

Sorption behavior of thorium onto montmorillonite and illite

Yoshihisa IIDA*¹ Logan BARR*¹ Tetsuji YAMAGUCHI*¹ Ko HEMMI*¹

高レベル放射性廃棄物処分の安全評価において、Th-229は重要核種の一つである。モンモリロナイトおよびイライトを対象としたThのバッチ吸着試験を、pHおよび炭酸濃度をパラメータとして実施した。モンモリロナイトに対する分配係数はイライトに比べ高い値を示した。分配係数は炭酸濃度の上昇に伴い減少し、pH 10付近で極小値を示した。

Thの吸着挙動を、静電項を考慮しない表面錯体モデル(NEM)により解析した。モデル計算は実験結果をよく説明し、分配係数の減少は、Thの水酸化炭酸錯体形成による溶存種の安定化によるものであることが示唆された。

Keywords: トリウム, 炭酸, 分配係数, 表面錯体, モンモリロナイト, イライト

Thorium (Th) -229 is one of the important radionuclides for the performance assessment calculations for high-level radioactive waste repositories. The sorption behavior of Th onto montmorillonite and illite were investigated by batch sorption experiments. Experiments were carried out under variable pH and carbonate concentrations. The sorbability of montmorillonite was higher than that of illite. Distribution coefficients, K_d ($\text{m}^3 \text{kg}^{-1}$), decreased with increased carbonate concentrations and showed the minimal value at around pH 10.

The sorption behaviors of Th were analyzed by the non-electrostatic surface complex model with PHREEQC computer program. The model calculations were able to explain the experimental results reasonably well. The decreases of K_d was likely due to the stabilization of aqueous species by hydroxo-carbonate complexations in the solutions.

Keywords: thorium, carbonate, distribution coefficient, surface complex, montmorillonite, illite

1 Introduction

Retardation of radionuclide migration by sorption in natural barrier systems is one of the important factors that influence the performance of a radioactive waste disposal system. Performance assessment calculations for hypothetical high-level radioactive waste (HLW) repositories [1] show that ^{229}Th which is a member of the neptunium series ($4n+1$) is one of the radionuclides dominating the long-term radiological hazard. Thorium exists only in the tetravalent oxidation state independent of the redox conditions of the groundwater [2,3]. The carbonate concentrations in reference groundwaters for the performance assessment of HLW repositories are $3.4 \times 10^{-3} \text{ mol dm}^{-3}$ (fresh type) and $1.2 \times 10^{-2} \text{ mol dm}^{-3}$ (saline type) [4], and that in the reference groundwater at Horonobe area are $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ [5]. The dominant aqueous species of Th in the reference groundwaters were estimated to be hydroxide-carbonate complexes from thermodynamic calculations [6]. In the long term, the sorption behavior of Th would change because the pH and carbonate concentration of groundwater is likely to be changed [4-7]. Hence, it is necessary to understand the sorption behavior of Th under variable groundwater conditions for a long-term safety assessment of geological disposal of HLW.

Clay minerals such as smectite and illite are important components in sedimentary rocks because of their strong radionuclide retention properties [5,8,9]. Several sorption data of Th onto clay minerals have been reported [9-11]. For montmorillonite which is a member of the smectite group, sorption data of Th in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ solutions were reported by Bradbury and Baeyens [11] and the pH dependence

of the sorption has been modeled [12]. Bradbury and Baeyens [9] also reported the sorption data of Th onto illite in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ solutions and modeled the pH dependence of the sorption. However, the influence of carbonate on the sorption has not been clarified.

In the present study, sorption data of Th onto montmorillonite and illite were obtained by batch sorption experiments. Experiments were carried out under variable pH and carbonate concentrations. The sorption behaviors of Th were analyzed by surface complexation model (SCM) with a widely-used and verified geochemical code, PHREEQC ver. 3.3.0 [13].

2 Experimental

2.1 Experimental solutions

A Th stock solution was prepared by the following procedure. Thorium nitrate hydrate ($\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$, $4 \leq n \leq 5$) was purchased from Fluka Chemika Co. One gram of $\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$ was dissolved in 10 cm^3 volume of 0.1 mol dm^{-3} hydrochloric acid (HCl). Diluting 0.1 cm^3 volume of the solution to 10 cm^3 with 0.1 mol dm^{-3} HCl, Th stock solution was prepared (the concentration of Th is approximately $2 \times 10^{-3} \text{ mol dm}^{-3}$). Experimental solutions were prepared in a controlled-atmosphere glove box under Ar to avoid dissolution of carbon dioxide gas from the atmosphere. Three types of solutions, 0.01, 0.05, and 0.1 mol dm^{-3} sodium hydrogen carbonate (NaHCO_3), were prepared. Considering the solubility of Th [2,3], experimental solutions were prepared by adding the Th stock solution into the above-mentioned NaHCO_3 solutions. The initial concentrations of Th in the experimental solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC, PerkinElmer Inc.) to be 2.1×10^{-9} , 4.2×10^{-9} and $2.2 \times 10^{-8} \text{ mol dm}^{-3}$ for the 0.01, 0.05 and $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ solutions, respectively.

2.2 Solid samples

The employed montmorillonite material was Kunipia F

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(Received 5 November 2015; accepted 21 January 2016)

montmorillonite (Kunimine Industries Co. Ltd.). Illite sample in granulated form ($< 100 \mu\text{m}$) was purchased from Nichika Inc. These samples were used without pretreatment. The specific surface area of illite sample was measured as $9.1 \text{ m}^2 \text{ g}^{-1}$ by the Brunauer-Emmett-Teller (BET) N_2 gas adsorption method [14] (NOVA 1200e, Quantachrome Instruments). The specific surface area of Kunipia F has been measured by the BET method and ethylene glycol monoethyl ether (EGME) adsorption method by Ohashi et al. [15]. The measured specific surface areas by the BET method were $45 \text{ m}^2 \text{ g}^{-1}$ for coarse-grained samples and $62 \text{ m}^2 \text{ g}^{-1}$ for fine-grained samples, and those by EGME method for both samples were $700 \text{ m}^2 \text{ g}^{-1}$.

2.3 Sorption experiments

Sorption experiments were performed in a controlled-atmosphere glove box under Ar. The experimental runs were made following the procedure of the ‘‘Measurement Method of the Distribution Coefficient on the Sorption Process’’ compiled by the Atomic Energy Society of Japan [16]. Liquid-to-solid ratio of $10 \text{ cm}^3 \text{ g}^{-1}$ is recommended in this literature, but $1000 \text{ cm}^3 \text{ g}^{-1}$ was selected because of the water-absorbing property of montmorillonite and high sorbability of Th [16]. The solid samples (0.01 g) were immersed in 10 cm^3 volume of the Th experimental solutions in polypropylene test tubes. The pH of the sample suspension was adjusted to 8.5-11 with NaOH solution. Dissolution of montmorillonite and illite can be negligible at pH 4-11 [8,17]. The sample suspensions were agitated once a day. After two weeks, the pH and the concentration of Th were measured. The pH was measured with a Sure-Flow combination glass electrode (ROSS 8172BNWP, Thermo Fisher Scientific Inc.) calibrated with standard pH buffer solutions of 7.00, 10.01, and 12.46. A 1 cm^3 aliquot was sampled and filtered through a 10,000 NMWL ultrafilter (USY-1, Toyo Roshi Kaisha, Ltd.). The filtrate was sampled (0.5 cm^3 for 0.01 and $0.05 \text{ mol dm}^{-3} \text{ NaHCO}_3$, or 0.2 cm^3 for $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$) and diluted to 3 cm^3 with 5% HNO_3 . The concentrations of Th were determined by ICP-MS.

3 Results and discussion

3.1 Experimental results

The distribution coefficient, K_d ($\text{m}^3 \text{ kg}^{-1}$), was calculated from the following equation

$$K_d = \frac{c_{\text{ini}} - c_{\text{eq}}}{c_{\text{eq}}} \frac{V_{\text{ini}}}{M} \quad (1)$$

c_{ini} : initial concentration of Th [mol dm^{-3}]

c_{eq} : equilibrated concentration of Th [mol dm^{-3}]

V_{ini} : initial volume of the solution [m^3]

M : weight of the solid phase [kg]

The K_d values for montmorillonite are plotted versus pH in Figure 1(a). For the K_d data obtained from the lower

concentrations of Th than the detection limit of ICP-MS ($2 \times 10^{-11} \text{ mol dm}^{-3}$ for 0.01 and 0.05 mol dm^{-3}), the lowest K_d values were plotted in the figure. All the K_d values for $0.01 \text{ mol dm}^{-3} \text{ NaHCO}_3$ were higher than $100 \text{ m}^3 \text{ kg}^{-1}$ at pH 9.35-10.53. The K_d values for $0.05 \text{ mol dm}^{-3} \text{ NaHCO}_3$ were from 42 to $81 \text{ m}^3 \text{ kg}^{-1}$ at pH 9.31-10.52. The K_d values for $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ were from 2.2 to $13 \text{ m}^3 \text{ kg}^{-1}$ at pH 8.74-10.66. The K_d values decreased with increasing NaHCO_3 concentration and the minimal value was seen at around pH 10 under $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$. The values were lower than the literature K_d values for Wyoming Na-montmorillonite (SWy-1) under the conditions of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ reported by Bradbury and Baeyens [11] those are the only existing dataset of Th for montmorillonite reported with pH values of the experimental solutions.

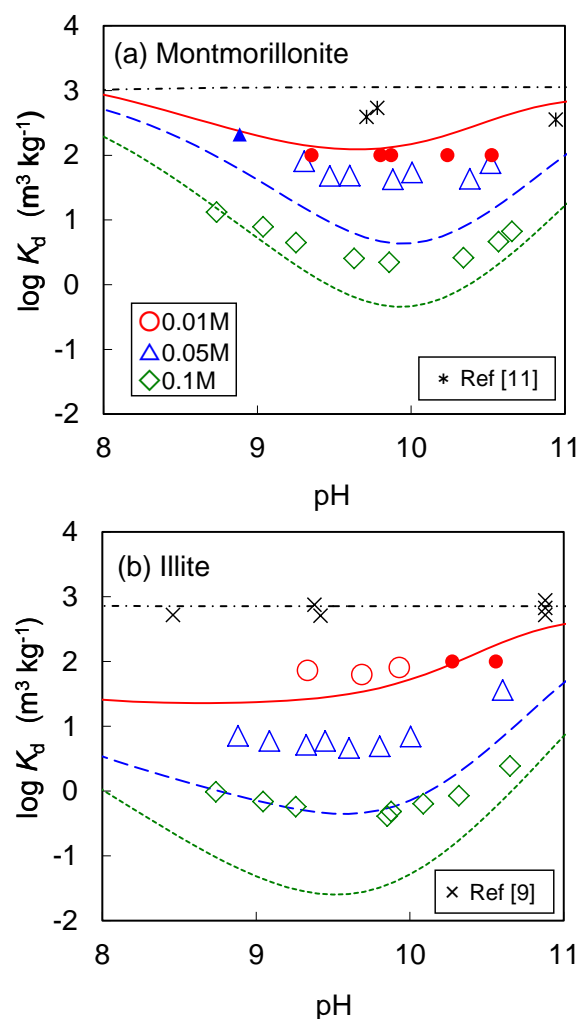


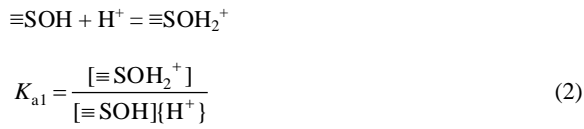
Fig. 1 Comparison of K_d values obtained in this study and literature values ($0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ conditions): (a) montmorillonite [11] and (b) illite [9]. Closed marks show the lowest values. ‘‘0.01 M’’ represents the $0.01 \text{ mol dm}^{-3} \text{ NaHCO}_3$ concentration. Lines show the predicted values by the NEM (NaClO_4 and NaHCO_3 conditions)

The K_d values for illite are plotted versus pH in Figure 1(b). The K_d values for $0.01 \text{ mol dm}^{-3} \text{ NaHCO}_3$ were from 63 to 80

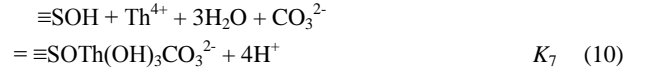
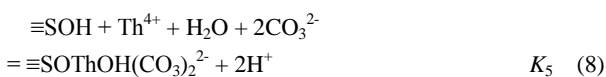
$\text{m}^3 \text{kg}^{-1}$ at pH 9.34–9.93 and higher than $100 \text{ m}^3 \text{kg}^{-1}$ at pH 10.28–10.56. The K_d values for $0.05 \text{ mol dm}^{-3} \text{ NaHCO}_3$ were from 4.6 to $36 \text{ m}^3 \text{kg}^{-1}$ at pH 8.88–10.60. The K_d values for $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ were from 0.41 to $2.4 \text{ m}^3 \text{kg}^{-1}$ at pH 8.74–10.65. The K_d values decreased with increasing NaHCO_3 concentration and increased at higher pH than 10. The K_d values for illite were lower than those for montmorillonite, the pH dependences of K_d for illite showed the same tendency as those for montmorillonite. The obtained K_d values for illite were lower than the literature values for Na-illite (illite du Puy) under the conditions of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ reported by Bradbury and Baeyens [9] those are the only existing dataset of Th for illite reported with pH values of the experimental solutions.

3.2 Analysis of the sorption behavior by the SCM

The mole fractions of aqueous species of Th under $0.01 \text{ mol dm}^{-3} \text{ NaHCO}_3$ conditions calculated using thermodynamic data (Table 1) [3] are shown in Figure 2. The dominant aqueous species are neutral or negatively charged; the cation-exchange sorption was ignored although montmorillonite and illite have large cation exchange capacities. Considering the surface complexation of Th with surface hydroxyl groups of the minerals, the sorption behaviors onto montmorillonite and illite were analyzed by the non-electrostatic surface complex model (NEM) [9,12]. The NEM was calculated by the PHREEQC computer program. The protonation and deprotonation reactions of surface hydroxyl groups ($\equiv\text{SOH}$) are expressed by



where the square brackets represent concentrations (mol dm^{-3}) and the curly brackets represent activities. Based on the aqueous Th species (Table 1), the surface species were assumed as follows.



The sorption of Th was estimated as inner-sphere surface complexation [18,19]. On the other hand, the sorption of the electrolyte ions was outer-sphere surface complexation [20,21]. The NEM assumes only one sorption plane, it cannot distinguish these sorption mechanisms. Therefore, the sorption of background electrolytes was ignored [22,23]. The K_d value was calculated as

$$K_d = \frac{\sum[\text{surface Th species}]}{\sum[\text{aqueous Th species}]} \frac{V_{\text{ini}}}{M} \quad (11)$$

Nuclear energy agency (NEA) [24] reported the indicative values for SCM parameters of important minerals. In the calculations for montmorillonite, the surface site density ($n_s = 2.41 \text{ sites nm}^{-2}$) reported by NEA [24] was adopted. The specific surface area of Kunipia F montmorillonite measured by N_2 -BET method (45 or $62 \text{ m}^2 \text{g}^{-1}$) was about 1 order of magnitude lower than that by EGME method ($700 \text{ m}^2 \text{g}^{-1}$) [15]. Nitrogen gas cannot access the interlayer planes of expandable clay minerals such as montmorillonite, therefore the external surface areas can be estimated by N_2 -BET method. In contrast, EGME can penetrate into interlayer planes and can estimate the total surface area. The surface complexation sites exist on the edges of clay mineral crystallites, the external surface area measured by N_2 -BET method is appropriate for the SCM. The montmorillonite sample used in this study was not preconditioned; the value of $45 \text{ m}^2 \text{g}^{-1}$ for

Table 1 Thermodynamic data for aqueous Th species

Reaction	log K
$\text{Th}^{4+} + \text{H}_2\text{O} = \text{Th(OH)}^{3+} + \text{H}^+$	-2.500 ± 0.500
$\text{Th}^{4+} + 2\text{H}_2\text{O} = \text{Th(OH)}_2^{2+} + 2\text{H}^+$	-6.200 ± 0.500
$\text{Th}^{4+} + 4\text{H}_2\text{O} = \text{Th(OH)}_4^0 + 4\text{H}^+$	-17.400 ± 0.700
$2\text{Th}^{4+} + 2\text{H}_2\text{O} = \text{Th}_2(\text{OH})_2^{6+} + 2\text{H}^+$	-5.900 ± 0.500
$2\text{Th}^{4+} + 3\text{H}_2\text{O} = \text{Th}_2(\text{OH})_3^{5+} + 3\text{H}^+$	-6.800 ± 0.200
$4\text{Th}^{4+} + 8\text{H}_2\text{O} = \text{Th}_4(\text{OH})_8^{8+} + 8\text{H}^+$	-20.400 ± 0.400
$4\text{Th}^{4+} + 12\text{H}_2\text{O} = \text{Th}_4(\text{OH})_{12}^{4+} + 12\text{H}^+$	-26.600 ± 0.200
$6\text{Th}^{4+} + 14\text{H}_2\text{O} = \text{Th}_6(\text{OH})_{14}^{10+} + 14\text{H}^+$	-36.800 ± 1.200
$6\text{Th}^{4+} + 15\text{H}_2\text{O} = \text{Th}_6(\text{OH})_{15}^{9+} + 15\text{H}^+$	-36.800 ± 1.500
$\text{Th}^{4+} + 5\text{CO}_3^{2-} = \text{Th(CO}_3)_5^{6-}$	31.000 ± 0.700
$\text{Th}^{4+} + 2\text{H}_2\text{O} + 2\text{CO}_3^{2-} = \text{Th(OH)}_2(\text{CO}_3)_2^{2-} + 2\text{H}^+$	8.798 ± 0.501
$\text{Th}^{4+} + \text{H}_2\text{O} + 4\text{CO}_3^{2-} = \text{ThOH(CO}_3)_4^{5-} + \text{H}^+$	21.599 ± 0.500
$\text{Th}^{4+} + 4\text{H}_2\text{O} + \text{CO}_3^{2-} = \text{Th(OH)}_4\text{CO}_3^{2-} + 4\text{H}^+$	-15.605 ± 0.603

coarse-grained samples was adopted. This value is almost the same as $41 \text{ m}^2 \text{ g}^{-1}$ reported by NEA for montmorillonite [24]. The surface acidity constants ($\log K_{a1} = 4.5$ and $\log K_{a2} = -7.9$) and the equilibrium constants of K_1 - K_4 reported by Bradbury and Baeyens [12] were adopted. Bradbury and Baeyens [12] assumed that the Th hydroxo-complex species sorbed on the strong site which account for about 2.4% of all sorption sites. In the same manner, 2.4% of the total site density was assigned to the strong site density ($0.06 \text{ sites nm}^{-2}$) in this calculation. The model parameters for the surface carbonato-complex species of Th are not available. Fernandes et al. [25] modeled the sorption of U onto montmorillonite in the presence of carbonate and reported that the ternary uranyl-carbonate complex ($\equiv\text{SOUO}_2\text{CO}_3$) on the weak site was necessary to reproduce the obtained sorption data in addition to that on the strong site. Therefore, the carbonate-complex species of Th were assumed to be sorbed on all sites. The formation constants of surface carbonato-complex species (K_5 - K_7) were estimated by linear free energy relationships (LFER). Bradbury and Baeyens [12] formulates the interrelation between the formation constants of aqueous hydroxo-complex species of metal ions (${}^{\text{OH}}K_x$) and those of surface species for montmorillonite (${}^{\text{S}}K_{x-1}$) as

$$\log {}^{\text{S}}K_{x-1} = 8.1 \pm 0.3 + (0.90 \pm 0.02) \log {}^{\text{OH}}K_x \quad (12)$$

The K_5 - K_7 values were estimated from the formation constants of aqueous carbonate complex species (${}^{\text{aq}}K_x$) listed in Table 1



and those of surface species for montmorillonite (${}^{\text{sur}}K_{x-1}$).

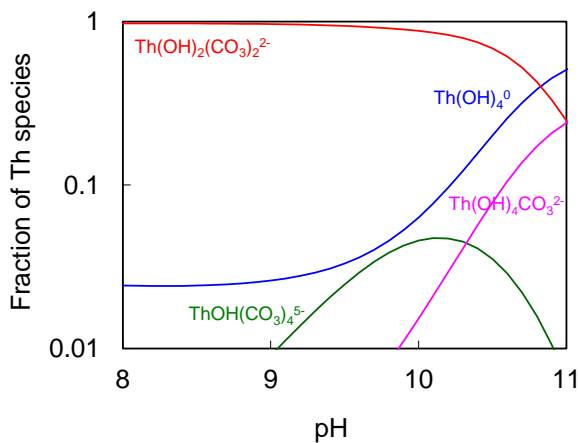
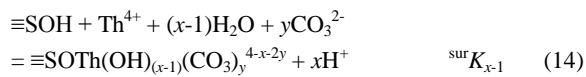


Fig. 2 Calculated mole fraction of aqueous Th species under $0.01 \text{ mol dm}^{-3} \text{ NaHCO}_3$ conditions

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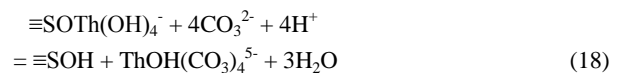
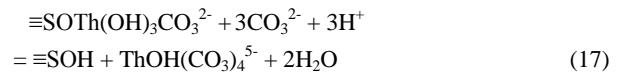
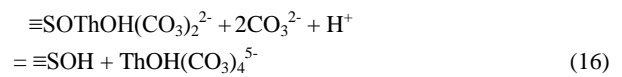
$$\log {}^{\text{sur}}K_{x-1} = 8.1 + 0.90 \log {}^{\text{aq}}K_x \quad (15)$$

The employed surface parameters and equilibrium constants are summarized in Table 2.

Table 2 Surface parameters and equilibrium constants for the NEM calculation

		Montmorillonite		Illite	
		Strong	Total	Strong	Total
Surface area ($\text{m}^2 \text{ g}^{-1}$)	S	45		36	
Site density (sites nm^{-2})	n_s	0.06	2.41	0.06	2.39
Equilibrium constant	$\log K_{a1}$	4.5	4.5	4.0	4.0
	$\log K_{a2}$	-7.9	-7.9	-6.2	-6.2
	$\log K_1$	7.2	—	7.4	—
	$\log K_2$	2.7	—	2.3	—
	$\log K_3$	-9.1	—	-8.8	—
	$\log K_4$	-16.9	—	-15.3	—
	$\log K_5$	—	16.0	—	15.2
	$\log K_6$	—	27.5	—	25.8
	$\log K_7$	—	-5.9	—	-5.1

Figure 1(a) shows the comparison of the predicted K_d values for montmorillonite with the experimentally measured ones and the literature values [11]. The calculation results explain the experimental results reasonably well, but slightly underestimated. The strong site density might be underestimated because of the difference between Kunipia F and SWy-1. Figure 3(a) shows the calculated mole fractions of Th species under $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ conditions. It is shown that the dominant sorption species are $\equiv\text{SOT}(\text{OH})(\text{CO}_3)_2^{2-}$, $\equiv\text{SOT}(\text{OH})_3\text{CO}_3^{2-}$ and $\equiv\text{SOT}(\text{OH})_4^-$, and the dominant aqueous species is $\text{ThOH}(\text{CO}_3)_4^{5-}$. The relation equation between these sorption species and $\text{ThOH}(\text{CO}_3)_4^{5-}$ are



involving CO_3^{2-} ions on the left-hand side. Therefore, the stability of aqueous $\text{ThOH}(\text{CO}_3)_4^{5-}$ species increased with increasing NaHCO_3 concentration more than those of sorption species, the K_d values decreased with increasing NaHCO_3 concentration. The minimal K_d value at around pH 10 was also

due to the stabilization of aqueous species by hydroxo-carbonate complexation.

In the calculations for illite, the surface site density (2.39 sites nm^{-2}) reported by NEA [24] was adopted. The specific surface area of illite measured by N_2 -BET method ($9.1 \text{ m}^2 \text{ g}^{-1}$) is about 1 order of magnitude lower than that reported by Bradbury and Baeyens [9] ($97 \text{ m}^2 \text{ g}^{-1}$), and that reported by NEA [24] ($36 \text{ m}^2 \text{ g}^{-1}$) is the intermediate value between the two. In this calculation, the value of $36 \text{ m}^2 \text{ g}^{-1}$ was adopted by considering the consistency with the site density. The surface acidity constants ($\log K_{a1} = 4.0$ and $\log K_{a2} = -6.2$) and the equilibrium constants of K_1 – K_4 reported by Bradbury and Baeyens [9] were adopted. For illite, Bradbury and Baeyens [9] assumed that the Th hydroxo-complex species sorbed on the strong site which account for about 2.4% of all sorption sites, as well as montmorillonite. The strong site density was estimated to be $0.06 \text{ sites nm}^{-2}$ in this calculation. The carbonate-complex species of Th were assumed to be sorbed on all sites. The formation constants of carbonato-surface complex (K_5 – K_7) were estimated by LFER. Bradbury and Baeyens [9] formulates the interrelation between $^{\text{OH}}K_x$ and $^{\text{s}}K_{x-1}$ for illite as

$$\log ^{\text{sur}}K_{x-1} = 7.9 \pm 0.4 + (0.83 \pm 0.02) \log ^{\text{aq}}K_x \quad (19)$$

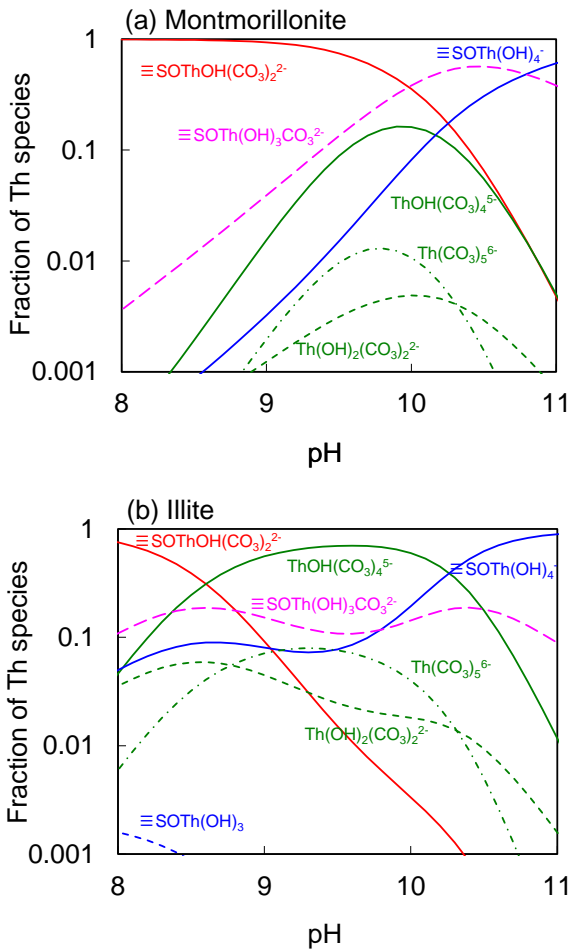


Fig. 3 Calculated mole fraction of Th species under $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ conditions

The values of K_5 – K_7 were calculated from the formation constants of aqueous carbonate complex species as

$$\log ^{\text{sur}}K_{x-1} = 7.9 + 0.83 \log ^{\text{aq}}K_x \quad (20)$$

Figure 1(b) shows the comparison of the predicted K_d values for illite with the experimentally measured ones and the literature values [9]. The calculation results explain the experimental results reasonably well, but underestimated especially at low pH and high carbonate concentration. Figure 3(b) shows the calculated mole fractions of Th species under $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ conditions. This underestimation might be due to the underestimation of the formation constant of $\equiv\text{SOTH}(\text{OH})(\text{CO}_3)_2^{2-}$ (K_5) estimated by the extrapolation of data for some metal species [9] using equation (20). The mole fractions of aqueous species, $\text{ThOH}(\text{CO}_3)_4^{5-}$, $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{ThOH}_2(\text{CO}_3)_2^{2-}$, are higher than the case for montmorillonite, which causes the lower K_d values than montmorillonite.

4 Conclusion

The K_d values of Th for montmorillonite and illite were obtained at pH 8.5–11 under 0.01 , 0.05 and $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ conditions. The sorbability of montmorillonite was higher than that of illite. The obtained K_d values were lower than the literature values obtained under $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ conditions. The K_d decreased with increased carbonate concentrations, and the minimal value was seen at around pH 10.

The NEM calculations using the existing model parameters and estimated formation constants of surface carbonato-complex species were able to explain the experimental results well. It was indicated that the decreases of K_d value under high concentration of carbonate and around pH 10 were due to the stabilization of aqueous species by hydroxo-carbonate complexations.

Acknowledgements

The authors acknowledge Mr. Y. Kawasaki for experimental measurements.

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