Sorption Behavior of Cesium, Strontium and Americium Ions on Clay Materials

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The sorption behavior of Cs, Sr and Am ions on loams, which is widely distributed in Tohoku district of Japan, was studied under static and flowing conditions.

The measurements of ion distribution ratios, which span a range of nearly three orders of magnitude, were fitted to Freundlich or Langmuir isotherms and the sorption parameters of isotherm equations were determined. It was found that the sorption of these ions on loams is due to the ionic exchange with Na, Ca and Mg ions of the loams. Analyzing the breakthrough curve of Cs ion sorption on a loam sorbent yielded $0.2 \, \mathrm{s}^{-1}$ and $0.32 \, \mathrm{cm}$ for values of the overall mass transfer coefficient and of the length of adsorption zone, respectively.

I. INTRODUCTION

The geological disposal systems have currently been investigated to isolate the radioactive wastes from the biosphere over a long time. In those circumstances the wastes are immobilized as a solid form and protected in a geological formation with other artificial multi-barriers. On the other hand, as it seems difficult in our country to find a stable rock formation with few fissures, the artificial barriers become to play an important part in those systems.

From the points of a low water permeability and relatively high cation sorption capability, bentonite consisting of montmorillonite and silt sand is well known as one of the leading candidates of backfill materials. However bentonite is considered inferior in mechanical strength, and thus an addition of some sort of reinforcing material such as quartz sand (sand) is proposed[1].

In the previous papers[2] some works on the cation sorption behavior of bentonite and bentonite-sand mixtures have been carried out, and it was found that the uptake of cations by bentonite from solutions prepared similarly to groundwater was mainly caused by the cation exchange reaction of montmorillonite of bentonite and that the cation sorption capability of sand was lower at least by a factor of several hundreds than that of bentonite. This means that the further addition of sand to bentonite as a reinforcer brings about a change for the worse of cation sorption capacity and of water permeability of the bentonite-backfill. Therefore, it is hoped to find a suitable substitute material for sand. The substitute should be one which is intimate with bentonite, distributed widely, capable of sorbing cations and usable for increasing mechanical strength of backfill.

We have investigated some loams distributed widely in Tohoku district on their applicability as an admixture to bentonite. Experimental results of the cation sorption behavior of these loams are presented in this paper.

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II. EXPERIMENTAL

1. Sample Preparation

Sample loams used here were collected at Takadate and Hachinohe in Tohoku district. Before use these were air-dried, sieved and analyzed by X-ray diffractometry, X-ray fluorescent spectroscopy and thermogravimetry. The standard BET method was applied to determine the specific surface area of samples. Bentonite marketed (by Kunimine Kogyo, Co. Ltd.) for building material was also tested as reference.

2. Procedure

The sorption of Cs, Sr and Am ions in deionized water (D. W.) or synthetic groundwater (S. W.) on sample materials was measured by the aid of the batch technique mostly identical to that described previously[2]; namely, the centrifugation of 39,000 G was applied to separate liquid phase from solid phase after one week equilibration at room temperature. Then, an aliquot of the supernatant fluid was taken out from the centrifuge tube to analyze for pH and for cations of interest by atomic absorption spectroscope and γ-counting with a NaI(Tl) scintillator.

To observe the sorption under flowing condition, $2\sim3$ g of the Takadate loam was packed into a glass tube of 22 mm I. D. for making sample column of 10 mm thick. The breakthrough curves of cations were determined by analyzing effluents collected fractionally.

III. RESULTS AND DISCUSSION

1. Characterization of Sample Sorbents

Results of the physical analyses of sample sorbents are listed in **Table 1**, where particle size and specific surface area are only of the dried sorbents and liable to change on soaking in aqueous solution owing to their swelling nature. From Table 1, Takadate loam was found to be a tuff containing about 40% of clay minerals of hydrohalloysite and some of allophane, and showed cation exchange capacity (CEC) of $0.1\sim0.3$ meq/g. Hachinohe loam was, on the other hand, comprised of silt sand, amorphous allophane and a few amounts of hydrohalloysite, among these minerals amorphous allophane has larger CEC $(0.3\sim 1.35$ meq/g[3]$)$ than others. Bentonite used here contained 70% of montmorillonite as a clay mineral, mainly taking part in the cation sorption, and showed the CEC of about 0.6 meq/g.

Table 1 Properties of sample sorbents

Sample	Minerals	Content (%)	Max. size (μm)	Sp. s. area (cm²/g)
Takadate loam†	Clay hydrohalloysite allophane Silt quartz	40 60	175	130
Hachinohe loam†	Clay allophane hydrohalloysite Silt quartz	10 90	175	60
Bentonite	Clay montmorillonite Silt quartz	70 30	65	70

† Contains a small amount of colored minerals such as mica, olivine, pyroxene and feldsper.

2. Cation Sorption on Sorbents

(1) Distribution Ratio

Cation distribution ratio for each sorbent Kd expressed in terms of the amounts of the ion sorbed by unit mass of solid sorbent q (mol/g) divided by the equilibrium ion concentration of aqueous phase C (mol/ml) was obtained by the batch technique. At constant

temperature q can often be represented by the Freundlich or the Langmuir type equation

$$q=kC^{1/n} \quad \text{or} \quad q=\frac{\alpha\beta C}{1+\alpha C}, \qquad (1)$$

where k, n, α and β are constants under the given conditions.

Combining Kd and Eq. (1) gives Eq. (2),

$$Kd=kC^{m-1} \quad \text{or} \quad Kd=\frac{\alpha\beta}{1+\alpha C}, \qquad (2)$$

where $m=1/n$.

The q's were measured at various concentration of ions both in deionized and synthetic groundwater, ranging nearly three orders of magnitude.

Some data on q were plotted as a function of C, as shown in **Fig. 1**(a) and (b), which gives mostly straight lines allowable to calculate the constants in Eq. (1). The results obtained for each ion were summarized in **Table 2**, where Kd's are estimated by taking the concentration being 1×10^{-5} mol/l for Cs and Sr ions, and 2×10^{-9} mol/l for Am ion.
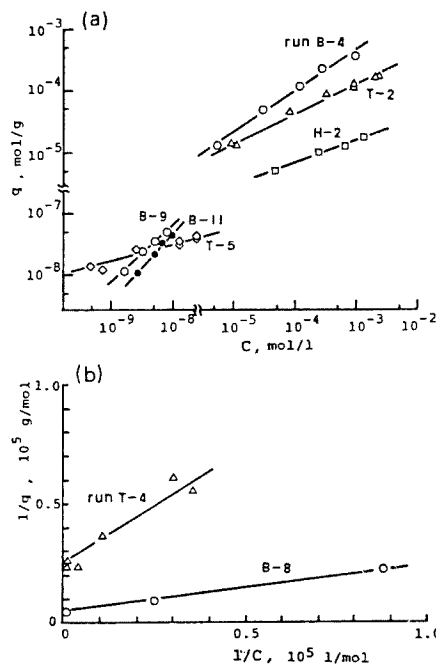

Fig. 1   Adsorption isotherm plots of Cs, Sr and Am ions on bentonite and loams

Table 2   Results of cation sorption on clay materials

Run	Material	Ion	Solution	pH	Kd[†] (ml/g)	k	m	α	β
						Constants in Eq. (2)			
B-1	Bentonite	Cs	D.W.	2.4	140	2.2 E-1[††]	1.1		
2				9.3	1,500	1.7 E-2	0.53		
3			S.W.	2.4	160	1.3 E-1	1.0		
4				9.3	1,100	4.8 E-2	0.67		
5		Sr	D.W.	2.7	60	8.1 E-3	0.77		
6				9.4	6,300			2.6 E-4	3.1 E-4
7			S.W.	2.7	40	2.3 E-3	0.71		
8				9.4	4,020			2.3 E-4	2.2 E-4
9		Am	D.W.	2.0	6,800	2.1	0.91		
10				6.0	23,000	1.1 E-1	0.59		
11			S.W.	2.0	3,800	16.2	1.1		
T-1	Takadate loam	Cs	D.W.	6.1	4,100	5.1 E-4	0.21		
2			S.W.	7.7	1,400	3.0 E-3	0.48		
3		Sr	D.W.	6.4	1,800	5.4 E-4	0.26		
4			S.W.	8.0	950			2.3 E-4	4.3 E-5
5		Am	D.W.	6.0	11,000	9.6 E-4	0.29		
H-1	Hachinohe loam	Cs	D.W.	6.6	1,100	1.3 E-5	0.013		
2			S.W.	8.3	280	2.3 E-5	0.38		
3		Sr	D.W.	6.5	550	1.7 E-4	0.27		
4			S.W.	8.2	260				
5		Am	D.W.	6.5	1,300			2.6 E-4	1.0 E-5

† Calculated by taking ion concentration as 10^{-5} mol/l for Cs, Sr and 2×10^{-9} mol/l for Am.
†† Read as 2.2×10^{-1}.

Equation (1) was also valid for Am ion in solution of lower pH, but not of higher pH than 7, probably because of its hydrolyzable and carbonate-complex forming properties in higher pH region[4].

From Fig. 1(a) and Table 2 the change in solution from D. W. to S. W. makes in general little effect on sorption of the ions on the sorbents, though somewhat larger Kd's in D. W. than in S. W. are observed. Takadate loam can sorb Cs from solution of low concentration up to the same degree or more of bentonite and shows high Kd's for these ions in solution of pH nearly equal to that of natural groundwater. Hachinohe, on the other hand, shows low Kd by a factor of 5 on that of bentonite. This is due to the differences in the kind and in the content of clay minerals of the samples.

(2) Breakthrough Curve

To obtain information on the sorption behavior of ions on solids under the flowing condition, the breakthrough curves of ions through the sorbent column were observed. Because of the higher sorption capability of Takadate than Hachinohe, the former was packed into a glass tube and the solution of sample ions in D. W. or S. W. was pumped into the tube at a constant rate. Then, the effluent was fractionally collected and analyzed in order of time for Na, Ca and Ce or Sr. The typical breakthrough curves obtained are shown in **Figs. 2** and **3**, where C_0 is the initial concentration of sorbable ion (100 ppm). The elution of Na and Ca ions during the sorption of Cs or Sr ion was also measured and depicted in Figs. 2 and 3. As seen from Figs. 2 and 3, Na ion is eluted from the loam, followed by Ca ion which approaches to zero, corresponding to termination of the sorption. Small amounts of Mg ion as compared with former ions were also detected in the effluent. The amounts of eluted ions estimated from the area under each elution curve are shown near by the curves, and the sum of these is found nearly in accord with the amount of sorbed ion in deionized water (Fig. 3), but not in the case of using synthetic groundwater (Fig. 2).
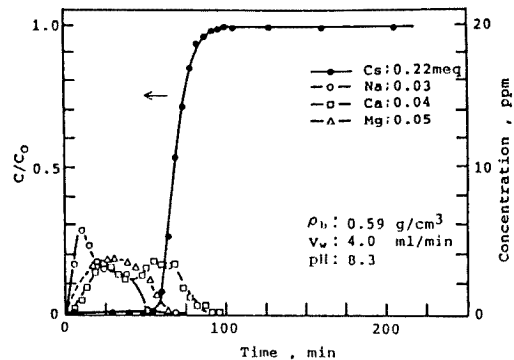

Fig. 2 Breakthrough curve of Cs ion and elution curves of Na, Ca and Mg ions, respectively, in S. W. on Takadate loam
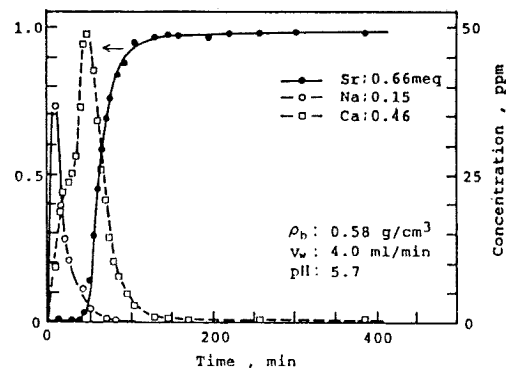

Fig. 3 Breakthrough curve of Sr ion and elution curves of Na and Ca, respectively, in D. W. on Takadate loam

These observations imply that the cation sorption by Takadate loam is mainly based on the ion exchange reaction of hydrohalloysite of the loam as well as montmorillonite of bentonite[2].

According to the model[5] based on the assumption of the diffusion limited process on a solid surface, the mass transfer zone proceeds along the sorption bed as more sorbable cation is fed. Provided that the concentration profile of cation in the zone is kept up the same until breakthrough occurs, application of the model to the present case yields the followings for the time difference between the ending and starting points of breakthrough,

$$t_E - t_B = \frac{\rho_b q_0}{K_f a_v C_0} \int_{c_B}^{c_E} \frac{dC}{C - C^*}, \qquad (3)$$

and for the velocity of the zone v_a,

$$v_a = \frac{u}{\varepsilon_b + \rho_b(q_0/C_0)}. \qquad (4)$$

Hence, the length of the zone Z_a is

$$Z_a = v_a(t_E - t_B) = \frac{u}{K_f a_v} \int_{c_B}^{c_E} \frac{dC}{C - C^*}, \qquad (5)$$

by neglecting $\varepsilon_b C_0$, where u is the linear flow rate of solution, $K_f a_v$ the overall mass transfer coefficient, ρ_b and ε_b the bulk density and void fraction of the bed, C, C^*, C_B and C_E the cation concentrations of feed solution, on the solid surface equilibrated with the solution of C in the zone, at t_B and t_E, respectively, and q_0 the amount of cation sorbed on solid equilibrated with the feed solution. In this connection, graphical integration of Eq. (5) for the sorption of Cs ion (Fig. 2) was applied, yielding the value of 3.59, which gives $0.2\,s^{-1}$ for the overall mass transfer coefficient and 0.32 cm for length of the zone, respectively.

The breakthrough curve for the Sr ion sorption (Fig. 3) shows a steeper slope than that for Cs, and thus seems possible to be described by the same model as well.

3. Water Permeability

As for a desirable backfill material, its low water permeability is one of the required properties as well as high cation sorption capability and mechanical strength.

Some of the data on water permeation obtained from preliminary examinations are shown in **Fig. 4**, where the high sample density is attained by compaction with a usual pressurizer. Figure 4 shows that bentonite is a material of very low water permeability even though on mixed with sand up to four times. Water permeates the Takadate loam of $1.6\,g/cm^3$ in compacted density about 100 times higher than bentonite-sand mixture, while almost 100 times lower than the Hachinohe, probably because of its lower content of silt sand. Considering the decrease in cation sorbability of bentonite on mixing with sand, it may be expected to improve the functions of bentonite backfill by replacing a part of sand by the loam. Further work on the composite backfill material of bentonite-loam is clearly needed.
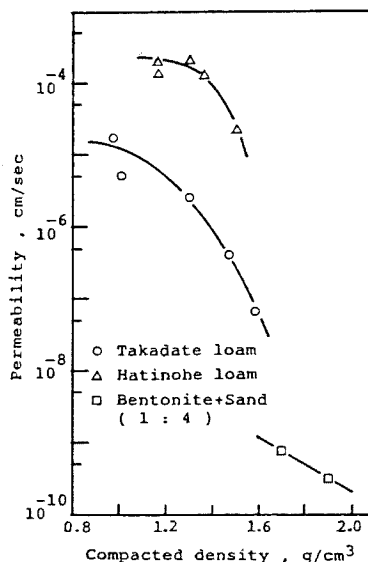

Fig. 4 Water permeability *vs.* compact density

IV. CONCLUSION

The sorption of Cs, Sr and Am ions on loams collected from Takadate and Hachinohe in Tohoku district were studied and it was found that the measurements are conformable to Freundlich or Langmuir isotherm. These loams contain clay minerals capable of sorbing cations and have Kd's over 250 for Cs and Sr ions of $10^{-5}\,mol/l$. Takadate loam has Kd on the order of 10^4 for Am ion of $10^{-9}\,mol/l$ in solution of $pH \leq 6$. This implies Takadate loam seems useful as one of admixtures to bentonite rather than sand, though the mechanical properties of the blended backfill are still to be surveyed.

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