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Surface complexation modeling for description of actinide sorption at the buffer materials/water interface

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Abstract

As mechanistic modeling becomes more feasible, surface complexation modeling was applied to actinide sorption reactions with the edge-surface hydroxyl groups of montmorillinite contained in bentonite, which is a potential buffer material for radwaste disposal. The determined surface properties of Japanese bentonite samples suggested possible interactions between positively charged surface sites and anionic Np(V) species in alkaline pH region under high inorganic carbon concentration conditions. The interfacial capacitance density affected determination of the bentonite surface parameters and the Np(V) surface complexation constants. The valence of the aqueous sorbing species was clarified to be useful in determining surface complexation constants of actinide sorption. © 1997 Elsevier Science B.V.

1. Introduction

Bentonite is a potential candidate for buffer materials used in ground/geological disposal of radioactive wastes. Sorption of radionuclides onto bentonite plays an important role in retarding radionuclide migration. Surface complexation modeling technique was used to mechanistically interpret actinide sorption behaviors affected by solution conditions, i.e., pH etc. [1–10]. The technique has been applied to simple materials such as iron oxides/hydroxides [1–6,11]. However, bentonite has not been sufficiently studied, though its main clay mineral, i.e., montmorillonite has edge-surface hydroxyl groups contributing the surface complexation. The edge-surface hydroxyl groups existing at the surface of the pore in compacted bentonite sorb actinide by the surface complexation and thus the modeling approach can be applied also to the buffer with high density by taking into account the characteristics of the pore water, such as high ionic strength. The technique involves arbitrary selection of surface complexation reactions and determination process for equilibrium reaction constants. Efforts should, therefore, be made to solve these problems as it is normally difficult to directly determine an equilibrium constant of a certain surface complexation reaction existing in mixtures such as Np(V) solution in the presence of carbonate ions.

In this study, bentonite surface properties which are important to surface complexation modeling are described. The effect of interfacial capacitance density, which defines charge–potential relationship at the bentonite surface, on the determination of surface complexation constants can be simulated using literature data of Np(V) sorption onto bentonite and a computer code GESPER [8]. The correlation of surface complexation constants and the valence of sorbing species are discussed to help determine the constants in the model calculation by referring to the previously determined surface complexation data of actinides for bentonite and hydrous ferric oxides.

2. Description of the sorption model

2.1. Constant capacitance model

A constant capacitance model [12] was used to describe the linear charge–potential relationship of the bentonite surface when considering actinide interaction with the

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surface. An interfacial capacitance density is a constant of the relationship, which is an adjustable model parameter:

$$\sigma = G\psi, \tag{1}$$

where σ is surface charge density (C/m^2), G is interfacial capacitance density (F/m^2) and ψ is surface potential (V). The details of the model are discussed elsewhere [12]. A brief description of mass action expressions of surface complexations is given below.

For surface proton association and dissociation reactions, and the surface complexation of only charged species, the following general equations are defined:

$$\mathrm{SOH_{(s)}} + \mathrm{H^+} = \mathrm{SOH^+_{2(s)}}, \tag{2}$$

$$\mathrm{SOH_{(s)}} = \mathrm{SO^-_{(s)}} + \mathrm{H^+}, \tag{3}$$

$$\mathrm{SOH_{(s)}} + \mathrm{H^+} + \mathrm{A}^{m-} = \mathrm{SOH_2A_{(s)}^{(m-1)-}}, \tag{4}$$

$$\mathrm{SOH_{(s)}} + \mathrm{C}^{n+} = \mathrm{SOC_{(s)}^{(n-1)+}} + \mathrm{H^+}, \tag{5}$$

where SOH is a hydroxyl site bound to an ion, S, in the bentonite and (s) represents the species existing on solid surface, C^{n+} and A^{m-} are ionic species. Equilibrium constants of Eqs. (2)–(5) are

$$K_+ = \frac{[\mathrm{SOH^+_{2(s)}}]}{[\mathrm{SOH_{(s)}}][\mathrm{H^+}]}\exp[F\psi/RT], \tag{6}$$

$$K_- = \frac{[\mathrm{SO^-_{(s)}}][\mathrm{H^+}]}{[\mathrm{SOH_{(s)}}]}\exp[-F\psi/RT], \tag{7}$$

$$\mathrm{K}_i = \frac{[\mathrm{SOH_2A_{(s)}^{(m-1)-}}]}{[\mathrm{SOH_{(s)}}][\mathrm{H^+}][\mathrm{A}^{m-}]}\exp[-(m-1)F\psi/RT], \tag{8}$$

$$\mathrm{K}_i = \frac{[\mathrm{SOC_{(s)}^{(n-1)+}}][\mathrm{H^+}]}{[\mathrm{SOH_{(s)}}][\mathrm{C}^{n+}]}\exp[(n-1)F\psi/RT], \tag{9}$$

where K_+ and K_- are proton association/dissociation constants, respectively, K_i is a surface complexation equilibrium constant for species i, R is an universal gas constant and T is absolute temperature (K).

Charged neptunyl species which are predominant in the bentonite suspension [7] were assumed to be sorbed on the edge-surface hydroxyl groups of monmorillonite with K_i in parenthesis: $\mathrm{SONpO_2}$ (K_1), $\mathrm{SOH_2NpO_2CO_3}$ (K_2), $\mathrm{SOH_2NpO_2(CO_3)_2^{2-}}$ (K_3), and $\mathrm{SOH_2NpO_2(CO_3)_3^{4-}}$ (K_4). Also surface complexations of carbonate ions are taken into account: $\mathrm{SOH_2CO_3^-}$ (K_5) and $\mathrm{SOH_2HCO_3}$ (K_6).

2.2. Surface property determination

Acid–base titration was carried out to determine the surface properties of various Japanese bentonite samples (see Table 1), i.e., K_+, K_-, and surface site density, N_s (mol/g) in a similar manner described by Fujita et al. [10]. FITEQL [13] was used to fit the parameters to the titration data. The value of G was basically fixed at 1.06 F/m^2 [14] and was parametrically changed for the Kunipia-F® sample. Specific surface area was determined by the glycerol and/or the BET methods.

2.3. Thermodynamic database

The thermodynamic data of Np(V) aqueous complexes and of carbonate ions used in the modeling study has been compiled by Fujita et al. [10]. Only the reactions of Np(V)

Table 1
Survey of surface properties for various bentonite and clay minerals

Solid phase	Temp. (°C)	SSA [a] (m^2/g)	N_s (10^{-5} mol/g)	log K_+	log K_-	G (F/m^2)	ZPC [b]	Supporting electrolyte	Comments
KUNIPIA-F	26	566^{GL}	7.7	9.4	−10.4	2.0	9.9	0.01 M NaCl	See Fig. 1.
Hoyo Bentonite	25	384^{GL}	19.7	9.1	−9.3	1.84	9.15	0.01 M NaCl	This work
KUNIBOND	25	112^{B}	19.5	7.8	−9.1	1.06	8.5	0.01 M NaCl	This work
KUNIBOND	25	242^{GL}	19.8	7.7	−9.3	1.06	8.5	0.01 M NaCl	This work
SMECTON	25	523^{GL}	73.4	7.7	−8.9	1.06	8.3	0.01 M NaCl	This work
CLAY-No. 1 [c]	25	790^{GL}	16.4	9.3	−10.3	–	9.8	0.01 M NaCl	This work
SUPERCLAY [c]	26	350^{GL}	8.0	7.8	−8.6	–	8.2	0.01 M NaCl	This work
KUNIPIA-F	25	566^{GL}	18.8	9.6	−11.4	0.15	10.5	0.01 M NaCl	Ref. [7]
KUNIPIA-F	26	566^{GL}	7.8	9.3	−10.3	1.06	9.8	0.01 M NaCl	Ref. [8].
KUNIGEL-V1	25	760^{GL}	–	–	–	–	–	0.01 M NaCl	Ref. [7].
Montmorillonite	–	18.6^{B}	–	9.87	−10.73	1.06	10.3	–	Ref. [17].
Illite	–	11.8^{B}	–	10.77	−10.08	1.06	10.4	–	Ref. [17].
Kaolinite	–	8.1^{B}	–	7.30	−10.38	1.06	8.8	–	Ref. [17].

[a] Specific surface area. Superscripts ‘GL’ and ‘B’ mean data by the glycerol and the BET methods.

[b] Calculated using the relationship: ZPC = 0.5(log K_+ − log K_-).

[c] A method using Langmuir type plotting [7] was used in the surface parameter determination.

with hydroxyl and carbonates ions were considered. Reactions with other anions such as nitrate, sulfate and perchlorate are assumed to be negligible [7].

2.4. Determination of Np surface complexation equilibrium constants

The equilibrium constants of Np(V) surface complexation reactions, K_1–K_4, were chosen with the following assumptions: (1) interaction between charged sites and charged species due to electrostatic attraction are assumed considering larger constant values with higher charge; (2) species with larger hydrated ion radius have smaller constant values because of the interference of sorption due to collision with neighboring outer-sphere surface complex; (3) coordination numbers have no effect on the size of species [15]. The third is not important since the hydrated Np(V) species are considered to have similar radii when calculated by the Stokes–Einstein equation [16] and the radius of the ions in the composition [15]. Constants K_5 and K_6 were referred from literature data [8] and fixed. The effect of inorganic carbon concentration on Np(V) sorption and chemical speciation was assigned from observed data [7]. GESPER [8] was used to solve the non-linear simultaneous equations and corresponding mass balance equations. Details of the calculation are shown elsewhere [7,8].

3. Results and discussions

3.1. Surface charge development

The determined bentonite surface properties are summarized in Table 1 which includes literature data for constant capacitance model. Bentonite samples have ZPC (zero point of charge) of the range 8–10, showing similar log K_+ and log K_- values as montmorillonite [17]. Among oxides of ions composing montmorillonite, Al_2O_3 [18] gives a similar ZPC to that of bentonite. The ZPC values for SiO_2 and ion oxides/hydroxides [18] are lower. This may indicate that of the edge-surface hydroxyl groups found on clay mineral surfaces, i.e., silanol and aluminol groups, the characteristics of the latter appear in the samples in this study. Fig. 1 plots the obtained parameters for the titration data (25°C) of Kunipia-F® with various G. The parameters vary drastically with G below 0.5 F/m², though the absolute change of N_s is not large. The tendency for surface parameters to be insensitive to larger G than about 1 F/m² is also found in oxide mineral titration data [19].

Fig. 2 shows the distribution of surface sites calculated using the parameters [8] for the Kunipia-F® with G of 1.06 F/m², which is an optimal value for Al_2O_3 [14]. The effective concentration of protonated surface sites SOH_2^+ decreases with the pH increases. The ratio of effective concentrations of SOH_2^+ and SO^- is unitary at ZPC and is about 10^{-5} at the pH of 12. Chemical speciation calculation of Np(V) in the bentonite suspensions [7] indicated that the concentrations of anionic Np(V) carbonate species are predominant in alkaline pH region, where the concentration of cationic NpO_2^+ decreases as the pH increases. These data suggest that the interaction with large K between anionic Np(V) carbonate species and the SOH_2^+ surface sites exceeds that between NpO_2^+ and the SO^- sites under this experimental condition [7] and support the surface complexation reactions selected in the previous studies [7–10].

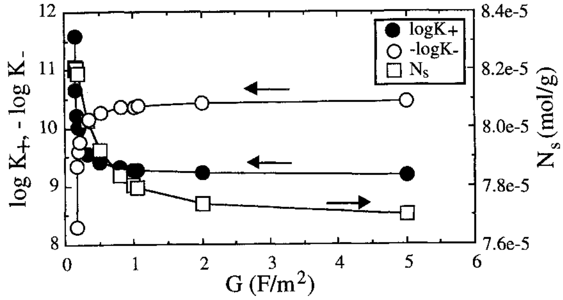

Fig. 1. Log K_+, log K_-, and N_s vs. G by FITEQL calculations for the pH titration data (25°C) of Kunipia-F®.

3.2. The effect of interfacial capacitance on simulation of the Np(V) sorption behavior

The model was applied to the observed data [7] of Np(V) sorption onto bentonite with the range of G 0.2 and 5 F/m² using the corresponding surface parameters (see Fig. 1). First the K values for the case with G of 1.06 F/m² [8] were applied to the all G cases. Fig. 3 shows slightly different shapes for the sorption envelopes and the extent of the winding is larger when the G differs more from 1.06 F/m². This tendency is obvious from Eqs. (1),

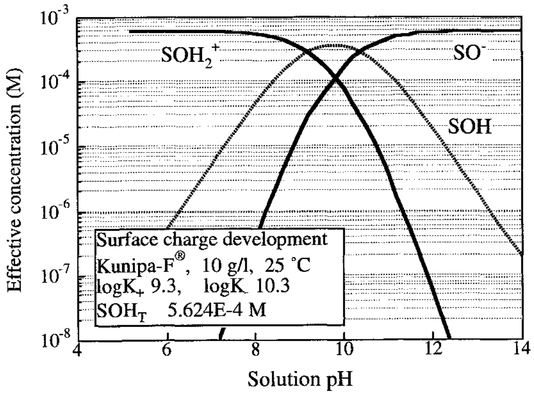

Fig. 2. Distribution of the surface sites calculated using the parameters for Kunipia-F® with G of 1.06 F/m².

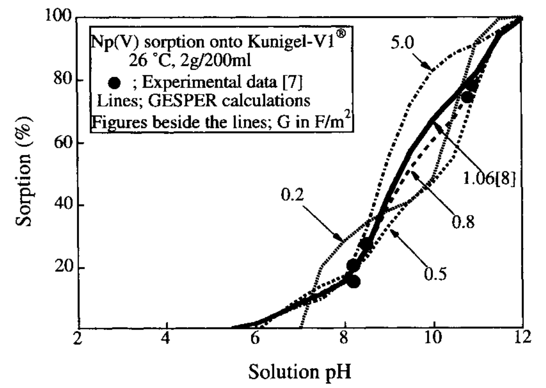

Fig. 3. Calculated Np(V) sorption behaviors onto Kunigel-V1® bentonite using surface parameters for various G in Fig. 1. A unique set of log K_i was used.

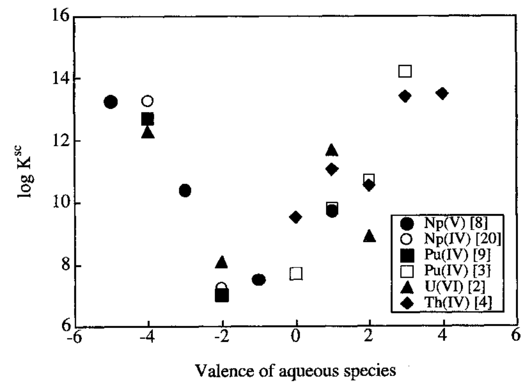

Fig. 4. Relationship between log K^{SC} of various actinides sorption onto bentonite/iron mineral samples and valence of the corresponding aqueous species.

(8) and (9) that sorption of highly charged complexes is easily affected by G.

The Np(V) surface complexation constant K as it fits the observed sorption data is tabulated in Table 2. The value comparison for various G with those for 1.06 F/m^2 [8] indicates that the sensitivity of G to K is larger in higher valence species, in particular, in the case with G of 0.2 F/m^2. Simulating the observed data of Np(V) sorption onto the bentonite using surface parameter sets for various G required slight modification of K of Np(V) surface complexation reactions.

3.3. Tendency of determined surface complexation constants

The correlation between surface complexation constants and the valence of sorbing aqueous complexes was examined. To obtain equilibrium reaction constants between charged surface sites and aqueous species, the determined log K_i were converted using the following equation:

$$\log K_i - \log K_+ = \log K_i^{\mathrm{SC}}, \qquad (10)$$

where K_i^{SC} is an equilibrium reaction constants between protonated surface site ($\mathrm{SOH_2^+}$) and anionic species. Similar equations is obtained for the sorption of cationic species and deprotonated site ($\mathrm{SO^-}$) by substituting log K_+ for log K_- in Eq. (6).

Fig. 4 is a plot of log K_i^{SC} of actinides for bentonite [8,9,20] and of hydrous ferric oxides [2–4,6] calculated using Eq. (6) with the corresponding aqueous complexation constants complied in Ref. [7] and log K_+/log K_- in the literature. The plot shows a positive relationship with the valence of the aqueous complexes considered as sorbing species. This may indicate that the assumptions described above were adequate and that electrostatic charge of sorbing aqueous species is important. The tendency is useful in determining surface complexation constants of actinide sorption onto buffer materials as well as the relationship between surface complexation constants and aqueous complexation constants [7,18], and the systematics of surface complexation constants among various solids [18].

Table 2
Surface complexation constants (log K_i) determined for various G

	G (F/m^2)				
	0.2	0.5	0.8	1.06 [a]	5.0
$\mathrm{SONpO_2}$	−1.5	−0.70	−0.60	−0.60	−0.45
$\mathrm{SOH_2NpO_2CO_3}$	16.1	16.6	16.7	16.8	17.0
$\mathrm{SOH_2NpO_2(CO_3)_2^{2-}}$	20.6	19.9	19.8	19.7	19.5
$\mathrm{SOH_2NpO_2(CO_3)_3^{4-}}$	25.3	23.3	22.8	22.6	22.1
$\mathrm{SOH_2CO_3^-}$ [b]	18.8				
$\mathrm{SOH_2HCO_3}$ [b]	15.2				

[a] Ref. [8].

[b] Fixed to the values in the reference.

4. Conclusion

The surface properties of bentonite samples suggested the possible interaction of positively charged surface site and anionic species in liquid phase, supporting the sorption reactions selected in the previous studies [7–10]. Interfacial capacitance density affected in both the determination of surface parameter sets for the bentonite and surface complexation constants reproducing the Np sorption behavior. The valence of sorbing ionic species gives useful information in determining surface complexation constants. Such the systematic approach is important in finding a unique set of the constants.

References

[1] D.C. Girvin, L.L. Ames, A.P. Schwab, J.E. McGarrah, J. Colloid Interf. Sci. 141 (1991) 67.

[2] C.-K. Hsi, D. Langmuir, Geochim. Cosmochim. Acta 49 (1985) 1931.

[3] A.L. Sanchez, J.W. Murray, Geochim. Cosmochim. Acta 49 (1985) 2297.

[4] B.D. LaFlamme, J.W. Murray, Geochim. Cosmochim. Acta 51 (1987) 243.

[5] K.A. Bond, J.E. Cross, F.T. Ewart, Radiochim. Acta 52&53 (1991) 433.

[6] T.E. Payne, T.D. Waite, Radiochim. Acta 52&53 (1991) 487.

[7] T. Ohe, M. Tsukamoto, T. Fujita, R. Hesböl, H.-P. Hermansson, Proc. 1993 Int. Conf. on Nuclear Waste Management and Environmental Remediation, Prague, Czech., 1993, pp. 197–205.

[8] M. Tsukamoto, T. Ohe, T. Fujita, R. Hesböl, H.-P. Hermansson, Radiochim. Acta 66&67 (1994) 397.

[9] M. Tsukamoto, T. Ohe, T. Fujita, R. Hesböl, H.-P. Hermansson, Mater. Res. Soc. Symp. Proc. 353 (1995) 291.

[10] T. Fujita, M. Tsukamoto, T. Ohe, S. Nakayama, Y. Sakamoto, Mater. Res. Soc. Symp. Proc. 353 (1995) 965.

[11] D.A. Dzombak, F.M.M. Morel, Surface Complexation Modeling, Hydrous Ferric Oxide (Wiley, New York, 1990).

[12] W. Stumm, R. Kummert, L. Sigg, Croat. Chem. Acta 53 (1980) 291.

[13] J C. Westall, FITEQL Version 2.0: A computer program for determining of chemical equilibrium constants for experimental data Report 82-01, Dept. of Chem., Oregon State Univ., Corvallis, OR, 1982.

[14] J.C. Westall, H. Hohl, Adv. Colloid Interf. Sci. 12 (1980) 265.

[15] R.A. Robinson, R.H. Stokes, Electrolyte Solutions (Butterworths Scientific, London, 1955) p. 12.

[16] R.D. Shannon, Acta Crystallogr. A32 (1976) 751.

[17] S. Goldberg, R.A. Glaubig, Soil Sci. Soc. Am. J. 50 (1986) 1442.

[18] P.W. Schindler, W. Stumm, in: Aquatic Surface Chemistry, ed. W. Stumm (Wiley, New York, 1987) p. 83.

[19] K.F. Hayes, G. Redden, W. Ela, J.O. Leckie, J. Colloid Interf. Sci. 142 (1991) 448.

[20] M. Tsukamoto, J. Jpn. Health Phys. Soc. 31 (1996) 297, (in Japanese).