

Sorption behavior of Np(V) on illite, shale and MX-80 in high ionic strength solutions

Shinya Nagasaki¹ · Takumi Saito² · Tammy Tianxiao Yang³

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Abstract Sorption of Np(V) on illite, shale and MX-80 under oxidizing conditions were first studied in two types of high ionic strength solutions: (i) a reference brine solution (SR-270-PW) with an ionic strength of 6.0 M, and (ii) Na–Ca–Cl solutions. The effects of pH_c , Na/Ca ratio, and ionic strength on Np(V) sorption in Na–Ca–Cl solutions were investigated. The K_d values and the sorption isotherms in SR-270-PW and Na–Ca–Cl solutions were also evaluated.

Keywords Np(V) · Sorption · High ionic strength solutions · Illite · Shale · MX-80

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 contain Na–Ca–Cl brine solutions with total dissolved solids (TDS) concentrations up to 200–400 g/L, for example, groundwaters in Southern Ontario, Michigan Basin [1]. 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 sub-surface transport to the surface environment [2–7]. Therefore, it is important to elucidate the sorption behaviour of radionuclides not only on host rocks, but also on engineered barrier materials such as MX-80 bentonite [2].

The Nuclear Waste Management Organization (NWMO) has been developing a sorption database of sorption coefficient values for Canadian sedimentary rocks and bentonite [2, 8]. The principal objective of this study is to investigate the sorption behavior of Np(V) 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 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} M in a diluted neutral pH solution [9]) and its interaction with bentonite and rocks is strong [3, 10, 11]. On the other hand, Np(V) is more soluble (e.g. the solubility of Np(V) is approximately 10^{-4} M in a diluted neutral pH solution [12]) and has moderate interaction with bentonite and rocks [3, 10, 11, 13]. 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. [14] observed partial reduction of Np(V) to Np(IV) on the illite surface although the measurement of redox potentials suggested the predominance of Np(V). This indicates that the redox reaction of Np on the solid/liquid interface is critical in the sorption behavior of Np on some minerals.

Recently, several extensive reviews on the aqueous chemistry of actinides have been published [3, 15–20].

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✉ Shinya Nagasaki
nagasas@mcmaster.ca

¹ McMaster University, 1280 Main Street West, Hamilton, ON L8S 4L7, Canada

² Japan Atomic Energy Agency, 2-4 Shirakata, Tokai, Ibaraki 319-1195, Japan

³ Nuclear Waste Management Organization, 22 St. Clair Ave. East, 6th Floor, Toronto, ON M4T 2S3, Canada

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 [3, 21–26]. Note that fresh water has a TDS < 2 g/L, saline water has a TDS of 10–100 g/L (keeping in mind that seawater has a TDS of 33–37 g/L), and brine water has a TDS > 100 g/L. As mentioned in Ref. [8], some sorption experiments [27–33] have been carried out in solutions with higher ionic strengths. However, there are no published sorption measurements of Np(V) on Canadian sedimentary rocks and MX-80 in brine solutions.

This paper presents the results of a study conducted of the sorption behavior of Np(V) on shale, illite, which is the main mineral of shale [2], and MX-80 bentonite in brine solutions under oxidizing conditions. This work includes: (1) measurement of the sorption distribution coefficient, K_d [mL g^{-1}], of Np(V) on illite, shale and MX-80 in the SR-270-PW reference brine solution with ionic strength (I) of 6.0 M and the Na–Ca–Cl solution ($I = 4.6$ M); (2) investigation of the pH_c dependence of Np(V) sorption at $6 < \text{pH}_c < 10$; (3) investigation of ionic strengths effects on Np(V) sorption at $0.10 \text{ M} \leq I \leq 4.6 \text{ M}$; (4) investigation of the dependence of Np(V) sorption on Na/Ca molar concentration ratio (pure CaCl_2 solution, Ca–Na–Cl solution, Na–Ca–Cl solution, and pure NaCl solution); and (5) measurement of Np(V) sorption isotherm with initial Np(V) concentrations ranging from 1.0×10^{-4} M to 1.0×10^{-8} M.

This is the first experimental research which systematically studied the sorption behavior of Np(V) under a wide range of high ionic strength conditions. The sorption distribution coefficient values determined in this work will contribute to the NWMO's database of sorption values for Canadian sedimentary rocks and bentonite [2, 8].

Experimental

Chemicals and soils

All chemicals used were reagent grade and supplied from Fisher Scientific. Deionized water was prepared using a Milli-Q Direct 8. The shale sample was from Queenston Formation of the Michigan Basin. The mineralogy of the shale is described in [2]. Illite (Silver Hill Montana USA, Cambrian Shale) was purchased from the Clay Minerals Society, USA, and was characterized by Hower et al. [34]. Shale and illite samples were crushed using a super hard cylinder of Nichika Inc., and sieved using stainless steel sieves in deionized water. Grain sizes between 150 and 75 μm were used in the sorption experiments. The MX-80 bentonite sample was supplied by the American Colloid Company, and was used as received. A Precise Controlled

Atmosphere Glove Box (GB) supplied by Labconco was filled with N_2 gas (>99.999 %). The GB was used to exclude CO_2 , but not O_2 .

Preparation of Np(V) stock solution

The Np-237 solution was purchased from Stuart Hunt & Associates Ltd. Np in HNO_3 solutions may contain different oxidation states: Np(IV), Np(V) and Np(VI). A 0.01 M HClO_4 solution containing only Np(V) was prepared using established procedures [35, 36].

The oxidation state of the prepared Np stock solution was confirmed to be pentavalent by UV–VIS–NIR spectroscopy (Agilent 8453 UV–Vis spectrometer). The Np(V) stock solution was stored in a N_2 gas filled GB. The concentration of the Np(V) stock solution was determined to be 1.0×10^{-3} M from the molar absorption coefficient of Np(V) at 981 nm, $\epsilon = 385 \text{ L/mol}\cdot\text{cm}$ [36]. Based on the detection efficiency of germanium (Ge) detection (Canberra) at McMaster University, the concentration of the Np(V) stock solution was also confirmed to be $(1.0 \pm 0.1) \times 10^{-3}$ M.

pH_c evaluation and Eh measurement

The pH values indicated on the pH meter ($\text{pH}_{\text{measure}}$) should be considered as operational values [37]. The relationship between the operational $\text{pH}_{\text{measure}}$ and the molar H^+ concentrations ($\text{pH}_c = -\log c_{\text{H}^+}$) or the molal H^+ concentration ($\text{pH}_m = -\log m_{\text{H}^+}$) were discussed in detail by Altmaier et al. [38, 39]. In this study, the relationship between $\text{pH}_{\text{measure}}$ and pH_c in solutions were determined by titration (Metrohm Ti-Touch 916), and the $\text{pH}_{\text{measure}}$ values were converted to the pH_c values.

The redox potentials of 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 standard hydrogen electrode by the calibration of the electrode with a standard ORP solution. In this study, the Eh value was used as a relative indicator, by which we confirmed that the experiments were conducted under the oxidizing conditions. The measured Eh values are summarized in the Supplementary Information.

Preparation of solutions

SR-270-PW reference brine solution

The SR-270-PW reference brine solution (water type Na–Ca–Cl) has an Eh of -200 mV and pH of 6.0 [28]. Given that in this research sorption experiments were performed under oxidizing conditions, the experimental SR-270-PW

reference brine solution was prepared under oxidizing conditions using the chemical compounds given in Table 1, excluding the minor ions of Li, F, I, Br, and Si. No visible precipitates were observed during the preparation of the reference brine solution. The prepared reference brine solution was stored in a GB, and was decanted and centrifuged before use in order to ensure that any precipitates were not present. The prepared experimental solution has the ionic strength of 6.0 M, and is referred to as SR-270-PW reference brine solution in this paper.

Na–Ca–Cl (I = 4.6 M) solution

A Na–Ca–Cl solution was prepared using the same weights of NaCl and CaCl₂·2H₂O used to prepare 1 L of SR-270-PW reference brine solution (Table 2), and was stored in the GB. The prepared Na–Ca–Cl solution has an ionic strength of 4.6 M and a Na/Ca molar concentration ratio of 2.7. This established Na–Ca–Cl solution is referred to as Na–Ca–Cl (I = 4.6 M) brine solution in this paper.

Na–Ca–Cl solutions with various ionic strengths

Six Na–Ca–Cl solutions with the same Na/Ca molar concentration ratio of 2.7 as above were prepared to study the ionic strength effect on the Np(V) sorption. The weights of NaCl and CaCl₂·2H₂O for preparation of 1 L of the six Na–Ca–Cl solutions were: (NaCl (g), CaCl₂·2H₂O (g)) = (2.777, 2.572), (13.884, 12.861), (27.767, 25.722), (55.534, 51.444), (83.301, 77.166), and (111.068, 102.888). These Na–Ca–Cl solutions have ionic strengths of 0.10, 0.50, 1.0, 2.0, 3.0, and 4.0 M, respectively.

Table 1 Preparation of 1 L of SR-270-PW reference brine solution

Compound	Mass (g) of compound
KCl	22.249
NaCl	126.719
CaCl ₂ ·2H ₂ O	117.383
MgCl ₂ ·6H ₂ O	68.590
SrCl ₂ ·6H ₂ O	3.652
NaHCO ₃	0.151
Na ₂ SO ₄	0.651
KBr	2.532

Table 2 Preparation of 1 L of Na–Ca–Cl (I = 4.6 M) brine solution

Compound	Mass (g) of compound
NaCl	126.719
CaCl ₂ ·2H ₂ O	117.383

Na–Ca–Cl solutions with various Na/Ca ratios

Four Na–Ca–Cl/Ca–Na–Cl solutions with the ionic strength of 4.6 M but with different Na/Ca molar concentration ratios, as well as pure CaCl₂ and NaCl solutions with the ionic strength of 4.6 M were prepared. The weights of NaCl and CaCl₂·2H₂O for preparation of 1 L of pure CaCl₂, Ca–Na–Cl, Na–Ca–Cl and pure NaCl solutions are: (NaCl (g), CaCl₂·2H₂O (g)) = (0, 223.65), (8.603, 216.430), (66.675, 167.735), (166.687, 83.8675), (205.153, 51.611), and (266.70, 0). The prepared CaCl₂, Ca–Na–Cl, Na–Ca–Cl, and NaCl solutions have Na/Ca molar concentration ratios of 0.0, 0.10, 1.0, 5.0, 10, and infinite, respectively.

Sorption experiments

All sorption experiments were carried out in triplicate at 25 °C. In preliminary tests, the sorption of Np(V) on the wall of a polycarbonate reaction vessel was found to be negligible when the initial Np(V) concentration was 1×10^{-6} M and above. In the experiments with initial Np(V) concentrations below 1×10^{-6} M, the sorption of Np(V) on the reaction vessel wall was measured in blank tests. Assuming that the Np(V) sorption on the reaction vessel wall follows ideal sorption in the presence and in the absence of solids, the sorption on the wall was taken into account in the estimation of the sorption amounts of Np(V) on the solid.

In order to investigate the sorption mechanisms in detail, not only sorption experiments, but also desorption experiments are important. Because this is the first systematic study on the sorption behavior of Np(V) on illite, shale and MX-80 in high ionic strength brine solutions, the sorption behavior of Np(V) was studied in this work; the desorption behavior will be investigated in future research.

Kinetics of Np(V) sorption

Sorption kinetics of Np(V) on illite, shale and MX-80 in the SR-270-PW reference brine solution and the Na–Ca–Cl (I = 4.6 M) brine solution were measured. The sorption kinetic measurements were conducted at two solid/liquid (S/L) ratios of 0.50 g/5.0 mL and 0.10 g/5.0 mL. The procedures for conducting sorption kinetics experiments are described below and will be used for the subsequent sorption experiments.

In the GB, 0.50 or 0.10 g of illite, shale or MX-80 was added into a polycarbonate reaction vessel and 5.0 mL of SR-270-PW or Na–Ca–Cl (I = 4.6 M) brine solution was added into the reaction vessel. The suspensions were kept in the GB for 3–4 days for pre-equilibration (the pH_c and Eh of solutions in contact with illite, shale and MX-80 had stabilized within 1 day in the preliminary tests).

The reaction vessels were removed from the GB and the liquid and solid were separated by centrifugation for 30 min at 12,000 rpm (Beckman Coulter, Allegra X-30R). The reactions vessels were then transferred back into the GB and the liquid was removed by pipette. SR-270-PW or the Na–Ca–Cl ($I = 4.6$ M) brine solution was then added into the reaction vessel again, and a portion of the Np(V) stock solution was spiked into the reaction vessel. The initial Np(V) concentration in the liquid of the reaction vessel was 1.0×10^{-5} M. The final volume of the liquid was 5.0 mL. After one day, the pH_c and Eh (Fisher Scientific Accumet AB 150/Accumet pH/ORP electrodes) of the liquid in the reaction vessel were measured (also in the GB) and the reaction vessel was then tightly re-sealed.

The reaction vessels were transferred from the GB to an incubator at 25 °C (Infors HT Ectron) and were shaken for pre-decided periods. After each pre-decided period, the liquid was separated from the solid by centrifugation for 30 min at 12,000 rpm at 25 °C. The pH_c and Eh of the liquid were measured in the GB, and an aliquot was sampled from the liquid phase of each reaction vessel. The concentration of Np in the aliquot was measured using the Ge detector. The concentration of Np sorbed on the solid was evaluated, and the percent sorption of Np(V) was calculated by:

Percent sorption

$$= \frac{\text{Np(V) mass removed from solution} \times 100\%}{\text{Total Np(V) available for sorption}} \quad (1)$$

As discussed in the “Results and Discussion” section below, the sorption equilibrium for Np(V) on illite, shale and MX-80 (i.e. the kinetics of Np(V) sorption) was achieved within 3 days. Hence, the sorption reaction time was set to one week or longer in subsequent experiments.

Effect of the solid/liquid (S/L) ratio on Np(V) sorption

The S/L ratio dependence of Np(V) sorption onto illite, shale and MX-80 in the SR-270-PW and the Na–Ca–Cl ($I = 4.6$ M) brine solutions was measured at S/L ratios of 0.20 g/5.0 mL, 0.30 g/5.0 mL, and 0.40 g/5.0 mL.

Sorption results were expressed as K_d (mL g^{-1}), which is calculated as follows:

$$K_d = \frac{(C_0 - C_e) V}{C_e W} \quad (2)$$

where C_0 (M) is the initial concentration of Np(V) in the liquid phase, C_e (M) the equilibrium concentration of Np(V) in the liquid phase, V (mL) the volume of liquid phase, and W (g) the mass of the solid phase.

As discussed in the “Results and Discussion” section below, the K_d values were found to be independent of the S/L ratio at S/L ratios above 0.30 g/5.0 mL. Therefore, the

S/L ratio was set to 0.50 g/5.0 mL in the subsequent experiments.

In general, it is useful to normalize the sorption amount using the cation exchange capacity (CEC) for solid on which the ion exchange reaction is dominant and using the specific surface area for non-interlayered solid. In this research, the sorption of Np(V) could be normalized by the specific surface area because of high ionic strengths (except for several experiments) in the experimental conditions. However, since, under the experimental conditions, N_2 can contribute to the sorption on the interlayer of clay minerals in BET (Brunauer–Emmett–Teller) measurements, it may not be adequate to use the specific surface area determined by the BET method. It may be better to normalize the sorption amount using the sorption site density or the specific surface area of the relevant edge faces. However, since the principal objective of this study is to investigate the sorption behavior of Np(V) in highly saline solutions, and this is the first research which systematically studied the sorption behavior of Np(V) under a wide range of high ionic strength conditions, the K_d value was used to express the sorption amount in this work. In the future study, not only the sorption site density or the specific surface area of the edge faces in each solid but also the amount of each mineral in solid and the fractionation of sorption sites available to the sorption in the mineral will be taken into consideration to study the sorption behavior of Np(V) on illite, shale and MX-80.

K_d measurements in reference brine and Na–Ca–Cl solutions

The K_d values of Np(V) on illite, shale and MX-80 in the SR-270-PW reference brine solution and the Na–Ca–Cl ($I = 4.6$ M) brine solution were measured.

Effect of pH_c on K_d value

The pH_c dependence of the K_d value of Np(V) on illite, shale and MX-80 in the Na–Ca–Cl ($I = 4.6$ M) brine solution was measured. The pH_c of the liquid in reaction vessels was adjusted to values between $6 < \text{pH}_c < 10$ by addition of 0.01 M HClO_4 or 0.01 M NaOH solution in the GB. The pH_c in the reaction vessel was measured twice a day, and the pH_c was re-adjusted to the original pH_c value. In this experiment, the sorption reaction time was set to two weeks.

Effect of the ionic strength on K_d value

The ionic strength dependence of the K_d value of Np(V) on illite, shale and MX-80 in the Na–Ca–Cl solutions with various ionic strengths was measured. In the preliminary

test, the reproducibility of the solid/liquid separation by centrifugation for 30 min at 12,000 rpm was confirmed, but colloids might be produced and present in the separated solutions in MX-80 series at lower ionic strengths.

Effect of the Na/Ca ratio on K_d value

The Na/Ca molar concentration ratio dependence of the K_d value of Np(V) on illite, shale and MX-80 in CaCl₂, Ca–Na–Cl, Na–Ca–Cl and NaCl solutions with various Na/Ca ratios was investigated.

Sorption isotherms in SR-270-PW and Na–Ca–Cl solutions

The sorption isotherms of Np(V) on illite, shale and MX-80 in the SR-270-PW reference brine solution and the Na–Ca–Cl ($I = 4.6$ M) brine solution were measured. The initial Np(V) concentrations ranged from 1.0×10^{-4} M to 1.0×10^{-8} M. The concentration of Np(V) in the liquid phase after centrifugation was measured by ICP-MS (Agilent ICP-MS 8800). For the initial Np(V) concentration below 1×10^{-6} M, the sorption of Np(V) on the wall was taken into account to calculate the K_d values.

Results and discussion

Kinetics of Np(V) sorption

The percent sorption of Np(V) measured on illite, shale and MX-80 at the S/L ratio of 0.10 g/5.0 mL and 0.50 g/5.0 mL in the SR-270-PW reference brine solution and the Na–Ca–Cl ($I = 4.6$ M) brine solution is shown in Figs. 1 and 2, respectively. The values of pH_c and Eh at the sorption equilibrium are shown in the Supplementary Information ($S/L = 0.10$ g/5.0 mL and 0.50 g/5.0 mL in Table 1). These results illustrate that sorption equilibrium for Np(V) on illite, 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. [40] measured the sorption kinetics of Np(V) on poorly crystallized ferric oxide and found that sorption equilibrium was achieved in 1 h. Snow et al. [41] found that no significant changes in the Np(V) sorption on goethite were observed from 1 to 8 days, suggesting that the sorption equilibrium was achieved in 1 day. On the other hand, Nagasaki et al. [42, 43] measured the sorption kinetics of Np(V) on illite and Na-montmorillonite, and found that more than 1 day was required to reach sorption equilibrium. This difference in equilibration times may be due to the difference in structure between clay minerals and Fe(III) oxides. The solid structures of illite, shale and MX-

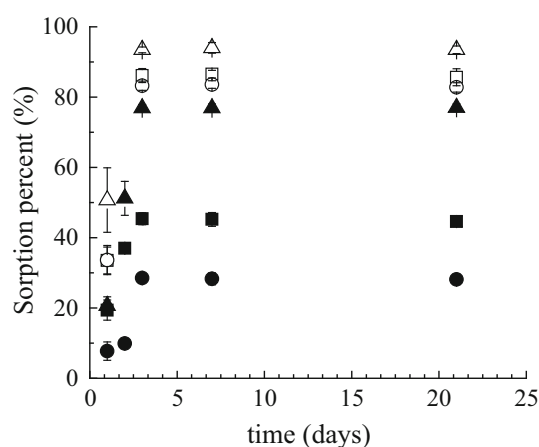


Fig. 1 Sorption kinetics in the SR-270-PW reference brine solution at S/L of 0.10 g/5.0 mL (filled square illite; filled circle shale; filled triangle MX-80) and 0.50 g/5.0 mL (open square illite; open circle shale; open triangle MX-80). The initial concentration of Np(V) was 1.0×10^{-5} M. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 1)

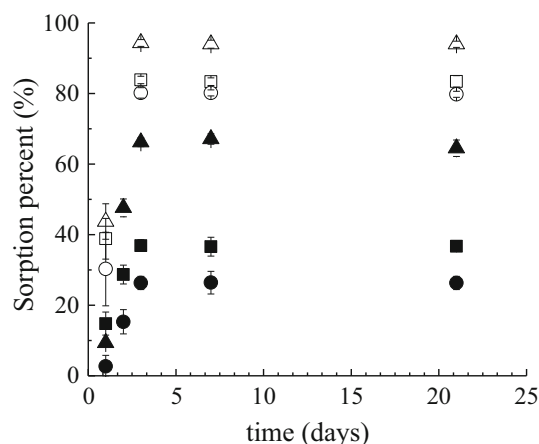


Fig. 2 Sorption kinetics in the Na–Ca–Cl ($I = 4.6$ M) brine solution at S/L of 0.10 g/5.0 mL (filled square illite; filled circle shale; filled triangle MX-80) and 0.50 g/5.0 mL (open square illite; open circle shale; open triangle MX-80). The initial concentration of Np(V) was 1.0×10^{-5} M. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 1)

80 and the brine conditions considered in this current study may contribute to the slightly longer times required to reach sorption equilibrium.

Effect of the solid/liquid (S/L) ratio on K_d value

The dependence of the K_d value of Np(V) on the solid/liquid (S/L) ratio in the SR-270-PW and the Na–Ca–Cl ($I = 4.6$ M) brine solutions is illustrated in Fig. 3. The data at the S/L ratio of 0.10 g/5.0 mL and 0.50 g/5.0 mL in Fig. 3 were taken from the results of sorption kinetics experiments. The pH_c and Eh values of solutions at

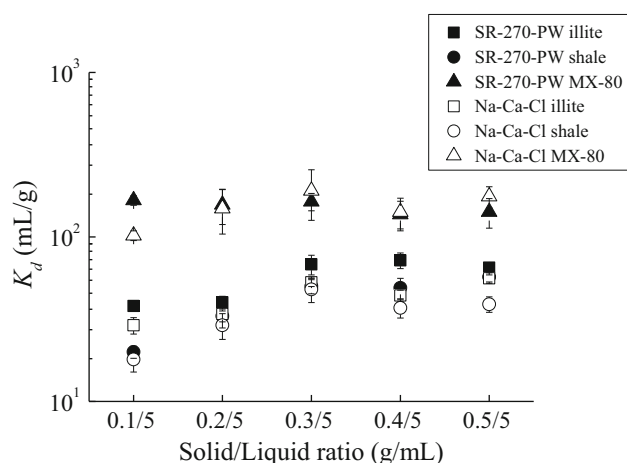


Fig. 3 Dependence of K_d values on the solid/liquid ratio for illite, shale and MX-80 in SR-270-PW and Na–Ca–Cl ($I = 4.6$ M) brine solutions. The initial concentration of Np(V) was 1.0×10^{-5} M. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 1)

sorption equilibrium are summarized in the Supplementary Information (Table 1). It was found that the pH_c value was dependent on the solid phase, 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, shale and MX-80 increased as the S/L ratio increased from 0.10 g/5.0 mL to 0.20 g/5.0 mL, and reached plateaus at the S/L ratios above 0.30 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. Namely, Fig. 3 illustrates that the ideal sorption range under the selected experimental conditions is reached at $S/L \geq 0.30$ 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. [44]); whereas, others reported that the K_d value was independent of the S/L ratio (e.g. [45]). 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 [46] and on attapulgite [47]. 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 [46, 47]. The effect of the S/L ratio on Np(V) sorption will be further investigated in future research.

K_d values in SR-270-PW and Na–Ca–Cl solutions

The K_d values of Np(V) on illite, shale, and MX-80 in the SR-270-PW and the Na–Ca–Cl ($I = 4.6$ M) brine solutions are summarized in Table 3. Table 3 also lists the K_d values

calculated from the kinetics experiment conducted at a S/L ratio of 0.50 g/5.0 mL. The average K_d values on illite and shale in the SR-270-PW reference brine solution are slightly larger than those in the Na–Ca–Cl ($I = 4.6$ M) brine solution, and the average K_d values on MX-80 in the SR-270-PW reference brine solution are slightly smaller than those in the Na–Ca–Cl ($I = 4.6$ M) brine 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 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 appreciably larger than those in the Na–Ca–Cl ($I = 4.6$ M) brine solution, even when the experimental errors in the K_d values and the difference of pH_c are taken into account.

The content of illite in the Queenston shale used in this study is 60 % [2]. Assuming that the simple mineral additivity is appropriate for the evaluation of K_d values and that illite dominates the sorption of Np(V) on shale [2, 8], the K_d value of Np(V) on illite can be used to estimate the K_d value on shale [8]. However, it was found that the K_d values on shale obtained in this work were much larger than 60 % of the K_d values on illite. This suggests that Np(V) also sorbs onto other minerals in shale (e.g. chlorite and dolomite) in brine conditions, or that the simple mineral additivity is questionable. It is important to normalize the sorption amounts on illite and shale using the specific surface area or the sorption site density, and estimate the K_d value using the normalized sorption amount.

Marsac et al. [14] found the reduction of Np(V) on the purified illite surface in 0.1 M NaCl solution under Ar atmosphere. In this work, we did not examine whether Np(V) was reduced to Np(IV). However, because our K_d values of Np(V) on the illite are similar to those reported in the previous researches [33, 48, 49] which will be discussed later, and our K_d values are much smaller than those reported by Marsac et al. [14], we think the possibility of reduction of Np(V) to Np(IV) in the experiments of this work is very small.

Bradbury and Baeyens [50, 51] proposed a methodology to predict the K_d values of actinides and some heavy metals on montmorillonite and illite. The model and the methodology of Bradbury and Baeyens [50, 51] were not applied to this work because (1) our experimental conditions, such as the solution compositions (Na–Ca–Cl brine solutions with an ionic strength of 4.6 and 6.0 M were used in this work) and the pre-conditioning procedures of the solids, were not identical to those of what Bradbury and Baeyens used, and (2) the Pitzer model parameters which should be used for the model calculation are not fully compiled. We appreciate that it would be interesting to investigate the applicability of the model of Bradbury and Baeyens at the higher ionic conditions and to develop a sorption model

Table 3 K_d values of illite, shale and MX-80 measured in the SR-270-PW and Na–Ca–Cl ($I = 4.6$ M) brine solutions

Solid	Illite	Shale	MX-80
Solution	SR-270-PW		
K_d (mL/g) (ave.)	65 ± 4.4 (pHc = 7.6)	57 ± 4.7 (pHc = 7.4)	142 ± 29 (pHc = 8.1)
Sorption experiment	(Eh = 347 mV)	(Eh = 354 mV)	(Eh = 356 mV)
K_d (mL/g) (ave.)	65 ± 7.9 (pHc = 7.6)	51 ± 4.1 (pHc = 7.4)	161 ± 38 (pHc = 8.1)
Kinetics experiment	(Eh = 349 mV)	(Eh = 353 mV)	(Eh = 354 mV)
Solution	Na–Ca–Cl ($I = 4.6$ M)		
K_d (mL/g) (ave.)	56 ± 2.8 (pHc = 7.7)	39 ± 4.2 (pHc = 7.9)	176 ± 26 (pHc = 9.0)
Sorption experiment	(Eh = 349 mV)	(Eh = 364 mV)	(Eh = 310 mV)
K_d (mL/g) (ave.)	50 ± 3.9 (pHc = 7.8)	40 ± 2.1 (pHc = 8.0)	160 ± 35 (pHc = 9.1)
Kinetics experiment	(Eh = 343 mV)	(Eh = 362 mV)	(Eh = 311 mV)

The initial concentration of Np(V) was 1.0×10^{-5} M

and methodology available under the wider brine and solid conditions.

Sorption in Na–Ca–Cl solutions

Effect of pH_c on K_d value

The pH_c dependence of K_d value of Np(V) in the Na–Ca–Cl ($I = 4.6$ M) brine solution is illustrated in Fig. 4. The values of pH_c and Eh at the sorption equilibrium are shown in the Supplementary Information (Table 2). Figure 4 shows that the K_d values of Np(V) on illite, shale and MX-80 increase with pH_c. This tendency is consistent with the results of the previous studies [8, 33, 48, 50–53], 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 was similar to that for shale, and slightly smaller than that for MX-80. We will continue to examine

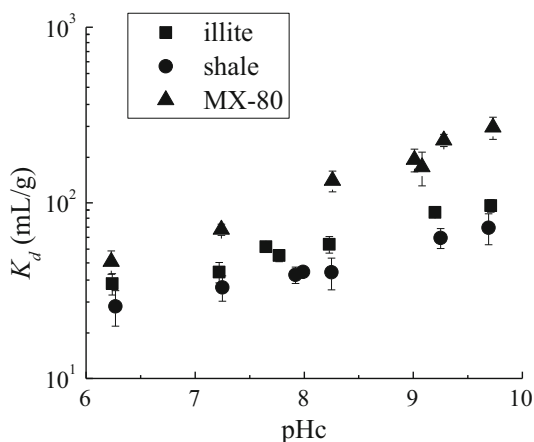


Fig. 4 pH_c dependence of the K_d values in the Na–Ca–Cl ($I = 4.6$ M) brine solution. The initial concentration of Np(V) was 1.0×10^{-5} M. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 2)

the physical and chemical meanings of the similarity and the difference in the slope of K_d value vs. pH_c.

In April 2014, the Japan Atomic Energy Agency (JAEA) updated their Thermodynamic Database and the SIT (Specific Ion Interaction Theory) model parameters [54]. Using simulations conducted with the geochemical code PHREEQC (version 3.1.2) [55] and JAEA’s SIT thermodynamic database for Na–Ca–Cl solutions with an ionic strength of less than 4 M, it was predicted that NpO_2^+ is dominant at pH values from 6 to 9. If NpO_2^+ is the dominant species in both the SR-270-PW reference brine solution and the Na–Ca–Cl ($I = 4.6$ M) brine solution, this pH_c dependence of the K_d value 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 [50, 51].

Mucciardi et al. [33] measured the sorption of Np(V) on illite in CaCl_2 solution ($I = 5.2$ M) at pH of 7, and reported the K_d values of 13–44 mL g^{-1} . Gorgeon [48] reported the K_d values of 60–195 mL g^{-1} on illite in NaClO_4 solution ($I = 1.0$ M) at pH of 6–7. There are some reported K_d values measured under low ionic strength conditions. Torstenfelt et al. [49] observed the K_d values of 80–90 mL g^{-1} in Na–Ca– HCO_3 – SO_4 solution ($I = 0.004$ M) at pH of 8.5. Mucciardi et al. [33] also reported the the K_d values of 150–460 mL g^{-1} in NaHCO_3 solution ($I = 0.025$ M) at pH 8–9, and 13–74 mL g^{-1} in NaCl solution ($I = 0.03$ M) at pH of 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 agree with those reported by previous researches.

Mucciardi et al. [33] also studied the sorption of Np(V) on montmorillonite, and reported the K_d values of 18–24 mL g^{-1} in CaCl_2 solution ($I = 5.2$ M) at pH of 7–8. Gorgeon [48] reported the K_d values of 25–130 mL g^{-1} on smectite in NaClO_4 solution ($I = 1.0$ M) at pH of 6–7.

Kitamura and Tomura [52] measured the K_d values of 2–21 mL g⁻¹ on smectite in NaCl solution ($I = 1$ M) at pH of 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 [48], but were larger than the K_d values by Mucciardi et al. [33] and Kitamura and Tomura. [52].

Vilks [8] conducted an extensive review of the K_d values of Np(V) onto shale, limestone and bentonite published in scientific papers, reports and international sorption databases, discussed the validity of these K_d values in brine conditions, and recommended a range of K_d values for brine solutions. The recommended K_d values for shale were 7.8–120 mL g⁻¹ at $6.1 \leq \text{pH} \leq 7.1$. The recommended K_d values for bentonite were 2–130 mL g⁻¹ at $6 \leq \text{pH} \leq 8$. The measured K_d values on shale at $\text{pH}_c = 6.3$ (26 mL g⁻¹) and on MX-80 at $\text{pH}_c = 6.2$ and 7.2 (46 and 70 mL g⁻¹, respectively) in the Na–Ca–Cl ($I = 4.6$ M) solution (Fig. 4) are within the recommended K_d values by Vilks [8].

Effect of the ionic strength on K_d value

The ionic strength dependence of the K_d value of Np(V) in Na–Ca–Cl solutions is illustrated in Fig. 5. The pH_c and Eh values at sorption equilibrium are summarized in the Supplementary Information (Table 3).

The pH_c value changed slightly over a series of sorption experiments on illite ($\text{pH}_c = 7.1$ –7.8), shale ($\text{pH}_c = 7.6$ –8.1) and MX-80 ($\text{pH}_c = 8.5$ –9.1). Considering the variation of pH_c of the Na–Ca–Cl solutions with different ionic strengths and the pH_c dependence of K_d values (Fig. 4), the K_d values on illite and shale can be considered

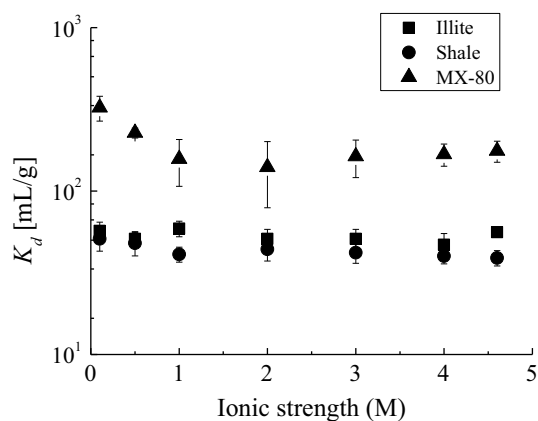


Fig. 5 Ionic strength dependence of the K_d values in the Na–Ca–Cl brine solutions. The initial concentration of Np(V) was 1.0×10^{-5} M. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 3)

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 0.10 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 and MX-80 may be explained by (i) the difference in the structures of interlayer of illite and MX-80, and (ii) sorption by ionic exchange reactions at ionic strengths below 1 M. Furthermore, as Schnurr et al. [27] pointed out, the coagulation effects of MX-80 might also be a possibility for the decrease in sorption with increasing ionic strength. However, the coagulation effects are marked at relatively low salt concentration such as 0.01–0.1 M.

Gorgeon [48] measured the sorption of Np(V) on Na-smectite in 0.025 and 0.1 M NaClO₄ solutions and reported the K_d value of 60–160 mL g⁻¹ at pH of 7–9. Turner et al. [56] reported the K_d value of 50–200 mL g⁻¹ on Namontmorillonite in 0.1 M NaNO₃ solution at pH of 7.5–9. Sakamoto et al. [57] reported the K_d value of 15–44 mL g⁻¹ on bentonite in 0.01 M NaClO₄. Higgs et al. [58] reported the K_d value of 1100–12,400 mL g⁻¹ on smectite in sea water. Morgan et al. [59] studied the sorption of Np(V) on bentonite in deionized water and reported the K_d value of 110–4000 mL g⁻¹. As discussed above, the K_d values on illite and 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 previous researches. However, the K_d values on MX-80 ($I = 0.10$ and 0.50 M) are higher than those reported by Gorgeon [48], Turner et al. [56], and Sakamoto et al. [57], but much smaller than those by Higgs et al. [58], and Morgan et al. [59]. As explained previously, the reproducibility of the solid/liquid separation by centrifugation for 30 min at 12,000 rpm was confirmed, but colloids might be produced and present in the separated solutions in MX-80 series at $I = 0.10$ and 0.50 M. It will be useful to further investigate the different Np(V) sorption behavior on illite, shale and MX-80 over a wide range of high ionic strength conditions, including the influence of smaller size colloids.

Effect of the Na/Ca ratio on K_d value

The effect of the Na/Ca molar concentration ratio on the K_d value of Np(V) in CaCl₂, Ca–Na–Cl, Na–Ca–Cl, and NaCl solutions with an ionic strength of 4.6 M is summarized in Table 4. The pH_c and Eh values of the solutions at the sorption equilibrium are shown in the Supplementary Information (Table 4).

Although the pH_c value of the solution varied over a series of sorption experiments on illite ($\text{pH}_c = 6.9$ –8.6), shale ($\text{pH}_c = 7.4$ –9.2) and MX-80 ($\text{pH}_c = 8.5$ –10.2), the K_d value seemed to increase as the Na/Ca ratio increased in

Table 4 Na/Ca ratio dependence of K_d values measured in CaCl_2 , Ca-Na-Cl / Na-Ca-Cl , and NaCl solutions with the ionic strength of 4.6 M

Solution	CaCl_2 solution		$\text{Ca-Na-Cl}/\text{Na-Ca-Cl}$ solution				NaCl solution
	Na/Ca ratio	0	0.10	1.0	5.0	10	∞
K_d (mL/g)							
Illite		9.9 ± 1.3	18 ± 2.2	58 ± 6.2	60 ± 6.8	102 ± 14	189 ± 24
Shale		9.0 ± 0.39	17 ± 1.2	40 ± 5.1	42 ± 4.2	88 ± 9.3	122 ± 18
MX-80		32 ± 2.7	71 ± 3.8	135 ± 4.4	139 ± 8.8	282 ± 37	512 ± 52

The initial concentration of Np(V) was 1.0×10^{-5} M. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 4)

experiments conducted with all three solids, suggesting that the presence of Ca in solution reduces the sorption of Np(V) on illite, shale and MX-80. Possible explanations may be the competition of Ca with Np(V) for sorption sites, or the change in the aqueous speciation of Np(V) induced by high concentrations of Ca. However, these cannot explain the ionic strength dependence and the Na/Ca ratio dependence simultaneously. Schnurr et al. [27] observed a similar effect in the Eu sorption on illite and smectite, and considered that the competition for the same sorption sites might not be a sufficient explanation. Bradbury and Baeyens [50] found that the K_d value of Eu(III) on smectite in NaCl solution is more than one order of magnitude higher than that in CaCl_2 solution. Activity coefficients in the solution containing Ca might be different from those in the solution containing Na, but this effect has not yet been understood. The effect of Na/Ca ratio on Np(V) sorption including the effect of pH_c will be further investigated in the future research.

Isotherms of Np(V) sorption in SR-270-PW and Na-Ca-Cl solutions

Sorption isotherms in the SR-270-PW reference brine solution and the Na-Ca-Cl ($I = 4.6$ M) brine solution are illustrated in Figs. 6 and 7, respectively. The data at the initial Np(V) concentration of 1.0×10^{-5} M were from the experimental results of K_d value measurement in the SR-270-PW and Na-Ca-Cl ($I = 4.6$ M) brine solutions. The pH_c and Eh values of the solutions at the sorption equilibrium are shown in the Supplementary Information (Table 5).

In both solutions, the measured 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} M (the initial Np(V) concentration was 1.0×10^{-5} M). The data points at a Np(V) equilibrium concentrations of 1×10^{-5} to 2×10^{-5} M in the liquid (the initial Np(V) concentration was 1.0×10^{-4} M) slightly deviate from a linear relationship (Figs. 6 and 7). Figures 6 and 7 illustrate that the ideal sorption range under the selected experimental conditions is reached at the Np(V) concentration in the liquid of less than 2×10^{-6} M.

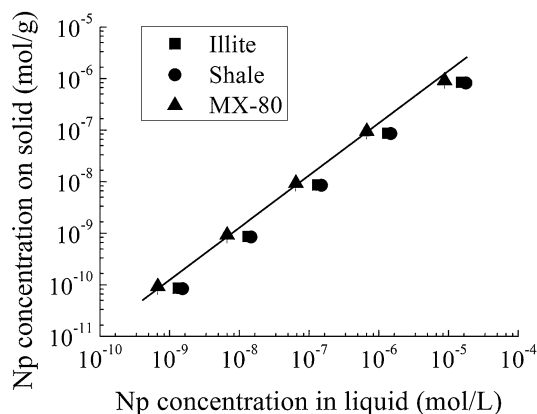


Fig. 6 Sorption isotherms in the SR-270-PW reference brine solution. The data at the initial concentration of 1.0×10^{-5} M was from the K_d value measurement in the SR-270-PW. A solid line represents a sorption isotherm on MX-80 with the slope of 1. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 5)

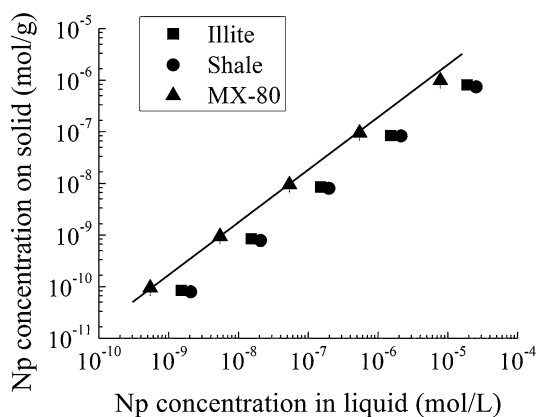


Fig. 7 Sorption isotherms in the Na-Ca-Cl ($I = 4.6$ M) brine solution. The data at the initial concentration of 1.0×10^{-5} M was from the K_d value measurement in the Na-Ca-Cl ($I = 4.6$ M). A solid line represents a sorption isotherm on MX-80 with the slope of 1. pH_c and Eh at sorption equilibrium are summarized in the Supplementary Information (Table 5)

Conclusions

This is the first research systematically studying the sorption behavior of Np(V) under a wide range of high ionic strength. The K_d values of Np(V) on illite, shale and MX-80 in the SR-

270-PW reference brine solution and in the Na–Ca–Cl ($I = 4.6$ M) brine solution were evaluated using batch sorption experiments. 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 Na–Ca–Cl brine solution.

The sorption equilibrium of Np(V) on illite, shale and MX-80 was achieved within 3 days and was independent of the compositions of the studied solutions. The K_d values of Np(V) on MX-80 in the reference SR-270-PW and Na–Ca–Cl ($I = 4.6$ M) brines were independent of the S/L ratios. Those on illite and shale in the reference SR-270-PW and Na–Ca–Cl ($I = 4.6$ M) brine solutions as well as those on MX-80 in the Na–Ca–Cl ($I = 4.6$ M) solution increased with the S/L ratio and reached plateaus at S/L ratios above 0.30 g/5.0 mL. The K_d value of Np(V) on the 3 solids (illite, shale and MX-80) in the Na–Ca–Cl ($I = 4.6$ M) brine solution increased with pH_c . The K_d values of Np(V) on shale and MX-80 obtained in this work fall into the range of recommended Np(V) K_d values for brine solutions recommended by Vilks [8]. The K_d values on illite and shale in Na–Ca–Cl solutions were independent of the ionic strength in the range of 0.10–4.6 M. The K_d values on MX-80 in Na–Ca–Cl solutions decreased with increasing the ionic strength from 0.10 M to 1.0 M and became independent of the ionic strength of 1.0–4.6 M. The K_d values on 3 solids were all observed to increase with the Na/Ca molar concentration ratio of solutions. The slopes of the sorption isotherms for the minerals in both the reference SR-270-PW brine and Na–Ca–Cl ($I = 4.6$ M) solutions were approximately 1 at the Np(V) equilibrium concentration of less than 2×10^{-6} M.

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