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Sorption of Tc(IV) in Saline Solutions – II. Sorption on MX-80, Illite, Shale and Limestone in Na-Ca-Cl Solutions

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Technetium has been identified as an element of interest for the safety assessment of a deep geological repository for used nuclear fuel. In this study, the sorption of Tc(IV) onto MX-80 bentonite, illite, and shale in ionic strength (*I*) 0.1–6 mol·kgw^{-1} (m) Na-Ca-Cl solutions at pH$_m$ = 4–9 and limestone at pH$_m$ = 5–9 was studied. Tc(IV) sorption on MX-80 increased with pH$_m$ from 4 to 6, reached the maximum at pH$_m$ = 6–7, and then gradually decreased with pH$_m$ from 7 to 9. Tc(IV) sorption on illite gradually increased with pH$_m$ from 4 to 7, and then decreased as pH$_m$ increased. The sorption properties of Tc(IV) on shale were quite similar to those on illite. Tc(IV) sorption on limestone slightly increased with pH$_m$ from 5 to 6 and then seemed to be constant at pH$_m$ = 6–9. Tc(IV) sorption on all four solids was independent of ionic strength (0.1–6 m). The 2 site protolysis non-electrostatic surface complexation and cation exchange model successfully simulated the sorption of Tc(IV) onto MX-80 and illite and the optimized values of surface complexation constants were estimated.

Keywords: Technetium(IV), Sorption, MX-80 bentonite, Illite, Shale, Limestone

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1. Introduction

Today's scientific consensus is that deep geological repositories (DGRs) are a safe and effective approach to permanently manage and dispose of used nuclear fuel and high-level radioactive wastes. In Canada, the Nuclear Waste Management Organization (NWMO) is responsible for the safe, long-term management of Canada's used nuclear fuel. The used nuclear fuel will be safely isolated and contained in a DGR in suitable sedimentary or crystalline rock. This paper focuses on the study of sorption of Tc(IV) on sedimentary rock samples (including shale and limestone), illite and bentonite as the second paper in this series.

There are some previous studies on the sorption of Tc(IV) on bentonite, minerals and various rocks including sedimentary rocks. The previous studies on the sorption of Tc(IV) onto bentonite were reviewed in the first paper of this series [1].

Walton et al. [2] studied interactions of Tc(IV) with $Fe(OH)_3$ and Fe_2O_3 in bicarbonate media using demineralized water under anoxic conditions and found that Tc(IV) was rapidly removed from anoxic bicarbonate solutions by Fe(III) oxyhydroxides by chemisorption. Tkáč et al. [3] studied sorption of Tc(IV) on soils in the presence of humic material in pure water and showed that about 99% of reduced technetium was absorbed by the soils. Uezu et al. [4] reported that migration of Tc(VII) was faster than Tc(IV) in distilled water through soil samples. Kumar et al. [5] investigated the sorption of Tc(IV) on alumina in the absence and presence of humic acid in I = 0.1 M $NaClO_4$ solution at pH 3–10. They found that sorption of Tc(IV) in the presence of humic acid enhanced significantly at pH < 7. Sorption of Tc(IV) decreased at higher pH compared to sorption in the absence of humic acid. Hallam et al. [6] carried out batch sorption experiment of Tc(IV) for hematite, goethite, plagioclase feldspar, quartz, sand and shale in diluted solutions at pH = 3–13 and applied the surface complexation models. They found that sorption was strongly dependent on pH for all solids.

There are some previous studies which discussed that the reduction of Tc(VII) to Tc(IV) contributed to Tc adsorption. Fredrickson et al. [7] studied the potential for reduction of TcO_4^- to poorly soluble $TcO_2 \cdot nH_2O(s)$ by biogenic sediment-associated Fe(II) in 30 mM bicarbonate solutions and concluded that TcO_4^- was immobilized by the in situ microbial reduction of sediment-associated Fe(III), either naturally or via redox manipulation. Yalçıntaş et al. [8] examined the mechanisms for the reduction and uptake of Tc by magnetite (Fe_3O_4) and mackinawite (FeS) in 0.1 M NaCl solution using X-ray absorption spectroscopy (XANES and EXAFS) and thermodynamic calculation of the Tc/Fe systems. They found that the uptake of Tc(IV) by magnetite and mackinawite strongly depended on the loading of Tc and pH. Rodríguez et al. [9] studied Tc(VII) uptake by synthetic pure pyrite in 0.1 M NaCl solution at 21°C in a pH range from 3.5 to 10.5 using batch experiments, scanning electron microscopy, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, and Raman microscopy. They confirmed the uptake mechanism involved the reduction of Tc(VII) to Tc(IV). Mayordome et al. [10] studied the retention of Tc on gamma alumina nanoparticles (γ-Al_2O_3 NPs) in the absence and presence of previously sorbed Fe^{2+} on γ-Al_2O_3 NPs as a reducing agent in 0.01 M NaCl solution and found that Tc scavenging was predominantly controlled by the presence of sorbed Fe^{2+} species on γ-Al_2O_3 NP. Mayordomo et al. [11] studied the retention of Tc(VII) on Fe(II)-Al(III)-Cl layered double hydroxides in ionic strength range from 0.1 M NaCl solution to Milli-Q water at pH = 3.5–10.5 and Tc concentration from 10^{-11} to 10^{-3} M under ambient and inert gas (N_2) atmosphere. Most of the Tc uptake was caused by an initial Tc(VII) reduction to Tc(IV) and consecutive Tc(IV) interaction with the solid. Rodríguez et al. [12] studied reductive immobilization of Tc(VII) by a synthetic FeS_2 mixture (marcasite-pyrite 60:40) in water and 0.1 M NaCl solution by batch experiments, powder X-ray diffraction, X-ray photoelectron spectroscopy and Raman microscopy. Tc(VII) was completely removed from the solution after 7 days of interaction with the FeS_2 mixture at $6.0 < pH \leq 9.0$. Schmeide et al. [13] investigated the uptake of Tc by chukanovite in 0.1 M and 1 M NaCl solutions under anoxic, alkaline to hyperalkaline conditions (pH from 7.8 to 12.6), and confirmed the complete reduction of Tc(VII) to Tc(IV) by chukanovite under all experimental conditions.

Sedimentary rocks including shale and limestone are being considered as potential host rocks for a DGR for used nuclear fuel waste in Canada. Within deep-seated groundwater systems, these sediments have been observed to contain highly saline Na-Ca-Cl brine solutions with I up to 7 $mol \cdot kgw^{-1}$ (m) in a reducing environment (e.g., porewaters in Southern Ontario) [14]. SR-270-PW is an NWMO reference porewater for sedimentary rock which represents the potential groundwater chemistry at repository depths, with a total dissolved solids (TDS) concentration of about 275 $g \cdot L^{-1}$ (I of 6 m, Na-Ca-Cl type, Na/Ca molal ratio = 2.7) [15].

Bertetti [16] measured the sorption of Tc on MX-80 bentonite, shale and limestone in SR-270-PW and a dilute solution ($I = 0.01$ m) under reducing conditions. To our best knowledge, however, there are no previous studies that systematically investigated the effects of pH and ionic strength on Tc(IV) sorption on MX-80, illite (a main mineral composition of shale), shale and limestone in highly saline solutions. This paper studied the effect of pH ($4 \leq pH_m \leq 9$ for MX-80, illite, shale; $5 \leq pH_m \leq 9$ for limestone) and I (0.1 m – 6 m) on sorption of Tc(IV) on MX-80, illite, shale and limestone in Na-Ca-Cl solutions by batch experiments. The 2 site protolysis nonelectrostatic surface complexation and cation exchange sorption model (2SPNE SC/CE model) was applied for the sorption of Tc(IV) on MX-80 and illite.

2. Experimental

Many of experimental procedures such as preparation of Tc(IV) solution, sorption kinetics measurements and pH_m and I dependence measurements were the same as those described in the first paper of this series [1]. Therefore, the experimental procedures which were different from those in the first paper are mainly explained in this paper.

2.1 Materials

All chemicals used in this work were certified ACS reagent grade and purchased from Fisher Scientific and MilliporeSigma. Deionized water prepared with a Milli-Q Direct 8 (18.2 $M\Omega \cdot cm^{-1}$) system was used.

MX-80 bentonite sample was provided by the American Colloid Company and was used as received. The specific surface area of MX-80 is 26.2 $m^2 \cdot g^{-1}$ [16]. Other information including the mineralogy of this material is described elsewhere [16]. IMt-2 Na-illite (Silver Hill Montana USA, Cambrian Shale) was supplied from the Clay Minerals Society, USA, and was characterized by Hower et al. [17]. The specific surface area of illite is 70 $m^2 \cdot g^{-1}$ [18]. Other information including the mineralogy is described elsewhere [19]. Queenston shale core sample (DGR5-548.02 collected from the Queenston Formation of the Michigan Basin at the Bruce Nuclear Site in Ontario, Canada; specific surface area = 10.3 $m^2 \cdot g^{-1}$) and limestone core sample (DGR5-729.91 collected from Cobourg Formation at the Bruce Nuclear Site in Ontario, Canada; specific surface area = 2.8 $m^2 \cdot g^{-1}$) were provided by the NWMO. The major minerals of the Queenston shale are clay (41.5%, i.e., 25% illite, 10% chlorite, 2% kaolinite, 4% illite/smectite), carbonate (39.5%, i.e., 25.5% calcite, 14% dolomite) and quartz (17.5%). Queenston shale also contains trace minerals such as pyrite, gypsum, anhydrite, halite, hematite, and goethite [20]. The major minerals of the limestone are calcite (81%), dolomite (8%), clay (6%) and quartz (3%). Limestone also contains trace minerals such as microcline, pyrite, halite and anhydrite [21]. Illite, shale and limestone samples were crushed using a super hard cylinder of Nichika Inc. and sieved using stainless steel sieves in deionized water. Particle sizes between 150 μm and 300 μm were used in the

Table 1. Masses of chemical compounds added to 1 kg deionized water for preparation of SR-270-PW reference porewater

Compound	Mass of compound (g)
KCl	22.2
NaCl	127
$CaCl_2 \cdot 2H_2O$	117
$MgCl_2 \cdot 6H_2O$	68.6
$SrCl_2 \cdot 6H_2O$	3.65
$NaHCO_3$	0.151
Na_2SO_4	0.651
KBr	2.53

sorption experiments.

Na-Ca-Cl solutions were prepared by adding NaCl and $CaCl_2 \cdot 2H_2O$ salts to deionized water to achieve the desired I of 0.1, 0.5, 1, 2, 3 and 6 m. A Na/Ca molar ratio of 2.7 was used for the Na-Ca-Cl solutions which is the same as the SR-270-PW reference porewater. The SR-270-PW reference porewater (Na/Ca molal ratio = 2.7; I = 6 m) was prepared using the masses of reagents shown in Table 1. All reagents were dissolved into 1 kg of deionized water in total.

As explained in the first paper of this series [1], Tc(VII) in Tc-99 solution supplied by the Health Physics Department at McMaster University was electrochemically reduced to Tc(IV). Technetium(IV) solution was prepared just before the sorption experiments.

A Glove Box (GB) was filled with N_2 gas (> 99.998%) to exclude CO_2 and O_2. The concentration of O_2 in the running N_2 gas was confirmed to be less than 2 ppm by an oxygen sensor (Inert Technology). All sorption experiments were carried out in the GB.

In this study, the pH_m in solutions was determined by acid-base titration (Metrohm Ti-Touch 916) according to the procedures we used in the first paper of this series [1]. We also measured the redox potentials in the solutions and converted them into Eh versus SHE. The Eh measurement and calibration are also described in the first paper of this series [1].

2.2 Sorption Experiment

2.2.1 Sorption kinetics

All experiments were conducted at 25°C in the GB. The experimental procedures were the same as those described in the first paper of this series [1]. In this work, the R_d [$cm^3 \cdot g^{-1}$] (sorption distribution coefficient) was used to express the results of the sorption experiment:

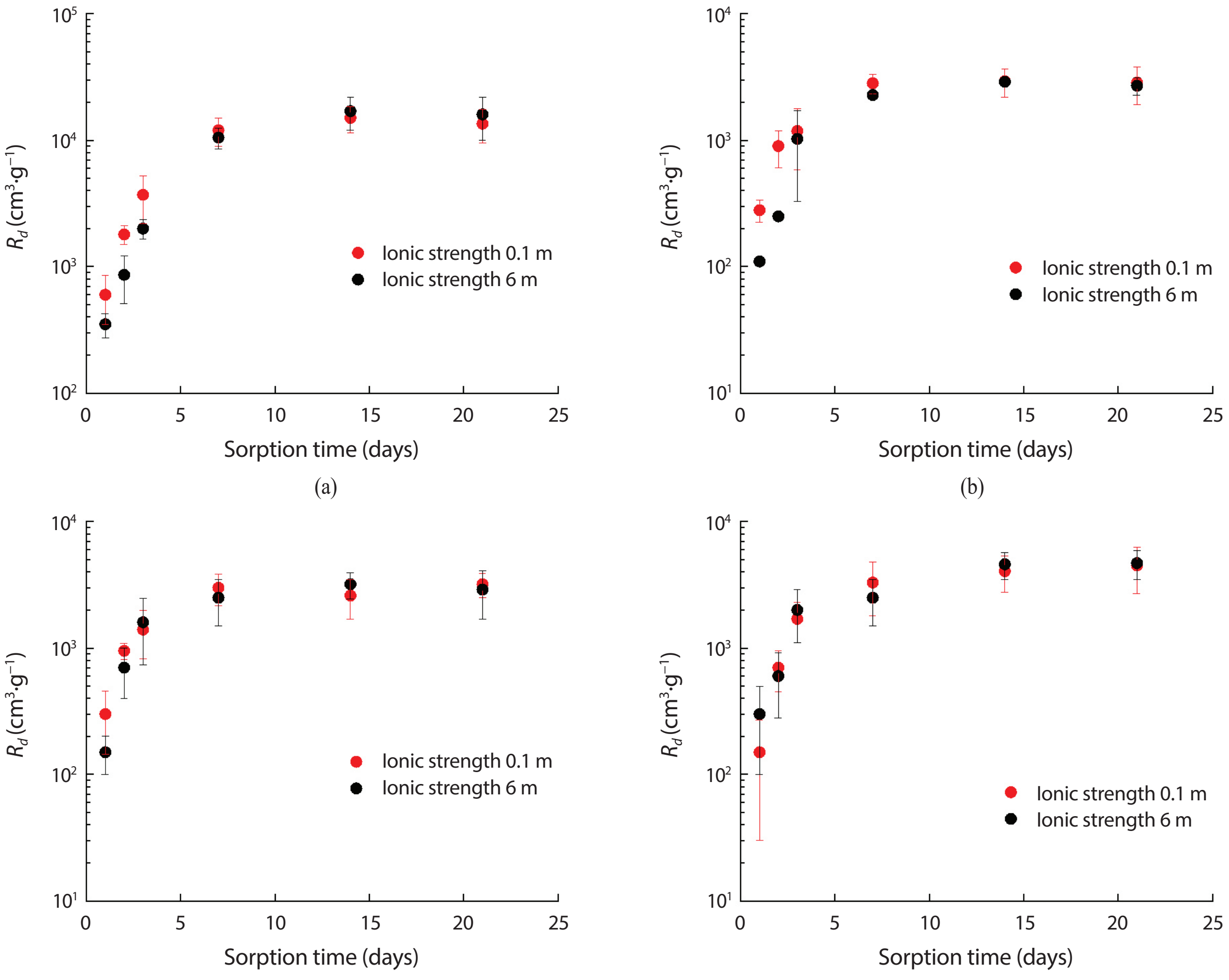
$$R_d = \frac{(C_0 - C_e)}{C_e} \frac{V}{W} \tag{1}$$

where C_0 (m) is the initial concentration of Tc(IV) in solution (1×10^{-9} m), C_e [m] is the Tc(IV) concentration in solution at sorption equilibrium, V [cm^3] is the volume of the solution, and W [g] the mass of MX-80, illite, shale or limestone.

The solid/liquid ratio for all sorption experiments was 0.01 g/10 cm^3. All sorption experiments were preceded by pre-equilibration, where 10 cm^3 of Na-Ca-Cl solution with respective I (0.1, 0.5, 1, 2, 3 and 6 m) were mixed with 0.01 g MX-80, illite, shale or limestone. The sorption kinetics of Tc(IV) on MX-80, illite, shale and limestone in Na-Ca-Cl solutions were conducted for I = 0.1 and 6 m. After the Tc(IV) solution was spiked, the value of pH_m was adjusted to around 6. The value of pH_m was measured daily in the GB. When the pH_m value shifted more than ± 0.3 from the initial value, it was adjusted by adding small amounts of HCl or NaOH solution. The initial concentration of Tc(IV) was 1×10^{-9} m.

2.2.2 pH_m and Ionic Strength Dependence of R_d

The pH_m dependences of the R_d of Tc(IV) sorption on MX-80, illite, and shale in Na-Ca-Cl solutions were measured at pH_m = 4–9. Since we could not adjust the pH_m of the Na-Ca-Cl solutions contacting with limestone to around 4 adequately, the study of pH_m dependence of the R_d of Tc(IV) sorption on limestone was conducted at pH_m



(a)

(b)

(c)

(d)

Fig. 1. Sorption kinetics of Tc(IV) measured on (a) MX-80, (b) illite, (c) shale, and (d) limestone in Na-Ca-Cl solutions with $I = 0.1$ and 6 m.

= 5–9. The effect of ionic strength on Tc(IV) sorption was studied at $I = 0.1$, 0.5, 1, 2, 3 and 6 m. All experiments were conducted in triplicate. As shown in the Results and Discussion section, the sorption equilibrium under the experimental conditions in this study was reached in 7 days. Therefore, the sorption period was established as 14 days for the pH_m and I dependence of R_d sorption experiments. Furthermore, R_d values for Tc(IV) sorption onto MX-80, illite, shale and limestone in the SR-270-PW reference porewater were also measured. The pH_m was adjusted to 6.5 ± 0.5 using a small amount of HCl or NaOH solution when the value of pH_m changed by more than ± 0.3 from the initial value. Other procedures were the same as those used in the first paper of this series [1].

3. Results and Discussion

3.1 Sorption Kinetics

The sorption kinetics results of Tc(IV) measured for MX-80, illite, shale and limestone in Na-Ca-Cl solutions at $I = 0.1$ m and 6 m are shown in Fig. 1. It was found that the sorption of Tc(IV) on all four solids reached equilibrium

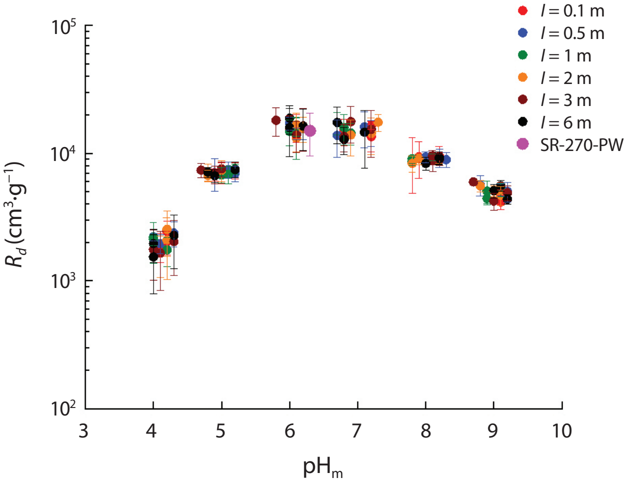


Fig. 2. pH$_m$ and ionic strength dependences of R_d values of Tc(IV) sorption on MX-80 in Na-Ca-Cl solutions.

within 7 days at both $I = 0.1$ and 6 m. Based on the sorption kinetics results, the sorption reaction time for experiments on pH$_m$ and I dependence of R_d was set at 14 days. The Eh values of the solutions were measured as –250 ~ –200 mV.

3.2 Sorption on MX-80

The pH$_m$ and I dependence of Tc(IV) sorption onto MX-80 measured in Na-Ca-Cl solutions is illustrated in Fig. 2. The R_d values of Tc(IV) on MX-80 increased with pH$_m$ from pH$_m$ = 4 to 6, reached the maximum at pH$_m$ = 6–7 and then gradually decreased from pH$_m$ = 7 to 9. This trend was the same as that observed in the sorption of Tc(IV) on MX-80 in Ca-Na-Cl solutions with $I = 0.05$–1 m [1] and was qualitatively similar to that reported by Grambow et al. [22]. The measured R_d values of Tc(IV) were also found to be similar to those measured in Ca-Na-Cl solutions ($I = 0.05$–1 m) at the same pH [1], suggesting that the effect of competition of sorption sites with Ca^{2+} and other cations in Na-Ca-Cl solutions was negligible. It was found that the R_d values of Tc(IV) did not depend on I at the pH$_m$ range we studied in this work. The Eh values of the solutions were measured as from –250 mV to –200 mV.

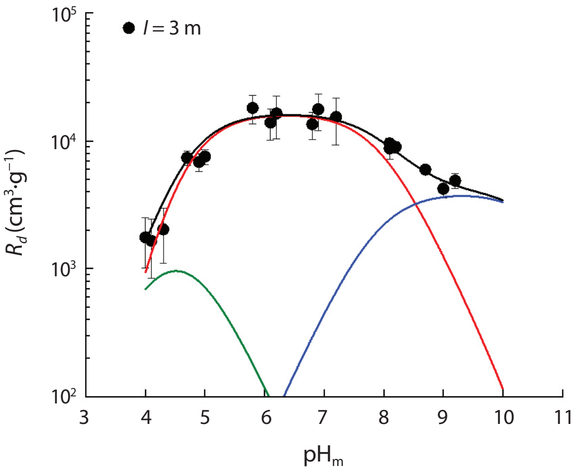


Fig. 3. Fitting results for Tc(IV) sorption on MX-80 in ionic strength 3 m Na-Ca-Cl solution by 2SPNE SC/CE model using SIT parameters. The red, blue, and green lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows SOTcO(OH)_2^- + 3H^+$, and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$, respectively. The black line represents the total of modelled sorption.

The R_d value of Tc(IV) on MX-80 measured in the SR-270-PW solution was estimated as $1.5 \times 10^4 \pm 5.5 \times 10^3$ cm³·g⁻¹ (at pH$_m$ = 6.3, Eh = –200 mV). This is within the range of the R_d values measured in the Na-Ca-Cl solutions around pH$_m$ = 6–7 as shown in Fig. 2, suggesting that the impact of minor ions such as Mg^{2+}, K^+, Sr^{2+}, HCO_3^- and SO_4^{2-} on the sorption of Tc(IV) at pH$_m$ = 6–7 would be small. Bertetti [16] measured R_d of Tc(IV) on MX-80 in SR-270-PW solution as 5×10^3 cm³·g⁻¹ at pH = 7 and Eh = –20 mV. A possible explanation for a lower R_d value by Bertetti could be that Bertetti used $Na_2S \cdot 9H_2O$ to reduce Tc(VII) to Tc(IV) and some Tc(VII) might not be reduced to Tc(IV).

For the sorption of Tc(IV) on MX-80 in Na-Ca-Cl solutions, we applied the 2SPNE SC/CE model to simulate the pH$_m$ and I dependences of R_d values of Tc(IV) sorption on MX-80. The experimental data were used for sorption modelling to identify the surface complexation reactions and evaluate the surface complexation constants (log K^0). For the experimental data measured at I up to 3 m, the specific ion interaction theory (SIT) [24] was used to estimate the

Table 2. Surface complexation constants log K^0 of Tc(IV) sorption on MX-80 obtained in this work with SIT parameters and literature values

Surface complexation reaction	log K^0 (this work)	log K^0 [1]	log K^0 [22]
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	3.3	3.4	2.38
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOTcO(OH)_2^- + 3H^+$	7.2	7.4	-
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOH_2TcO(OH)_2^+ + H^+$	−5.2	−5.1	-
$2\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv (SO)_2TcO(OH)^- + 3H^+$	-	-	−4.27

activity coefficients of species in solutions. The JAEA thermodynamic database [25] which contains SIT parameters for Tc(IV) species was used.

For the highly saline solution with $I = 6$ m, Pitzer model is preferred for ion activity correction.

The main limitation of application of the Pitzer approach for radionuclides is the lack of Pitzer parameters. The Pitzer thermodynamic database DGR-Pitzer-TDB (version 2) being developed by the NWMO [23] was also used for the sorption modelling for experimental data measured at I up to 6 m. To our best knowledge, this would be the first sorption modelling work using the Pitzer model.

To initiate the fitting of the model, the constants of surface complexation reactions for Tc(IV) sorption on MX-80 derived by our sorption study in Ca-Na-Cl solutions [1] were used as the initial values of constants for MX-80. Values of other parameters such as protolysis constants of MX-80 are described elsewhere [16]. Since the concentration of Tc(IV) in the Na-Ca-Cl solution was small, we considered only strong sites in this study.

Fig. 3 illustrates the fitting results at $I = 3$ m using SIT parameters. Other fitting results with SIT parameters at $I =$ 0.1, 0.5, 1 and 2 m are shown in Supplementary Materials (Figs. S1–S4). The optimized values of log K^0 for Tc(IV) sorption on MX-80 by this study in Na-Ca-Cl solutions, by our study in 0.24 m Ca-Na-Cl solution [1] and by Grambow et al. [22] in 0.05 m synthetic groundwater (Na-Ca-Mg-Cl-SO_4 type) are summarized in Table 2. It was found that the 2SPNE SC/CE model well simulated the sorption of Tc(IV) on MX-80 in the wide ranges of pH_m (4–9) and I (0.1–3 m) (Fig. 3, Figs. S1–S4). Furthermore, the surface complexation reactions of Tc(IV) sorption on MX-80 in Na-Ca-Cl solutions determined in this model calculation and the optimized value of log K^0 for each surface complexation reaction were identical to those we reported in Ca-Na-Cl solutions [1]. Hence, it is considered that the Tc(IV) sorption on MX-80 in saline solution is dominated by two inner-sphere surface complexation reactions ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$ and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$) and one outer-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$).

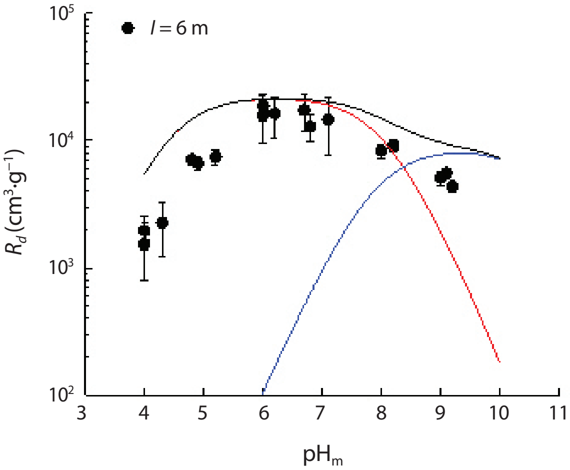


Fig. 4. Fitting results for Tc(IV) sorption on MX-80 in ionic strength 6 m Na-Ca-Cl solution by 2SPNE SC/CE model using Pitzer parameters. The red and blue lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SSOTcO(OH)_2^- + 3H^+$, respectively. The black line represents the total of modelled sorption.

Fig. 4 illustrates the fitting results at $I = 6$ m using Pitzer parameters. Other fitting results with the Pitzer parameters at $I =$ 0.1, 0.5, 1, 2 and 3 m are shown in Supplementary

Table 3. Surface complexation constants log K^0 of Tc(IV) sorption on MX-80 obtained with Pitzer parameters

Surface complexation reaction	log K^0 (this work)
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	3.7
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOTcO(OH)_2^- + 3H^+$	−4.6

Materials (Figs. S5–S9). It was found that the 2SPNE SC/CE model using Pitzer parameters simulated well the sorption of Tc(IV) on MX-80 in the pH_m of 6–9 at $I = 0.1–6$ m (Fig. 4, Figs. S5–S9), but slightly overestimated the sorption in pH_m of 4–5, especially at $I = 6$ m. This slight overestimate is considered to result from uncertainties related to the lack of the appropriate set of Pitzer parameters and the thermodynamic data for Tc. Furthermore, it was found that Tc(IV) sorption on MX-80 in saline solutions using Pitzer parameters was fitted only by two inner-sphere surface complexation reactions ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$ and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$). The optimized values of log K^0 for Tc(IV) sorption on MX-80 in Na-Ca-Cl solutions obtained by Pitzer parameters are summarized in Table 3. When we included the outer-sphere surface complexation reaction in the sorption model, the difference between the experimental data and the model in the pH_m of 4–5 became larger. This will leave for future research with further development of the Pitzer database.

3.3 Sorption on Illite

The pH_m and I dependence of Tc(IV) sorption onto illite measured in Na-Ca-Cl solutions is shown in Fig. 5. The R_d values of Tc(IV) sorption on illite gradually increased with pH_m from 4 to 7 and then decreased with pH_m from 7 to 9. It was also found that the R_d values of Tc(IV) were independent of I at the pH_m range we studied in this work. The Eh values of the solutions were measured as –250 ~ –200 mV.

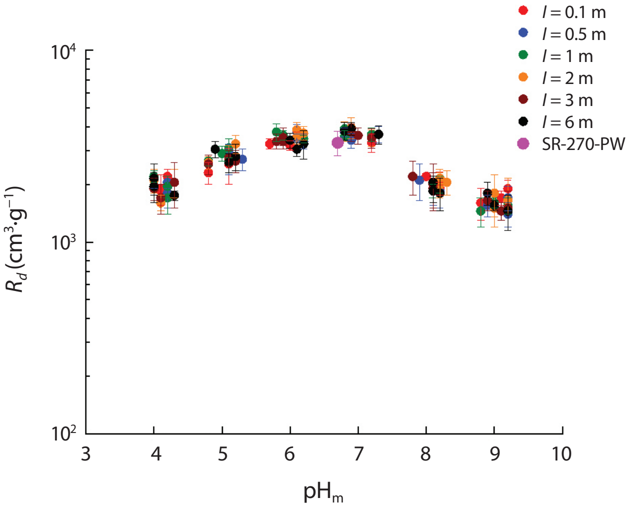


Fig. 5. pH_m and ionic strength dependences of R_d values of Tc(IV) sorption on illite in Na-Ca-Cl solutions.

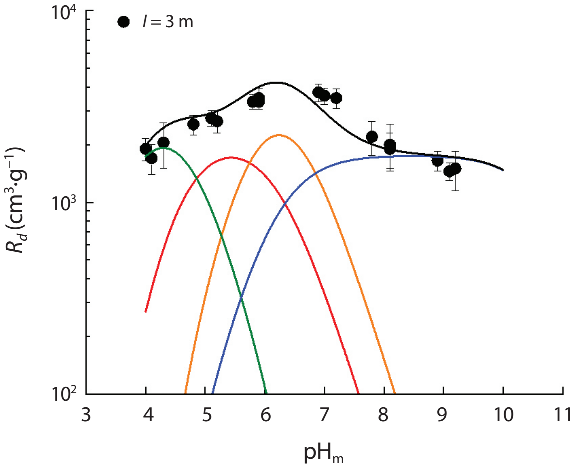


Fig. 6. Fitting results for Tc(IV) sorption on illite in ionic strength 3 m Na-Ca-Cl solution by 2SPNE SC/CE model using SIT parameters. The red, blue, green and orange lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$, and $2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcOOH^- + 3H^+$, respectively. The black line represents the total of modelled sorption.

The R_d value of Tc(IV) sorption on illite in the SR-270-PW solution was estimated as $3.3 \times 10^3 \pm 4.8 \times 10^2$ cm³·g⁻¹ (at $pH_m = 6.7$, Eh = –200 mV). This is within the range of the R_d values measured in the Na-Ca-Cl solutions around $pH_m = 6–7$ (see Fig. 5), suggesting that the impact of minor ions such as Mg^{2+}, K^+, Sr^{2+}, HCO_3^- and SO_4^{2-} on the sorption of Tc(IV) at $pH_m = 6–7$ would be small.

For the sorption of Tc(IV) on illite, we also applied the

Table 4. Surface complexation reactions and surface complexation constants log K^0 of Tc(IV) sorption on illite obtained in this work using SIT parameters

Surface complexation reaction	log K^0
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	2.2
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOTcO(OH)_2^- + 3H^+$	7.1
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOH_2TcO(OH)_2^+ + H^+$	−4.1
$2\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons (\equiv SO)_2TcO(OH)^- + 3H^+$	−3.1

2SPNE SC/CE model to simulate the pH_m and I dependences of R_d values of Tc(IV) sorption on illite. To initiate the fitting of the model, we adopted the values of surface complexation constants for Tc(IV) sorption on MX-80 shown in Table 2. This was because there is no previous modelling work on Tc(IV) sorption on illite we could refer to. Values of other parameters such as protolysis constants of illite were the same as those used by Walker et al. [19]. Since the concentration of Tc(IV) used in the sorption measurements was small, we also considered only strong sites in this study. Same as the sorption modelling for MX-80 bentonite, the JAEA SIT thermodynamic database [24, 25] was used to simulate the experimental data measured at I up to 3 m and the NWMO Pitzer database [23] was used to simulate the experimental data measured at I up to 6 m for illite.

Fig. 6 illustrates the fitting results at I = 3 m using SIT model. Other fitting results at I = 0.1, 0.5, 1 and 2 m are shown in Supplementary Materials (Figs. S10–S13). The optimized values of log K^0 for Tc(IV) sorption on illite obtained in this study are summarized in Table 4. It was found that the 2SPNE SC/CE model well simulated the sorption of Tc(IV) on illite in the wide range of pH_m (4–9) and I (0.1–3 m) although the model slightly underestimated the R_d values around pH_m = 7. The reason for this underestimation is not clear at the present. Compared to the modelling results for MX-80, it was found that the bidentate surface complexation reaction ($2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcOOH^- + 3H^+$) also contributed to the sorption on illite at pH_m = 6–7. If the dominant range of the bidentate surface complexation reaction had been expanded to pH_m of 7.5–8, the underestimation of the R_d value by modelling would have been resolved. The reason for the underestimation by the model will be examined in the future by further study on the stability of bidentate surface complexation reaction. From the modelling results, it is considered that the Tc(IV) sorption on illite in saline solution is dominated by two monodentate inner-sphere surface complexation reactions ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$ and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$), one bidentate inner-sphere surface complexation reaction ($2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcOOH^- + 3H^+$) and one monodentate outer-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$).

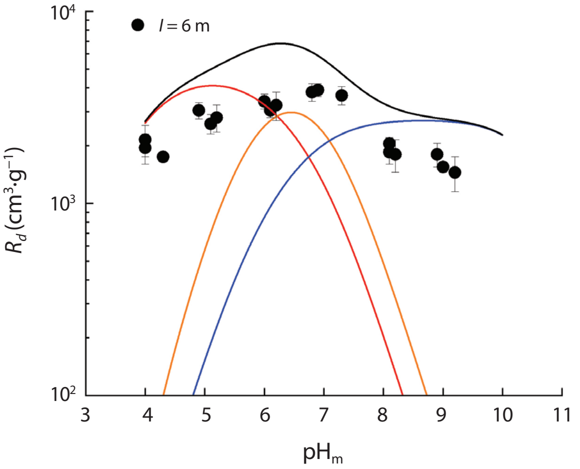


Fig. 7. Fitting results for Tc(IV) sorption on illite in ionic strength 6 m Na-Ca-Cl solution by 2SPNE SC/CE model using Pitzer parameters. The red, blue and orange lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$, and $2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcOOH^- + 3H^+$, respectively. The black line represents the total of modelled sorption.

Fig. 7 illustrates the fitting results at I = 6 m using Pitzer parameters. Other fitting results using Pitzer parameters at I = 0.1, 0.5, 1, 2 and 3 m are shown in Supplementary Materials (Figs. S14–S18). It was found that the 2SPNE SC/CE model using Pitzer parameters simulated well the sorption of Tc(IV) on illite in the pH_m range of 6–9 at I = 0.1–2 m (Figs. S14–S17), but overestimated the sorption of Tc(IV) on illite in the pH_m range of 4–9 at I = 3 m

Table 5. Surface complexation constants log K^0 of Tc(IV) sorption on illite obtained using Pitzer parameters

Surface complexation reaction	log K^0
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	2.3
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOTcO(OH)_2^- + 3H^+$	−4.1
$2\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv (SO)_2TcO(OH)^- + 3H^+$	−3.2

and 6 m (see Fig. S18 and Fig. 7, respectively). It was also found that Tc(IV) sorption on illite in saline solution was fitted using Pitzer parameters by two monodentate inner-sphere surface complexation reactions ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$ and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$), and one bidentate inner-sphere surface complexation reaction ($2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcOOH^- + 3H^+$). The optimized values of log K^0 for Tc(IV) sorption on illite in Na-Ca-Cl solutions obtained using Pitzer parameters are summarized in Table 5. When the outer-sphere surface complexation was included in the model, the difference between the experimental data and the model in the pH_m range of 4–6 became larger. These discrepancies likely are due to a lack of thermodynamic data and Pitzer parameters for Tc [23]. This remains for future study with further development of the Pitzer parameters for Tc.

3.4 Sorption on Shale and Limestone

The pH_m and I dependences of Tc(IV) sorption onto shale and limestone measured in Na-Ca-Cl solutions are shown in Figs. 8 and 9, respectively. The Eh values of the solutions were measured as –250 ~ –200 mV.

The R_d values of Tc(IV) sorption on shale gradually increased with pH_m from 4 to 7 and then decreased with pH_m from 7 to 9. This trend of pH_m dependence of Tc(IV) sorption on shale was found to be similar to that of Tc(IV) sorption on illite. The R_d values of Tc(IV) sorption on shale were also similar to those of Tc(IV) sorption on illite measured at the same pH_m. This can be considered because the major sorbing mineral of Queenston shale used in this study is illite. It was found that the I dependence of R_d values of Tc(IV) sorption on shale was negligibly small. Hallam et al. [7] measured the pH dependence of R_d values of Tc(IV) sorption on shale in diluted solutions. The R_d values measured by Hallam et al. [7] at pH = 5.6 (R_d = 1,552 $cm^3 \cdot g^{-1}$), 6.44 (R_d = 2,501 $cm^3 \cdot g^{-1}$), 6.51 (R_d = 3,681 $cm^3 \cdot g^{-1}$) and 7.14 (R_d = 4,236 $cm^3 \cdot g^{-1}$) are similar to that measured in this

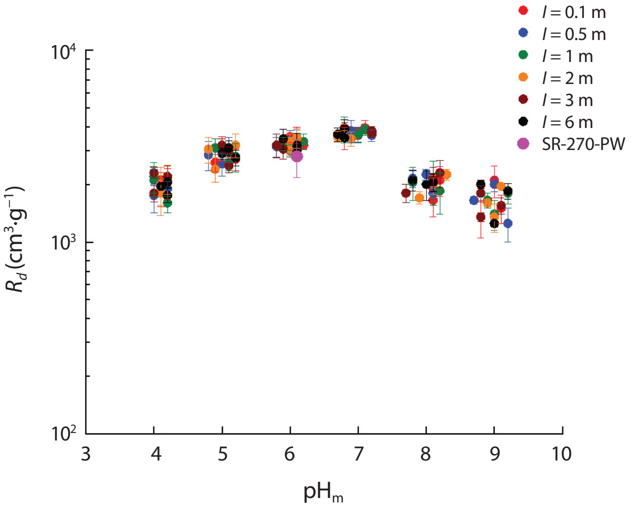


Fig. 8. pH_m and ionic strength dependences of R_d values of Tc(IV) sorption on shale in Na-Ca-Cl solutions.

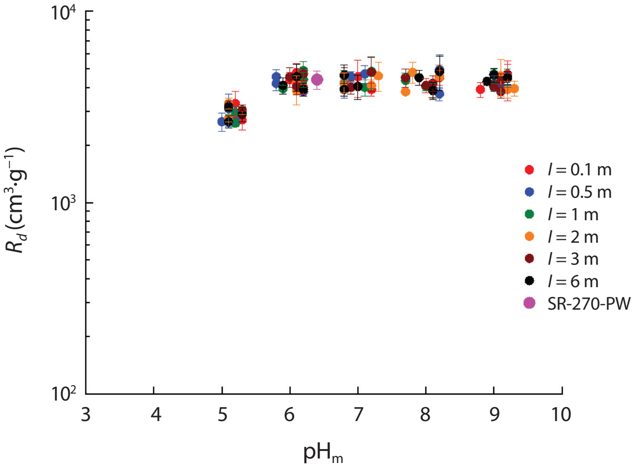


Fig. 9. pH_m and ionic strength dependences of R_d values of Tc(IV) sorption on limestone in Na-Ca-Cl solutions.

study at similar pH. Assuming the homogeneous surface property for shale, they considered one monodentate and one bidentate surface complexation reaction to fit their experimental data. We will characterize the surface properties of mineral components of Queenston shale and conduct the surface complexation modelling in the future.

The R_d values of Tc(IV) sorption on limestone measured at $pH_m = 6–9$ seemed constant but those measured at $pH_m = 5$ were slightly smaller than those at $pH_m = 6–9$. It was also found that the effect of I on the R_d values of Tc(IV) sorption on limestone was negligible.

The R_d value of Tc(IV) on shale and limestone in the SR-270-PW solution was measured as $2.8 \times 10^3 \pm 6.3 \times 10^2$ $cm^3 \cdot g^{-1}$ (at $pH_m = 6.1$, Eh = –200 mV) and $4.4 \times 10^3 \pm 4.8 \times 10^2$ $cm^3 \cdot g^{-1}$ (at $pH_m = 6.4$, Eh = –200 mV), respectively. These are within the range of the R_d values measured in the Na-Ca-Cl solutions around $pH_m = 6–7$ (see Figs. 8 and 9), suggesting that the impact of minor ions such as Mg^{2+}, K^+, Sr^{2+}, HCO_3^- and SO_4^{2-} on the sorption of Tc(IV) on shale and limestone at $pH_m = 6–7$ would also be small. Bertetti [16] measured the R_d values of 20 $cm^3 \cdot g^{-1}$ and 10^4 $cm^3 \cdot g^{-1}$ for shale and limestone at pH = 7 and Eh = –20 mV, respectively. The reason for these differences is not clear and remains for future study.

To apply the 2SPNE SC/CE model and other sorption models, it is required to evaluate the surface characterization of constituent minerals of shale and limestone quantitatively. Therefore, the sorption modelling for shale and limestone remains for future study.

4. Conclusions

A systematic study was carried out to study the sorption of Tc(IV) in Na-Ca-Cl solutions with I of 0.1 m – 6 m at pH_m of 4–9 for MX-80, illite and shale and pH_m of 5–9 for limestone. The sorption kinetics were conducted for all four solids at $I = 0.1$ and 6 m. It was found that the sorption of Tc(IV) reached equilibrium within 7 days on all four solids. It was also confirmed that Tc(IV) sorption on all four solids was independent of I in the range of 0.1 to 6 m. Tc(IV) sorption on MX-80 showed that the R_d values increased with increasing pH_m until $pH_m = 6$ and reached the maximum at $pH_m = 6–7$. Then, the R_d values gradually decreased with pH_m until $pH_m = 9$. The R_d value of Tc(IV) sorption on illite gradually increased with increasing pH_m until $pH_m = 7$, where the maximum value of R_d was observed. Then, the R_d value decreased as pH_m increased. The sorption properties of Tc(IV) on shale were very similar to that on illite. The R_d value of Tc(IV) sorption on limestone slightly increased with pH_m from 5 to 6 and then seemed to be constant at $pH_m = 6–9$. From the results of Tc(IV) sorption in Na-Ca-Cl solutions and the SR-270-PW reference porewater, it was found that the impact of minor ions such as Mg^{2+}, K^+, Sr^{2+}, HCO_3^- and SO_4^{2-} on the sorption of Tc(IV) onto all four solids at $pH_m = 6–7$ was small.

The 2SPNE SC/CE model was able to successfully simulate the sorption of Tc(IV) onto MX-80 and illite using SIT parameters for the experimental results measured at I up to 3 m. Two monodentate inner-sphere surface complexation reactions and one monodentate outer-sphere surface complexation reaction were identified for Tc(IV) sorption onto MX-80 bentonite. For Tc(IV) sorption onto illite, two monodentate inner-sphere surface complexation reactions, one bidentate inner-sphere surface complexation reaction and one monodentate outer-sphere surface complexation reaction were identified. Pitzer parameters were also used in the 2SPNE SC/CE model to simulate experimental results measured at I up to 6 m. To our best knowledge, this is the first sorption modelling work using the Pitzer parameters. It was found that the model calculations could simulate the experimental results without outer-sphere surface complexation reaction both for MX-80 and illite. However, the calculation results using Pitzer parameters slightly overestimated the sorption in the pH_m of 4–5, especially at $I = 6$ m for MX-80 and overestimated the sorption of Tc(IV) in the pH_m of 4–9 at $I = 3$ m and 6 m for illite. These discrepancies likely are due to a lack of thermodynamic data and Pitzer parameters for Tc. Sorption modelling of Tc(IV) using Pitzer parameters for highly saline solutions remains for future study with further development of Pitzer parameters for Tc. The optimized value of log K^0 of each surface complexation reaction was evaluated using both SIT and Pitzer parameters.

Conflict of Interest

No potential conflict of interest was reported by the authors.

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