PLUTONIUM DIFFUSIVITY IN COMPACTED BENTONITE

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PLUTONIUM DIFFUSIVITY IN COMPACTED BENTONITE

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要　旨

本論文は，1988年10月5〜7日にスウェーデンのルンドで開催された「高レベル廃棄物処分場のための粘土系人工バリア」の会議（SKB[***]主催）で発表したものである。

目的　水で飽和した圧縮ベントナイト中のプルトニウムの拡散係数を測定する。

方法　直径20 mm，高さ20 mmの円柱試験中にプルトニウムを約1カ月間拡散させ，その濃度分布から拡散係数を算出した。用いた材料は，山形県月布産，青森県黒石産のベントナイトである。月布産ベントナイトは更に(1)無処理，(2)精製物（Na-型），(3)塩酸処理物（H-型）に分けられた。H-型はNa-型に比べpH・膨潤圧が低く拡散係数が大きくなると予想され，試料中の濃度分布を測定するのに都合が良いので標準試料として用いた。試料のバルク密度は1200〜1800 kg/m^{3}である。

結果　試料中のプルトニウム濃度分布は一定濃度源からの拡散で説明できた。得られた拡散係数は，$10^{-13} \sim 10^{-12}$ m^2/s（H-型，黒石産），10^{-14} m^2/s以下（Na-型，月布産）であった。H-型ベントナイト中の拡散係数は，バルク密度の上昇と共に減少する傾向があるが，石英砂（50％まで）とヘマタイト（1％まで）の混合による影響は認められなかった。

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ABSTRACT

Measurement on plutonium diffusivity in water-saturated compacted bentonite was carried out. Representative specimens of sodium bentonite were taken from Tsukinuno and Kuroishi mines situated in northeast Japan. Tsukinuno bentonite was divided into three types; raw type, purified Na-type, and H-type which was prepared by treating Na-type bentonite with hydrochloric acid. Kuroishi bentonite contained chlorite as impurity. H-type bentonite was used as reference for the convenience of profile measurement in bentonite, since plutonium diffusivity in H-type bentonite was considered to be larger than that in Na-type bentonite because of low pH and low swelling pressure of H-type bentonite.

Sampled bentonite was compacted into pellet of 20 mm in diameter and 20 mm in height. Bulk densies of these specimens were 1200 to 1800 kg/m^3 for purified Na-type and H-type bentonite and 1600 kg/m^3 for raw type bentonite.

Plutonium profiles obtained in H-type bentonite can be explained by diffusion equation with constant concentration source. Diffusivity ranges from 10^{-13} to 10^{-12} m^2/s for H-type and Kuroishi impure sodium bentonite. Diffusivity in both raw type and purified Tsukinuno bentonite was estimated to be less than 10^{-14} m^2/s. Diffusivity in H-type bentonite showed a tendency to decrease with increasing density. Influence of

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quartz and hematite contents in bentonite was also studied. Quartz content up to 50% or hematite content up to 1% did not influence diffusivity significantly in H-type bentonite.

The chemical species of plutonium in pore water of Na-type and H-type were estimated $Pu(OH)_3^+$ and PuO_2^+ respectively.

INTRODUCTION

Compacted bentonite has been proposed as a suitable backfill material for vitrified high-level waste disposal (KBS, 1978). Diffusion is usually the predominant mass transport mechanism in materials that contains swelling clays or minerals because of their low water conductivity. Diffusion is expected to be slow, since the porosity of the clay is low and many radionuclides are strongly sorbed on the clay. Diffusion of plutonium has been studied in four kinds of bentonite with diffusion cell (Trestenfelt et al., 1982), in which diffusion take place axially from the surface where two compacted bentonite cylinders were connected.

EXPERIMENTAL

Specimens of sodium bentonite were selected for representative from Tsukinuno and Kuroishi mines situated in northeast Japan. Three types of Tsukinuno bentonite were prepared: raw type, purified Na-type, and H-type which was produced by treating Na-type bentonite with hydrochloric acid. Kuroishi bentonite was raw type and contained chlorite as impurity. Composition of bentonites used in these experiments are shown in Table 1. A remarkable feature of H-type bentonite is its lower sodium content than others. It means that sodium ions were substituted by H ions. Kuroishi raw bentonite had higher potassium, magnesium and iron content than others. Magnesium and iron might be contained as chlorite. High potassium content means that Kuroishi raw bentonite might be metamorphosed.

Since diffusivity in Na-type might be too slow to obtain distinct profile, H-type bentonite was used as reference for convenience of profile measurement.

Plutonium tracer used in this experiment was aqueous solution of Pu(IV) in 0.1 to 1.0 M HCl. Concentration of plutonium was 3.3×10 Ci/m^3 (2 gPu/m^3).

Cylinders of bentonite were prepared in cylindrical diffusion cells which were composed of coupled stainless steel columns shown in Figure 1.

This design is similar to the one reported Torestenfelt et al. (1982), but cells used in these experiments include no polymeric seal material. Bentonite was isostatically pressed into the diffusion cell. Densities of these specimens were 1200 to 1800 kg/m^3 for purified Na-type and H-type, and 1600 kg/m^3 for raw type bentonite. Water content of these bentonites was almost 10%. Two cylinders of bentonite, each 20 mm in diameter and 20 mm in height, were used for each cell. Porous discs were placed and fixed on open ends of column. Each closed cell was immersed in distilled water. Approximately two weeks were allowed for the bentonite to be saturated by water. The degree of saturation was checked by weight gain measurement.

Plutonium tracer was added into columns by disassembling the cell and placing $30 \times 10^{-9} \ m^3$ of $PuCl_4$ solution between the bentonite cylinders. Each cell was reassembled after the plutonium tracer was introduced. After time intervals in the range of 28 to 36 days at ambient temperature, all of the cylinders within the cells were sectioned. The final profiles of plutonium concentration were determined by alpha-ray counting. Sectioning was accomplished by pushing a bentonite cylinder out of its diffusion cell in approximately 1 mm increments and cutting off each exposed section with a blade. Alpha-ray from plutonium on the exposed surface was counted with ZnS(Ag) scintillation counter. The final plutonium profiles were used to calculate apparent diffusivities.

Experimental conditions are shown in the first four columns of Table 2.

Since the concentration of plutonium introduced into bentonite was much higher than solubility of plutonium in water (Allard, 1982), the resulting concentration profiles were fitted to curves derived from a theoretical relationship (Crank, 1956) that describes one-dimensional diffusion from a constant concentration source.

$$C/C_0 = \mathrm{erfc}(x/2\sqrt{Dat})$$

where:

    C = concentration of plutonium at distance x, $mole/m^3$,

    C_0 = constant concentration of the source, $mole/m^3$,

    Da = apparent diffusivity, m^2/s,

    x = distance from constant concentration source, m ,

and t = time after inroduction of the source, s.

The value of Da that yielded the best fit was chosen to characterize the concentration profile for each experimental column.

RESULTS

Alpha-activities (cpm) that represent plutonium concentrations are plotted in Figure 2 versus longitudinal distance from the center of the column. Plutonium diffusion was not observed in each column of Na-type and raw type bentonite from Tsukinuno mine. Apparent diffusivity of plutonium was estimated to be less than 10^{-14} m^2/s in these cases, on the assumption that plutonium was diffused within 1 mm of cylinder slice thickness. This value is similar to that reported by Trestenfelt et al. (1983) and Eriksen et al. (1984). In H-type bentonite, plutonium diffusion was observed, and apparent diffusivity Da = 3×10^{-13} m^2/s was chosen as the best fit. In raw type bentonite from Kuroishi mine, apparent diffusivity Da = 6×10^{-13} m^2/s was chosen as the best fit. Results for these diffusion experiments are given in fifth column of Table 2. The calculated values of apparent diffusivity were in the range 10^{-13} to 10^{-12} m^2/s in H-type bentonite. Diffusivity in H-type bentonite showed a tendency to decrease with increasing density. Influence of quartz and hematite content in bentonite was also studied. Quartz content up to 50% or hematite up to 1% did not influence plutonium diffusivity significantly in H-type bentonite.

Water chemistry in the bentonite was also studied. Oxidation potential, Eh, and pH in suspensions were measured in several ratio of distilled water and buffer materials such as purified Na-type, H-type bentonite and quartz with or without 30×10^{-9} m^3 of 0.5 M hydrochloric acid. These data were used to estimate pH and Eh in pore water of compacted bentonite. The estimated values of pH and Eh are shown in Table 3. The pH and Eh in quartz suspension were significantly influenced by adding of hydrochloric acid. The pH and Eh in purified Na-type bentonite were 8.2 and 0.31 to 0.32 V respectively and were not influenced by adding of hydrochloric acid because of chemical buffering activity of sodium bentonite. The pH and Eh in H-type bentonite were 3.2 to 3.5 and 0.66 V respectively.

We tried to estimate speciation of plutonium in compacted bentonite. The pH-Eh diagrams of plutonium (Jensen, 1982) are shown in Figure 3. Solid phase of plutonium is estimated plutonium dioxide in both purified

Na-type and H-type bentonite. Aqueous phase of bentonite in purified Na-type and H-type are estimated $Pu(OH)_3^+$ and PuO_2^+ respectively.

CONCLUSION

Apparent diffusivity of plutonium in purified and Tsukinuno raw bentonite was estimated to be lower than 10^{-14} m^2/s. This value was similar to that reported by Torestenfelt et al. Plutonium diffusivity in the range of 10^{-13} to 10^{-12} m^2/s was obtained for H-type bentonite. Distinct profiles were obtained in H-type bentonite, and were explained by diffusion equation with constant concentration source. In spite of high pH, diffusivity in raw bentonite from Kuroishi mine was similar to that in H-type bentonite. This result may be led by impurities such as chlorite.

Further work is needed to examine the influence of chemical environment such as pH, Eh and chemical species in ground water.

ACKNOWLEDGEMENTS

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Table 1　Chemical compositions of bentonites
used in Pu diffusion test

	Purified Na-type (wt%)	H-type treated with HCl (wt%)	Raw type from Tsuki-nuno mine (wt%)	Raw type from Kuro-ishi mine (wt%)
SiO_2	55.68	58.29	53.02	53.62
TiO_2	0.23	0.12	0.09	0.53
Al_2O_3	19.96	20.45	19.23	17.75
Fe_2O_3	1.95	3.71	2.90	5.68
MnO	0.01	0.003	0.02	0.02
MgO	3.64	3.14	2.51	7.43
CaO	0.41	0.08	0.74	0.89
Na_2O	3.22	0.26	2.40	1.65
K_2O	0.07	0.035	0.09	0.57
H_2O	14.23	12.27	18.67	11.54

Table 2 Experimental conditions and measured diffusivities

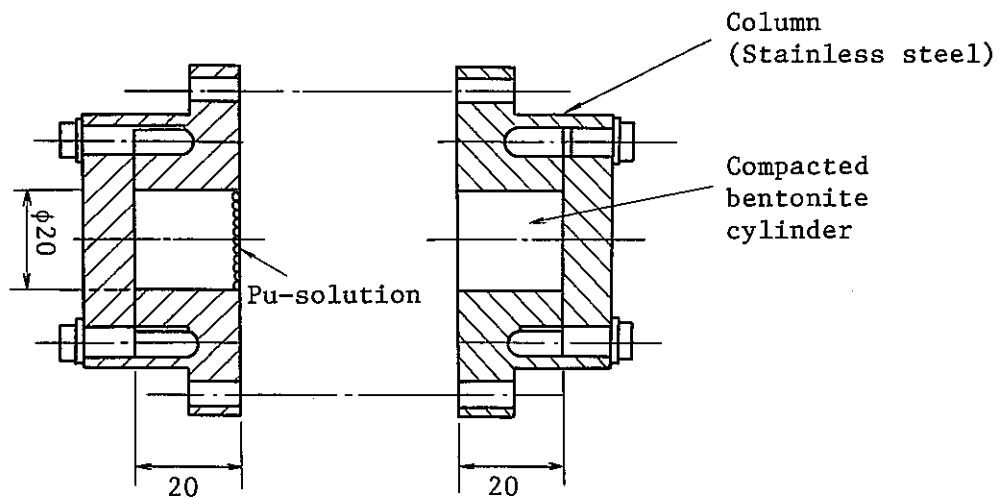| No.	Material	HCl conc. in Pu solution (M)	Packing density (Kg/m^3)	Apparent diffusivity (m^2/s)
1	Na-type	0.1	1600	– **
2	Na-type	0.5	1400	–
3	Na-type	0.5	1600	–
4	Na-type	0.5	1800	–
5	Na-type	1.0	1600	–
6	H -type	0.5	1200	7×10^{-13}
7	H -type	0.5	1400	3×10^{-12}
8	H -type	0.5	1600	3×10^{-13}
9	H -type	0.5	1800	1×10^{-13}
10	Raw type from Kuroishi	0.5	1600	6×10^{-13}
11	Na-type/Quartz(85/15)*	0.5	1600	–
12	Na-type/Quartz(70/30)	0.5	1600	–
13	Na-type/Quartz(50/50)	0.5	1600	–
14	Na-type/Quartz(30/70)	0.5	1600	–
15	H -type/Quartz(85/15)	0.5	1600	5×10^{-13}
16	H -type/Quartz(70/30)	0.5	1600	3×10^{-13}
17	H -type/Quartz(50/50)	0.5	1600	3×10^{-13}
18	Raw type from Tsukinuno	0.5	1600	–
19	H-type/Hematite(99.5/0.05)	0.5	1600	3×10^{-13}
20	H-type/Hematite(99/1)	0.5	1600	3×10^{-13}

*   Numbers in parentheses show weight percent.

** The mark, –, means less than 10^{-14} m/s.

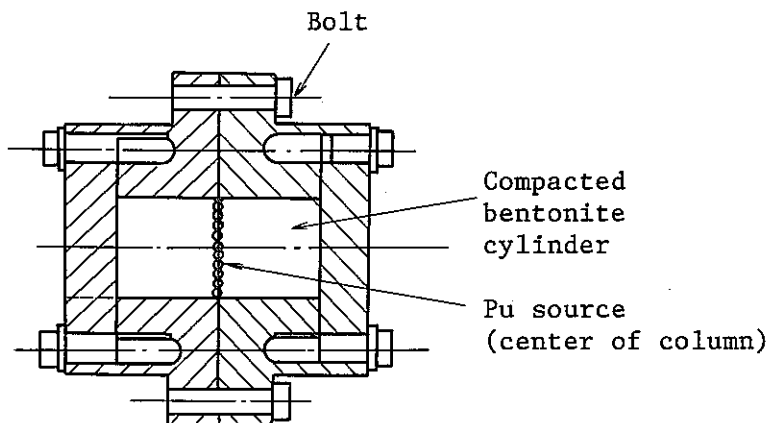Table 3 Estimated values of the pH and Eh in suspension
of buffer materials

Buffer materials		pH	Eh(V)
Na-type bentonite	not added	8.2 *	0.32 *
	HCl added	8.2 *	0.31 *
H-type bentonite	not added	3.2 *	0.66 *
	HCl added	3.5 **	0.66 **
Quartz	not added	8.6 **	0.36 **
	HCl added	2.6 **	0.74 **

    * Water/clay weight ratio is 1.

  ** Water/clay weight ratio is 10.

Column
(Stainless steel)

Compacted
bentonite
cylinder

$\phi 20$

Pu-solution

20   20

(1) Diffusion column within water-saturated bentonite

Bolt

Compacted
bentonite
cylinder

Pu source
(center of column)

(2) Assembled column

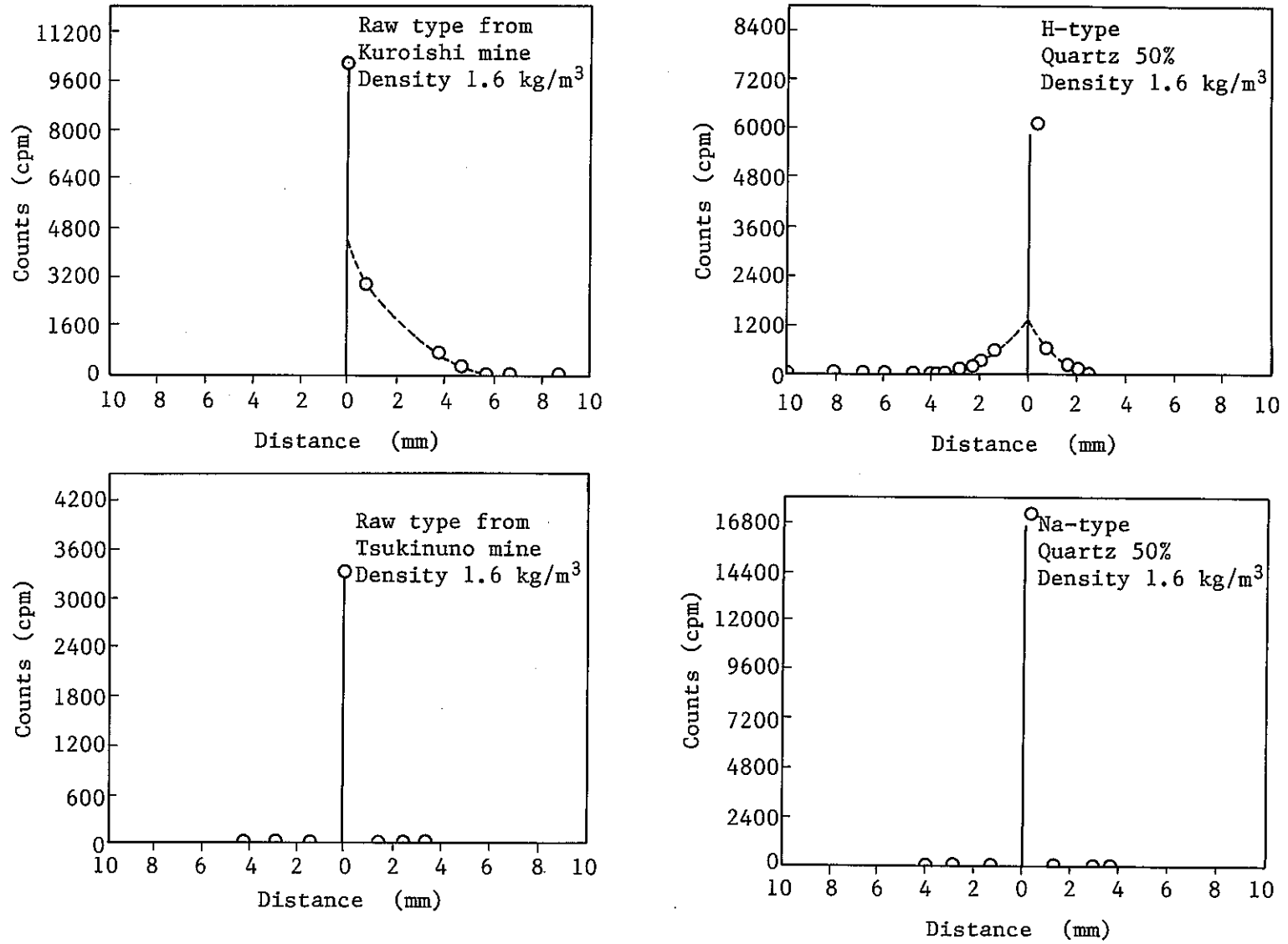Figure 1   Compacted bentonite cylinders assembled
          in stainless-steel column

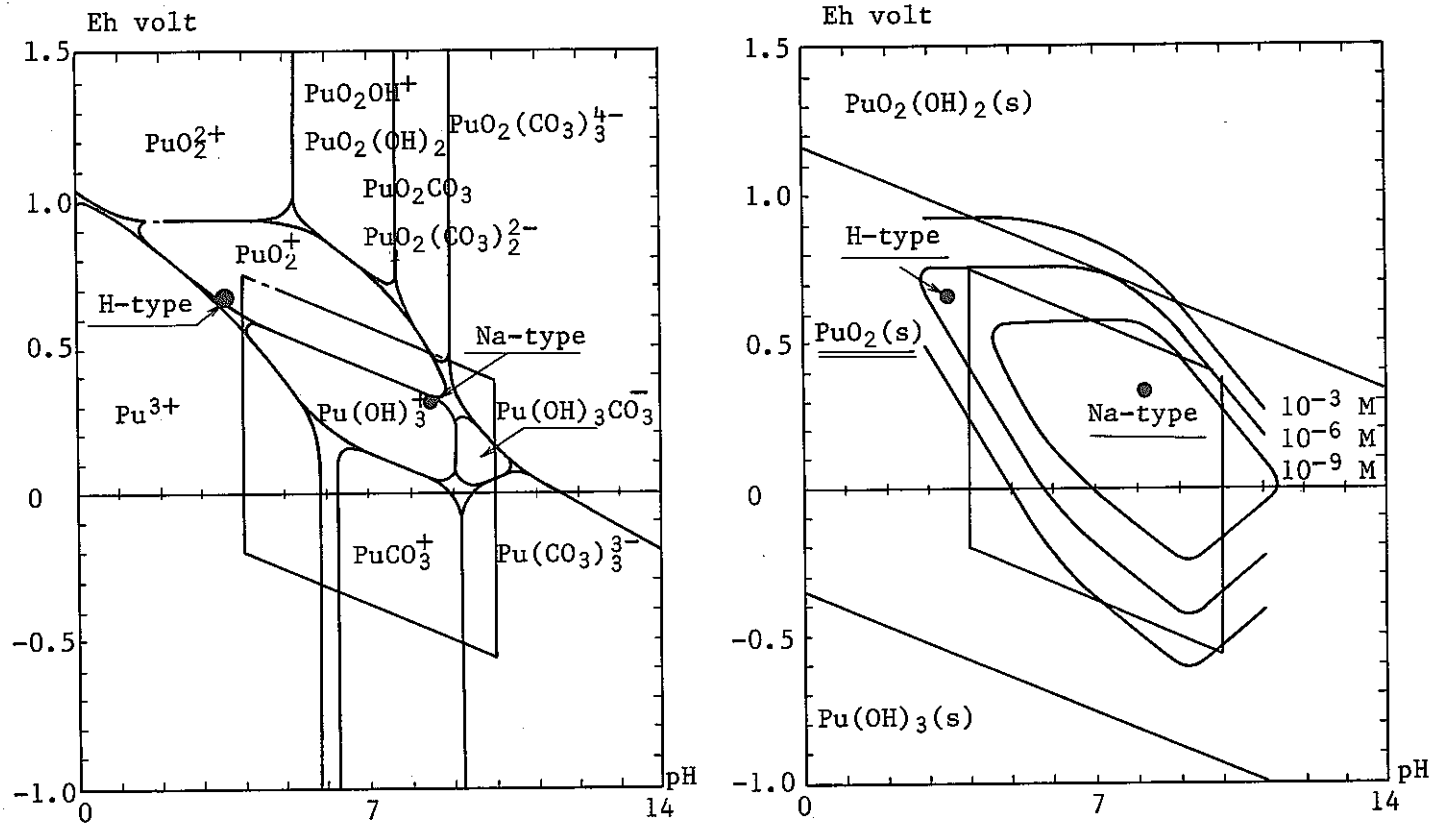Figure 2 Plutonium diffusion profiles in the bentonite cylinders

Figure 3 The pH-Eh diagrams of plutonium at $P_{CO_2} = 10^{-3.5}$ atm. (Jensen, 1982)

Left: Aqueous phase. Right: Solid phase.
Na-type and H-type in the diagram mean the conditions in purified
Na-type and H-type bentonites respectively.