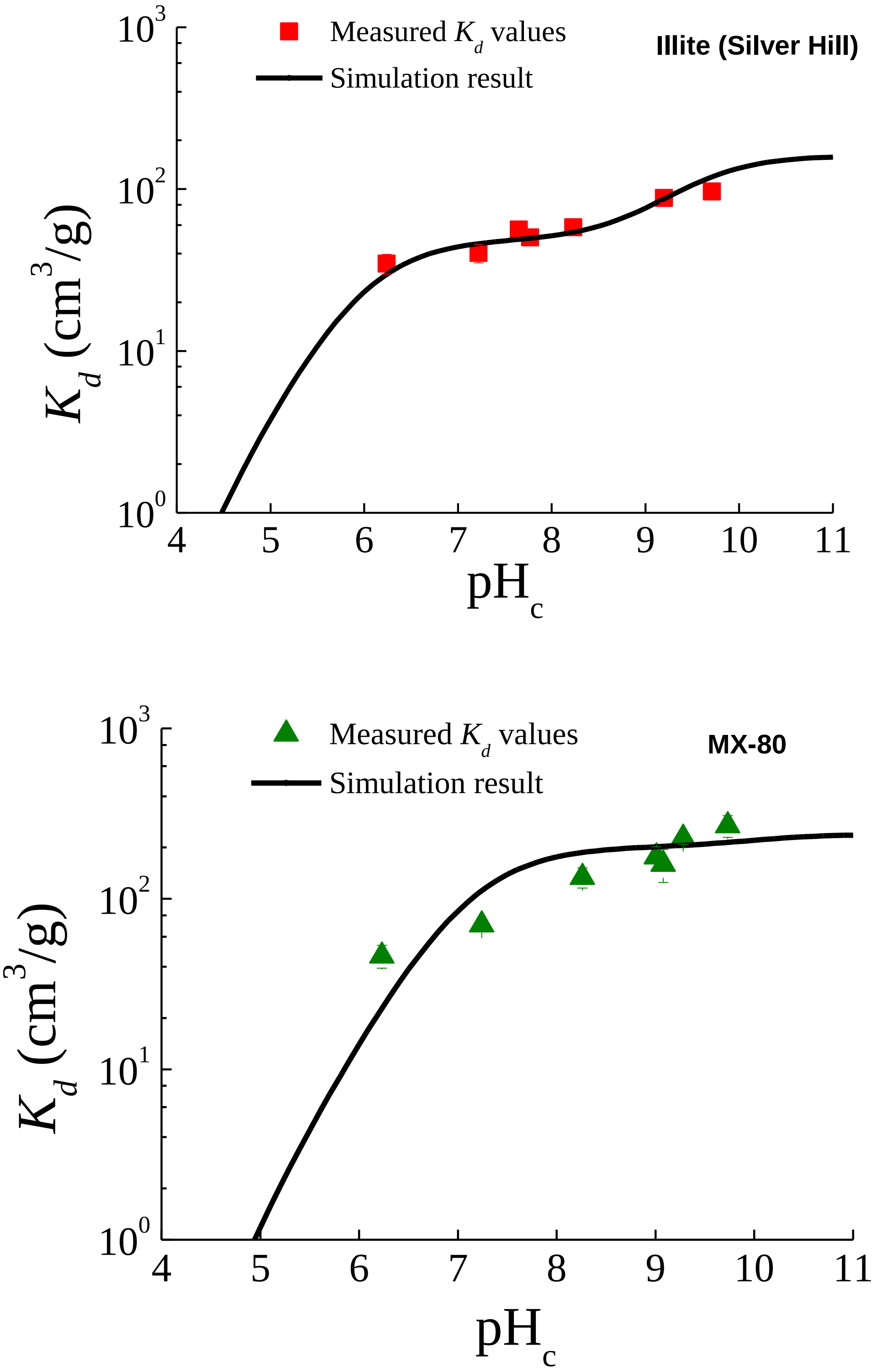


Figure 15: Simulation Results Using 2 SPNE SC /CE Model for Np(V) Sorption on Illite (Silver Hill) and MX-80

5. SUMMARY

This is the first research systematically studying the sorption behaviors of Np(V) and Np(IV) on illite (Silver Hill), Queenston shale and MX-80 under a wide range of high ionic strength solutions.

The sorption equilibrium of Np(V) on illite (Silver Hill), Queenston shale and MX-80 was achieved within 3 days and was independent of the compositions of the studied solutions. The respective K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 are $(6.5 \pm 0.44) \times 10^1$ cm^3/g, $(5.7 \pm 0.47) \times 10^1$ cm^3/g and $(1.42 \pm 0.29) \times 10^2$ cm^3/g in the SR-270-PW reference brine solution (I = 6 M), and $(5.6 \pm 0.28) \times 10^1$ cm^3/g, $(3.9 \pm 0.42) \times 10^1$ cm^3/g and $(1.76 \pm 0.26) \times 10^2$ cm^3/g in the NaCl-$CaCl_2$ (I = 4.6 M) solution. Considering the experimental errors in the K_d values and the difference of pH_c, there may be no marked difference in the K_d values on illite and MX-80 between these two solutions. On the other hand, the K_d value on shale in the SR-270-PW reference brine solution is observed to be larger than those in the NaCl-$CaCl_2$ (I = 4.6 M) brine solution.

The K_d values of Np(V) on MX-80 in the SR-270-PW brine were independent of the S/L ratios. Those on illite (Silver Hill) and Queenston shale in the SR-270-PW brine and NaCl-$CaCl_2$ (I = 4.6 M) solution as well as those on MX-80 in the NaCl-$CaCl_2$ (I = 4.6 M) solution increased with the S/L ratio and reached plateaus at S/L ratios above 0.3 g/5.0 mL. The K_d value of Np(V) on illite (Silver Hill), Queenston shale and MX-80 in the NaCl-$CaCl_2$ (I = 4.6 M) solution increased with $pH_{c.}$ The K_d values of Np(V) on illite and shale were independent of the ionic strength in the range of 0.10 - 4.6 M. That on MX-80 decreased with increasing the ionic strength from 0.10 M to 1.0 M, but was independent of ionic strength at the ionic strength over 1.0 M. The K_d values of Np(V) on illite (Silver Hill), Queenston shale and MX-80 were all observed to increase with the Na/Ca molar concentration ratio of solutions. The slopes of the sorption isotherms of Np(V) for illite (Silver Hill), Queenston shale and MX-80 in both the SR-270-PW brine and NaCl-$CaCl_2$ (I = 4.6 M) solution were approximately 1 at the Np(V) equilibrium concentration less than 2×10^{-6} mol/L.

The sorption equilibrium of Np(IV) for illite (Silver Hill), Queenstone shale and MX-80 in NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) solution were achieved within 3 to 7 days. The K_d values of Np(IV) sorption for illite (Silver Hill), Queenston shale and MX-80 in the SR-270-PW reference brine solutions were $(9.2 \pm 1.5) \times 10^4$ cm^3/g, $(9.8 \pm 0.93) \times 10^4$ cm^3/g and $(1.3 \pm 0.31) \times 10^5$ cm^3/g, respectively. The average K_d values for illite (Silver Hill), Queenston shale, and MX-80 in NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) solution measured in sorption kinetics and pH_c and ionic strength dependence experiments were in the range of $(1.2 - 1.6) \times 10^5$ cm^3/g, $(1.3 - 1.8) \times 10^5$ cm^3/g, and $(1.7 - 2.2) \times 10^5$ cm^3/g, respectively. Considering the uncertainties of the K_d values, the variation in the K_d values for illite (Silver Hill), Queenston shale and MX-80 between the SR-270-PW reference brine solution and the NaCl-$CaCl_2$-$NaClO_4$ (I = 6 M) solution was considered to be insignificant. Np(IV) sorption K_d values for illite, shale and bentonite are three orders of magnitude larger than Np(V). Np(IV) is strongly sorbed into illite, shale and bentonite in highly saline solutions.

The overall trend of pH_c dependence of Np(IV) on illite (Silver Hill), Queenston shale and MX-80 was that the K_d values increased with pH_c at $pH_c \leq 5$ and were independent of pH_c at $5 \leq pH_c \leq 10$. The overall trend of ionic strength dependence of Np(IV) on illite (Silver Hill), Queenston shale and MX-80 was that the K_d values decreased from I = 0.1 M to 0.5 M, and did not depend on ionic strength at 0.5 M ≤ I ≤ 6 M. The K_d values of Np(IV) increased with Na/Ca ratio for illite (Silver Hill), Queenston shale and MX-80.

The surface complexation constants for Np(IV) sorption on illite (Silver Hill) and MX-80 were estimated by fitting the 2 SPNE SC/CE model to the measured pH_c dependence of the K_d values. It was found that the 2 SPNE SC/CE model is a valuable tool to simulate the pH_c dependence of the K_d values of Np(IV) in high ionic strength solutions (0.5 M ≤ I ≤ 4 M) for illite (Silver Hill) and MX-80 in the wide range of pH_c ($3 \le pH_c \le 10$). However, because it neglects an electrostatic part of surface complexation reaction, the 2 SPNE SC/CE model could not simulate the decrease in the K_d values from I = 0.1 M to 0.5 M. The contribution of electrostatic interaction and cation exchange reactions needs to be considered for Np(IV) sorption on illite (Silver Hill) and MX-80 in low ionic strength solutions. The surface complexation constants for Np(V) sorption on illite (Silver Hill) and MX-80 were estimated. The simulation results for Np(V) sorption on illite (Silver Hill) and MX-80 agree with the measured K_d values.

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APPENDIX A: PH AND EH VALUES IN NP(V) AND NP(IV) SORPTION EXPERIMENTS

CONTENTS

A.1 pH and Eh values in deionized water prepared for Np(IV) sorption experiments

(1) pH and Eh (vs. Ag/AgCl) in the deionized water after Fe powder was removed

pH	7.1 – 7.3
Eh (vs. Ag/AgCl) (mV)	-450 – -500

(2) pH and Eh (vs. Ag/AgCl) in the solution after 1 x 10^{-2} mol/L $Na_2S_2O_4$ was added

pH	6.1 – 6.5
Eh (vs. Ag/AgCl) (mV)	-450 – -500

(3) Change in the pH_c and Eh (vs. SHE) in $NaCl$-$CaCl_2$-$NaClO_4$ (I = 6 M) brine solution with time

Time (day)	pH_c	Eh (vs. SHE) (mV)
1	6.0 - 6.7	–250 – –170
3	6.2 - 6.5	–250 – –180
7	6.5 - 7.0	–250 – –190
14	6.1 - 6.9	–220 – –170
30	6.3 - 6.8	–220 – –180

A.2 pH_c, Eh (vs. Ag/AgCl) and sorption percent values of solutions in Np(V) sorption kinetics experiments

***S*/*L* = 0.1 g/5.0 mL**

SR-270-PW	Illite		Shale		MX-80	
	pH_c	Eh (mV)	pH_c	Eh (mV)	pH_c	Eh (mV)
	Sorption percent (%)		Sorption percent (%)		Sorption percent (%)	
1 day	8.0	192	7.9	187	8.5	196
	19.4±2.89		7.73±2.61		20.6±2.61	
2 days	8.1	189	7.9	191	8.4	195
	37.0±1.39		9.86±1.04		51.2±4.84	
3 days	8.0	189	7.9	188	8.4	187
	45.4±1.71		28.5±1.00		76.9±1.01	
1 week	8.1	191	7.8	189	8.4	189
	45.2±1.95		28.3±1.71		76.9±1.18	
3 weeks	8.1	190	7.9	190	8.5	192
	44.6±1.43		28.1±1.32		77.0±1.08	

***S*/*L* = 0.5 g/5.0 mL**

SR-270-PW	Illite		Shale		MX-80	
	pH_c	Eh (mV)	pH_c	Eh (mV)	pH_c	Eh (mV)
	Sorption percent (%)		Sorption percent (%)		Sorption percent (%)	
1 day	8.3	179	8.4	191	8.8	189
	33.5±3.80		33.6±4.17		50.7±9.19	
3 days	8.2	191187	8.5	201192	8.7	
	86.2±1.98		83.2±1.28		93.4±0.80	
1 week	8.1	194189	8.4	199193	8.5	191
	86.5±1.10		83.6±1.07		94.0±1.50	
3 weeks	8.3	193192	8.2	201190	8.5	194
	85.6±2.40		82.8±1.34		93.5±1.08	

***S/L* = 0.1 g/5.0 mL**

NaCl-CaCl$_2$ (I = 4.6 M) solution	Illite		Shale		MX-80	
	pH$_c$	Eh (mV)	pH$_c$	Eh (mV)	pH$_c$	Eh (mV)
	Sorption percent (%)		Sorption percent (%)		Sorption percent (%)	
1 day	8.3	199	8.4	201	9.4	193
	14.8±3.24		2.68±3.10		9.30±0.52	
2 days	8.0	190	8.4	201	9.2	196
	28.7±2.69		15.3±3.45		47.6±2.54	
3 days	8.2	191	8.5	201	9.3	195
	36.9±1.67		26.3±1.88		66.2±1.25	
1 week	8.1	194	8.4	199	9.5	195
	36.6±2.68		26.4±3.20		67.1±1.50	
3 weeks	8.2	193	8.2	201	9.5	195
	36.7±1.29		26.3±3.00		64.5±2.33	

***S/L* = 0.5 g/5.0 mL**

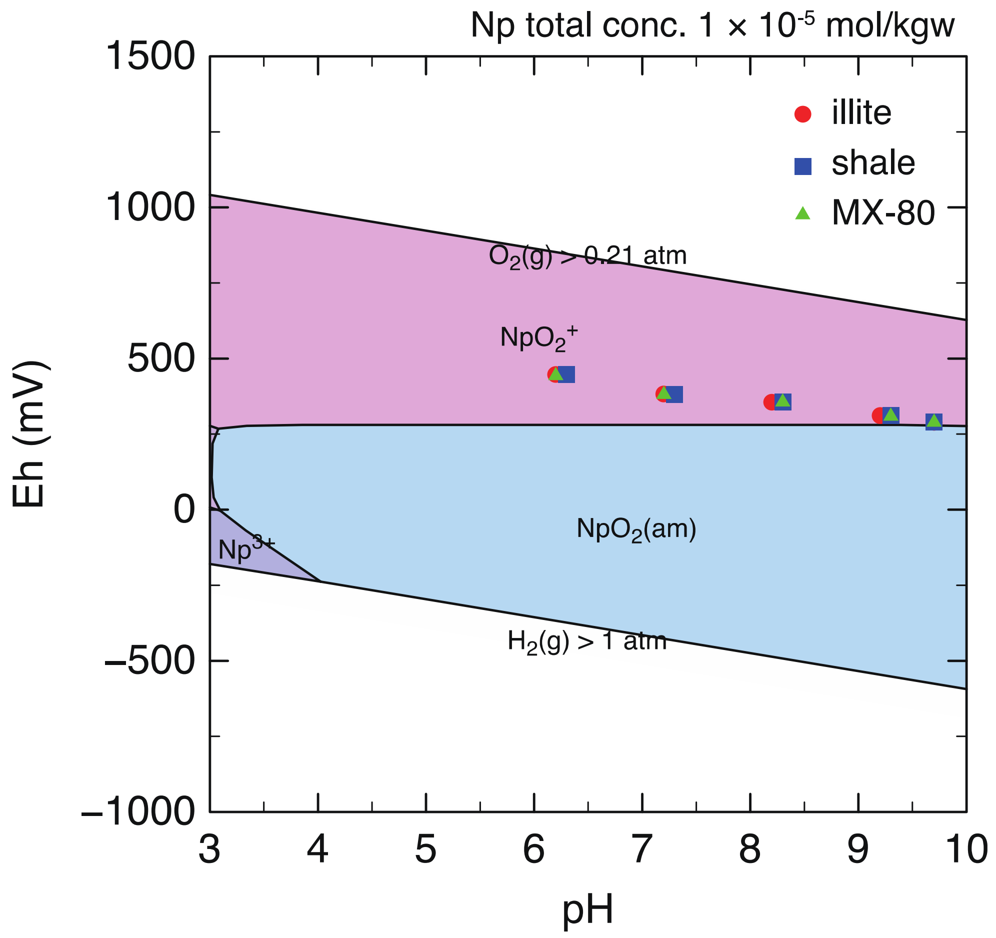
NaCl-CaCl$_2$ (I = 4.6 M) solution	Illite		Shale		MX-80	
	pH$_c$	Eh (mV)	pH$_c$	Eh (mV)	pH$_c$	Eh (mV)
	Sorption percent (%)		Sorption percent (%)		Sorption percent (%)	
1 day	8.1	188	8.4	199	9.4	192
	38.8±5.76		30.3±10.4		43.7±5.04	
3 days	8.2	179	8.5	203	9.1	196
	83.8±1.03		80.2±1.46		94.3±0.97	
1 week	8.2	183	8.5	202	9.1	201
	83.3±1.09		80.2±0.83		94.0±1.14	
3 weeks	8.1	189	8.5	203	9.2	196
	83.4±1.63		79.8±0.85		94.0±0.87	

A.3 $\mathrm{pH_c}$, Eh (mV) (vs. SHE) and K_d values of the solid/liquid ratio dependence of Np(V) K_d values experiments in SR-270-PW reference brine and $\mathrm{NaCl\text{-}CaCl_2}$ (I = 4.6 M) solutions

SR-270-PW				
Solid		Illite	Shale	MX-80
S/L = 0.10 g/5.0 mL	$\mathrm{pH_c}$	7.7	7.4	7.9
	Eh (mV)	351	349	349
	K_d (cm^3/g)	38±2.7	20±1.7	167±11
S/L = 0.20 g/5.0 mL	$\mathrm{pH_c}$	7.6	7.7	8.0
	Eh (mV)	348	359	356
	K_d (cm^3/g)	40±3.6	33±2.5	157±38
S/L =0.30 g/5.0 mL	$\mathrm{pH_c}$	7.7	7.4	8.0
	Eh (mV)	347	356	353
	K_d (cm^3/g)	68±9.3	50±4.9	164±20
S/L = 0.40 g/5.0 mL	$\mathrm{pH_c}$	7.7	7.4	8.0
	Eh (mV)	335	352	359
	K_d (cm^3/g)	72±7.8	49±7.0	137±28
S/L = 0.50 g/5.0 mL	$\mathrm{pH_c}$	7.6	7.4	8.1
	Eh (mV)	349	353	354
	K_d (cm^3/g)	65±4.4	57±4.7	142±29
$\mathrm{NaCl\text{-}CaCl_2}$ (I = 4.6 M) solution				
Solid		Illite	Shale	MX-80
S/L = 0.10 g/5.0 mL	$\mathrm{pH_c}$	7.7	8.0	9.0
	Eh (mV)	359	361	306
	K_d (cm^3/g)	29±3.3	18±2.9	102±6.9
S/L = 0.20 g/5.0 mL	$\mathrm{pH_c}$	7.7	8.1	9.1
	Eh (mV)	348	362	305
	K_d (cm^3/g)	34±6.0	29±5.2	149±45
S/L = 0.30 g/5.0 mL	$\mathrm{pH_c}$	7.7	7.9	8.9
	Eh (mV)	349	360	308
	K_d (cm^3/g)	53±3.1	48±8.1	191±65
S/L = 0.40 g/5.0 mL	$\mathrm{pH_c}$	7.7	7.8	9.0
	Eh (mV)	348	358	310
	K_d (cm^3/g)	44±3.4	37±4.9	142±30
S/L = 0.50 g/5.0 mL	$\mathrm{pH_c}$	7.8	8.0	9.1
	Eh (mV)	343	362	311
	K_d (cm^3/g)	56±2.8	39±4.2	176±26

A. 4 pH$_c$, Eh (mV) (vs. SHE) and K_d values of the pH$_c$ dependence of Np(V) K_d values experiments in the NaCl-CaCl$_2$ (I = 4.6 M) solution

Illite	pH$_c$	6.2	7.2	8.2	9.2	9.7
	Eh (mV)	448	383	356	311	289
	K_d (cm^3/g)	35±4.8	40±5.3	58±6.3	88±5.5	96±7.9
Shale	pH$_c$	6.3	7.3	8.3	9.3	9.7
	Eh (mV)	447	381	356	311	290
	K_d (cm^3/g)	26±5.9	33±5.4	40±8.2	63±8.2	72±14
MX-80	pH$_c$	6.2	7.2	8.3	9.3	9.7
	Eh (mV)	443	381	356	309	289
	K_d (cm^3/g)	46±7.0	70±5.2	134±18	227±18	269±39


Np pH/Eh diagram (I = 4.6 M)

A.5 pH$_c$, Eh (mV) (vs. SHE) and K_d values of the ionic strength dependence of Np(V) K_d values experiments in NaCl-CaCl$_2$ solutions

Ionic Strength (M)		0.10	0.50	1.0	2.0	3.0	4.0	4.6
Illite	pH$_c$	7.8	7.2	7.1	7.3	7.2	7.4	7.7
	Eh (mV)	341	346	347	348	350	348	349
	K_d (cm^3/g)	57±7.6	51±5.4	59±6.4	51±7.3	51±7.3	47±7.9	56±2.8
Shale	pH$_c$	8.1	7.8	7.6	7.6	7.7	7.8	7.9
	Eh (mV)	358	362	363	362	364	361	364
	K_d (cm^3/g)	51±8.1	48±7.9	41±4.3	44±6.7	42±5.9	40±4.1	39±4.2
MX-80	pH$_c$	9.1	8.8	8.5	8.6	8.6	8.9	9.0
	Eh (mV)	306	311	320	321	325	312	310
	K_d (cm^3/g)	320±56	230±16	160±50	140±61	160±42	170±26	180±26

A.6 pH$_c$ and Eh (mV) (vs. SHE) values of CaCl$_2$, NaCl-CaCl$_2$ and NaCl solutions in the Na/Ca ratio dependence of Np(V) K_d values experiments

Solution		CaCl$_2$ solution	NaCl-CaCl$_2$ solution				NaCl solution
Na/Ca ratio		0	0.1	1	5	10	∞
Illite	pH$_c$	8.6	8.5	7.9	7.3	6.9	8.0
	Eh (mV)	339	335	354	384	393	351
Shale	pH$_c$	9.2	9.0	8.3	7.7	7.4	8.6
	Eh (mV)	313	315	343	361	359	326
MX-80	pH$_c$	10.2	10.0	9.4	8.7	8.5	8.7
	Eh (mV)	233	234	302	322	320	314

A.7 pH$_c$ and Eh (mV) (vs. SHE) values of SR-270-PW reference brine and NaCl-CaCl$_2$ (*I* = 4.6 M) solutions in Np(V) isotherm experiments

SR-270-PW					
Initial Np(V) Concentration (mol/L)		1 x 10^{-8}	1 x 10^{-7}	1 x 10^{-6}	1 x 10^{-4}
Illite	pH$_c$	7.6	7.7	7.6	7.6
	Eh (mv)	348	348	348	349
Shale	pH$_c$	7.5	7.5	7.5	7.4
	Eh (mv)	353	352	353	353
MX-80	pH$_c$	8.0	8.0	8.0	8.0
	Eh (mv)	355	354	355	356
NaCl-CaCl$_2$ (*I* = 4.6 M) solution					
Initial Np(V) Concentration (mol/L)		1 x 10^{-8}	1 x 10^{-7}	1 x 10^{-6}	1 x 10^{-4}
Illite	pH$_c$	7.6	7.6	7.8	7.6
	Eh (mv)	348	350	348	348
Shale	pH$_c$	8.0	7.9	7.9	8.0
	Eh (mv)	364	364	363	362
MX-80	pH$_c$	9.0	9.0	9.1	9.0
	Eh (mv)	310	309	309	309

A.8 pH_c, Eh (vs SHE) and K_d values of Np(IV) sorption kinetics experiments in NaCl-$CaCl_2$-$NaClO_4$ solutions

Solid/Liquid ratio = 0.1 (g)/1 (L)

		Illite	Shale	MX-80
1 day	pH_c	7.9	8.2	9.0
	Eh (mv)	−200	−190	−-200
	K_d (cm^3/g)	$(1.0\pm0.06)\times10^5$	$(9.5\pm1.35)\times10^4$	$(1.9\pm0.22)\times10^5$
2 days	pH_c	8.0	8.1	8.8
	Eh (mv)	−200	−180	−190
	K_d (cm^3/g)	$(1.1\pm0.13)\times10^5$	$(1.1\pm0.21)\times10^5$	$(2.0\pm0.11)\times10^5$
3 days	pH_c	7.9	8.2	8.9
	Eh (mv)	−190	−170	−160
	K_d (cm^3/g)	$(1.1\pm0.13)\times10^5$	$(1.1\pm0.45)\times10^5$	$(2.0\pm0.34)\times10^5$
7 days	pH_c	7.9	8.0	8.9
	Eh (mv)	−180	−170	−180
	K_d (cm^3/g)	$(1.3\pm0.18)\times10^5$	$(1.1\pm0.10)\times10^5$	$(2.2\pm0.39)\times10^5$
14 days	pH_c	8.0	8.1	8.9
	Eh (mv)	−150	−160	−170
	K_d (cm^3/g)	$(1.1\pm0.17)\times10^5$	$(1.2\pm0.13)\times10^5$	$(2.3\pm0.83)\times10^5$
30 days	pH_c	8.1	8.2	8.9
	Eh (mv)	−160	−160	−150
	K_d (cm^3/g)	$(1.2\pm0.15)\times10^5$	$(1.1\pm0.15)\times10^5$	$(2.3\pm0.34)\times10^5$

Solid/Liquid ratio = 0.2 (g)/1 (L)

		Illite	Shale	MX-80
1 day	pH_c	7.8	8.0	9.1
	Eh (mv)	−190	−200	−200
	K_d (cm^3/g)	$(1.2\pm0.07)\times10^5$	$(1.1\pm0.16)\times10^5$	$(1.5\pm0.18)\times10^5$
2 days	pH_c	8.1	8.0	9.0
	Eh (mv)	−190	−180	−200
	K_d (cm^3/g)	$(1.3\pm0.16)\times10^5$	$(1.3\pm0.25)\times10^5$	$(1.6\pm0.09)\times10^5$
3 days	pH_c	7.9	8.1	8.8
	Eh (mv)	−200	−180	−180
	K_d (cm^3/g)	$(1.3\pm0.15)\times10^5$	$(1.4\pm0.05)\times10^5$	$(1.6\pm0.27)\times10^5$
7 days	pH_c	7.8	8.0	8.8
	Eh (mv)	−190	−180	−170
	K_d (cm^3/g)	$(1.5\pm0.22)\times10^5$	$(1.3\pm0.12)\times10^5$	$(1.8\pm0.31)\times10^5$
14 days	pH_c	8.2	7.8	8.9
	Eh (mv)	−170	−160	−160
	K_d (cm^3/g)	$(1.4\pm0.20)\times10^5$	$(1.5\pm0.16)\times10^5$	$(1.9\pm0.66)\times10^5$
30 days	pH_c	8.1	7.9	8.8
	Eh (mv)	−160	−170	−140
	K_d (cm^3/g)	$(1.4\pm0.18)\times10^5$	$(1.3\pm0.18)\times10^5$	$(1.9\pm0.27)\times10^5$

A.9 Initial and final pH$_c$ and Eh (vs. SHE) values of SR-270-PW reference brine solution in Np(IV) sorption experiments

Solid	pH$_c$ initial	pH$_c$ final	Eh (mV) initial	Eh (mV) final
illite	7.7	7.8	−100	−80
shale	7.4	7.6	−90	−80
MX-80	8.0	8.1	−90	−80

A.10 Initial and final pH_c and Eh (vs. SHE) of solutions and K_d values in pH_c dependence of Np(IV) K_d values experiments

(1) Ionic strength = 4 M (NaCl-$CaCl_2$ solution)

	Illite	Shale	MX-80
pH_c initial	3.2	3.1	3.2
pH_c final	3.3	3.3	3.2
Eh (mV) initial	−120	−100	−110
Eh (mV) final	−110	−110	−100
K_d (cm^3/g)	$(8.5\pm0.34)\times10^4$	$(8.7\pm2.0)\times10^4$	$(1.5\pm0.15)\times10^5$
pH_c initial	4.0	4.1	4.3
pH_c final	4.2	3.9	3.9
Eh (mV) initial	−100	−100	−100
Eh (mV) final	−110	−90	−90
K_d (cm^3/g)	$(8.4\pm1.4)\times10^4$	$(1.1\pm0.04)\times10^5$	$(1.1\pm0.05)\times10^5$
pH_c initial	5.1	4.9	4.8
pH_c final	5.1	5.2	5.1
Eh (mV) initial	−120	−110	−110
Eh (mV) final	−100	−80	−90
K_d (cm^3/g)	$(1.5\pm0.23)\times10^5$	$(1.6\pm0.06)\times10^5$	$(1.9\pm0.19)\times10^5$
pH_c initial	6.1	6.2	6.2
pH_c final	6.2	6.2	6.2
Eh (mV) initial	−130	−120	−120
Eh (mV) final	−120	−110	−110
K_d (cm^3/g)	$(1.1\pm0.15)\times10^5$	$(1.2\pm0.06)\times10^5$	$(1.5\pm0.09)\times10^5$
pH_c initial	7.0	6.9	7.2
pH_c final	7.1	7.0	7.1
Eh (mV) initial	−130	−130	−120
Eh (mV) final	−130	−110	−120
K_d (cm^3/g)	$(1.3\pm0.09)\times10^5$	$(1.2\pm0.02)\times10^5$	$(1.3\pm0.15)\times10^5$
pH_c initial	8.0	8.1	8.1
pH_c final	8.0	8.0	8.1
Eh (mV) initial	−160	−150	−120
Eh (mV) final	−150	−140	−110
K_d (cm^3/g)	$(1.1\pm0.09)\times10^5$	$(1.4\pm0.13)\times10^5$	$(1.5\pm0.13)\times10^5$
pH_c initial	9.1	9.1	9.0
pH_c final	9.0	9.1	9.1
Eh (mV) initial	−150	−150	−140
Eh (mV) final	−140	−130	−120
K_d (cm^3/g)	$(1.1\pm0.07)\times10^5$	$(1.7\pm0.10)\times10^5$	$(1.7\pm0.07)\times10^5$
pH_c initial	9.9	10.0	10.0
pH_c final	9.9	10.0	10.0
Eh (mV) initial	−170	−150	−140
Eh (mV) final	−150	−140	−120
K_d (cm^3/g)	$(1.1\pm0.07)\times10^5$	$(1.7\pm0.45)\times10^5$	$(1.5\pm0.17)\times10^5$

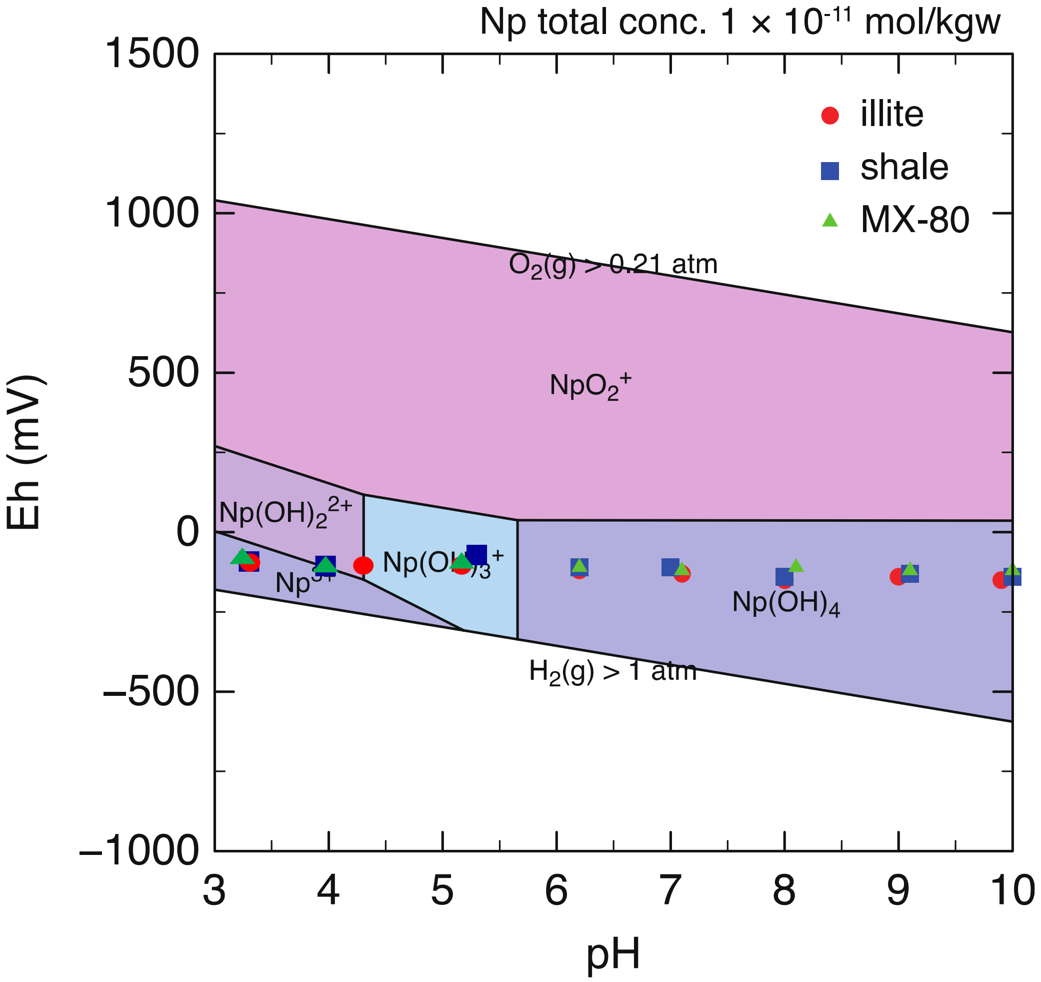
(2) Ionic strength = 6 M
(NaCl-CaCl$_2$-NaClO$_4$ solution)

	Illite	Shale	MX-80
pH$_c$ initial	3.1	3.2	3.3
pH$_c$ final	3.2	3.2	3.3
Eh (mV) initial	−100	−90	−100
Eh (mV) final	−80	−90	−80
K_d (cm^3/g)	$(7.8\pm1.3)\times10^4$	$(8.4\pm1.4)\times10^4$	$(9.3\pm0.87)\times10^4$
pH$_c$ initial	3.9	4.0	4.0
pH$_c$ final	4.1	4.2	3.9
Eh (mV) initial	−90	−110	−90
Eh (mV) final	−100	−100	−90
K_d (cm^3/g)	$(1.4\pm0.24)\times10^5$	$(1.1\pm0.03)\times10^5$	$(1.5\pm0.05)\times10^5$
pH$_c$ initial	5.0	5.0	4.9
pH$_c$ final	5.2	5.1	5.2
Eh (mV) initial	−120	−110	−100
Eh (mV) final	−100	−110	−90
K_d (cm^3/g)	$(1.0\pm0.02)\times10^5$	$(1.6\pm0.32)\times10^5$	$(1.7\pm0.13)\times10^5$
pH$_c$ initial	6.1	6.1	6.0
pH$_c$ final	6.1	6.0	6.1
Eh (mV) initial	−130	−120	−120
Eh (mV) final	−110	−100	−100
K_d (cm^3/g)	$(1.5\pm0.27)\times10^5$	$(1.5\pm0.04)\times10^5$	$(1.4\pm0.40)\times10^5$
pH$_c$ initial	6.9	6.9	7.1
pH$_c$ final	7.1	7.0	7.0
Eh (mV) initial	−140	−110	−100
Eh (mV) final	−120	−110	−100
K_d (cm^3/g)	$(1.6\pm0.20)\times10^5$	$(1.6\pm0.28)\times10^5$	$(1.4\pm0.11)\times10^5$
pH$_c$ initial	8.0	7.9	8.2
pH$_c$ final	8.1	8.1	8.0
Eh (mV) initial	−130	−130	−140
Eh (mV) final	−110	−120	−100
K_d (cm^3/g)	$(1.2\pm0.06)\times10^5$	$(1.7\pm0.37)\times10^5$	$(1.3\pm0.15)\times10^5$
pH$_c$ initial	9.0	8.9	9.0
pH$_c$ final	8.9	9.1	9.1
Eh (mV) initial	−150	−160	−150
Eh (mV) final	−140	−140	−120
K_d (cm^3/g)	$(1.4\pm0.07)\times10^5$	$(1.0\pm0.07)\times10^5$	$(1.7\pm0.07)\times10^5$
pH$_c$ initial	10.1	10.1	9.9
pH$_c$ final	10.0	10.1	10.0
Eh (mV) initial	−140	−170	−130
Eh (mV) final	−140	−130	−130
K_d (cm^3/g)	$(1.5\pm0.15)\times10^5$	$(9.5\pm0.27)\times10^4$	$(1.7\pm0.13)\times10^5$

(3) Ionic strength = 0.1 M (NaCl-$CaCl_2$ solution)

	Illite	MX-80
pH_c initial	3.0	2.8
pH_c final	3.1	3.0
Eh (mV) initial	−90	−90
Eh (mV) final	−90	−100
K_d (cm^3/g)	$(9.0 \pm 0.28) \times 10^4$	$(9.9 \pm 1.0) \times 10^4$
pH_c initial	4.1	4.0
pH_c final	4.2	3.9
Eh (mV) initial	−90	−100
Eh (mV) final	−100	−100
K_d (cm^3/g)	$(1.8 \pm 0.37) \times 10^5$	$(1.9 \pm 0.18) \times 10^5$
pH_c initial	5.1	5.2
pH_c final	5.0	5.0
Eh (mV) initial	−110	−100
Eh (mV) final	−100	−110
K_d (cm^3/g)	$(2.4 \pm 0.22) \times 10^5$	$(2.5 \pm 0.04) \times 10^5$
pH_c initial	7.3	6.8
pH_c final	7.2	7.2
Eh (mV) initial	−120	−100
Eh (mV) final	−120	−100
K_d (cm^3/g)	$(2.2 \pm 0.14) \times 10^5$	$(2.4 \pm 0.21) \times 10^5$
pH_c initial	8.8	9.0
pH_c final	9.1	9.1
Eh (mV) initial	−130	−120
Eh (mV) final	−120	−110
K_d (cm^3/g)	$(2.3 \pm 0.28) \times 10^5$	$(2.4 \pm 0.84) \times 10^5$
pH_c initial	10.2	10.1
pH_c final	10.1	9.9
Eh (mV) initial	−140	−140
Eh (mV) final	−120	−130
K_d (cm^3/g)	$(2.3 \pm 0.10) \times 10^5$	$(2.6 \pm 0.60) \times 10^5$

Np pH/Eh diagram (I = 4.0 M)



A.11 Initial and final pH$_c$ and Eh (vs. SHE) of solutions and K_d values of the ionic strength dependence of Np(IV) K_d values experiments.

I (M)		Illite	Shale	MX-80
0.1	pH$_c$ initial	8.1	8.1	8.9
	pH$_c$ final	8.0	8.2	9.1
	Eh (mV) initial	−170	−160	−150
	Eh (mV) final	−160	−150	−150
	K_d (cm^3/g)	$(2.6\pm0.88)\times10^5$	$(3.1\pm0.11)\times10^5$	$(3.0\pm1.1)\times10^5$
0.1	pH$_c$ initial	8.1	8.1	8.7
	pH$_c$ final	8.1	8.1	8.9
	Eh (mV) initial	−160	−140	−160
	Eh (mV) final	−150	−130	−130
	K_d (cm^3/g)	$(2.7\pm0.13)\times10^5$	$(2.6\pm0.43)\times10^5$	$(1.9\pm0.47)\times10^5$
0.5	pH$_c$ initial	8.0	8.2	9.0
	pH$_c$ final	8.2	8.3	9.0
	Eh (mV) initial	−170	−160	−140
	Eh (mV) final	−170	−160	−150
	K_d (cm^3/g)	$(1.9\pm0.23)\times10^5$	$(1.8\pm0.34)\times10^5$	$(2.1\pm0.58)\times10^5$
1	pH$_c$ initial	8.1	8.2	8.8
	pH$_c$ final	8.1	8.3	8.8
	Eh (mV) initial	−150	−150	−160
	Eh (mV) final	−150	−150	−140
	K_d (cm^3/g)	$(1.5\pm0.087)\times10^5$	$(1.2\pm0.13)\times10^5$	$(2.0\pm0.078)\times10^5$
2	pH$_c$ initial	7.9	8.3	9.0
	pH$_c$ final	7.8	8.4	8.9
	Eh (mV) initial	−180	−170	−150
	Eh (mV) final	−150	−150	−150
	K_d (cm^3/g)	$(1.2\pm0.27)\times10^5$	$(1.7\pm0.18)\times10^5$	$(1.6\pm0.089)\times10^5$
2	pH$_c$ initial	8.0	8.3	8.9
	pH$_c$ final	8.1	8.1	8.8
	Eh (mV) initial	−160	−140	−170
	Eh (mV) final	−160	−140	−150
	K_d (cm^3/g)	$(1.5\pm0.12)\times10^5$	$(1.5\pm0.087)\times10^5$	$(1.9\pm0.13)\times10^5$
3	pH$_c$ initial	8.0	8.4	9.1
	pH$_c$ final	8.1	8.1	9.0
	Eh (mV) initial	−180	−170	−160
	Eh (mV) final	−160	−150	−150
	K_d (cm^3/g)	$(1.5\pm0.54)\times10^5$	$(1.8\pm0.27)\times10^5$	$(1.5\pm0.32)\times10^5$
3	pH$_c$ initial	8.1	8.2	8.7
	pH$_c$ final	8.0	8.3	8.8
	Eh (mV) initial	−140	−160	−150
	Eh (mV) final	−150	−150	−130
	K_d (cm^3/g)	$(1.5\pm0.059)\times10^5$	$(1.5\pm0.10)\times10^5$	$(2.0\pm0.48)\times10^5$
4	pH$_c$ initial	8.3	8.1	8.6
	pH$_c$ final	8.1	8.2	8.9
	Eh (mV) initial	−170	−180	−160
	Eh (mV) final	−150	−160	−150

	K_d (cm^3/g)	$(1.3\pm0.20)\times10^5$	$(1.3\pm0.078)\times10^5$	$(1.9\pm0.085)\times10^5$
4	pH$_c$ initial	8.0	8.2	8.8
	pH$_c$ final	8.0	8.1	8.8
	Eh (mV) initial	−160	−150	−140
	Eh (mV) final	−160	−140	−140
	K_d (cm^3/g)	$(1.6\pm0.053)\times10^5$	$(1.6\pm0.26)\times10^5$	$(2.0\pm0.11)\times10^5$
6	pH$_c$ initial	8.0	8.3	9.0
	pH$_c$ final	8.3	8.4	9.1
	Eh (mV) initial	−170	−170	−160
	Eh (mV) final	−160	−160	−140
	K_d (cm^3/g)	$(1.3\pm0.087)\times10^5$	$(1.8\pm0.15)\times10^5$	$(1.7\pm0.17)\times10^5$
6	pH$_c$ initial	8.1	8.3	8.9
	pH$_c$ final	8.1	8.2	8.7
	Eh (mV) initial	−150	−160	−160
	Eh (mV) final	−140	−150	−140
	K_d (cm^3/g)	$(1.6\pm0.073)\times10^5$	$(1.3\pm0.16)\times10^5$	$(2.2\pm0.26)\times10^5$

A.12 Initial and final pH_c and Eh (vs, SHE) values of $CaCl_2$, $NaCl$-$CaCl_2$-$NaClO_4$, and NaCl solutions in Na/Ca ratio dependence of Np(IV) K_d values experiments

Illite

Na/Ca ratio	pH_c initial	pH_c final	Eh (mV) initial	Eh (mV) final
0 ($CaCl_2$ solution)	7.9	7.9	-130	-120
0.1	8.0	8.0	-120	-120
1	8.1	8.2	-110	-120
5	8.2	7.9	-120	-110
1×10^1	8.2	8.0	-120	-120
∞ (NaCl solution)	8.0	8.1	-130	-110

Shale

Na/Ca ratio	pH_c initial	pH_c final	Eh (mV) initial	Eh (mV) final
0 ($CaCl_2$ solution)	8.3	8.1	-120	-120
0.1	8.3	8.2	-130	-120
1	8.1	8.2	-130	-130
5	8.0	8.3	-120	-130
1×10^1	8.4	8.2	-110	-120
∞ (NaCl solution)	8.2	8.3	-120	-120

MX-80

Na/Ca ratio	pH_c initial	pH_c final	Eh (mV) initial	Eh (mV) final
0 ($CaCl_2$ solution)	8.9	8.7	-130	-120
0.1	9.0	8.8	-140	-120
1	8.7	8.9	-130	-110
5	9.0	8.9	-120	-120
1×10^1	8.8	9.0	-110	-100
∞ (NaCl solution)	8.9	8.9	-120	-110

APPENDIX B: PHREEQC INPUT FILES FOR NP(IV) K_d VALUES

CONTENTS

Page

B.1 PHREEQC input file for Np(IV) K_d values on illite using the surface complexation constants by Marsac et al. (Marsac et al. 2015)

```
DATABASE C:\Users\pc-nagasaki-jg\Desktop\Np(IV)
SCM\THEREDA\THEREDA_PIT_PHRC_R07.DAT

TITLE Neptunium(IV) Sorption onto Illite

KNOBS
   -logfile                   true
   -iterations                100
   -step_size                 100
   -tolerance                 1e-15
   -convergence_tolerance     1e-8
   -diagonal_scale            true

PITZER
         -macinnes            false
         -use_etheta          true

SURFACE_MASTER_SPECIES
Ill_s Ill_sOH

SURFACE_SPECIES
# Illite Surface Complexation Reactions
# Surface Sites - A-B
Ill_sOH = Ill_sOH
log_k 0.0
Ill_sOH + H+ = Ill_sOH2+
log_k 4.0
Ill_sOH = Ill_sO- + H+
log_k -6.2

# Inner/Outer Sphere Complexes - Metal Binding
Ill_sOH + Np+4 + 2H2O = Ill_sONp(OH)2+ + 3H+
log_k 6.4
Ill_sOH + Np+4 + 3H2O = Ill_sONp(OH)3 + 4H+
log_k 0.7
Ill_sOH + Np+4 + 4H2O = Ill_sONp(OH)4- + 5H+
log_k -5.7

SOLUTION 1 I = 0.1M
         temp    25
         units   mol/kgw
         density 1
         water   1 # kg
```

```
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.01754
        Na      0.04737
        Cl      0.08246
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_III_0.1
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 1" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END

SOLUTION 2 I = 4M
        temp    25
        units   mol/kgw
        density 1
        water   1 # kg
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.70175
        Na      1.89474
        Cl      3.29824
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_III_4.0
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 2" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END

PHASES
```

```
Fix_H+
H+ = H+
log_k 0.0
END

SURFACE 1
Ill_sOH 1.44e-6 70.0 1
-no_edl

SELECTED_OUTPUT
-file NpSCM.out
-reset true
-simulation false
-state false
-solution true
-distance false
-time false
-reaction false
-temperature false
-alkalinity false
-charge false
-percent_error false
-water false
-step false
-molalities       Np+4
                  Ill_sOH Ill_sOH2+ Ill_sO- Ill_sONp+3 Ill_sONpOH+2 Ill_sONp(OH)2+
Ill_sONp(OH)3 Ill_sONp(OH)4- Ill_sONpCl+2

USER_PUNCH
10
USER_GRAPH 1 Neptunium Sorption onto Illite (I = 0.1M)
-headings mu kd
-chart_title "Neptunium Sorption onto Illtmoronillite (I = 0.1M)"
-axis_titles "pH" "Kd [m3/kg]"
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Ill")/TOT("Np"))
-end
INCLUDE$ NpSCM_Ill_0.1
END
USER_GRAPH 1
    -detach
END

USER_PUNCH
10
USER_GRAPH 2 Neptunium Sorption onto Illite (I = 4.0M)
-headings mu kd
-chart_title "Neptunium Sorption onto Illite (I = 4.0M)"
-axis_titles "pH" "Kd [m3/kg]"
```

```
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","III")/TOT("Np"))
-end
INCLUDE$ NpSCM_III_4.0
END
USER_GRAPH 2
     -detach
END
```

B.2 PHREEQC input file for Np(IV) K_d values on illite using the surface complexation constants estimated in this work

```
DATABASE C:\Users\pc-nagasaki-jg\Desktop\Np(IV)
SCM\THEREDA\THEREDA_PIT_PHRC_R07.DAT

TITLE Neptunium(IV) Sorption Onto Illite With Optimized Constants

KNOBS
   -logfile                        true
   -iterations                     100
   -step_size                      100
   -tolerance                      1e-15
   -convergence_tolerance    1e-8
   -diagonal_scale              true

PITZER
         -macinnes                 false
         -use_etheta               true

SURFACE_MASTER_SPECIES
Ill_s Ill_sOH

SURFACE_SPECIES
# Illite Surface Complexation Reactions
# Surface Sites - A-B
Ill_sOH = Ill_sOH
log_k 0.0
Ill_sOH + H+ = Ill_sOH2+
log_k 4.0
Ill_sOH = Ill_sO- + H+
log_k -6.2

# Inner/Outer Sphere Complexes - Metal Binding
Ill_sOH + Np+4 = Ill_sONp+3 + H+
log_k 7.4
Ill_sOH + Np+4 + H2O = Ill_sONpOH+2 + 2H+
log_k 9.3
Ill_sOH + Np+4 + 2H2O = Ill_sONp(OH)2+ + 3H+
log_k 5.5
Ill_sOH + Np+4 + 3H2O = Ill_sONp(OH)3 + 4H+
log_k -0.2
Ill_sOH + Np+4 + 4H2O = Ill_sONp(OH)4- + 5H+
log_k -6.4

# Ternary Complexes (Type A) - Only One Ternary Surface Complexation Reaction
Ill_sOH + Np+4 + Cl- = Ill_sONpCl+2 + H+
log_k = 9.45
```

```
SOLUTION 1 I = 0.1M
        temp    25
        units   mol/kgw
        density 1
        water   1 # kg
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.01754
        Na      0.04737
        Cl      0.08246
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_Ill_0.1
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 1" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END

SOLUTION 2 I = 4M
        temp    25
        units   mol/kgw
        density 1
        water   1 # kg
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.70175
        Na      1.89474
        Cl      3.29824
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_Ill_4.0
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 2" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
```

```
60 PUNCH a$
70 NEXT i
END

PHASES
Fix_H+
H+ = H+
log_k 0.0
END

SURFACE 1
Ill_sOH 1.44e-6 70.0 1
-no_edl

SELECTED_OUTPUT
-file NpSCM.out
-reset true
-simulation false
-state false
-solution true
-distance false
-time false
-reaction false
-temperature false
-alkalinity false
-charge false
-percent_error false
-water false
-step false
-molalities      Np+4
                 Ill_sOH Ill_sOH2+ Ill_sO- Ill_sONp+3 Ill_sONpOH+2 Ill_sONp(OH)2+
Ill_sONp(OH)3 Ill_sONp(OH)4- Ill_sONpCl+2

USER_PUNCH
10
USER_GRAPH 1 Neptunium Sorption onto Illite (I = 0.1M)
-headings mu kd
-chart_title "Neptunium Sorption onto Illtmoronillite (I = 0.1M)"
-axis_titles "pH" "Kd [m3/kg]"
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Ill")/TOT("Np"))
-end
INCLUDE$ NpSCM_Ill_0.1
END
USER_GRAPH 1
    -detach
END

USER_PUNCH
```

```
10
USER_GRAPH 2 Neptunium Sorption onto Illite (I = 4.0M)
-headings mu kd
-chart_title "Neptunium Sorption onto Illite (I = 4.0M)"
-axis_titles "pH" "Kd [m3/kg]"
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Ill")/TOT("Np"))
-end
INCLUDE$ NpSCM_Ill_4.0
END
USER_GRAPH 2
    -detach
END
```

B.3 PHREEQC input file for Np(IV) K_d values on MX-80 using the surface complexation constants by Bradbury and Baeyens (Bradbury and Baeyens. 2005)

```
DATABASE C:\Users\pc-nagasaki-jg\Desktop\Np(IV)
SCM\THEREDA\THEREDA_PIT_PHRC_R07.DAT

TITLE Neptunium(IV) Sorption onto Montmorillonite

KNOBS
   -logfile                    true
   -iterations                 100
   -step_size                  100
   -tolerance                  1e-15
   -convergence_tolerance      1e-8
   -diagonal_scale             true

PITZER
        -macinnes              false
        -use_etheta            true

SURFACE_MASTER_SPECIES
Mon_s Mon_sOH

SURFACE_SPECIES
# Montmorillonite Surface Complexation Reactions
# Surface Sites - A-B
Mon_sOH = Mon_sOH
log_k 0.0
Mon_sOH + H+ = Mon_sOH2+
log_k 4.5
Mon_sOH = Mon_sO- + H+
log_k -7.9

# Inner/Outer Sphere Complexes - Metal Binding
Mon_sOH + Np+4 = Mon_sONp+3 + H+
log_k 8.5
Mon_sOH + Np+4 + H2O = Mon_sONpOH+2 + 2H+
log_k 8.3
Mon_sOH + Np+4 + 2H2O = Mon_sONp(OH)2+ + 3H+
log_k 5.5
Mon_sOH + Np+4 + 3H2O = Mon_sONp(OH)3 + 4H+
log_k 0.1

SOLUTION 1 I = 0.1M
        temp     25
        units    mol/kgw
        density  1
        water    1 # kg
        redox    pe
```

```
        pH      6
        pe      -3.378
        Ca      0.01754
        Na      0.04737
        Cl      0.08246
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_Mon_0.1
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 1" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END

SOLUTION 2 I = 4M
        temp    25
        units   mol/kgw
        density 1
        water   1 # kg
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.70175
        Na      1.89474
        Cl      3.29824
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_Mon_4.0
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 2" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END

PHASES
Fix_H+
```

```
H+ = H+
log_k 0.0
END

SURFACE 1
Mon_sOH 2e-6 26.2 1
-no_edl

SELECTED_OUTPUT
-file NpSCM.out
-reset true
-simulation false
-state false
-solution true
-distance false
-time false
-reaction false
-temperature false
-alkalinity false
-charge false
-percent_error false
-water false
-step false
-molalities      Np+4
                 Mon_sOH Mon_sOH2+ Mon_sO- Mon_sONp+3 Mon_sONpOH+2
Mon_sONp(OH)2+ Mon_sONp(OH)3 Mon_sONp(OH)4- Mon_sONpCl+2

USER_PUNCH
10
USER_GRAPH 1 Neptunium Sorption onto Montmorillonite (I = 0.1M)
-headings mu kd
-chart_title "Neptunium Sorption onto Montmoronillite (I = 0.1M)"
-axis_titles "pH" "Kd [m3/kg]"
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Mon")/TOT("Np"))
-end
INCLUDE$ NpSCM_Mon_0.1
END
USER_GRAPH 1
    -detach
END

USER_PUNCH
10
USER_GRAPH 2 Neptunium Sorption onto Montmorillonite (I = 4.0M)
-headings mu kd
-chart_title "Neptunium Sorption onto Montmorillonite (I = 4.0M)"
-axis_titles "pH" "Kd [m3/kg]"
-start
```

```
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Mon")/TOT("Np"))
-end
INCLUDE$ NpSCM_Mon_4.0
END
USER_GRAPH 2
     -detach
END
```

B.4 PHREEQC input file for Np(IV) K_d values on MX-80 using the surface complexation constants estimated in this work

```
DATABASE C:\Users\pc-nagasaki-jg\Desktop\Np(IV)
SCM\THEREDA\THEREDA_PIT_PHRC_R07.DAT

TITLE Neptunium(IV) Sorption Onto Montmorillonite With Optimized Constants

KNOBS
   -logfile                  true
   -iterations               100
   -step_size                100
   -tolerance                1e-15
   -convergence_tolerance    1e-8
   -diagonal_scale           true

PITZER
         -macinnes           false
         -use_etheta         true

SURFACE_MASTER_SPECIES
Mon_s Mon_sOH

SURFACE_SPECIES
# Montmorillonite Surface Complexation Reactions
# Surface Sites - A-B
Mon_sOH = Mon_sOH
log_k 0.0
Mon_sOH + H+ = Mon_sOH2+
log_k 4.5
Mon_sOH = Mon_sO- + H+
log_k -7.9

# Inner/Outer Sphere Complexes - Metal Binding
Mon_sOH + Np+4 = Mon_sONp+3 + H+
log_k 8.1
Mon_sOH + Np+4 + H2O = Mon_sONpOH+2 + 2H+
log_k 9.8
Mon_sOH + Np+4 + 2H2O = Mon_sONp(OH)2+ + 3H+
log_k 5.3
Mon_sOH + Np+4 + 3H2O = Mon_sONp(OH)3 + 4H+
log_k -0.3
Mon_sOH + Np+4 + 4H2O = Mon_sONp(OH)4- + 5H+
log_k -8.2

SOLUTION 1 I = 0.1M
         temp    25
         units   mol/kgw
         density 1
```

```
        water   1 # kg
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.01754
        Na      0.04737
        Cl      0.08246
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_Mon_0.1
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 1" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END

SOLUTION 2 I = 4M
        temp    25
        units   mol/kgw
        density1
        water   1 # kg
        redox   pe
        pH      6
        pe      -3.378
        Ca      0.70175
        Na      1.89474
        Cl      3.29824
        Np      1E-11

SELECTED_OUTPUT
        file NpSCM_Mon_4.0
        reset false

USER_PUNCH
10 FOR i = 2.0 to 12 STEP 0.1
20 a$ = EOL$ + "USE solution 2" + CHR$(59) + " USE surface 1" + EOL$
30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
40 a$ = a$ + " Fix_H+" + STR$(-i) + " NaOH 10.0" + EOL$
50 a$ = a$ + "END" + EOL$
60 PUNCH a$
70 NEXT i
END
```

```
PHASES
Fix_H+
H+ = H+
log_k 0.0
END

SURFACE 1
Mon_sOH 2e-6 26.2 1
-no_edl

SELECTED_OUTPUT
-file NpSCM.out
-reset true
-simulation false
-state false
-solution true
-distance false
-time false
-reaction false
-temperature false
-alkalinity false
-charge false
-percent_error false
-water false
-step false
-molalities       Np+4
                  Mon_sOH Mon_sOH2+ Mon_sO- Mon_sONp+3 Mon_sONpOH+2
Mon_sONp(OH)2+ Mon_sONp(OH)3 Mon_sONp(OH)4- Mon_sONpCl+2

USER_PUNCH
10
USER_GRAPH 1 Neptunium Sorption onto Montmorillonite (I = 0.1M)
-headings mu kd
-chart_title "Neptunium Sorption onto Montmoronillite (I = 0.1M)"
-axis_titles "pH" "Kd [m3/kg]"
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Mon")/TOT("Np"))
-end
INCLUDE$ NpSCM_Mon_0.1
END
USER_GRAPH 1
    -detach
END

USER_PUNCH
10
USER_GRAPH 2 Neptunium Sorption onto Montmorillonite (I = 4.0M)
-headings mu kd
-chart_title "Neptunium Sorption onto Montmorillonite (I = 4.0M)"
```

```
-axis_titles "pH" "Kd [m3/kg]"
-start
10 GRAPH_X -LA("H+")
20 GRAPH_Y (SURF("Np","Mon")/TOT("Np"))
-end
INCLUDE$ NpSCM_Mon_4.0
END
USER_GRAPH 2
     -detach
END
```