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Section 12. Interfacial actinide chemistry in radioactive waste management

Interfacial behavior of actinides with colloids in the geosphere

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Abstract

A column experiment was carried out to assess the migration behavior of trivalent ^{241}Am and pentavalent ^{237}Np in the presence of montmorillonite colloids. The breakthrough phenomena of montmorillonite colloids and pseudocolloids (actinide-bearing montmorillonite colloids) are measured as a function of pH and ionic strength, and are explained by using DLVO theory where the attractive van der Waals and the repulsive electrostatic potentials are taken into account. By using the sorption data cited from the literature [Nagasaki et al., J. Radioanal. Nucl. Chem. Lett. 214 (1996) 381; Technical Report on Research and Development of High-level Radioactive Waste Repositories, Power Reactor and Nuclear Fuel Development Corp. Technical Report PNC TN 1410 92-081, 1992], the actinide migration behavior in the column is simulated. © 1997 Elsevier Science B.V.

1. Introduction

Groundwater colloids, existing in all groundwaters, are composed of inorganic and organic molecular constituents and microorganisms. Groundwater colloids are chemically surface-active and readily sorbed actinide ions, namely generate pseudocolloids of actinides [1]. Depending on their charge relative to the surrounding geologic media and their size distribution, the colloids can migrate faster or slower than the average velocity of the groundwater [2]. When the colloids act as a third phase that can increase the amount of actinides that can migrate in a natural aquifer system, failure to account for the colloid migration, as a potential vehicle for actinides, can lead to serious underestimates of the distances that actinides can migrate. In our previous works [3–5], we have pointed out that it is indispensable to elucidate the interfacial interactions among actinide ions, groundwater colloids and geologic media for evaluating the actinide migration quantitatively, and have studied the generation, diffusion, dispersion and desorption of colloids by using DLVO (Derjaguin–Landau–Verwey–Overbeek) theory.

In the present work, we studied the influence of montmorillonite colloids on the migration of actinide ions by column experiments, and compared the experimental results with the calculated prediction based on DLVO theory.

2. Experimental

Montmorillonite colloid is one of the typical inorganic groundwater colloids [6]. In the safety assessment of high-level radioactive waste disposal, actinides such as Am and Np are considered to dominate the potential hazard to the biosphere [7]. In the present work, the column experiments were carried out to assess the migration behavior of montmorillonite colloids and also assess the migration behavior of ^{241}Am(III) and ^{237}Np(V) in the presence of montmorillonite colloids.

2.1. Sorption / desorption of montmorillonite colloidal particles

Experiments were performed under ambient aerobic conditions. All chemicals except Am-241 and Np-237 solutions were reagent grade and used without further purification. Water was prepared from doubly distilled

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water by further purification with a Milli-Q system (Millipore).

The column had an inner diameter of 5 mm and was filled with the quartz powder (diameter = 8 μm) up to a height of 300 mm. The porosity of the column was found to be 40% from the breakthrough phenomenon of non-sorbing tracer, HTO. The temperature of the column was controlled at 25 ± 1°C by a water jacket. The quartz powder used was supplied from APPIE (Association of Powder Process Industry and Engineering, Japan) and immersed in 0.5 M NaCl solution (pH = 6.0 or 8.5) for more than one year. The detailed characterization of the quartz powder is described elsewhere [8].

Montmorillonite supplied from Nichika, Japan, was dispersed into 0.5 M NaCl solution of which pH value had been adjusted to pH = 6.0 or pH = 8.5 by using HCl or NaOH. Montmorillonite colloids (diameter: < 0.45 μm) were prepared by filtering the supernatant of the dispersed solution with a 0.45 μm membrane filter. Montmorillonite colloids do not aggregate to settle down in a 0.5 M NaCl solution at both pH values.

The salt solution, of which the ionic strength was adjusted to 0.5 M by addition of NaCl and the pH value was adjusted to pH = 6.0 or pH = 8.5 with HCl or NaOH respectively, had been continuously pumped through the column at the flow velocity of 1×10^{-4} cm/s, before the montmorillonite colloids were injected. After pre-equilibrium in the column was achieved by this procedure, the solution of montmorillonite colloids (pH = 6.0 or 8.5; ionic strength = 0.5 M) was introduced into the column for three days and the montmorillonite colloids were sorbed onto the quartz powder. Next, the washing solution at an ionic strength of 0.5 M was pumped through the column to remove the montmorillonite colloids existing in the pore spaces in the column. We found no release of montmorillonite by this washing procedure.

In order to study the dependence of the release of montmorillonite colloids from quartz powder on ionic strength, the flow was changed abruptly from the washing solution to the eluent with the same pH condition (pH = 6.0 or pH = 8.5). The ionic strengths (NaCl) in the eluent were in the 0 to 0.1 M range in the present work. We introduced an amount of more than ten times the effective pore volume of the column into the column.

The concentration of montmorillonite colloids in the eluate leaving the column was measured by using a UV-VIS-NIR scanning spectrophotometer (Shimadzu UV-3100PC).

2.2. Migration of Am(III) and Np(V) in the presence of montmorillonite colloids

Americium-241 in 0.5 M HNO_3 was supplied from Amersham (Am source solution) and Np-237 in 1 M HNO_3 from LMRI (Np source solution). By repeatedly mixing the Am source solution or the Np source solution with CMPO (*n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide), we prepared an Am(III) stock solution and a Np(V) stock solution.

A feed solution of Am or Np was prepared by adding each stock solution into a solution of montmorillonite colloids and equilibrating for one month. The pH of the feed solution was adjusted to pH = 6.0 or pH = 8.5 (HCl/NaOH) and the ionic strength to 0.01 or 0.1 M (NaCl). The concentration of Am in the feed solution was 1×10^{-6} M and that of Np was 1×10^{-7} M. We confirmed that all Am species and about 60% of Np species in the feed solutions were trapped by a 2 nm pore size ultrafilter under all experimental conditions, while no precipitates were measured in the solutions which were prepared by the same procedure as mentioned above but contained no montmorillonite colloids.

After the salt solution (ionic strength = 0.01 or 0.1 M; pH = 6.0 or 8.5) was pumped through the same column as described above and the column conditions were pre-equilibrated, two ml of the feed solution of Am or Np was injected into the column. The concentrations of Am or Np in eluate fractions were determined by α counting (2π gas flow counter) and γ counting (Ge counter).

3. Results and discussion

3.1. Sorption / desorption of montmorillonite colloidal particles

Table 1 summarizes the experimental results of the sorption/desorption of montmorillonite colloids. Symbols of 'O' and 'X' represent either that elution of montmorillonite was detected or was not detected, respectively. At pH = 6.0, elution of montmorillonite colloids was observed at an ionic strength below 0.05 M. At pH = 8.5, the same observation was made at an ionic strength below 0.08 M.

To explain the effects of pH and ionic strength on the elution of montmorillonite colloids, we analyzed the particle–wall interactions. Two types of geometric interactions, face–wall and edge–wall, exist between the montmorillonite colloids and the quartz powder. Since montmorillonite is platelet in shape and the edge can be treated as a

Table 1
Sorption/desorption of montmorillonite colloids on/from quartz powder

pH	NaCl concentration (M)								
	0	0.01	0.04	0.05	0.06	0.07	0.08	0.09	0.1
6.0	O	O	O	O	×	×	×	×	×
8.5	O	O	O	O	O	O	O	×	×

O Elution of montmorillonite was detected.
× Elution of montmorillonite was not detected.

cylinder, the plate–plate and the cylinder–plate interactions can be considered to represent the face–wall and edge–wall interactions, respectively. The total interaction potential between the montmorillonite colloids and the quartz powder is assumed to be given by the van der Waals potential and the double layer potential. We know that the face and edge surfaces of montmorillonite colloids are differently charged [9]. The face surfaces of montmorillonite carry a constant negative surface potential which is actually independent of the pH of the solution. The edge surface of montmorillonite readily interacts with the potential determining H^+ and OH^- ions and hence the edge surface potential depends on the pH. The formulation of interaction potentials and the data of surface potentials and Hamaker constant are summarized elsewhere in detail [5,10].

Fig. 1 illustrates the total interaction potential as a function of distance of separation at pH = 6.0. At the ionic strength above 0.055 M, the interaction between the montmorillonite colloids and the quartz powder is attractive and, hence, the elution of montmorillonite colloids from the column cannot be expected to take place. On the other hand, the total interaction is repulsive at the ionic strength below 0.055 M, the elution of montmorillonite colloids is expected to take place.

The total interaction potential at pH = 8.5 is shown in Fig. 2. At an ionic strength below 0.09 M, the total interaction is repulsive, while it is attractive at the ionic strength above 0.09 M. Therefore, we can expect the elution of montmorillonite colloids at the ionic strength below 0.09 M.

The calculated result at pH = 6.0 agreed well with the experimental result. However, the calculated result at pH = 8.5 was slightly different from the experimental result. A possible reason for this deviation is as follows. It is well known that adsorption behavior of colloidal particles under the stagnant flow conditions can be quantitatively predicted by considering the van der Waals potential and the double layer potential. In the present work, we observed the desorption behavior in the continuous flow fields. Therefore, we may have to take the Born potential [11], the stability of montmorillonite colloids and hydrodynamic force acting to montmorillonite colloids into account, for predicting the desorption and detachment behavior of montmorillonite colloids quantitatively. We are now investigating the stability of montmorillonite colloids not only under the stagnant flow conditions but also under the flow conditions, and the hydrodynamic force acting to montmorillonite colloids. The formulation of Born potential in the cylinder–plate system is not identified. We are planning to study the effect of the Born potential.

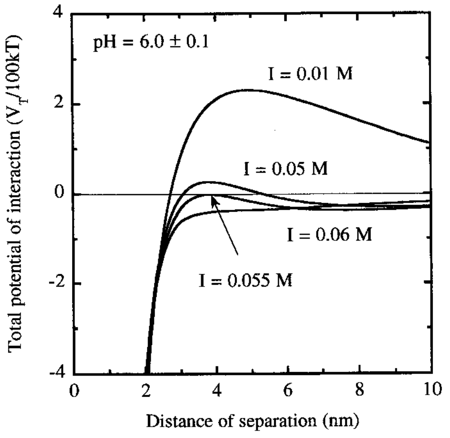

Fig. 1. Total interaction potential as a function of distance of separation and ionic strength at pH = 6.0.

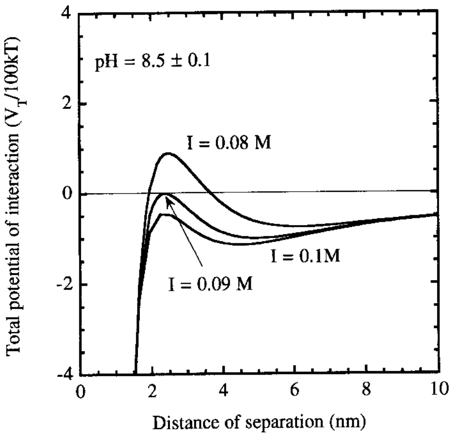

Fig. 2. Total interaction potential as a function of distance of separation and ionic strength at pH = 8.5.

3.2. Migration of Am(III) and Np(V) in the presence of montmorillonite colloids

Fig. 3 shows the breakthrough and recovery curves of ^{241}Am at an ionic strength of 0.01 M. In this figure, the Am concentration in eluates normalized to the injected Am concentration is displayed as a function of $V(i)/V_{\mathrm{eff}}$, where $V(i)$ is the eluted volume and V_{eff} is the effective

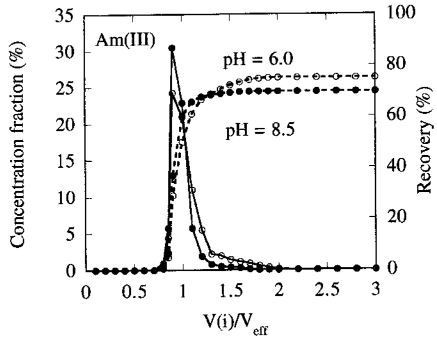

Fig. 3. Breakthrough and recovery curves for ^{241}Am(III) pseudo-colloids at an ionic strength of 0.01 M.

Table 2
Fractional distribution (%) of particle sizes of montmorillonite colloid, Am(III) pseudocolloid and Np(V) pseudocolloid in the feed and eluate solutions at an ionic strength of 0.01 M: (a) pH = 6.0; (b) pH = 8.5

	< 2 nm	2–100 nm	100–250 nm	250–450 nm	450 nm <
(a) pH = 6.0					
Montmo. in feed	ND	4	7	89	ND
Montmo. in eluate	ND	3	5	92	ND
Am(III) in feed	ND	2	10	88	ND
Am(III) in eluate	ND	2	13	85	ND
Np(V) in feed	40	2	3	55	ND
Np(V) in eluate	ND	4	6	90	ND
(b) pH = 8.5					
Montmo. in feed	ND	2	5	93	ND
Montmo. in eluate	ND	5	4	91	ND
Am(III) in feed	ND	3	7	90	ND
Am(III) in eluate	ND	6	9	85	ND
Np(V) in feed	41	4	4	51	ND
Np(V) in eluate	ND	7	5	88	ND

ND: Not detected.

pore volume of the column. The retardation factor is given as the ratio $V(i)/V_{\mathrm{eff}}$. At both pH, it was found that more than 70% of Am was recovered from the column. About 30% of Am was considered to be trapped by the filtration effect [12] of Am pseudocolloids and remained in the column. Our results indicate that a substantial portion of Am migrated through the column at a similar velocity as HTO at the ionic strength of 0.01 M when Am forms Am pseudocolloids (Am-bearing montmorillonite colloids). The size distributions of Am pseudocolloids and montmorillonite colloids in the feed and in the eluate determined by filtration are illustrated in Table 2. There was almost no change in the size distribution during the column experiments. These experimental results suggest that Am is stabilized by sorption on montmorillonite colloids which suppress the interaction with quartz powder. On the other hand, in the absence of montmorillonite colloids or in the experiment at the ionic strength of 0.1 M, no elution of Am was observed. Since Am is markedly sorbed on quartz powder, Am was strongly retained in the column in the absence of montmorillonite colloids. Because montmorillonite colloids are sorbed onto quartz powder and cannot migrate through the column at the ionic strength of 0.1 M, and because Am is strongly associated with the montmorillonite colloids, Am was retained in the column along with montmorillonite colloids at the ionic strength of 0.1 M.

Fig. 4 illustrates the breakthrough and recovery curves of ^{237}Np at the ionic strength of 0.01 M. It was found that approximately 30% of Np was eluted at pH = 6.0 and 50% at pH = 8.5, while no Np was recovered from the column in the absence of montmorillonite colloids or in the experiment at the ionic strength of 0.1 M. The experimental results also show that a substantial portion of Np was transported without interaction almost at the same flow velocity as HTO at the ionic strength of 0.01 M, when Np forms Np pseudocolloids (Np-bearing montmorillonite colloids). About 70% and 50% of Np at pH = 6.0 and 8.5 respectively, were considered to be retained in the column through the filtration effect of Np pseudocolloids and the sorption of ionic Np species. The total recoveries of Np were lower than those of Am. This might be explained by the large portion of non-colloidal Np (< 2 nm) in comparison with Am (Table 2).

By using the colloid migration model which we have developed [12] and with the sorption data of Am and Np cited from the literature [13,14], we tried to simulate the recovery curves from the column at the ionic strength of 0.01 M. In this calculation, we tried to fit the calculated amount recovered to that experimentally obtained by fitting the filtration coefficient. The optimal filtration coefficient was 10^{-3} m^{-1}. The calculated results at pH = 6.0 are shown in Fig. 5. The calculated curves relatively agreed with the experimental ones. However, we could not obtain the satisfied results at pH = 8.5. This is because Am

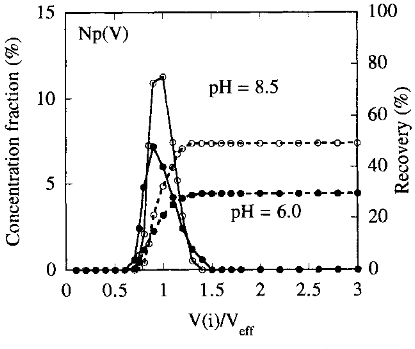

Fig. 4. Breakthrough and recovery curves for ^{237}Np(V) pseudocolloids at an ionic strength of 0.01 M.

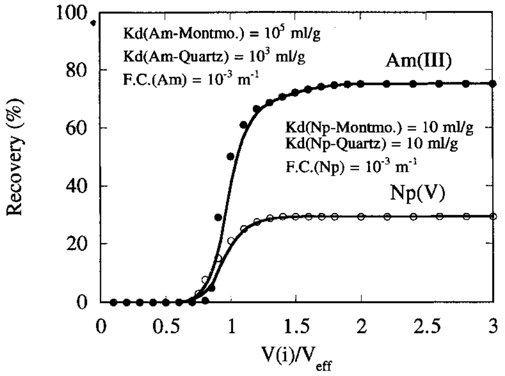

Fig. 5. Calculated recovery curves for Am and Np at pH = 6.0.

and Np show multi-species (ex. AmOH^{2+}, Am(OH)$_2^+$, Am(OH)$_3$, AmCO$_3^+$, Am(CO$_3$)$_2^-$, Am(CO$_3$)$_3^{3-}$ for Am; NpO$_2^+$, NpO$_2$CO$_3^-$, NpO$_2$(CO$_3$)$_2^{3-}$ for Np) at pH = 8.5 and the interactions are very complicated in our experimental system. In our colloid migration model, we can take the one sorption equilibrium among one species, one kind of sorption site on colloids and one kind of sorption site on the solids into account by using the sorption ratio. When one process of sorption is dominating, the concentration of the sorption sites is known, and the sorption properties are not changed by the sorption of other cations or anions, then sorption may be described by the sorption ratio. However, when several species and/or several kinds of sorption sites are involved, several sorption equilibria have to be taken into account. Therefore, in order to predict the migration behavior of actinides in natural multicomponent systems, we have to investigate very carefully all possible interactions for each species and for each sorption site in a given system. The sorption behaviors of each Np/Am species are under investigation, and the colloid migration model will be developed to take account of the multi-sorption equilibria in the near future.

4. Conclusions

- The dependence of the breakthrough behavior of montmorillonite colloid on pH and ionic strength is predicted by taking into account the van der Waals potential and the double layer potential.
- A substantial portion of Am(III) and Np(V) was found to migrate through the column when Am and Np form dispersed pseudocolloids (Am or Np bearing-montmorillonite colloids). These experimental results were compatible with the theoretical estimation by taking into account the van der Waals potential and the double layer potential.
- At pH = 6.0, the breakthrough behavior of pseudocolloids can be predicted. We have to make further effort to develop the colloid migration model in the complicated system.

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