

# Sorption of Eu on MX-80 Bentonite in Na–Ca–Cl Brine Solutions

Jieci Yang<sup>1</sup>, Joshua Racette<sup>1</sup>, Fabiola Guido Garcia<sup>1</sup>, Shinya Nagasaki<sup>1,\*</sup>, and Tammy Yang<sup>2</sup>

<sup>1</sup>McMaster University, 1280 Main Street West, Hamilton, ON, L8S 4L7, Canada

<sup>2</sup>Nuclear Waste Management Organization, 22 St. Clair Ave. East, 4th Floor, Toronto, ON, M4T 2S3, Canada

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The sorption of Eu on MX-80 bentonite in Na–Ca–Cl solutions is investigated at a molal proton concentration ( $\text{pH}_m$ ) range of 3 to 10 and an ionic strength ( $I$ ) range of 0.1 to 6 m ( $\text{mol}\cdot\text{kgw}^{-1}$ ). The sorption equilibrium of Eu on MX-80 is achieved within 14 to 21 d at  $I = 0.1$  and 6 m. The sorption distribution coefficient ( $K_d$ ) values of Eu for MX-80 increase as  $\text{pH}_m$  increases from 3 to 6 for all  $I$  values, and they are independent of  $\text{pH}_m$  between 8 and 10 at  $I \geq 0.5$  m. Meanwhile, at  $I = 0.1$  m, the  $K_d$  value at  $\text{pH}_m = 10$  is slightly lower than those at  $\text{pH}_m = 8$  and 9. The  $K_d$  values are not affected by the  $I$  values between 0.5 m and 6 m, whereas the  $K_d$  value at  $I = 0.1$  m is greater than those at  $I \geq 0.5$  m, except at  $\text{pH}_m = 10$ . A two-site protolysis nonelectrostatic surface complexation and cation exchange sorption model is applied to the Eu sorption data for  $I \leq 4$  m, and the equilibrium constants of the sorption reactions are estimated.

Keywords: Eu, MX-80 bentonite, Sorption, pH and ionic strength dependences, Sorption distribution coefficient, Two-site protolysis nonelectrostatic surface complexation and cation exchange sorption model (2SPNE SC/CE model)

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\*Corresponding Author.

Shinya Nagasaki, McMaster University, E-mail: [nagasas@mcmaster.ca](mailto:nagasas@mcmaster.ca), Tel: +1-905-525-9140

## ORCID

Jieci Yang

<http://orcid.org/0000-0002-3601-9622>

Joshua Racette

<http://orcid.org/0000-0001-5173-6681>

Fabiola Guido Garcia

<http://orcid.org/0000-0003-0208-9195>

Shinya Nagasaki

<http://orcid.org/0000-0002-6990-0811>

## 1. Introduction

The federal government of Canada approved Adaptive Phased Management (APM) as the long-term management plan for used nuclear fuel in Canada in 2007 [1]. The Nuclear Waste Management Organization (NWMO) is responsible for implementing the APM. Under the APM, used nuclear fuel will be placed within a deep geological repository (DGR) which is constructed in a suitable host rock formation. One of the candidate host rocks for a DGR in Canada is sedimentary rocks [1].

Brine solutions of Na–Ca–Cl type with a total dissolved solids (TDS) concentration up to  $350 \text{ g}\cdot\text{L}^{-1}$  have been observed in some of the sedimentary rocks in Southern Ontario (Michigan Basin) in Canada [1]. Sorption of radionuclides in engineered and natural barriers is an essential mechanism to retard their subsurface migration from the repository to the biosphere [2–6]. Hence, it is critical to investigate the sorption behavior of radionuclides on engineered barrier materials as well as natural barrier rocks. MX-80 is bentonite clay from the Clay Spur bed, Wyoming, USA, consisting of about 80wt% Na-rich montmorillonite and the candidate buffer material for the DGR project in Canada.

Plutonium(III) is one of the radionuclides of interest in the safety assessment of the DGR. Since the sorption behavior of Eu(III) is considered to be similar to that of trivalent actinides such as Pu(III), Am(III) and Cm(III), Eu is used as a chemical analogue for these trivalent actinides including Pu(III) [7].

There are many previous studies on the sorption of Eu on bentonite/montmorillonite using batch experiment, sorption modelling, laser spectroscopy and EXAFS (Extended X-ray Absorption Fine Structure) [3, 8–32]. However, to the best of our knowledge, there is only one research project that systematically studied the sorption of Eu on bentonite/montmorillonite in a wide range of pH and ionic strength [8]. Others investigated the sorption of Eu under relatively low ionic strength conditions or over a relatively small

range of pH. Schnurr et al. [8] investigated sorption of Eu on Na-SWy-2 montmorillonite in NaCl solutions at 0.09, 0.92 and 3.90 molal (m) by batch experiment and using a two-site protolysis nonelectrostatic surface complexation and cation exchange sorption model (2SPNE SC/CE). They also applied time-resolved laser fluorescence spectroscopy to study the Cm sorption at 0.1, 1.02 and 4.37 m. They found that (i) the sorption of Eu increased as  $\text{pH}_m$  increased for  $\text{pH}_m < 9$ , (ii) the sorption by cation exchange was suppressed with ionic strength at  $\text{pH}_m < 6$ , and (iii) the ionic strength dependence of Eu sorption at  $6 < \text{pH}_m < 8-9$  was small. The model prediction by 2SPNE SC/CE agreed well with the experimental data for  $\text{pH}_m < 9$ .

Due to the highly saline groundwater conditions in the Canadian sedimentary rocks, the sorption behavior of Eu on MX-80 in highly saline Na–Ca–Cl solutions has to be elucidated. In the presence of Ca ion, the sorption of Eu may compete with that of  $\text{Ca}^{2+}$ . In this study, Eu sorption on MX-80 in Na–Ca–Cl solutions ( $\text{pH}_m = 3-10$ , ionic strength ( $I$ ) = 0.1–6 m) was investigated by batch experiment and 2SPNE SC/CE model.

## 2. Experimental

### 2.1 Materials

All chemicals used in this work were reagent grade and purchased from Fisher Scientific. Deionized water prepared with a Milli-Q Direct 8 was used. The MX-80 bentonite sample was provided by the American Colloid Company and was used as received. The specific surface area of MX-80 is  $26.2 \text{ m}^2\cdot\text{g}^{-1}$  [33]. Other information including the mineralogy of this material is described elsewhere [33]. A Glove Box (GB) was filled with  $\text{N}_2$  gas (> 99.999%) to exclude  $\text{CO}_2$  and  $\text{O}_2$ . The concentration of  $\text{O}_2$  in the running  $\text{N}_2$  gas was confirmed to be less than 2 ppm by an oxygen sensor (Inert Technology).

A standard solution of Eu was purchased from Agilent

Technologies ( $1,000 \mu\text{g}\cdot\text{mL}^{-1}$  in 5%  $\text{HNO}_3$ ). This standard solution was diluted, and the Eu stock solution was prepared (Eu concentration:  $1 \times 10^{-5}$  m).

The Na/Ca ratio in molal concentration is 2.7 in the NWMO reference groundwater which represents the saline groundwater conditions at the repository depth in the Canadian sedimentary rocks (SR-270-PW, Na–Ca–Cl type, TDS =  $275 \text{ g}\cdot\text{L}^{-1}$ ) [2]. Therefore, Na–Ca–Cl solutions (Na/Ca = 2.7) with  $I = 0.1, 0.5, 1, 2, 4$  and  $6$  m were prepared with NaCl and  $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$  compounds. Since Eu(III) is dominant under both the oxidizing and reducing conditions, it is not necessary to adjust the Eh of the solution. However, in this study, to simulate the deep geological conditions, reducing conditions were established for the sorption measurements. To achieve the low Eh values such as  $-200$  mV versus SHE (standard hydrogen electrode), a small volume of hydrazine was added.

The pH values measured by the pH meter ( $\text{pH}_{\text{measure}}$ ) are operational values [34]. How to convert the  $\text{pH}_{\text{measure}}$  to the molar  $\text{H}^+$  concentrations ( $\text{pH}_c = -\log c_{\text{H}^+}$ ) or the molal  $\text{H}^+$  concentration ( $\text{pH}_m = -\log m_{\text{H}^+}$ ) were described elsewhere [35-37]. In this study, the  $\text{pH}_m$  in solutions was determined by acid-base titration (Metrohm Ti-Touch 916) according to the procedure described elsewhere [37]. Furthermore, we measured the redox potentials in the solutions and converted them into Eh versus SHE. The Eh measurement and calibration are also described elsewhere [37].

## 2.2 Sorption Experiment

All experiments were conducted at  $25^\circ\text{C}$  in triplicate in the GB. The experimental procedures were the same as those in our experiments on Np(IV) sorption in Na–Ca–Cl solutions [37]. In the present work, the sorption distribution coefficient ( $K_d$ ) [ $\text{mL}\cdot\text{g}^{-1}$ ] was used to express the results of the sorption experiment:

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

where  $C_0$  (m) is the initial concentration of Eu in the solution ( $1 \times 10^{-7}$  m as explained later),  $C_e$  [m] the Eu concentration in the solution at sorption equilibrium,  $V$  [mL] the volume of the solution, and  $W$  [g] the mass of the MX-80.

The solid/liquid ratio for all sorption experiments was  $10 \text{ mg}/10 \text{ mL}$  ( $10 \text{ mg}$  of MX-80 was added into a  $15 \text{ mL}$  test tube). All sorption experiments were preceded by pre-equilibration, in which  $10 \text{ mL}$  Na–Ca–Cl solution with each ionic strength ( $0.1, 0.5, 1, 2, 4$  or  $6$  m) were mixed with  $10 \text{ mg}$  MX-80. The suspensions were kept in the GB for one week. The solution was separated by centrifuge ( $6$  min at  $3,000$  rpm) and removed by pipette. Then,  $10 \text{ mL}$  of Na–Ca–Cl solution with the same ionic strength was added to the tube and the Eu stock solution was spiked. The initial concentration of Eu was  $1 \times 10^{-7}$  m. The solubility of  $\text{Eu}(\text{OH})_3(\text{am})$  in  $I = 1$  m Na–Ca–Cl solution is estimated to be  $3 \times 10^{-6}$  m at  $\text{pH} = 8$  by PHREEQC [38]. Schnurr et al. [8] used  $2 \times 10^{-7}$  m as the Eu initial concentration in their sorption measurements. Therefore,  $1 \times 10^{-7}$  m was considered lower than the Eu solubility and was used as Eu initial concentration throughout this work.

To study the Eu sorption kinetics, the Na–Ca–Cl solutions with  $I = 0.1$  and  $6$  m were used. After the Eu stock solution was spiked, the  $\text{pH}_m$  was adjusted to around  $6.5$  and Eh was checked to be around  $-200$  mV vs. SHE. During the experiment,  $\text{pH}_m$  and Eh were measured daily. When the  $\text{pH}_m$  value changed more than  $\pm 0.3$ , the  $\text{pH}_m$  was adjusted. During the kinetics measurement, Eh values of all test tubes were stable. After  $1, 2, 4, 7, 14$  and  $30$  d, the solution was separated from the solid by centrifugation ( $30$  min at  $18,000$  rpm) at  $25^\circ\text{C}$ . The  $\text{pH}_m$  and Eh of the solution were measured in the GB, and an aliquot was sampled from the solution of the test tube. The Eu concentration in the aliquot was measured with the ICP-MS (Agilent ICP-MS 8800). The detection limit of Eu was  $2 \times 10^{-12}$  m.

The  $\text{pH}_m$  and ionic strength dependences of  $K_d$  were measured at  $\text{pH}_m$  range from  $3$  to  $10$  and  $I = 0.1, 0.5, 1, 2, 4$  and  $6$  m. The  $\text{pH}_m$  of the solution was measured once a day in the GB. If the value of  $\text{pH}_m$  changed by more than  $\pm 0.3$

from the original one, it was re-adjusted to the original value of  $pH_m$  by addition of HCl or NaOH solution. Since the volume added was very small, the impact of change in the concentration of Eu on  $K_d$  evaluation was considered to be negligibly small. As explained in the following section, the sorption equilibrium under the experimental conditions of this study was reached within 21 d. Therefore, the sorption time was set 30 d throughout the  $pH_m$  and ionic strength dependence of  $K_d$  measurements. Other procedures were the same as those used in the kinetics measurements.

### 3. Results and Discussion

The results of the sorption kinetics of Eu for MX-80 in Na–Ca–Cl solutions at  $I = 0.1$  and 6 m are shown in Fig. 1. It was illustrated that the sorption of Eu reached the equilibrium within 14 to 21 d at both ionic strengths. Based on the sorption kinetics results, the sorption reaction time for experiments on  $pH_m$  and ionic strength dependence of  $K_d$  was set at 30 d.

The  $pH_m$  and ionic strength dependences of sorption of Eu in Na–Ca–Cl solutions are shown in Fig. 2. Fig. 2 illustrates that the  $K_d$  values of Eu on MX-80 increased with  $pH_m$  from 3 to 6 at all ionic strengths, which is consistent with the result on Na–SWy-2 montmorillonite by Schnurr et al. [8]. However, while the  $K_d$  values reported by Schnurr et al. [8] continued to increase slightly with  $pH_m$  up to 10, the  $K_d$  values obtained for MX-80 in this study seemed to be independent of  $pH_m$  between 8 and 10 at  $I \geq 0.5$  m. The pH independence has been reported in cation sorption onto montmorillonite [39]. This is considered because sorption apparently seems to be saturated at  $pH_m = 8-10$  where anionic species such as carbonate complexes and high-order hydrolyzed species are formed. At  $I = 0.1$  m, the  $K_d$  value at  $pH_m = 10$  slightly decreased, compared to that at  $pH_m = 8$  and 9.

In Figs. 1 and 2, a few measured data seemed to have relatively large experimental errors or uncertainties. How-

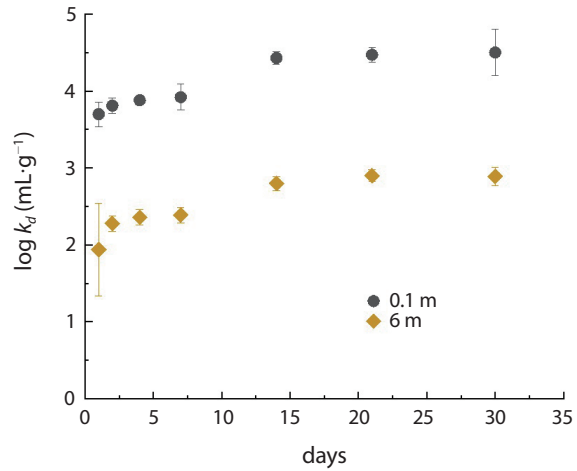


Fig. 1. Sorption kinetics of Eu on MX-80 in Na–Ca–Cl solutions at  $I = 0.1$  and 6 m. Initial concentration of Eu was  $1 \times 10^{-7}$  m.  $pH_m$  was adjusted to  $6.5 \pm 0.3$ .

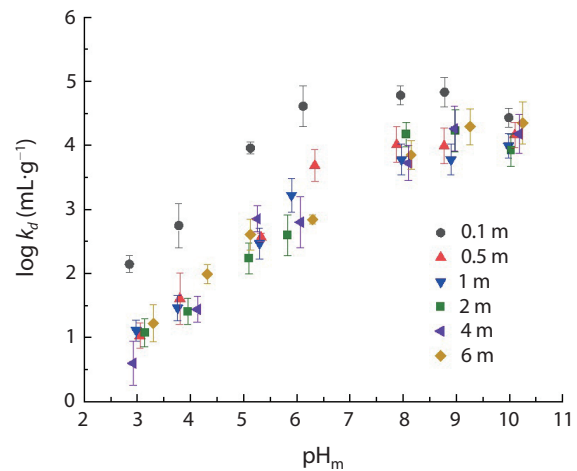


Fig. 2.  $pH_m$  and ionic strength dependence of  $K_d$  values of Eu in Na–Ca–Cl solutions. Initial concentration of Eu was  $1 \times 10^{-7}$  m.

ever, the error / uncertainty of  $0.5 \log K_d$  is not unusual [8]. On the other hand, there was a possibility that the colloidal particles released from MX-80 might not be removed completely by the centrifugation, leading to the experimental errors / uncertainties of  $K_d$  values, but the discussion in this paper would not be affected by these errors / uncertainties.

It was found that the  $K_d$  values of Eu for MX-80 at  $I$  values between 0.5 m and 6 m were independent of  $I$  values at a full range of  $pH_m$  investigated in this study, whereas the  $K_d$  value at  $I = 0.1$  m is greater than the  $K_d$  values at  $I \geq 0.5$  m

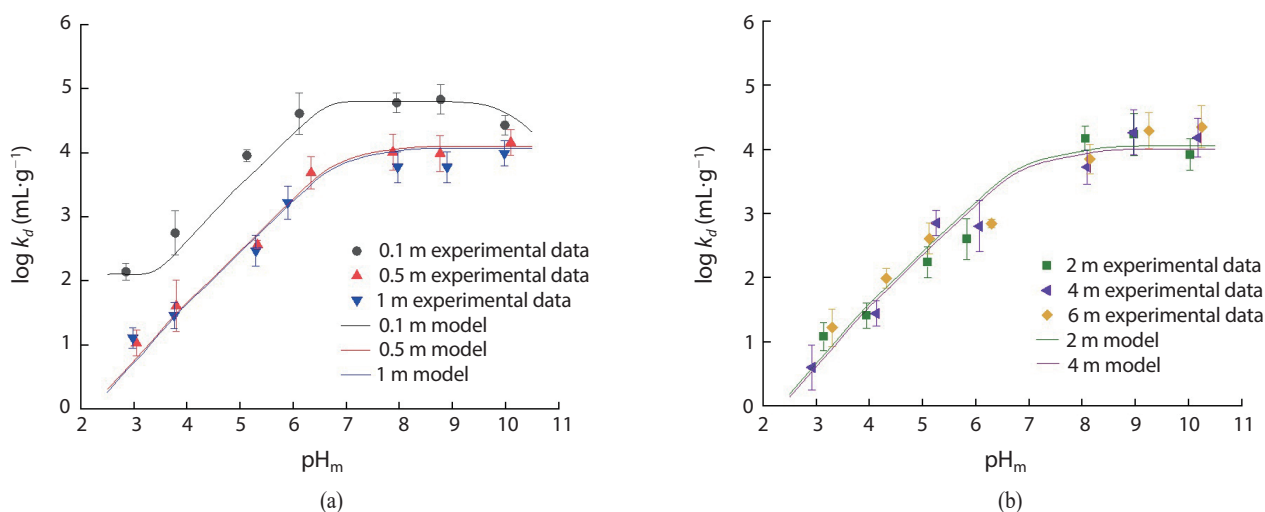


Fig. 3.  $K_d$  prediction by 2SPNE SC/CE model. (a) Ionic strength = 0.1, 0.5 and 1 m; (b) ionic strength = 2 and 4 m.

except  $\text{pH}_m = 10$ . Schnurr et al. [8] reported that at  $\text{pH}_m < 8-9$ , the  $K_d$  value at  $I = 0.09$  m is greater than that at  $I = 0.92$  m and 3.90 m and that the  $I$  dependence at  $I = 0.92$  m and 3.90 m was minor. Our results demonstrated that the same dependence on  $I$  was measured under the wider  $I$  conditions for MX-80. That the  $K_d$  values were not affected by  $I$  values was considered due to the formation of inner-sphere complexes. This is supported by the discussion and the TRLFS measurement by Schnurr et al. [8].

The  $K_d$  values obtained in this study were lower than those reported by Schnurr et al. measured in NaCl solution [8] and by Bradbury and Baeyens measured in NaClO<sub>4</sub> solution [39]. This was considered because not only Na<sup>+</sup> but also Ca<sup>2+</sup> competed for the sorption with Eu<sup>3+</sup>, and because Ca<sup>2+</sup> is well known as a strong coagulant for montmorillonite. The effects of the difference in the surface properties between MX-80 and Na-SWy-2, the difference in initial concentration (maybe negligible:  $1 \times 10^{-7}$  m in this study and  $2 \times 10^{-7}$  m) and the presence of Ca<sup>2+</sup> are left for future study.

The 2SPNE SC/CE model incorporated in PHREEQC [38] was applied to simulate the  $\text{pH}_m$  and ionic strength dependences of  $K_d$  values of Eu on MX-80. Since the Pitzer parameters for Eu in Na–Ca–Cl solution are not available, the dependences of  $K_d$  values of Eu on  $\text{pH}_m$  and  $I$  up to  $I = 4$

m were used to decide the surface complexation reactions and the constants of surface complexation reactions and cation exchange reaction. We adopted the specific ion interaction theory (SIT [40]) to estimate the activity coefficients of species in solutions and used thermodynamic constants for Eu aqueous species from the JAEA thermodynamic database [41] and from the study by Spahiu and Bruno (Eu-Cl complexations) [42]. The JAEA thermodynamic database contains the SIT parameters to estimate the activity coefficients [41]. The thermodynamic data used for the model calculation was shown in Supplementary Material (Table S1). To initiate the fitting of the model, the constants of surface complexation reactions and cation exchange reaction for Eu on Na-SWy-2 montmorillonite in NaCl solution reported by Schnurr et al. [8] were used for the initial values of constants. Values of other parameters such as protolysis constants were the same as those used by Walker et al. [43]. To simulate clay proton titration data, two types of high surface density protolysable sites (W1 and W2) were considered in the 2SPNE SC/CE model. However, in the latest version of the 2SPNE SC/CE model [44] and the study by Schnurr et al. [8], only strong sites, S, were used for modelling cation surface complexation data at trace metal ion concentrations, and the calculations successfully predicted the experimental data [8, 44]. Hence, we also considered

Table 1. Parameters to model Eu sorption for MX-80 in Na–Ca–Cl solutions with 2SPNE SC/CE model and the literature values for montmorillonite/bentonite [8, 15, 39]

	This work	Schnurr et al. [8]	Grambow et al. [15]	Bradbury and Baeyens [39]
Surface complexation reactions	$\log K_{sc}$			
$\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}^{2+} + \text{H}^+$	2.2	2.3	0.4	1.6
$\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_2^+ + 2\text{H}^+$	-7.7	-5.9	-6.5	-6.4
$\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_2 + 3\text{H}^+$	-15.0	-13.9	-	-15.7
$\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_3 + 4\text{H}^+$	-	-25.8	-24.5	-
Cation exchange reaction	$\log K_{ce}$			
$3\text{Na-MX-80} + \text{Eu}^{3+} \leftrightarrow \text{Eu-MX-80} + 3\text{Na}^+$	1.5	1.5	1.4	1.5

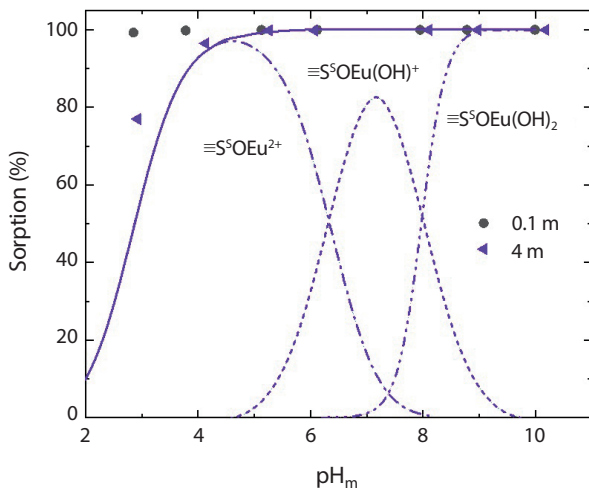


Fig. 4. Sorption edges of Eu on MX-80 as a function of  $\text{pH}_m$  at  $I = 0.1$  and  $4$  m. Sorption data (symbols) show percentage sorption. Curves represent calculation results with the 2SPNE SC/CE model. Eu surface complexation at  $I = 4$  m is illustrated in dashed lines.

only strong sites in this study.

The fitting results were shown in Figs. 3(a) and 3(b). The optimized parameters at an infinite dilute solution for MX-80 obtained in this study and other studies for montmorillonite/bentonite [8, 15, 39] are summarized in Table 1. Dominant surface complexation reactions at  $I = 4$  m are illustrated in Fig. 4 (shown as percentage sorption).

It was found that the  $\text{pH}_m$  and  $I$  dependences predicted by 2SPNE SC/CE model agreed well with the experimen-

tal data obtained in this study. The surface complexation constant value of the reaction  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}^{2+} + \text{H}^+$  optimized in this study ( $\log K_{sc} = 2.2$ ) was greater than the range of the surface complexation constant value of the linear free energy relationship (LFER) ( $0.6 \leq \log K_{sc} \leq 1.5$ ) [39], but it was similar to the value reported by Schnurr et al [8]. The optimized  $\log K_{sc}$  values for the surface complexation reactions  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_2^+ + 2\text{H}^+$  and  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_2 + 3\text{H}^+$  were lower than those reported by Schnurr et al. [8], but were within the range of LFER ( $-7.7 \leq \log K_{sc} \leq -6.5$  and  $-16.6 \leq \log K_{sc} \leq -14.9$ , respectively). Schnurr et al. [8] considered the surface complexation reaction  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_3 + 4\text{H}^+$  to improve the fitting between the model results and the experimental data at  $\text{pH}_m > 10$ . In this study, we measured the  $K_d$  values at  $\text{pH}_m \leq 10$  and could reproduce the experimental data well with the model without considering the surface complexation reaction  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{OEu}(\text{OH})_3 + 4\text{H}^+$ .

It was considered that cation exchange was a dominant sorption reaction which controlled the sorption of Eu onto MX-80 for  $\text{pH}_m < 4$  whereas the surface complexation of Eu with -OH groups at the surface of MX-80 dominated its sorption for  $\text{pH}_m > 4$ . It is well known that high background electrolyte concentrations suppress cation exchange reaction [8]. This explains the low sorption of Eu at  $\text{pH}_m < 4$



and high  $I$  ( $I \geq 0.5$  m).

These results suggest that the sorption of Eu on MX-80 in a Na–Ca–Cl solution at  $\text{pH} \leq 10$  and  $I = 0.1$  m to 4 m could be simulated by three surface complexation reactions and one cation exchange reaction. Grambow et al. [15] studied the sorption of Eu on MX-80 in  $0.066 \text{ mol} \cdot \text{L}^{-1}$   $\text{Ca}(\text{NO}_3)_2$  solution and showed that instead of the surface complexation reaction  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{O}(\text{OH})_2 + 3\text{H}^+$ , the surface complexation reaction  $\equiv\text{S}^{\circ}\text{OH} + \text{Eu}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{O}(\text{OH})_3 + 4\text{H}^+$  dominated sorption at  $\text{pH} > 9$ . On the other hand, Grambow et al. [15] also reported that the sorption of Am on MX-80 in  $0.1 \text{ mol} \cdot \text{L}^{-1}$   $\text{NaClO}_4$  at  $\text{pH} < 10$  could be simulated with three surface complexation reactions  $\equiv\text{S}^{\circ}\text{OH} + \text{Am}^{3+} \leftrightarrow \equiv\text{S}^{\circ}\text{O}(\text{OH})_2 + \text{H}^+$ ,  $\equiv\text{S}^{\circ}\text{OH} + \text{Am}^{3+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{O}(\text{OH})_2 + 2\text{H}^+$  and  $\equiv\text{S}^{\circ}\text{OH} + \text{Am}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\circ}\text{O}(\text{OH})_3 + 3\text{H}^+$  as well as cation exchange reaction. This also indicates that the effect of the type of electrolyte on the Eu sorption on MX-80 is a topic for future study.

#### 4. Conclusions

The dependence of  $K_d$  values of Eu onto MX-80 in Na–Ca–Cl solutions on  $\text{pH}_m$  (3–10) and  $I$  (0.1–6 m) was studied. The following conclusions were drawn in this work.

- The sorption of Eu on MX-80 in Na–Ca–Cl solutions at  $I = 0.1$  and 6 m reached equilibrium within 14 to 21 d.
- The  $K_d$  value of Eu for MX-80 was independent of  $\text{pH}_m$  at 8 to 10 at  $I \geq 0.5$  m, while the  $K_d$  value increased as  $\text{pH}_m$  increased up to 6 at all  $I$  values. At  $I = 0.1$  m, the  $K_d$  value at  $\text{pH}_m = 10$  slightly decreased, compared to that at  $\text{pH}_m = 8$  and 9.
- The  $K_d$  value of Eu for MX-80 was independent of  $I$  at  $\text{pH}_m = 3$ –10 at  $I \geq 0.5$  m, whereas the  $K_d$  value at  $I = 0.1$  m (except  $K_d$  at  $\text{pH}_m = 10$ ) was greater than that at  $I \geq 0.5$  m.
- The  $\text{pH}_m$  and  $I$  dependences of Eu on MX-80 in Na–Ca–

Cl solutions measured in this study could be simulated well with the 2SPNE SC/CE model. The optimized constants of three surface complexation reactions and one cation exchange reaction were evaluated.

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## Supplementary Material

Table S1. Thermodynamic data used for sorption model calculation

Formation reaction	Log K	Error
$\text{H}_2\text{O} - \text{H}^+ \leftrightarrow \text{OH}^-$	-14.001	0.015
$2\text{H}_2\text{O} + 4\text{H}^+ + 4\text{e}^- \leftrightarrow \text{O}_2$	-86.080	
$\text{Ca}^{+2} + \text{H}_2\text{O} - \text{H}^+ \leftrightarrow \text{CaOH}^+$	-12.850	0.500
$\text{Cl}^- + \text{H}_2\text{O} - \text{H}^+ - 2\text{e}^- \leftrightarrow \text{ClO}^-$	-57.933	0.170
$\text{Cl}^- + 2\text{H}_2\text{O} - 4\text{H}^+ - 4\text{e}^- \leftrightarrow \text{ClO}_2^-$	-107.874	0.709
$\text{Cl}^- + 3\text{H}_2\text{O} - 6\text{H}^+ - 6\text{e}^- \leftrightarrow \text{ClO}_3^-$	-146.238	0.236
$\text{Cl}^- + 4\text{H}_2\text{O} - 8\text{H}^+ - 8\text{e}^- \leftrightarrow \text{ClO}_4^-$	-187.785	0.108
$\text{Cl}^- + \text{H}_2\text{O} - \text{H}^+ - 2\text{e}^- \leftrightarrow \text{HClO}$	-50.513	0.109
$\text{Cl}^- + 2\text{H}_2\text{O} - 3\text{H}^+ - 4\text{e}^- \leftrightarrow \text{HClO}_2$	-105.913	0.708
$\text{Eu}^{+3} + \text{OH}^- \leftrightarrow \text{Eu}(\text{OH})^{+2}$	-7.800	
$\text{Eu}^{+3} + 2\text{OH}^- \leftrightarrow \text{Eu}(\text{OH})_2^+$	-16.900	
$\text{Eu}^{+3} + 3\text{OH}^- \leftrightarrow \text{Eu}(\text{OH})_3$	-26.500	
$\text{Eu}^{+3} + \text{Cl}^- \leftrightarrow \text{EuCl}^{+2}$	-0.34	0.05
$\text{Eu}^{+3} + 2\text{Cl}^- \leftrightarrow \text{EuCl}_2^+$	0.05	