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SORPTION MECHANISM OF Pu, Am AND Se ON SODIUM-BENTONITE

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ABSTRACT

The distribution coefficients (Kd) were measured for Pu, Am and Se on sodium-bentonite in bentonite-equilibrated distilled water in a pH range 4~10. Sodium-bentonite includes sodium-montmorillonite and ferrous minerals such as pyrite. The experiments were carried out by using the batch method under aerobic conditions for Pu, Am and under anaerobic conditions for Se. The distribution coefficients for Pu and Am were in the range $10^0 \sim 10^3 m^3/kg$ on sodium-bentonite in the above pH range. The sorption of Pu and Am was modeled by ion exchange of these cationic aqueous species with interlayer cations of sodium-bentonite. The distribution coefficients of Se on sodium-bentonite were interpreted by using a surface complexation model. The model was based on the assumption that the sorption behavior was dominated by ferric-oxyhydroxide, goethite, coating on the surface of pyrite. Sorption behavior of Am in compacted bentonite were also discussed by using cation exchange model.

INTRODUCTION

The research program for performance assessment of high-level waste isolation includes an investigation of the sorption mechanism for a number of important radioactive-elements to predict their migration behavior. Most of previous investigations have been carried out without consideration of the repository geochemical conditions and interpreted by the empirical methodologies only strictly valid under the experimental conditions in which they were measured. The distribution coefficient (Kd) is sensitive to aqueous chemistry and electro-chemical characteristics of solid surface and it would be possible to establish mechanistic model using these parameters. Sorption of Pu[1], Am[2] and Se[3] on sedimentary rocks has been studied. This paper presents the pH dependencies of the distribution coefficients for Pu, Am and Se on sodium-bentonite and goethite in a pH range 4~10 from batch sorption measurements. The applicability of mechanistic model of the ion exchange and the surface complexation was also discussed.

EXPERIMENTAL

The sodium-bentonite used in this study is Kunigel V1 (obtained from the Kunimine Industries Co. in Japan). The mineral assemblage of Kunigel V1 is shown in Table I. The cation exchange capacity (CEC) of sodium-montmorillonite is shown in Table II. The composition of the sodium-bentonite-equilibrated water is shown in Table III. The goethite used in this study is a reagent grade of α-FeOOH. The sorption experiment was carried out using the batch method. The pH was adjusted with NaOH or HCl. After 30 days, all samples were filtered through a 10,000MWCO (molecular weight cut off) filter for solid/solution separation. The blank test was carried out to measure sorption on the vessel walls and filter. Analysis of ^{239}Pu and ^{241}Am was conducted by α-spectrometry and Se was analyzed by ICP(inductively coupled plasma emission spectrometer). Distribution coefficient (Kd) was calculated from the ratio of the tracer element concentration in the solid and solution, and the Kd is given as (1)

$$Kd = \frac{C_b - C_t}{C_t} \times \frac{L}{S} \qquad (1)$$

Where Kd is the distribution coefficient (m^3/kg), Cb,Ct the concentration of tracer element in blank(Cb) and sample(Ct) (mol/l), L/S the solution/solid ratio(m^3/kg).

The experimental condition is shown in Table IV. The initial concentration of the tracer element in the solution was below the solubility limit. The solubility of the tracer element was calculated by PHREEQE[4], and thermodynamic data were taken from corresponding literatures for Pu, Se[5] and Am[6][7].

THERMODYNAMIC MODELLING OF SORPTION

The distribution coefficient of cationic species on sodium-bentonite is higher than the anionic species[8]. Sodium-montmorillonite have a structural permanent negative charge in interlayer of tetrahedral silicate. The zeta-potential of

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Table I. Mineralogical analyses of sodium-bentonite.

Mineral	wt% of bulk rock
montmorillonite	50-55
quartz	30-35
feldspar	5-10
calcite	1-3
dolomite	<2
zeolite	<2
mica	<2
pyrite	<2

Table II. Cation exchange capacity of sodium-bentonite.

Element	CEC(meq/g)
Na	1.078
K	0.012
Ca	0.183
Mg	0.031
Total	1.305

Table III. Composition of bentonite-equilibrated water. (solution/solid=0.5m^3/kg)

Component	Concentration(mol/l)
Na	8.696×10^{-4}
K	1.282×10^{-5}
Ca	3.000×10^{-5}
Mg	4.167×10^{-6}
Si	6.071×10^{-5}
Cl	8.451×10^{-6}
SO_4^{2-}	7.292×10^{-3}
HCO_3^-	4.918×10^{-4}

Table IV. Experimental condition.

tracer element	^{239}Pu	^{241}Am	Se
concentration(mol/l)	1×10^{-7}	1×10^{-9}	1×10^{-3}
solid	sodium-bentonite (Se ; α-FeOOH)		
solution/solid(m^3/kg)	0.5	0.5	0.05 (α-FeOOH ; 0.5)
pH range	5-9	5-9	4-10
temperature	room temperature		
atmosphere	air	air	N_2
time	30 days		

sodium-bentonite derived from the streaming potential measurement is negative, -20 through -10mV, in the experimental pH range, and the anionic species is not likely to be adsorbed on the sodium-bentonite. The zeta-potential of sodium-bentonite is shown in Fig.1. The sorption site of surface complexation for anion are decreasing with increasing pH, and anionic complexes such as carbonato-complexes are increasing with increasing pH. Sorption experimental results and predicted speciation of Pu and Am are shown in Fig.2. According to this figure, it is suggested that the sorption behavior of Pu can be concerned with $Pu(OH)_3^+$ and PuO_2^+, the sorption of Am with Am^{3+}, $AmOH^{2+}$ and $AmCO_3^+$, and the sorption of Se with SeO_3^{2-}.

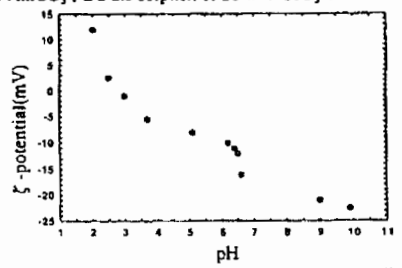

Fig.1. Zeta-potential of sodium-bentonite in bentonite-equilibrated water.

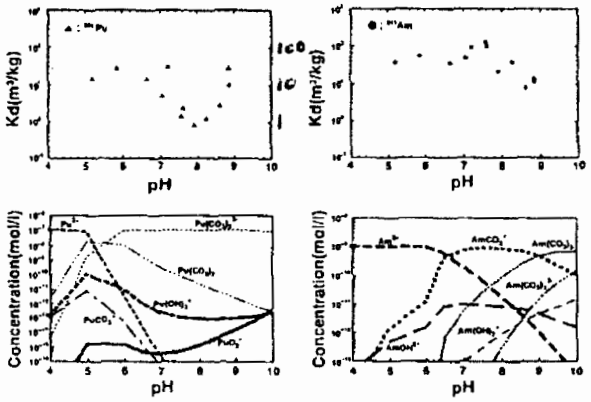

Fig.2. Experimental result and predicted speciation of Pu and Am.

Cation exchange model

The cation sorption mechanism of sodium-bentonite can be considered two types of sorption mechanisms, these are cation exchange between interlayer cations of sodium-montmorillonite and surface complexation of the edge silanol and aluminol groups of aluminosilicates included in sodium-bentonite respectively. In this sodium-montmorillonite, it can be considered that the effect of cation exchange is more significant than the surface complexation of silanol and aluminol groups, because CEC of ordinary clay minerals increases with increasing of pH owing to edge site increase, but its contribution to CEC is less than 15%[9]. The available cation exchange model was studied[12][10]. The schematic view of the cation exchange model is shown in Fig.3(a), in this model, the ion exchange reaction is shown as (2).

$$nZNa + M^{n+} \rightarrow Z_nM + nNa^+ \qquad (2)$$

The equilibrium constant(K) is described as (3).

$$K = \frac{[Z_nM][Na^+]^n}{[ZNa]^n[M^{n+}]} \qquad (3)$$

where Z^- is a reactive site in an interlayer and M^{n+} is a cationic species present in the solution.

In this model, cationic species(Am^{3+}, $AmOH^{2+}$, $AmCO_3^+$, PuO_2^+ and $Pu(OH)_3^+$) were assumed to be dominantly adsorbed on sodium-bentonite. The cation exchange constants were preliminarily estimated by best fitting from experimental results and the literatures[10][11]. This approach is adopted in other study[2]. These constants are shown in Table V. The distribution coefficients from the cation exchange model were calculated by using PHREEQE[4].

Surface complexation model

The dominant aqueous species of Se are predicted to be SeO_3^{2-} and $HSeO_3^-$. The dominant sorption mechanism of Se was inferred to be the surface complexation between solid surface and aqueous species of Se. In this study, generalized two-layer model[12] was selected to interpret Se sorption. The schematic view of this model is shown in Fig.3(b). The solid/solution interface is described in terms of two layers. All specifically adsorbed ions are assigned to the surface layer and counter ions assigned to a diffuse layer. The equilibrium constants for the surface reactions include an electrostatic term relating to the adsorbed ions in the surface plane(SOH). The concentration of surface species is related to the bulk concentration by using the Boltzmann distribution. The required input parameters arethe concentration of the surface sites, the specific surface area and equilibrium constants for the surface reactions. Anion sorption site in sodium-bentonite can be considered edge silanol and aluminol groups, but these site are too many amount to explain the Se sorption. Sorption mechanism of Se on ferric-oxyhydroxide can be considered surface

complexation. The ferric-oxyhydroxide was not observed in sodium-bentonite from X-ray diffraction, but formation of ferric- oxyhydroxide was supported by our observation of the altered surface of pyrite by using Electron Spectroscopy for Chemical Analysis(ESCA), as shown in Fig.4 and literature[13]. The model for Se sorption on sodium-bentonite was based on the assumption that the sorption behavior was dominated by small quantities of ferric-oxyhydroxide (goethite), coated on the surface of pyrite, which is 1wt% of sodium-bentonite. The surface complexation constants of Se was preliminarily estimated by best fitting from experimental results and other parameters were derived from the titration method. These constant are shown in Table VI. The distribution coefficient from surface complexation model was calculated by using HYDRAQL[14].

Table V. Ion Exchange Constants

Reaction	logK
$Z^- + Na^+ = ZNa$	20.0[9]
$Z^- + K^+ = ZK$	20.6[10]
$2Z^- + Ca^{2+} = Z_2Ca$	40.2[10]
$2Z^- + Mg^{2+} = Z_2Mg$	41.8[10]
$3Z^- + Am^{3+} = Z_3Am$	61.8
$2Z^- + AmOH^{2+} = Z_2AmOH$	43.7
$Z^- + AmCO_3^+ = ZAmCO_3$	22.3
$Z^- + Pu(OH)_3^+ = ZPu(OH)_3$	26.3
$Z^- + PuO_2^+ = ZPuO_2$	27.7

Table VI. Surface Complexation Constants and Parameters.

Reaction	logK
$SOH = SO^- + H^+$	-11.0
$SOH + H^+ = SOH_2^+$	3.4
$SOH + Na^+ = SONa + H^+$	-6.2
$SOH + Cl^- + H^+ = SOH_2Cl$	9.0
$SOH + H^+ + SeO_3^{2-} = SOH_2SeO_3^-$	15.1
Specific surface area	$10m^2/g$
Site density	1.8sites/nm

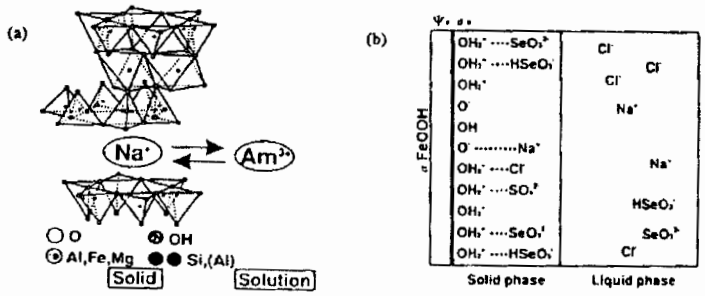

Fig.3. Schematic view of ion exchange model(a) and surface complexation model(b).

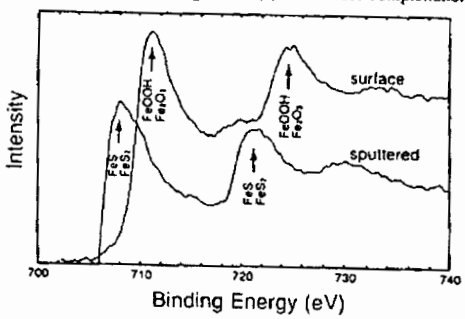

Fig.4. Characteristics of altered surface of pyrite.

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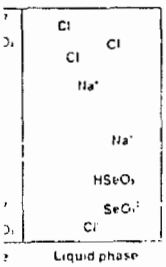
Constants and Parameters.

	logK
	-11.0
	3.4
	-6.2
Cl	9.0
)H,SeO,	15.1
	10m²/g
	1.8sites/nm



ation model(b).

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RESULT AND DISCUSSION

The distribution coefficients of Pu and Am were in the range $10^0 \sim 10^2 m^3/kg$ on sodium-bentonite in the above pH range. The sorbed ratio of Pu was in the range 60 ~ 100%, Am was 90 ~ 100% and Se was 0 ~ 20% on sodium-bentonite. The sorbed ratio of Se on the α-FeOOH were in the range 0 ~ 100% and these values increase with decreasing pH. Comparison of predicted with experimental data is shown in Fig. 5. The sorbed ratio of Pu and Am can be predicted by the cation exchange model, and Se can be predicted by the surface complexation model

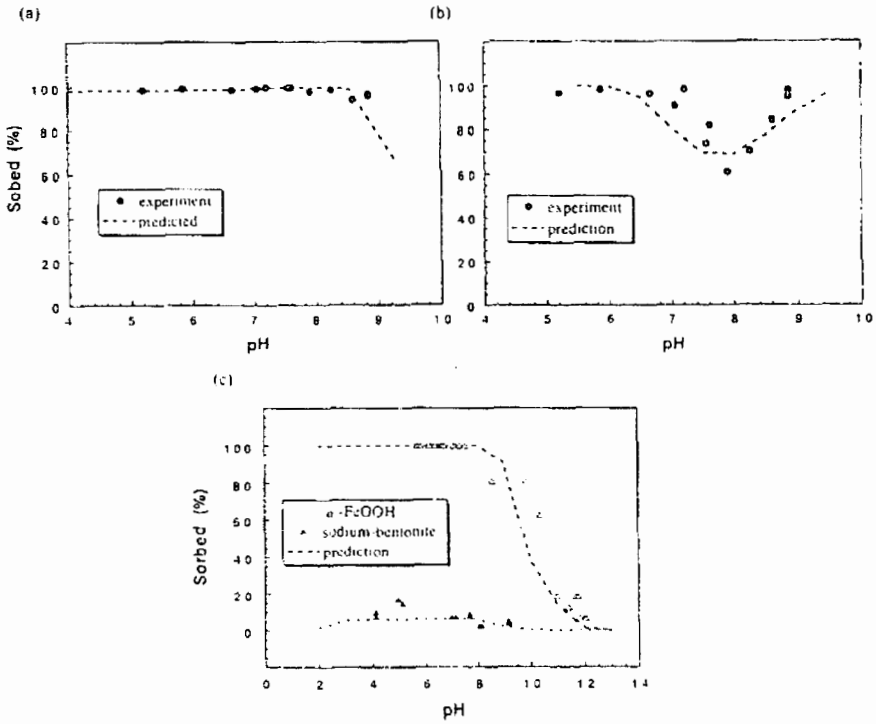

Fig.5. Results of the comparison of predicted and experimental data, where, (a) Am, (b) Pu and (c) Se.

Application for distribution coefficient of Am in compacted bentonite

The sodium-bentonite will be compacted at $1.8 g/cm^3$ in the isolation system of high-level radioactive waste. The principal retardation processes of nuclides in the compacted bentonite are considered to be two types of mechanisms[11-1], these are restriction of solute flow (i.e., molecular filtration, ion exclusion) and direct uptake onto the solid phase(i.e., ion exchange, physical adsorption). The direct uptake onto the solid phase can be estimated by distribution coefficient from the batch method. If the constrictivity is assumed 1, the apparent distribution coefficient of Am from the in-diffusion experiments[11-1] was estimated as $6.97 m^3/kg$. Pore water chemistry in compacted sodium-bentonite could not be measured at highly compacted sodium-bentonite, then pore water chemistry was predicted by calculation based on bentonite water interaction model[11-1]. The distribution coefficient of Am in compacted sodium-bentonite is predicted $1.32 m^3/kg$ by cation exchange model mentioned above. Difference between the experimental data and model prediction may be caused by the effects of molecular filtration and ion exclusion. The distribution coefficient estimated from in-diffusion experiment is given (4)[11-1].

$$Kd=\frac{\varepsilon}{\rho}\left(\frac{Do\,\delta}{Da\,\tau^2}-1\right) \quad (4)$$

Where ε is the total porosity calculated from the dry and theoretical density, ρ the dry density(kg/m^3), Do the ionic diffusion coefficient in free water(m^2/s), Da the apparent diffusion coefficient(m^2/s), δ are the constrictivity dependent on chemical formula of diffusion species and τ^2 the tortuosity related to path length. These values were cited from [8] except for the constrictivity(δ).

The constrictivity(δ) indicates the effects of molecular filtration and ion exclusion, and can be derived from equation (4). The input parameters are shown in Table VII. The derived constrictivity(δ) is 0.036.

Table VII. Parameters for Derivation of Constrictivity of Am in Compacted Bentonite.

ε	0.33	ρ	1800kg/m^3	Do	1.80×10^{-9}m^2/s
Kd	1.32m^3/kg	τ^2	7.03	Da	1.29×10^{-15}m^2/s

CONCLUSIONS

(1). The sorption mechanism of Pu and Am on sodium-bentonite is predicted to be cation exchange between interlayer cations and cationic species of actinides. (2). The sorption mechanism of Se on sodium-bentonite is predicted to be the surface complexation on the assumption that the sorption behavior was dominated by the small quantities of ferric-oxyhydroxide (α -FeOOH), coated on the surface of pyrite. (3). From the apparent distribution coefficient of Am in compacted sodium-bentonite and the distribution coefficient estimated from the cation exchange model, effective porosity for diffusion of Am is suggested. The effective diffusion porosity of Am is 3.6% of total porosity.

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