

DIFFUSION OF PLUTONIUM IN COMPACTED BENTONITES

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ABSTRACT

The diffusivities of plutonium have been measured in water-saturated naturally occurring Na-type bentonite and hydrogenated H-type bentonite. We also have tried to estimate the values of pH and Eh of the interstitial waters in these bentonite samples.

In cases of the Na-type bentonite with packing densities ranging from 1.6 to 2.0 g/cm³, no appreciable change in plutonium profile was detected after the diffusion time up to six months. This suggests the diffusivity to be much smaller than 10⁻⁹ cm²/s. Plutonium profiles in H-type bentonite suggested that diffusion actually proceeded from the center of the column where the Pu concentration was kept constant at its solubility. The diffusivity was estimated to be (3.0-4.3) × 10⁻⁹ cm²/s. Estimated pH values were 7.9-8.2 in the Na-type bentonite and 3.1-3.2 in the H-type bentonite.

These results suggest that the most probable chemical form of Pu in the bentonites is the tetravalent PuO₂ (crystalline or less crystalline), and that the observed difference in Pu migration at different pH values has resulted from the pH dependence of the solubility of this compound.

INTRODUCTION

Plutonium is present in nuclear wastes that are expected to be disposed in a deep geologic repository. These nuclear wastes may be protected by bentonite-containing buffer materials to retard the release of radioactive nuclides into the environment. The knowledge on the plutonium diffusion in bentonite is therefore important in assessing the effectiveness of such engineered barriers. However, the determination of plutonium diffusivity is not easy since the plutonium can assume various chemical forms at different oxidation states and the chemical characterization of the interstitial water in water-saturated bentonite is not easy.

A few data have been reported on the plutonium diffusivity in bentonite. Torstenfelt et al. (1) reported a value of 10⁻¹⁰ cm²/s for plutonium in groundwater-saturated bentonite at densities of 1.9-2.0 g/cm³. Nowak (2, 3) determined diffusivities for plutonium in brine-saturated bentonite to be (1-2) × 10⁻⁹ cm²/s at a density of 0.9 g/cm³ and (0.1-3) × 10⁻¹⁰ cm²/s at a density of 1.8 g/cm³. In these experiments, no measurement was carried out to determine the pH and Eh of the interstitial water of the bentonite samples.

We have determined diffusivities for plutonium in pure water-saturated, naturally occurring Na-type bentonite and hydrogenated H-type one, and also tried to estimate the pH and Eh of these samples. The results will be discussed in the

light of the plutonium solution chemistry presented so far.

EXPERIMENTAL

Materials

Buffer materials used in this experiment are Kunipia produced by Kunimine Industry Co., which was determined to be almost pure Na-montmorillonite by the X-ray diffraction analysis, and the hydrogenated Kunipia that was prepared by washing with 2 M HCl, drying, crushing and sieving with a 200-mesh sieve. The chemical compositions of these materials are shown in Table I. Hereafter, we describe the Kunipia as Na-type bentonite and the hydrogenated Kunipia as H-type bentonite.

In some samples, illite was mixed by 50% since montmorillonite may be changed to illite as a result of ion exchange with K⁺ in groundwater.

Apparatus

Diffusivities of plutonium were measured using cylindrical diffusion cells as shown in Fig. 1. The cell material is SUS316 stainless steel. The cell consists of two identical parts. Buffer materials are pressed into each part separately and saturated with pure water. Contact between the pure water and the buffer material was maintained through a sintered metal filter. The densities of the buffer materials were adjusted in a range between 1.6 and 2.0 g/cm³.

Plutonium tracer was supplied as a solid nitrate salt consisting of 95.3% ²³⁹Pu, 4.5% ²⁴⁰Pu and 0.2% ²⁴¹Pu. This was dissolved in a 0.5 M HCl solution to yield a plutonium

concentration of 8.37 mmol/l. The amount of 30 ul of this solution, which contains 3.55 uCi of Pu, was doped in each diffusion column.

TABLE I
Chemical Compositions of Buffer Materials

	Kunipia*	HCl washed +	Illite ++
SiO ₂	55.68	58.29	51.22
TiO ₂	0.23	0.12	0.53
Al ₂ O ₃	19.96	20.45	25.91
Fe ₂ O ₃	1.95	3.71	6.29
MnO	0.01	0.003	
MgO	3.64	3.14	2.84
CaO	0.41	0.08	0.16
Na ₂ O	3.22	0.26	0.17
K ₂ O	0.07	0.035	6.09
H ₂ O	14.23	12.27	8.59

*This is called Na-type bentonite in this paper.
 + This is called H-type bentonite in this paper.
 ++ Pennsylvania underclay, near Fithian, Ill., USA
 (11)

Measurement of Diffusivities

After water saturation was completed, the plutonium tracer solution was doped onto the surface of the buffer material in one half of the diffusion cell and assembled with the other half as shown in Fig. 1. Plutonium tracer was thus allowed to diffuse in the column towards both ends from the center. The temperature was maintained at 25 °C or 60 °C.

After time intervals ranging from 28 to 190 days, all of the columns within the cells were sectioned and analyzed to determine the final concentration profiles of plutonium. As shown in Fig. 2, both of the end plates are disassembled and a guide for extrusion is attached to one end. Sectioning was accomplished by forcing a column out of its diffusion cell in 0.5-2 mm increments and cutting off each exposed section with a sharp blade. The position of each section was calculated from the weights of the slices. The radioactivity of plutonium was then counted by a ZnS scintillation counter applied to the exposed end of the column. The detection limit for ²³⁹Pu of this method was about 2x10⁻⁸ mol/l.

The resulting radioactivity profiles were fitted to the solutions of the one-dimensional diffusion equation to estimate the apparent diffusivity of plutonium. As will be shown later, it was estimated that the plutonium concentration at the center of the column had been kept constant at its solubility. The theoretical relationship to describe such a situation is:

Eq. (1)

where x is the distance from the center, t the diffusion time, C the plutonium concentration, C₀ the plutonium

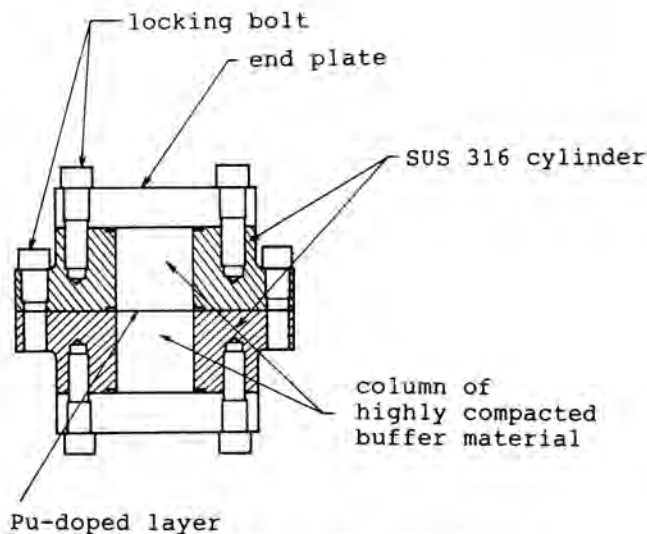


Fig. 1. Buffer Material Diffusion Column Assembled in SUS 316 Diffusion Cell.

solubility, and D denotes the apparent diffusivity.

Estimation of pH and Eh in Buffer Materials

Direct measurement of pH and Eh in the compacted bentonite is very difficult. So we have estimated the by measuring the values of pH and Eh of the clay suspensions as a function of the water-clay ratio, Mw/Mc, and ex-

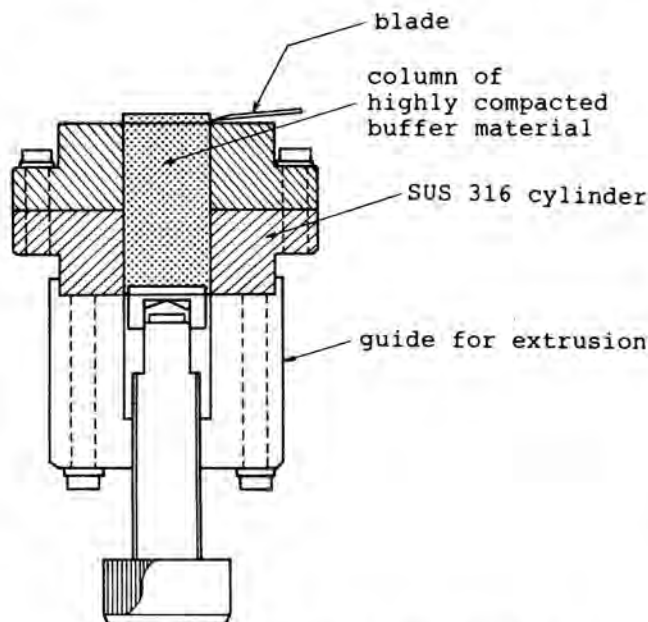


Fig. 2. Technique for Cutting Slices of Buffer Material to Measure Plutonium Radioactivity Profiles.

trapolating them to $Mw/Mc = 0.2$, which is a typical value for compacted bentonites. When $Mw/Mc > 20$, the suspension has fluidity and the pH and Eh could be measured with a usual combination glass electrode and a combination platinum electrode. The platinum electrode was allowed to equilibrate with the samples for about an hour. The suspensions of Na-type bentonite with $Mw/Mc < 20$ were very pasty and the pH was measured with a needle-like combination glass electrode. The clay and water were mixed by kneading in a polyethylene bag and allowed to become homogenized for 24 hours before measurement.

RESULTS AND DISCUSSION

Apparent Diffusivities for Plutonium

The results are summarized in Table II. A radioactivity profile in the column of the H-type bentonite with a packing density of 2.0 g/cm^3 is shown in Fig. 3. The diffusion time and temperature were 189 days and 60°C , respectively. Apparently the diffusion of plutonium occurred in this column. But the profile is not bisymmetric, though the diffusion should proceed bisymmetrically in this column, where plutonium was doped, coming to contact with the inner wall of the diffusion cell when the column was forced out of it.

Figure 3 also shows that the activity at $x = 0$ is much higher than expected from the extrapolation from the values at $x < 0$. This fact and the other profiles suggest that a part of the doped plutonium still remained undissolved and that the concentration of plutonium at $x = < 0$ may be kept constant at its solubility in the H-type bentonite.

The apparent diffusivity for plutonium estimated by the best fit of Fig. 3 to the curve of Eq. (1) is $4.3 \times 10^{-9} \text{ cm}^2/\text{s}$. The 1:1 mixture of the H-type bentonite and quartz sand gave similar diffusivities at 25°C , as shown in Table II.

Figure 4 shows a radioactivity profile in the column of the Na-type bentonite with a packing density of 1.2 g/cm^3 . the diffusion time and temperature were 189 days and 60°C , respectively.

Apparently, there is no significant elevation in radioactivity in the column except at $x = 0$, where the radioactivity is very high. The other columns of the Na-type bentonite or the mixture of the Na-type bentonite and quartz or illite showed similar profiles as in Fig. 4. This suggests two possibilities. One is that most of the doped plutonium remained as a solid with a solubility smaller than the detection limit of

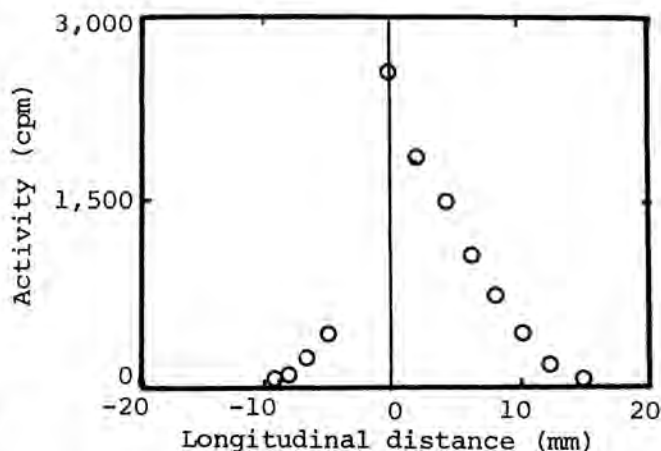


Fig. 3. Plutonium Radioactivity Profile in the H-type Bentonite Column. Packing Density is 2.0 g/cm^3 and the Temperature was 60°C .

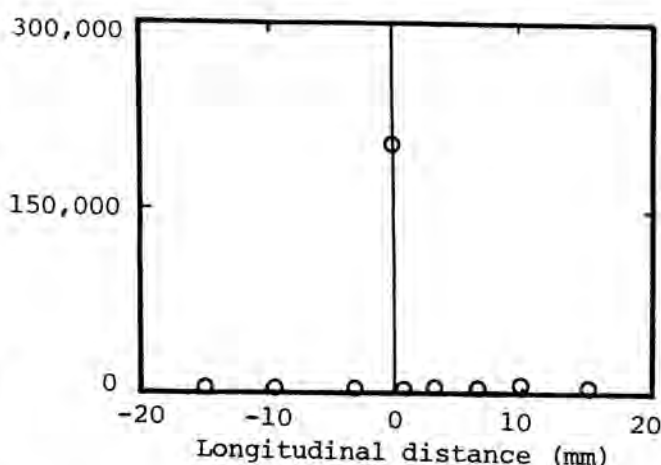


Fig. Fig. 4. Plutonium Radioactivity Profile in the Na-type Bentonite Column. Packing Density is 1.2 g/cm^3 and the Temperature was 60°C .

TABLE II

Apparent Diffusivities for Plutonium

Material	Packing density g/cm^3	Temperature $^\circ\text{C}$	Diffusion time days	Diffusivity cm^2
H-bent/Quartz *	1.6	25	36	3.1×10^{-9}
H-bent/Quartz *	1.6	25	36	3.0×10^{-9}
H-bentonite	2.0	60	189	4.3×10^{-9}

* 1:1 mixture of the H-type bentonite and quartz sand.

the scintillation counter. The other possibility is that the plutonium mostly or partly dissolved and began to diffuse at $x = 0$ but with an extremely small diffusivity. This problem will be resolved later with the aid of the pH and Eh analysis of the bentonite.

pH and Eh in Buffer Materials

In the diffusion experiments, the plutonium tracer that was dissolved in a 0.5 M HCl solution was doped into the bentonite column. It is therefore necessary to examine the effect of the presence of HCl on the pH of the interstitial water. The amount of the tracer solution doped was 30 μ l, which implies that the HCl added is 15 μ mol. The amount of the bentonite in a diffusion cell is 20 g when the packing density is 1.6 g/cm³. The cation exchange capacity of the Na-type bentonite is about 0.1 mmol/g (4). So the H⁺ added would be almost completely exchanged with Na⁺ in the Na-type bentonite and it would be negligible compared with the amount of exchangeable H⁺ in the H-type bentonite. Hence, the effect of HCl in the tracer solution on the pH of the buffer materials is not important.

Figure 5 shows the pH and Eh of the H-type bentonite suspension as a function of the water-clay mass ratio Mw/Mc. The suspension was prepared using distilled and ion-exchanged water. The value of pH gradually decreases with the decrease of Mw/Mc, approaching to 3.2 at Mw/Mc = 1. It is considered that more and more protons come to be released as the percentage of the H-type bentonite increases in the suspension. The Eh increased with the decrease of Mw/Mc. This tendency is explained from the change in pH by the pH dependence of Eh describe by:

$$Eh = Eh_0 - 0.059 \text{ pH} \quad \text{Eq.(2)}$$

The Na-type bentonite suspension showed a different tendency from the H-type one. Figure 6 shows that as the water-clay mass ratio decreases from 10⁴ to 10², the pH of the Na-type bentonite suspension sharply increases from 7 to 10, and with a further decrease in Mw/Mc it decreases back to 8.2 at Mw/Mc = 1. The change in Eh well corresponds to the change in pH.

The use of a needle-like pH electrode in measuring the pH of pasty suspensions with Mw/Mc < 20 may be responsible for such a difference in the water-clay mass ratio dependence of the pH observed at small values of the ratio. This possibility was examined by separating the interstitial water of samples with 7 < Mw/Mc < 20 by a high speed centrifugation at 15,000 rpm for an hour and measuring the pH with a usual combination glass electrode. This measurement gave similar pH values as the needle-like electrode, though a little higher by about 0.2. The observed decrease in pH at small water-clay ratio is thus believed to be definite. But the reason is left to be examined.

The pH of the illite suspension gradually decreased from 7.6 at Mw/Mc = 100 to 6.8 at Mw/Mc = 1. The quartz, when mixed with the bentonites, had negligible effects on the pH and Eh of the suspensions. The effects of temperature on the pH and Eh of suspensions were then examined. The results are that the values of pH are lower by 0.5 at 60° C than those at 25° C for both the Na- and H-type bentonites, and that Eh is lower by 70 mV for the Na-type and

higher by 30 mV for the H-type at 60° C.

The pH and Eh of water-saturated buffer materials were estimated by extrapolating the observed values to Mw/Mc = 1, though the actual value is about 0.2. The results are listed in Table III.

Chemical Compositions of Interstitial Waters

The chemical forms of plutonium compounds may be affected by the chemical species present in the interstitial water, as well as its pH and Eh, and the pH may depend on the chemical composition. Takahashi et al. (4) analyzed the chemical compositions of interstitial waters using the same bentonite samples as ours. We have determined chemical compositions at lower water-clay ratios with the same analytical procedure.

Figures 7(a) and (b) show respectively the cation and anion concentrations of the supernatant solutions separated from the Na-type bentonite suspensions as a function of Mw/Mc. It is found that the major cation is Na, its concentration being 30 mmol/l at Mw/Mc = 10, and that the major anion is SO₄²⁻, its concentration being 4 mmol/l at Mw/Mc = 10. The total amount of the cations is apparently an order of magnitude larger than the anions, meaning imbalance in ionic charge. This may be attributed to the presence of carbonate ions, and we have determined them in the supernatant solutions with a commercial TOC meter. The total carbonate concentration was 1.5 mmol/l at Mw/Mc = 10. This is too small. The problem of the imbalance in ionic charge should thus be examined further.

Chemical Form of Plutonium

Since the plutonium tracer was prepared as a 0.5 M HCl solution, the plutonium may exist as Pu(III) by 27.2 %, Pu(IV) by 58.4 %, Pu(V) by 0.8 % and Pu(VI) by 13.6 % (5). When this plutonium solution was doped into the buffer materials, the chemical forms may have changed depending on their chemical properties.

Figure 8 shows the pH-Eh diagram for plutonium (6). Two dotted areas in this figure show regions covering the

TABLE III
Estimated pH and Eh of Water-Saturated Buffer Materials at the Room Temperature

	pH	Eh
	-	(mV)
Na-bentonite	8.2	320
H -bentonite	3.2	660
Illite	6.9	290
Na-bent/illite *	7.9	440
H -bent/illite *	3.1	620

* 1:1 mixture with illite

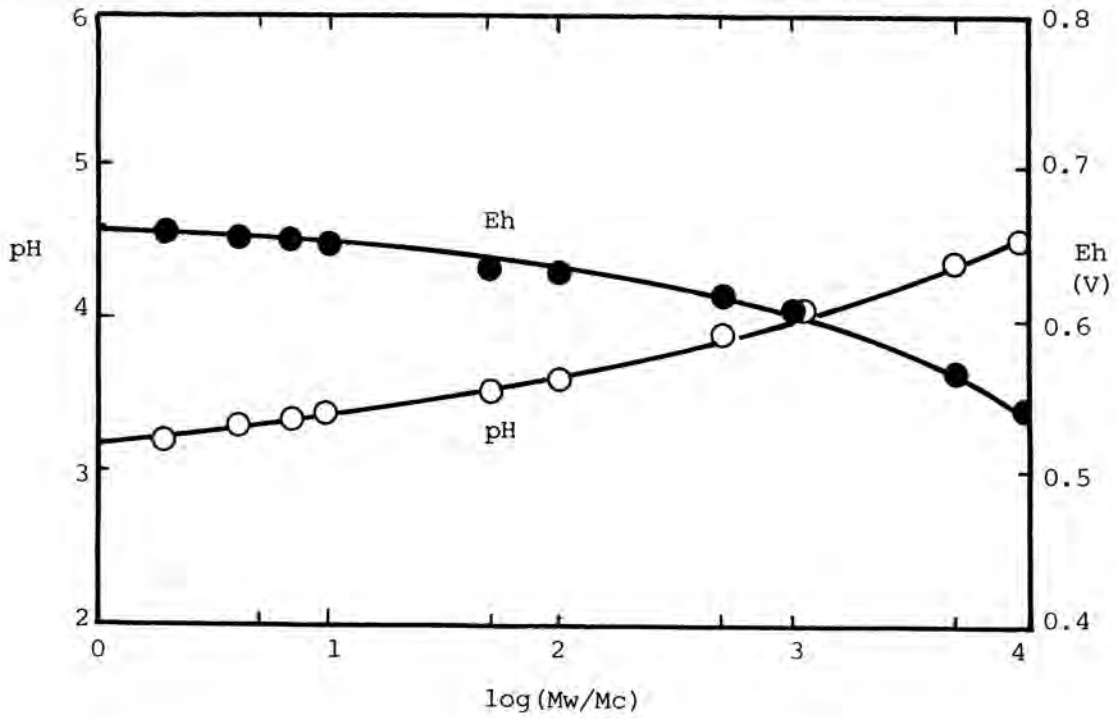


Fig. 5. The pH and Eh of the H-type Bentonite Suspensions as a Function of the Water-Clay Mass Ratio Mw/Mc.

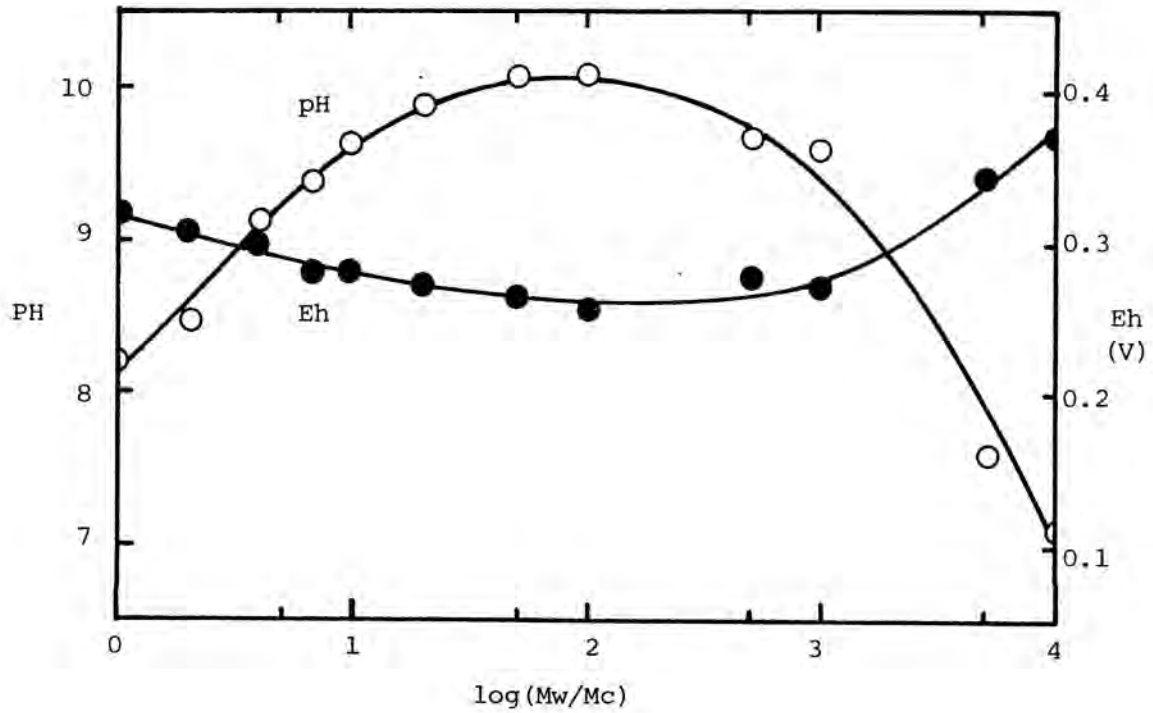


Fig. 6. The pH and Eh of the Na-type Bentonite Suspensions as a Function of the Water-Clay Mass Ratio Mw/Mc.

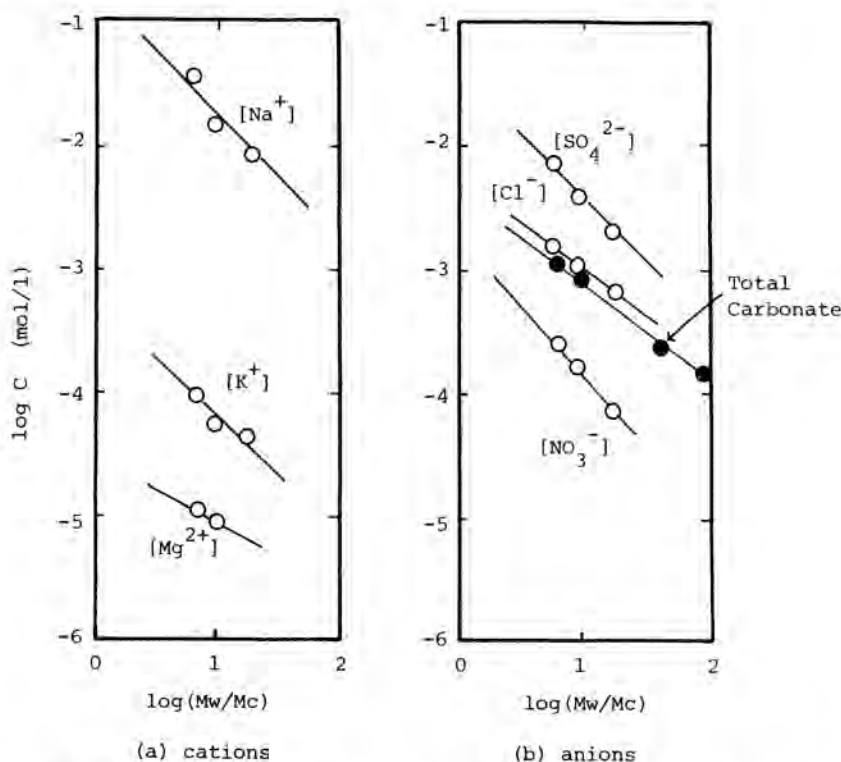


Fig. 7. Cations and anions concentrations of the supernatant solutions separated from the Na-type bentonite suspensions as a function of the water-clay mass ratio Mw/Mc.

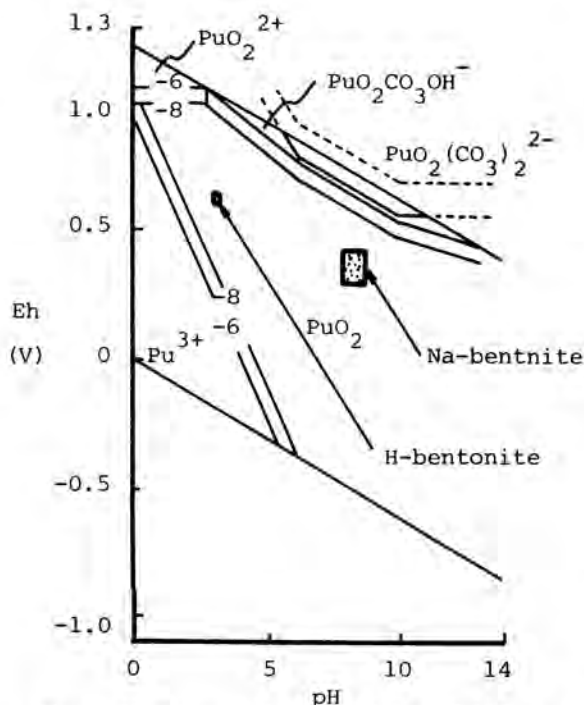


Fig. 8. The Eh-pH Diagram of Pu-C-O-H System at the Standard State (6).

pH and Eh values of the water-saturated Na- and H-type compacted bentonites. Both the areas lie in the region of PuO₂. It is also found that carbonate ions contained in the Na-type bentonite would unlikely form complexes with plutonium.

The solubility of PuO₂ was extensively investigated by many workers; for example, Rai et al. (7), Rai (8) and Ewart et al. (9), which cover a wide range in value of pH. Figure 9 shows a summary of these investigations. Plutonium(IV) can exist as the crystalline PuO₂(c) or amorphous Pu(OH)₄(am). These two have different solubilities, which strongly depend on the pH of solution as shown in Fig. 9.

Rai and Ryan (10) investigate the aging process of ²³⁹PuO₂(c) and ²³⁹PuO₂xH₂O(am) over a period of 1,300 days and found that both the compounds converted to PuO₂(1c; 1c = less crystalline) and hence had similar solubilities. If a similar process had proceeded in our experiments, the plutonium in the bentonites existed as PuO₂(1c). The solubility of PuO₂(c) is about 1x10⁻⁶ mol/l at pH = 3.2, a value for the H-type bentonite, and it is about 7x10⁻¹⁰ mol/l at pH = 8.2, a value for the Na-type bentonite. The solubilities of PuO₂(1c) may be a little larger than those values.

The diffusion experiments using the H-type bentonite showed that the radioactivity at the source seemed to be kept constant at the solubility, with an activity of about 1,000-2,000 cpm. This value may be converted to the plutonium concentration of (2-4)x10⁻⁴ mol/l. This is a concentration of the total plutonium, covering both the

dissolved and adsorbed forms. Suppose that the concentration of the dissolved plutonium is equal to the solubility, the above calculation implies that the adsorbed plutonium is about two orders of magnitude higher in concentration than the dissolved one. This means that the retardation factor is of the order of 100, and that the diffusivity for plutonium corrected for the adsorption onto the clay may be of the order of 10^{-7} cm²/s. This is not necessarily unrealistic.

In the case of the Na-type bentonite, the solubility estimated above is very small and it is understandable that changes in plutonium profile with time could not be traced by the present method.

Thus, the above estimation of the form of plutonium in the buffer materials seems consistent with the results of the present diffusion experiments.

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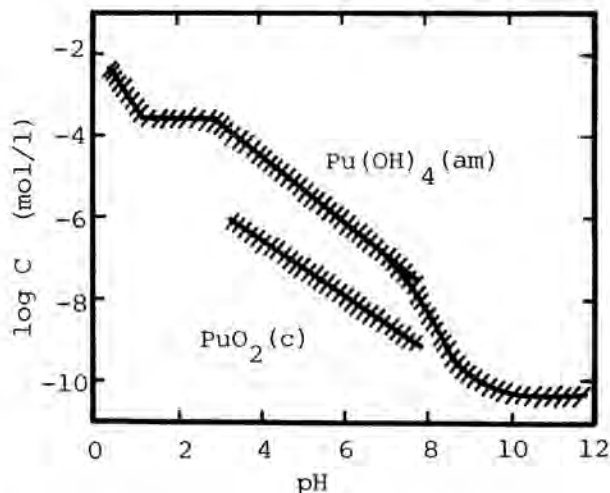


Fig. 9. Solubility of PuO₂(c) and Pu(OH)₄(am) as a function of pH. Data are compiled from the literature (7, 8, 9). Hatching shows scatter of the data.

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