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Sorption of Tc(IV) in Saline Solutions – I. Sorption on MX-80 and Granite in Ca-Na-Cl Solutions

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Technetium-99 is identified as an element of interest for the safety assessment of a deep geological repository for used nuclear fuel. The sorption behavior of Tc(IV) onto MX-80 and granite in Ca-Na-Cl solutions of varying ionic strength (0.05–1 mol·kgw^{-1} (m)) and across a pH$_m$ range of 4–9 was studied in this paper. Sorption of Tc(IV) was found to be independent of ionic strength in the range of 0.05 to 1 m for both MX-80 and granite. Sorption of Tc(IV) on MX-80 increased with pH$_m$ from 4 to 7 and then decreased with pH$_m$ from 8 to 9. Sorption of Tc(IV) on granite gradually increased with pH$_m$ from 4 to 8 and then became almost constant or slightly decreased with pH$_m$ from 8 to 9. A 2 site protolysis non-electrostatic surface complexation and cation exchange sorption model successfully simulated sorption of Tc(IV) on MX-80 and granite. Optimized values of surface complexation constants (log K^0) are proposed.

Keywords: Technetium(IV), Sorption, Granite, MX-80, Saline, 2SPNE SC/CE model

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1. Introduction

Technetium-99 (half-life: 2.1×10^5 years) is one of the fission products generated during the operation of nuclear power reactors and is one of the radionuclides of interest for the safety assessment of a deep geological repository (DGR) for used nuclear fuel. Technetium can be present in groundwater with different oxidation states (+II to +VII) which will have different physical and chemical behaviors during migration through the geosphere. When exposed to an aerobic environment, Tc exists as Tc(VII) and the dominant chemical species is TcO_4^- which is highly mobile due to the anionic charge and the high chemical stability of TcO_4^-. Tc(IV) is stable under anaerobic conditions and speciates predominately as $TcO(OH)_2$.

Sorption of radionuclides on the engineered and natural barrier materials is an important mechanism to retard their migration from the repository to the biosphere [1-3]. Potential geological media for a DGR for used nuclear fuel are crystalline and sedimentary rocks [4, 5]. Hence, it is critical to investigate the sorption behavior of radionuclides on engineered barrier materials, as well as natural barrier rocks such as granite. MX-80 bentonite clay consisting of about 80wt% Na-rich montmorillonite is widely considered for use as an engineered barrier material in the repository. This study focuses on the sorption of Tc(IV) onto MX-80 and granite. Sorption of Tc(IV) onto sedimentary rocks is described in another paper in this series.

There are some previous studies on Tc(IV) sorption on bentonite and granite. Oscarson et al. measured apparent diffusion coefficients of Tc in compacted 1:3 mixtures of Lake Agassiz clay and crushed granite with different particle size fraction in a Na-Ca-Cl-dominated synthetic groundwater solution (ionic strength of 0.22 $mol \cdot L^{-1}$) [6]. It was found that a decrease in granite particle size led to an increase in the extent of reduction of Tc(VII) to Tc(IV) (the reductants were probably Fe(II)-bearing minerals, such as magnetite) and its subsequent sorption on Fe(III) oxyhydroxides present in granite, which resulted in a the decrease in the apparent diffusion coefficient. Baston et al. studied the sorption of Tc onto bentonite, tuff and granodiorite in seawater (pH ~8.2) and de-ionized water (pH 9–10) under strongly-reducing and non-reducing conditions [7]. It was found that Tc was strongly sorbed from seawater and de-ionized water onto bentonite, tuff and granodiorite under strongly-reducing conditions but much weakly sorbed under non-reducing conditions. Baston et al. applied the triple layer models for silica, alumina and goethite to model sorption onto granodiorite and reported that the dominant surface complexation reaction and the surface complexation constants (log K^0) as $\equiv SOH + TcO(OH)_2 + H^+ \rightleftarrows \equiv SOH_2TcO(OH)_2^+$ (log K^0 (silica) = 9.0, log K^0 (alumina) = 12.2, and log K^0 (goethite) = 11.06) [7]. Baston et al. also studied the sorption of Tc onto bentonite, tuff and granodiorite in de-ionized water (pH 9–10) under strongly-reducing conditions at room temperature and 60ºC [8]. The goethite-based triple layer model was applied to all three solids and the surface complexation reaction and the surface complexation constant were reported as $\equiv SOH + TcO(OH)_2 + H^+ \rightleftarrows \equiv SOH_2TcO(OH)_2^+$ (log K^0 = 13.6) for bentonite, tuff and granodiorite. However, Baston et al. did not report how well the modelling results reproduced the experimental data [8]. Cui and Eriksen examined the migration of Tc in a granite fracture-groundwater system in column experiments with crushed Stripa granite fracture-filling material [9]. Cui and Eriksen found that under reducing conditions the Fe(II)-containing fracture-filling material reduced Tc(VII) to sparingly soluble $TcO_2 \cdot nH_2O(s)$ and $Tc(IV)_{aq}$ was rapidly sorbed by the material [9]. The reaction in the 15-hour column experiment was five times faster than that obtained from their previous 90-day batch experiment. The sorption of Tc(IV) was very fast under reducing conditions. Berry et al. measured the sorption behavior of Tc(IV) on granodiorite, tuff and bentonite in distilled water and synthesized seawater around pH = 8–10 at room temperature and at 60ºC [10]. Huber et al. studied the interaction of Tc(VII) with crushed crystalline rock (Äspö diorite; 1–2 mm size fraction) from the Äspö Hard Rock Laboratory by batch sorption and desorption experiments under

Ar atmosphere using natural Äspö groundwater (Na-Ca-Cl type, ionic strength (I) ≈ 0.17 m, pH = 7.8, Eh = −240 ± 50 mV), natural Grimsel groundwater (glacial melting water analogue with low ionic strength, pH = 9.67, Eh = 320 ± 50 mV) and a synthetic groundwater (Na-Ca-Cl type, I ≈ 0.17 m, pH = 8.0, Eh = 390 ± 50 mV) [11]. Huber et al. found that the uptake of Tc(VII) on the Äspö diorite strongly depended on the redox capacity of solids [11]. Uptake on the unoxidized rock sample was approximately 2 times greater compared to oxidized rock samples, most likely due to higher Fe(II) contents in the unoxidized rock. Huber et al. confirmed the reduction of Tc(VII) to Tc(IV) occurred at the rock surface by using X-ray photoelectron spectroscopy and K-edge X-ray absorption near edge structure spectroscopy [11]. Jedináková-Křížová et al. and Vinšová et al. investigated the sorption of Tc(VII) on bentonite, bentonite with Fe, bentonite with activated carbon, bentonite with Fe_3O_4, and bentonite with FeS under aerobic and anaerobic conditions [12, 13]. It was found that the main mechanism of retention of Tc on bentonite with activated carbon was the physical sorption of Tc(VII) anion (TcO_4^-) and that sorption of Tc on bentonite was caused by the reduction of Tc(VII) to Tc(IV) by Fe or FeS contained in bentonite. Grambow et al. applied a multi-site surface complexation/ion exchange model to sorption data of Tc(IV) on dispersed MX-80 bentonite measured by SUBATECH and identified the surface complexation reactions and their constants as $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcO(OH) + 2H^+$ ($\log K^0 = 2.38$) and $2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcO(OH)^- + 3H^+$ ($\log K^0 = -4.27$) [14]. Bruggeman et al. studied the interaction of Tc(IV) with dissolved boom clay and identified FeS_2 as one of the sorption sinks present within the boom clay through systematic experiments at pH = 8.3 ± 0.1 and Eh = −370 ~ −250 mV [15].

The crystalline rock in the Canadian Shield at repository depths (e.g., 500–800 m) in northern Ontario has been observed to have brackish to saline Ca-Na-Cl type groundwater in a reducing environment. CR-10 is a reference groundwater for crystalline rock representing the potential groundwater chemistry at repository depths, with a TDS concentration of about 11 $g \cdot L^{-1}$ ($I = 0.24\ mol \cdot kgw^{-1}$ (m), Ca-Na-Cl type, Na/Ca molal ratio = 1.6) [16]. In our knowledge, there is no previous study on sorption of Tc(IV) on granite and MX-80 in the saline solutions. In this paper, the dependence of sorption of Tc(IV) on granite and MX-80 in Ca-Na-Cl solutions on pH and I was systematically studied by batch experiments and a 2 site protolysis non-electrostatic surface complexation and cation exchange sorption model (2SPNE SC/CE model).

2. Experimental

2.1 Materials

All chemicals used in this work were certified ACS reagent grade and purchased from Fisher Scientific. 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. Bertetti measured the specific surface area of MX-80 as 26.2 $m^2 \cdot g^{-1}$ [17]. MX-80 has been widely used in the sorption study of various radionuclides, and its mineralogical information has been described in these studies [17-21]. The XRD pattern of MX-80 used is shown in Supplementary Materials (Fig. S1). The pattern is similar to that shown in the previous studies [17-21]. The granite sample was supplied by the NWMO and originated from the Lac du Bonnet batholith in Manitoba, Canada. Batholiths are common in the Canadian Shield. The main mineralogical composition of the Lac du Bonnet batholith granite being used in this work is plagioclase feldspar (37%), quartz (34%), alkali-feldspar (19%), biotite (3%), myrmekite (2%), chlorite (1.4%), muscovite (1%), opaques (0.9%), hornblende (0.9%), epidote (0.2%), and sphene (0.2%) (provided by the NWMO). The properties of the Lac du Bonnet batholith granite including its mineralogical information by XRD analysis have been studied previously [22-27]. The granite sample was crushed using a tungsten carbide cylinder supplied by Nichika. Using a range of stainless-steel sieves, granite particles with sizes between 150 μm – 300 μm were collected and used in all the subsequent sorption experiments. Ticknor and McMurry reported that the specific surface area of Lac du Bonnet batholith granite was 0.18 $m^2 \cdot g^{-1}$ measured at the particle size fraction of 106–180 μm by the BET method using N_2 [22]. This specific surface area of granite was used in our study although the particle size fraction we used was slightly different.

Ca-Na-Cl solutions (Na/Ca molal ratio = 1.6) with I = 0.05, 0.1, 0.24, 0.5 and 1 m were prepared using pure NaCl and $CaCl_2 \cdot 2H_2O$ compounds. The CR-10 reference groundwater (Na/Ca molal ratio = 1.6; I = 0.24 m) was also prepared using the masses of reagents shown in Table 1. All reagents were dissolved into 1 kg of deionized water in total.

Technetium-99 used was derived from a stock solution (ammonium pertechnetate) supplied by the Health Physics Department at McMaster University. A small aliquot was added with 1% nitric acid into a glass flask to prepare an aqueous solution containing Tc(VII) (Tc concentration = 1 × 10^{-7} m). An electrochemical reduction with ECstat-302 (EC Frontier Co., Ltd.) was applied to reduce Tc(VII) to Tc(IV) [28, 29]. The complete reduction to Tc(IV) was confirmed by a solvent extraction technique using tetraphenylphosphonium chloride in chloroform [30]. The Tc concentration of 1 × 10^{-7} m was considered smaller than the solubility of $TcO_2 \cdot 0.6H_2O$ at pH around 1 [31]. Furthermore, it was also confirmed that re-oxidation of Tc(IV) to Tc(VII) was negligible in the presence of 0.2 m hydrazine monohydrate for one month after the reduction. The Tc(IV) solution was prepared just before the sorption experiments.

A N_2 gas (> 99.999 %) filled Glove Box (GB) was used 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.

The pH values measured by the pH meter ($pH_{measure}$) are operational values [32, 33]. Altmaier et al. described how to convert the $pH_{measure}$ to the molar H^+ concentrations ($pH_c = -\log c_{H+}$) or the molal H^+ concentration ($pH_m = -\log m_{H+}$) [32, 33]. In this study, the pH_m in solutions was determined by acid-base titration (Metrohm Ti-Touch 916) according to the procedure described in the previous studies [32, 33]. We measured the redox potentials in the solutions and converted them into Eh versus SHE (standard hydrogen electrode). The Eh measurement and calibration were also described in our previous study [34]. The values of Eh versus SHE were from −250 to −200 mV.

Table 1. Masses of chemical compounds added to 1 kg deionized water for preparation of CR-10 reference groundwater

Reagents	Mass (mg)
KCl	28.6
NaCl	4,760
$CaCl_2 \cdot 2H_2O$	6,280
$Mg(OH)_2$	144
$SrCl_2 \cdot 6H_2O$	76.5
$NaHCO_3$	96.4
$(CaSO_4)_2 \cdot H_2O$	1,510

2.2 Sorption Experiment

2.2.1 Sorption Kinetics

All sorption experiments were conducted at 25°C in the GB. The experimental procedures were the same as those for our experiments on Np(IV) sorption in Na-Ca-Cl solutions [34]. In the present work, the sorption distribution coefficient, R_d [$cm^3 \cdot g^{-1}$], 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, 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] is the mass of MX-80 or granite.

The solid/liquid ratio for all sorption experiments was 0.01 g/10 mL. All sorption experiments were preceded by pre-equilibration, where 10 mL of Ca-Na-Cl solution with respective I (0.05, 0.1, 0.24, 0.5 or 1 m) were mixed with 0.01 g MX-80 or granite. The suspension was kept in the GB for a week, before the solution was separated by centrifugation (6 min at 3,000 rpm), and then removed with a pipette. Then, 10 mL of the same Ca-Na-Cl solution (with the same I) was added to the tube and spiked with Tc(IV) solution to reach an initial concentration of 1×10^{-9} m. The solubility of $TcO_2 \cdot 1.6H_2O$ in the 0.24 m Ca-Na-Cl solution at pH = 7 was estimated as 4×10^{-9} m by PHREEQC [35]. In this PHREEQC calculation, the JAEA (Japan Atomic Energy Agency) thermodynamic database was used [36]. This solubility was consistent with the calculated solubility of $TcO_2 \cdot 1.6H_2O$ in the reference groundwater CR-10 [37]. The solubility of $TcO_2 \cdot 0.6H_2O$ was also reported to be larger than 1×10^{-9} m [31].

The sorption kinetics of Tc(IV) on MX-80 and granite in Ca-Na-Cl solutions were conducted for I = 0.05 and 1 m. After the Tc(IV) solution was spiked, the value of pH_m was adjusted to 7.0–7.5. During the experiment, the sample tubes containing Tc(IV), solid and solution were gently shaken and kept at 25°C. The value of pH_m was measured daily in the GB and when the value shifted more than ± 0.3 from the initial value, the pH_m was adjusted by adding small amounts of HCl or NaOH solution. After the pre-fixed period of time, the solution was separated from the solid by ultracentrifugation using an Optima™ Max-XP Biosafe Ultracentrifuge System at 100,000 rpm for 15 min at 25°C. The pH_m of the solution was measured in the GB, and an aliquot was taken and transferred to a test tub. The Tc concentration in the test tube was measured by ICP-MS (Agilent ICP-MS 8800). The detection limit of Tc was smaller than 1×10^{-12} m.

2.2.2 pH_m and Ionic Strength Dependence of R_d

The pH_m and I dependences of the R_d of Tc(IV) sorption on MX-80 and granite in Ca-Na-Cl solutions were measured at pH_m = 4–9, and I = 0.05, 0.1, 0.24, 0.5 and 1 m in triplicate. The pH_m of the solution was measured once a day in the GB. When the value of pH_m changed by more than ± 0.3 from the initial one, the pH_m was re-adjusted by the addition of a small amount of HCl or NaOH solution. Due to the small volume of the added HCl or NaOH, the effect of HCl or NaOH addition on the final concentration of Tc(IV) and R_d calculation was considered to be negligible. 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 Tc(IV) sorption experiments. Furthermore, the R_d values of Tc(IV) sorption onto MX-80 and granite in the CR-10 reference groundwater were also measured and calculated. The pH_m was adjusted to 7 ± 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. All experimental procedures were the same as those for the sorption kinetics measurements.

3. Results and Discussion

3.1 Sorption Kinetics

The sorption kinetics of Tc(IV) on MX-80 and granite in Ca-Na-Cl solutions with I = 0.05 m and 1 m are shown in Fig. 1. It was found that the sorption of Tc(IV) reached the equilibrium in 7 days on both solids at both I = 0.05 m and 1 m. Based on these results, the sorption reaction period was set for 14 days for experiments on the dependence of Tc(IV) sorption on pH_m and I for both MX-80 and granite.

3.2 Sorption on MX-80

The pH_m and I dependence of sorption of Tc(IV) onto MX-80 in Ca-Na-Cl solutions is shown in Fig. 2. It was

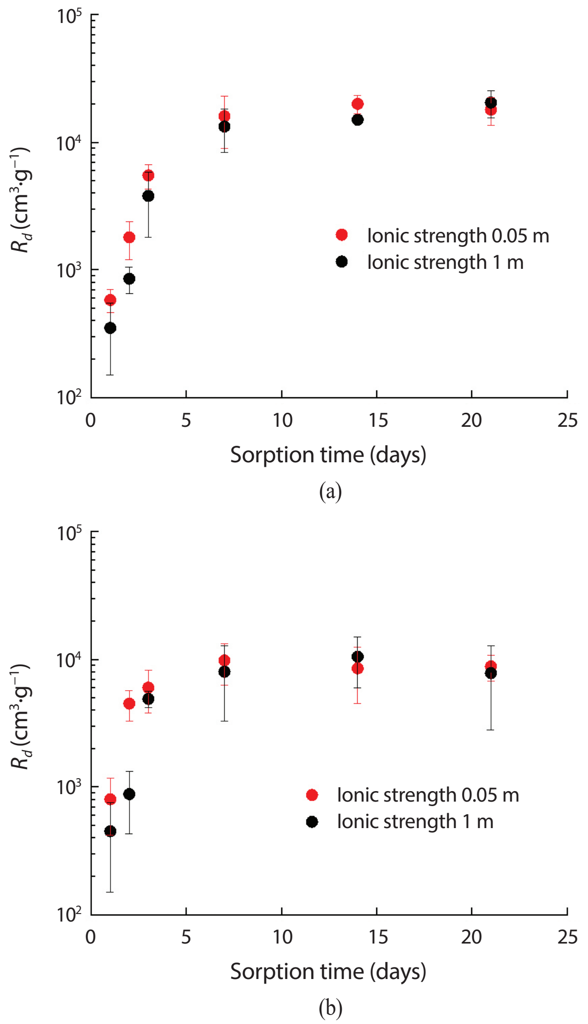

Fig. 1 Sorption kinetics of Tc(IV) on (a) MX-80 and (b) granite in Ca-Na-Cl solutions at ionic strength of 0.05 m and 1 m.

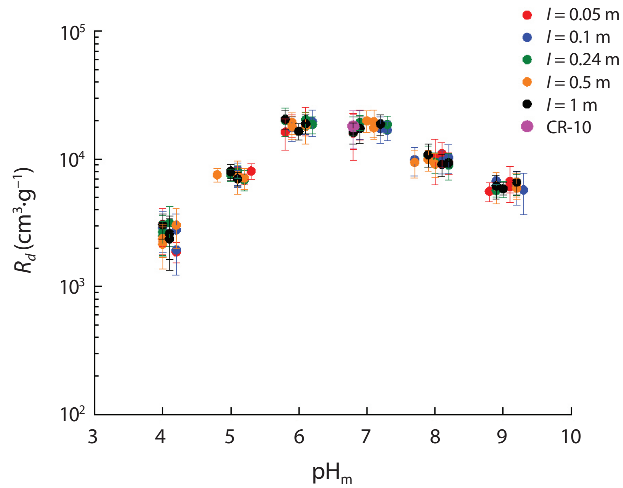

Fig. 2. pH_m and ionic strength dependence of R_d values of Tc(IV) on MX-80 in Ca-Na-Cl solutions.

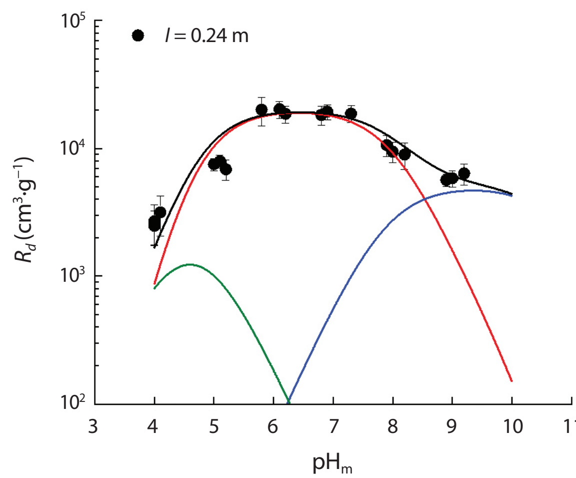

Fig. 3. Fitting results for Tc(IV) sorption on MX-80 in ionic strength 0.24 m Ca-Na-Cl solution with the 2SPNE SC/CE model. The red, blue, and green lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$, and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$, respectively. The black line represents the total of the modelled sorption.

found that the R_d values of Tc(IV) sorption on MX-80 increased with pH_m from 4 to 7 and then decreased with pH_m from 7 to 9. Grambow et al. also reported the pH_m dependence of Tc(IV) sorption on MX-80, while sorption increased with pH_m up to 8 and then decreased with pH_m sharply [14]. The reason for this difference of R_d with pH_m is not clear, but a possible explanation could be the difference of ions, especially anions in the solutions. The solutions used by Grambow et al. contained Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4^{2-}$and HCO_3^- [14]. Tc(IV) might form weakly adsorbed complexes with these coexisting ions. The values of R_d obtained in this work were consistent with those by Baston et al. and Berry et al. [8, 10].

It was also found that the R_d values of Tc(IV) sorption on MX-80 did not depend on I (0.05 m $\leq I \leq$ 1 m) in the range of pH_m = 4–9 studied in this work. Berry et al. measured R_d values of Tc(IV) on bentonite in artificial seawater (pH = 8) and de-ionized water (pH = 10.1) at water/bentonite

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

Surface complexation reaction	log K^0 (this work)	log K^0 [14]
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	3.4	2.38
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOTcO(OH)_2^- + 3H^+$	7.4	-
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOH_2TcO(OH)_2^+ + H^+$	−5.1	-
$2(\equiv SOH) + TcO^{2+} + H_2O \rightleftharpoons (\equiv SO)_2TcO(OH)^- + 3H^+$	-	−4.27

ratios = 20 and 100 $cm^3 \cdot g^{-1}$ [10]. Berry et al. found that at water/bentonite ratio = 100 $cm^3 \cdot g^{-1}$, the R_d values in the artificial seawater were about four times larger than those in the de-ionized water [10]. However, because of the different pH values in the two solutions, the I dependence of Tc(IV) sorption could not be concluded.

The R_d value of Tc(IV) on MX-80 in the CR-10 solution was measured as $1.8 \times 10^4 \pm 5.9 \times 10^3$ $cm^3 \cdot g^{-1}$ (at $pH_m = 6.8$, Eh = −200 mV). This is within the range of the R_d values measured in the Ca-Na-Cl solutions around $pH_m = 7$ (see Fig. 2), suggesting that the impact of coexisting ions such as Mg^{2+}, Sr^{2+}, HCO_3^-, and SO_4^{2-} on the sorption of Tc(IV) on MX-80 bentonite would be small.

Sorption models could help to understand the sorption mechanisms. In this study, the 2SPNE SC/CE model incorporated in PHREEQC was applied to simulate the dependences of R_d values of Tc(IV) sorption on MX-80 in Ca-Na-Cl solutions on pH_m and I [35]. The SIT (specific ion interaction theory) model in the thermodynamic database of the JAEA was used for the calculation [36, 38]. To initiate the fitting of the model, the constants of surface complexation reactions for Tc(IV) on MX-80 reported by Grambow et al. and those calculated by the linear free energy relationship equation for montmorillonite were used for the initial values of constants [14, 39]. Values of other parameters such as protolysis constants for MX-80 were the same as those used by Walker et al. [40]. Considering that the concentration of Tc(IV) is small in the Ca-Na-Cl solution, only strong sites were used for modelling surface complexation reactions at trace metal ion concentrations.

The fitting results of Tc(IV) sorption on MX-80 in the Ca-Na-Cl solution at I = 0.24 m are shown in Fig. 3. Other fitting results at I = 0.05, 0.1, 0.5 and 1 m are shown in Supplementary Materials (Figs. S2–S5). The optimized values of surface complexation constant log K^0 for MX-80 obtained in this study and those by Grambow et al. are summarized in Table 2 [14].

The dependence of Tc(IV) sorption onto MX-80 on pH_m and I simulated by the 2SPNE SC/CE model was found to be consistent with the experimental data measured in this work. Our model results showed that an inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$) dominated the Tc(IV) sorption on MX-80 at pH_m = 4–8.5, another inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$) was the dominant sorption of Tc(IV) at $pH_m > 8.5$, and one outer-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$) contributed to the sorption of Tc(IV) only around $pH_m = 4$ for the ionic strength range from 0.05 to 1 m. The contribution of ion exchange was found to be negligible at $4 \leq pH_m \leq 9$. In other words, under our experimental conditions, it was considered that the sorption of Tc(IV) on MX-80 at I = 0.05–1 m in Ca-Na-Cl solutions was simulated by two monodentate inner-sphere surface complexation reactions and one monodentate outer-sphere surface complexation reaction. On the other hand, Grambow et al. reported that the monodentate inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$) dominated the Tc(IV) sorption on MX-80 at pH = 4–7 and the bidentate inner-sphere surface complexation reaction ($2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcO(OH)^- + 3H^+$) dominated the sorption at pH ≥ 7 in the solutions containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^- (Na-Ca-Cl-SO_4 type water with ionic strength of 0.05 m) [14]. We tried to include this bidentate inner-sphere surface complexation reaction in our model calculation but could not fit the model to the experimental data well. At present, we have not elucidated the reason for this difference in the possible surface complexation reactions for Tc(IV) sorption on MX-80. One possible explanation is the difference in the coexisting ions in the solutions, leading to the formation of different complexes in the solutions. However, this still remains for future study.

It would be desirable to apply spectroscopy such as XRF, FT-IR and XPS to validate the sorption modelling results. However, we could not apply spectroscopy due to the low concentration of Tc. Therefore, the density functional theory simulations may help us justify the sorption modelling results. This also remains for future research.

3.3 Sorption on Granite

The dependence of sorption of Tc(IV) onto granite on pH_m and I in Ca-Na-Cl solutions is shown in Fig. 4. Fig. 4 illustrates that the R_d values of Tc(IV) sorption on granite gradually increased with pH_m from 4 to 8, and then became almost constant or slightly decreased with pH_m from 8 to 9 at all I values. The values of R_d measured in this work agreed with those measured by Baston et al. and Berry et al. [8, 10] but were larger than those reported by Huber et al. [11]. Huber et al. used Tc(VII) as an initial Tc species in the sorption measurements (in I = 0.2 M synthetic Äspö groundwater) and measured the R_d values of Tc which was reduced to Tc(IV) on the surface of the Fe(II)-containing minerals in granite [11]. Hence, some Tc(VII) might coexist in the sorption systems, leading to the smaller R_d values. It was also found that the R_d values of Tc(IV) sorption on granite were independent of I (0.05 m $\le I \le$ 1 m) in the range of pH_m (4–9) studied in this work.

The R_d value of Tc(IV) sorption on granite in the CR-10 solution was measured as $9.7 \times 10^3 \pm 1.0 \times 10^3$ $cm^3 \cdot g^{-1}$ (at

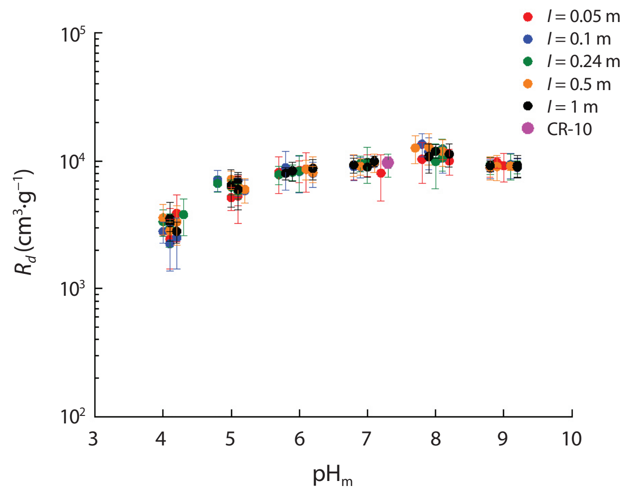

Fig. 4. pH_m and ionic strength dependence of R_d values of Tc(IV) sorption on granite in Ca-Na-Cl solutions.

pH_m = 7.3, Eh = –200 mV). This is within the range of the R_d values measured in the Ca-Na-Cl solutions around pH_m = 7, which suggests that the impact of coexisting ions such as Mg^{2+}, Sr^{2+}, HCO_3^-, and SO_4^{2-} on the sorption of Tc(IV) on granite would also be small.

The 2SPNE SC/CE model was also applied to simulate the dependences of R_d values of Tc(IV) sorption on granite on pH_m and I (Fig. 4). As mentioned before, the granite we used is composed of feldspar (plagioclase feldspar (37%) and K-feldspar (19%)), quartz (34%), biotite (3%), myrmekite (2%), chlorite (1.4%), muscovite (1%), opaques (0.9%), hornblende (0.9%), epidote (0.2%) and sphene (0.2%). In the modelling of Tc(IV) sorption on granite, we assumed that biotite contributed to the sorption of Tc(IV). The protolysis reaction constants of biotite in granite from the Lac du Bonnet batholith in Manitoba, Canada have not been studied yet. Hence, in this study, we assumed that the protolysis reaction constants and the site densities of biotite were the same as those of Inada granite used by Iida et al. for the simulation purpose [41]. Considering that the concentration of Tc(IV) in the studied Ca-Na-Cl solution is small, only strong sites of biotite were used for modelling surface complexation reactions at trace metal ion concentrations. In this study, we used the values of the surface

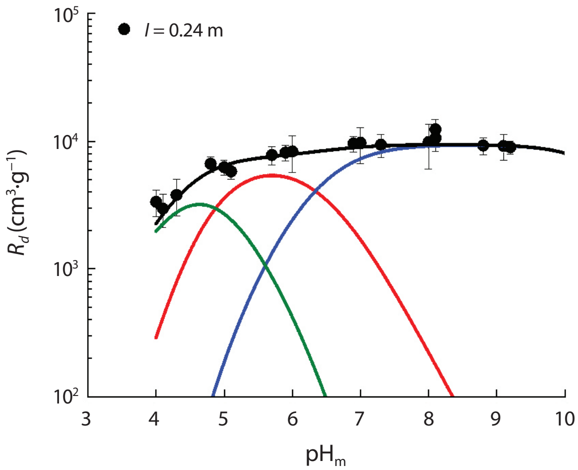

Fig. 5. Fitting results for Tc(IV) sorption on granite/biotite in ionic strength 0.24 m Ca-Na-Cl solution by the 2SPNE SC/CE model. The red, blue, and green lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$, and $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$, respectively. The black line represents the total of the modelled sorption.

complexation constant log K^0 reported by Grambow et al. as the initial values of constants to initiate the fitting of the model, although these values were for the sorption of Tc(IV) on MX-80 [14]. The main consideration was that there is no previous study that reported the log K^0 values for Tc(IV) sorption on granite/biotite and the surface complexation constants of Tc(IV) sorption on clay mineral (namely, MX-80) reported by Grambow et al. were the only available values [14].

The fitting results in I = 0.24 m Ca-Na-Cl solution are shown in Fig. 5. Other fitting results for I = 0.05, 0.1, 0.5 and 1 m are shown in Supplementary Materials (Figs. S6–S9). The 2SPNE SC/CE model was found to well reproduce the dependences of Tc(IV) sorption on granite on pH_m and I by considering the sorption on biotite in granite. The optimized values of log K^0 for granite/biotite obtained in this study are summarized in Table 3. We also performed the fitting using different initial values and confirmed that the same results as Table 5 were obtained. It was found that an inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$) was dominant at

Table 3. Surface complexation constants log K^0 of Tc(IV) sorption on granite/biotite obtained in this work

Surface complexation reaction	log K^0 (this work)
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	2.8
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOTcO(OH)_2^- + 3H^+$	7.7
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOH_2TcO(OH)_2^+ + H^+$	−3.4

Table 4. Protolysis reaction constants of chlorite used in this study

Protolysis reaction	Chlorite log K [42]
$\equiv SOH + H^+ \rightleftharpoons \equiv SOH_2^+$	5.6
$\equiv SOH \rightleftharpoons \equiv SO^- + H^+$	− 8.2

pH_m = around 5–6.5, an inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$) was dominant at pH_m > 6.5, and an outer-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$) was dominant at pH_m < around 5. It was found that the contribution of ion exchange was negligible at $4 \leq pH_m \leq 9$. When the biotite dominated the sorption of Tc(IV) on granite, the R_d values at pH_m = 8–9.5 were predicted to be constant.

It is known that chlorite is generated by hydrothermal alteration of biotite. Not only the mineral structure but also the sorption characteristics of chlorite might be similar to those of biotite. Therefore, although the composition of chlorite (1.4%) is about half of that of biotite (3%), chlorite might also dominate the sorption of Tc(IV) on granite. The 2SPNE SC/CE model was also applied to Tc(IV) sorption on chlorite. Surface characteristics of chlorite in the Lac du Bonnet batholith granite have not been studied, so the data of chlorite from other granites described elsewhere were used in this study [42, 43]. The protolysis reaction constants of chlorite being used in this study are summarized in Table 4 [42]. The site density of 2.3 sites·nm^{-2} was used [43]. It was assumed that the sorption of Tc(IV) on chlorite was dominated by the strong sites of chlorite.

The fitting results at I = 0.24 m in Ca-Na-Cl solution are shown in Fig. 6. The fitting results for I = 0.05, 0.1, 1 and 3

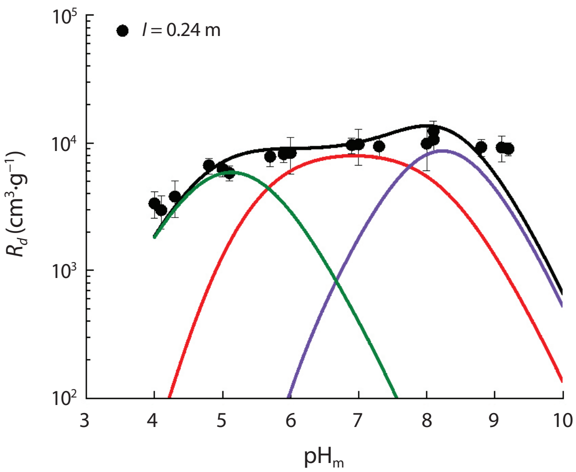

Fig. 6. Fitting results for Tc(IV) sorption on granite/chlorite in ionic strength 0.24 m Ca-Na-Cl solution with the 2SPNE SC/CE model. The red, green, and purple lines represent $\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$, $\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$, and $2(\equiv SOH) + TcO^{2+} + H_2O \rightleftarrows (\equiv SO)_2TcOOH^- + 3H^+$, respectively. The black line represents the total of the modelled sorption.

m are shown in Supplementary Materials (Figs. S10–S13). The optimized values of log K^0 for granite/chlorite obtained in this study are summarized in Table 5. Assuming chlorite being the sorbent (instead of biotite), the simulated results by 2SPNE SC/CE were found to also fit well with the pH$_m$ and I dependences of Tc(IV) sorption on granite observed in this study. From the model fitting results, it was found that an outer-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$), a monodentate inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$), and a bidentate inner-sphere surface complexation reaction ($2\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv (SO)_2TcO(OH)^- + 3H^+$) were the dominant reactions for the sorption of Tc(IV) on chlorite at pH$_m$ < around 5.5, around 5.5 < pH$_m$ < around 8, and pH$_m$ > around 8, respectively. The contribution of ion exchange was found to be negligible at 4 ≤ pH$_m$ ≤ 9. For Tc(IV) sorption on chlorite, the outer-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOH_2TcO(OH)_2^+ + H^+$) and the monodentate inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv SOTcOOH + 2H^+$) were found to be dominant in a wider pH range than those for biotite. Furthermore,

Table 5. Surface complexation constants log K^0 of Tc(IV) sorption on granite/chlorite obtained in this work

Surface complexation reaction	log K^0 (this work)
$\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv SOTcOOH + 2H^+$	2.9
$\equiv SOH + TcO^{2+} + 2H_2O \rightleftharpoons \equiv SOH_2TcO(OH)_2^+ + H^+$	8.7
$2\equiv SOH + TcO^{2+} + H_2O \rightleftharpoons \equiv (SO)_2TcO(OH)^- + 3H^+$	−4.3

the bidentate inner-sphere surface complexation reaction ($2\equiv SOH + TcO^{2+} + H_2O \rightleftarrows \equiv (SO)_2TcO(OH)^- + 3H^+$) predicted the small peak R_d values observed at pH$_m$ = 8. The model of Tc(IV) sorption on biotite predicted the constant R_d values at pH$_m$ = 8–9.5 by a monodentate inner-sphere surface complexation reaction ($\equiv SOH + TcO^{2+} + 2H_2O \rightleftarrows \equiv SOTcO(OH)_2^- + 3H^+$). The sorption of Tc(IV) on biotite and chlorite in granite would be possible. In this study, we did not investigate whether the sorption of Tc(IV) would be more preferential on biotite or chlorite in granite. If the measurements using the EPMA and SEM-EDX are applicable, a more detailed discussion will be possible. However, due to the low solubility of Tc(IV) in the Ca-Na-Cl solutions used in this study, such equipment is not capable. By studying the protolysis reactions of biotite and chlorite, measuring the R_d values on biotite and chlorite, and applying the quantum chemistry simulations such as density functional theory, we will further investigate the sorption mechanisms of Tc(IV) on granite in the future. In addition, although the outer-sphere complexation reaction was found to be dominant at pH$_m$ < around 5 (for biotite) and at pH$_m$ < around 5.5 (for chlorite), the I dependence of Tc(IV) sorption on granite was not observed. This will be also investigated in the future.

4. Conclusions

The sorption behavior of Tc(IV) onto MX-80 and granite in Ca-Na-Cl solutions with an ionic strength of 0.05 m–1 m was systematically studied. It was found that 7 days were sufficient for the sorption of Tc(IV) on both MX-80 and granite to reach sorption equilibrium. Tc(IV) sorption on both MX-80 and granite was independent of I in the range of 0.05 to 1 m. Sorption of Tc(IV) on MX-80 increased with pH_m from 4 to 7 and then decreased with pH_m from 7 to 9. Sorption of Tc(IV) on granite gradually increased with pH_m from 4 to 8 and then became almost constant or slightly decreased with pH_m from 8 to 9. The R_d values of Tc(IV) sorption onto MX-80 and granite in CR-10 reference groundwater were found to be within the range of the R_d values measured in the Ca-Na-Cl solutions at around $pH_m = 7$. The 2SPNE SC/CE model was able to successfully predict the sorption of Tc(IV) onto MX-80 and granite. Sorption of Tc(IV) on MX-80 at $I = 0.05–1$ m in Ca-Na-Cl solutions was simulated with two monodentate inner-sphere surface complexation reactions and one monodentate outer-sphere surface complexation reaction. For sorption of Tc(IV) on granite, assuming Tc(IV) preferentially sorbed on biotite in granite, sorption was simulated by two monodentate inner-sphere surface complexation reactions and one monodentate outer-sphere surface complexation reaction. On the other hand, assuming Tc(IV) dominantly sorbed on chlorite in granite, one bidentate inner-sphere complexation reaction, one monodentate inner-sphere surface complexation reaction and one monodentate outer-sphere surface complexation reaction simulated the sorption of Tc(IV). The optimized value of log K^0 of each surface complexation reaction was evaluated.

Conflict of Interest

No potential conflict of interest was reported by the authors.

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