Distribution Coefficients of Americium, Neptunium, and Protactinium for Selected Rocks

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(Received December 26, 1985)

Abstract

Distribution coefficients (K_D) were measured by a batch technique for sorption-desorption of americium(III), neptunium(V), and protactinium(V) between granite, tuff, or quartz mined in Japan, and water. Measurements were performed at room temperature. The effects of the surface area, pH, and the separation method of solid and liquid phases were studied. The K_D values of americium ranged from 50 to 370000 (mL/g), depending much on the separation methods adopted due to the presence of colloidal particles of americium in solutions. The K_D values of neptunium were small (0.67–13 mL/g), and were little affected by the experimental conditions employed. Protactinium had intermediate values of K_D. The physical adsorption was suggested in the sorption experiments for americium on latex particles.

I. Introduction

High–level radioactive wastes (HLW) generated from nuclear power plants are projected to be disposed in deep-geologic repositories. A major requirement for the long-term safety assessment is a thorough understanding of the migratory behaviors of some radionuclides in geologic media. Sorption due to interactions with the geologic media is the most important factor in the retardation of nuclide transport.

The parameter most commonly used for describing the sorption is the distribution coefficient, K_D, which is defined as the ratio of the radionuclide amount per unit weight of solid to the amount per unit volume of liquid. The phenomenological coefficient K_D is controlled by various factors such as temperature, solution pH, oxidation–reduction potential, cation exchange capacity, and chemical composition of the rock and of the solution.

Actinide elements are important in the safety assessment on a disposal of HLW. The K_D values for actinide elements have not yet been reported for rocks of Japan,

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despite the fact that extensive studies have been worldwidely made[1-7].

In this work, the K_D values for Am(III), Np(V), and Pa(V) were determined by a batch technique with spikes of [241]Am or [237]Np-[233]Pa into a solution of distilled water or rock pre-equilibriated water containing crushed granite, tuff, or quartz mined in Japan. In order to study the effect on K_D by the presence of particles in solutions, different separation methods, centrifugation and filtration, were applied to separte the solid phase from the liquid phase. The effects of pH and the surface area were also examined. Sorption experiments of americium on polystyrene latex particles were made to understand sorption mechanisms.

II. Experimental

1. Materials

The rock samples used in the experiments were Inada granite, Rokko granite, Ohya tuff, Itado tuff, and Myoken quartz. Each rock was crushed to the mesh sizes of <60 and 32-60. The specific surface areas listed in Table I were measured by

TABLE I   Specific Surface Areas of Crushed Rocks used for
Sorption-desorption Experiments[8]

rock	mesh size	specific surface area (m²/g)
Inada granite	32-60	ND
	<60	0.51
Rokko granite	32-60	ND
Ohya tuff	32-60	21.75
	<60	26.75
Itado tuff	32-60	43.00
Myoken quartz	32-60	ND
	<60	0.47

ND : Not determined because of small specific surface areas

the BET method, employing nitrogen as the adsorbate[8]. It should be kept in mind that the measured values of specific surface areas might vary depending on the measurement methods adopted[2]. No other characterizations of rock samples were made. The crushed rock samples were briefly washed with distilled water to remove dust.

The polystyrene latex particles provided by the Dow Chemical Company are tiny spheres with an extremely uniform size. The surface area is, accordingly, known exactly. Latex particles of 1.09 μm in diameter were selected for use.

Distilled water or rock pre-equilibriated water was used in the experiments. Rock pre-equilibriated water was prepared by contacting 2.5L of distilled water with 100g of crushed rock in a glass bottle for two weeks. Before use, the water was centri-

fuged at 5000rpm (4530g, g; acceleration of gravity) to remove rock particles present in the water.

Both [241]Am and [237]Np stock solutions of 0. 1N-HNO$_3$ were passed through a 0. 025μm-pore Millipore filter, and the pH was adjusted at about 7 with use of a solution of NaOH. The valence state of neptunium was identified to be +5 by the solvent extraction technique with tri-iso-octyl amine. Americium and protactinium are stable in +3 and +5 valence states, respectively, in aqueous solutions[9].

2. Procedures

The schematic diagram of the sorption experiment is shown in Fig. 1. All procedures were performed at room temperature. All solutions were treated in polypropylene tubes in order to avoid any release of, for example, silica from the vessel walls.
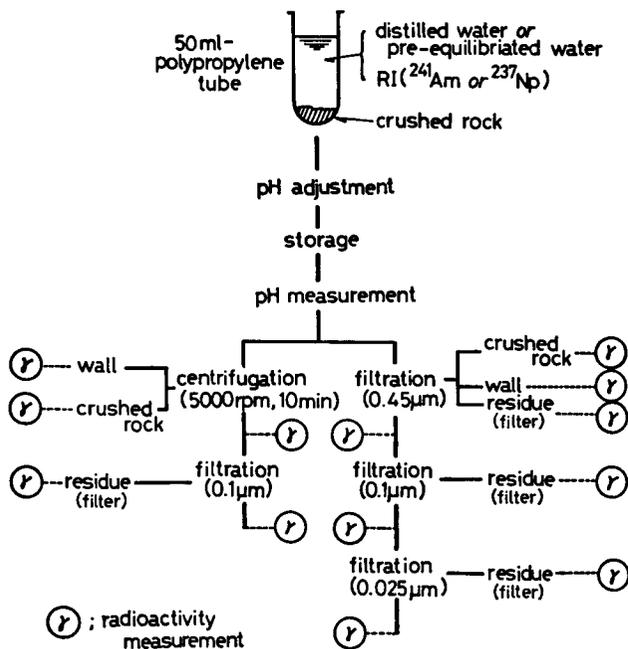

Fig. 1. Schematic diagram of the sorption experiment

Distilled water or rock pre-equilibriated water (30mL) was poured into a 50mL-centrifuge tube. Pre-equilibriated water was served for sorption-desorption experiments of americium in the Inada granite and the Ohya tuff systems. Distilled water was used in the other systems. The pH of the americium or neptunium stock solution was adjusted at about 7 by using a solution of NaOH and was added to obtain the concentrations of about 2×10^{-8}M and 1×10^{-4}M, respectively. One gram of crushed

rock, or latex particles with a total surface area of about 0.13m² was added to the solution. The pH of the mixture was adjusted by using a solution of NaOH. The tubes were sealed and were placed on a shaker for a week.

Water and crushed rock were separated either by centrifugation at 5000rpm for 10 min., or by filtration with a 0.45μm-pore Millipore filter followed by decantation. The size distributions of particles present in the liquid phase could be obtained by applying the subsequent filtrations with filters of decreasing pore-sizes of 0.1μm and 0.025μm to the filtrate obtained above. The samples including latex particles were subject only to these filtrations. Radionuclides remaining on a filter or sorbed on the vessel wall were dissolved in a 1N-HCl solution. The measurements of radioactivity in each sample were made with an intrinsic germanium detector.

Similar procedures were carried out for the desorption experiments of americium, in which distilled water was added to the crushed rock which had been separated in the sorption experiments.

III.   Results and Discussion

The results of the measurements are summarized in Table II. The K_D values of neptunium(V) and protactinium(V) are generally much smaller than those of americium(III). The K_D values of americium(III) range from 50 to 370000 (mL/g). The K_D values of neptunium(V), on the other hand, are not more than 13 (mL/g). Some results are mentioned below in more detail.

Sorption K_D and desorption K_D

The K_D values obtained from the desorption experiments are larger than those obtained from the sorption experiments. This probably shows that equilibrium in the sample solutions has not yet been established. The K_D in equilibrium may fall between both values.

The effect of separation methods

The comparison between K_D obtained by filtration (0.45μm) and that obtained by centrifugation (5000rpm, 10min) reveals that the centrifugation is not as effective as the filtration for removing particles which should be considered a part of the solid phase. Of particular interest is that the K_D values of americium(III) can be subject to vary by orders depending on the pore-size of the filter used to separate solids from liquids. It is very difficult to evaluate the true K_D values of americium because of the presence of the suspended particles. Little effect of the separation method can be observed, however, on the K_D values of neptunium(V).

In order to understand the effect of the separation method on the distribution coefficients, the distributions of radioactivities retained on each filter are shown in Fig. 2 for the sorption experiment on the Ohya tuff. Most of neptunium(V) in the liquid

TABLE II Distribution Coefficients for Americium, Neptunium, and Protactinium (mL/g)

rock	mesh size	pH	americium (^{241}Am)										neptunium (^{237}Np)			protactinium (^{233}Pa)		
			sorption					desorption					sorption			sorption		
			F_1	F_1+F_2	$F_1+F_2+F_3$	C	$C+F_2$	F_1	F_1+F_2	$F_1+F_2+F_3$	C	$C+F_2$	F_1	F_1+F_2	$F_1+F_2+F_3$	F_1	F_1+F_2	$F_1+F_2+F_3$
Granite Inada	32—60	~7	—	—	—	220	13000	—	—	—	3000	3700	1.3	1.4	1.7	2.5	3.3	6.2
		~11	1100	7700	7700	—	—	2100	12000	18000	—	—	3.3	3.5	3.7	2.4	5.6	7.3
	<60	~7	2700	9000	17000	430	43000	15000	74000	370000	5800	58000	—	—	—	—	—	—
Rokko	32—60	~7	—	—	—	2400	25000	—	—	—	3300	13000	—	—	—	—	—	—
Tuff Ohya	32—60	~7	—	—	—	98	1400	—	—	—	600	1600	3.5	3.3	3.5	1.5	40	52
		~11	50	1700	3600	—	—	440	6400	6400	—	—	13	12	13	3.4	42	65
	<60	~7	200	580	630	130	—	780	2000	2200	640	2300	—	—	—	—	—	—
Itado	32—60	~7	—	—	—	9300	23000	—	—	—	4400	—	—	—	—	—	—	—
Quartz Myoken	32—60	~7	—	—	—	220	1900	—	—	—	460	5700	0.67	0.73	0.92	0.61	6.5	16
		~11	—	—	—	22	350	—	—	—	92	1100	2.2	2.8	3.3	0.37	4.4	21
	<60	~7	4200	4200	4200	1300	18000	17000	17000	130000	12000	43000	—	—	—	—	—	—

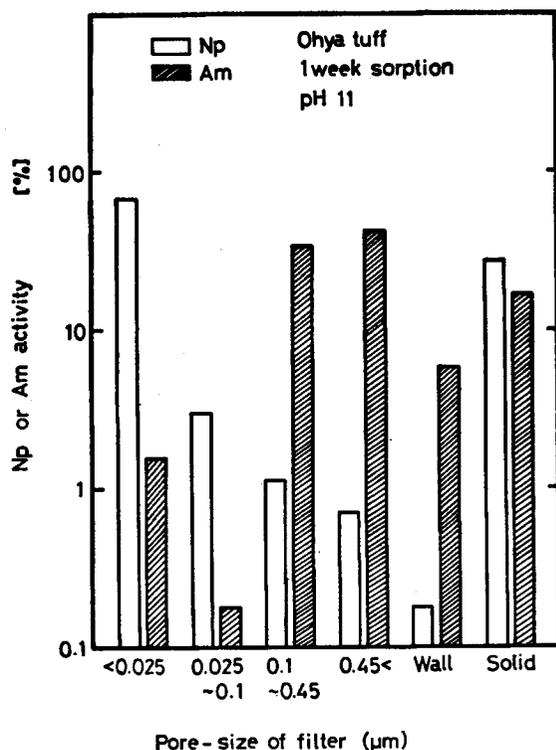F_1: 0.45μm filter, F_2: 0.1μm filter, F_3: 0.45μm filter, C: Centrifuge (5000rpm, 10min)

Fig. 2. Distribution of americium and neptunium in sorption experiments on Ohya
tuff. pH 11; equilibriation time 1 week; [Am] 2×10^{-8}M; [Np] 1×10^{-4}M.

phase is present in the fraction of $<0.025 \mu$m in sizes, which are likely to be mono-
mers. On the other hand, americium(III) has a wide range of particle sizes.

A very similar size distribution of particles was also obtained from the blank test,
to which no adsorbent was added[10]. The result of the blank test showed that pseudo
colloids of americium(III) were formed with iron which were present at a trace
quantity in distilled water. Thus, the fact that the K_D values of americium(III)
depend much on a pore-size of filter might be caused by colloidal particles of ameri-
cium(III) rather than by small particles of crushed rock.

The effect of surface area

It is interesting to note that a difference in surface areas is accompanied by a
difference in K_D values. This fact suggests that the distribution coefficient should be
defined with the surface area of the solid phase, not with its weight.

The possibility that adsorption may be limited on the surface of a solid phase
was examined by sorption experiments on americium(III), using distilled water and
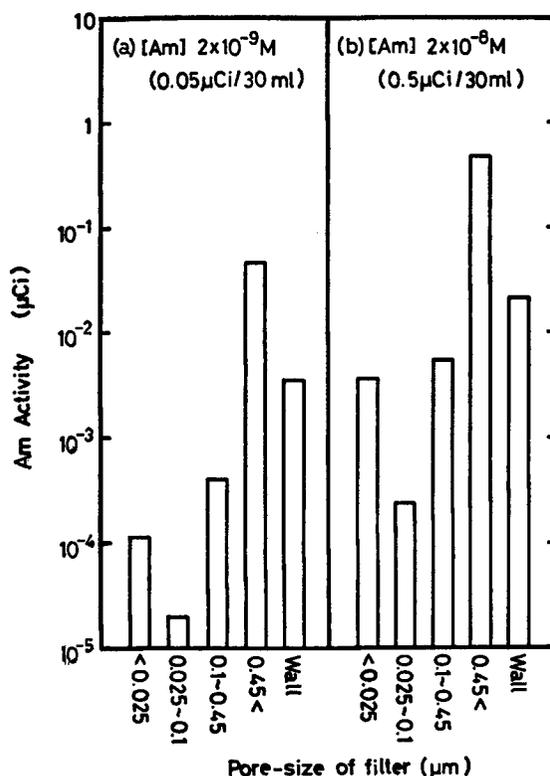latex particles. Figure 3(a) and (b) shows the distibutions of americium(III) obtained

Fig. 3. Distribution of americium in a distilled water–latex particle system. pH 7; equilibriation time 1 week; [Am] (a) 2×10^{-9}M, (b) 2×10^{-8}M.

by the sequential filtrations, in which the initial concentrations of americium(III) were 2×10^{-9}M and 2×10^{-8}M, respectively. The latex particles are present in the $>0.45 \mu$m fraction. Most of the radioactivity in the $>0.45 \mu$m fraction comes from americium (III) sorbed on the latex particles. The surface areas of latex particles per sample and the inner wall of the vessel are about 0.13m² and 0.005m², respectively. The ratios of the amounts of americium(III) sorbed on the two surfaces are about 14 and 22 in Fig. 3(a) and (b), respectively, which are close to the ratio of the two surface areas of 26. The proportionality between the amount sorbed and the surface area suggests the surface adsorption of americium(III). In addition, the sorption on the non–electrolytic adsorbents (polystyrene and polypropylene) may occur physically rather than electrostatically.

The K_D values of neptunium and protactinium

Although the K_D data on neptunium are scarce, the values are generally smaller than those for other actinide elements. The same tendency is observed in this work.

The K_D values of neptunium are small also for basalt, as observed in the sorption experiments with synthetic groundwater carried out by Ames and McGarrah[5]. Their results show that the K_D values of neptunium are little affected by such experimental conditions as temperature, equilibration time, and solution-solid ratio. The results of this work show that the difference in the separation method also little affects the K_D. It should be noted, however, that the concentration of neptunium in this work is, probably, as high as the solubility limit, although data on the solubility are limited at present. If the concentration exceeds the solubility limit, the measured K_D values reflect not only sorption but also precipitation. Precise experiments are required, in which the solubility limit is taken into account.

The K_D values of protactinium are also much smaller than those of americium (III), and are little affected by the experimental conditions adopted.

IV. Conclusion

The distribution coefficients of americium(III), neptunium(V), and protactinium (V) for some selected rocks were determined by a batch technique with spikes of ^{241}Am and ^{237}Np. The K_D values of neptunium(V) and protactinium(V) were far smaller than those of americium(III).

The K_D values of americium(III) depend much on the methods used to separate the solid phase from the liquid phase. The difficulty results from the presence of colloidal particles of americium(III) in solutions. A thorough understanding is needed about the stability and migratory behaviors of the colloidal particles. As suggested from the results of the sorption experiments of americium(III) on latex particles, the sorption of actinide elements is possibly limited on a surface of solid phase.

The K_D values of neptunium(V), which is one of the most important nuclides for a long-term safety assessment on disposal of HLW, are not so much affected by the difference in the separation methods. No rock was found that has a strong sorptivity for neptunium(V).

V. Acknowledgements

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