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Sorption Characteristics of Actinium and Protactinium onto Soils

Yoshiaki, SAKAMOTO*[1], Tomoaki, ISHII[2], Satoru, INAGAWA[3], Yasuyoshi, GUNJI[2], Shinichi, TAKEBE[4], Hiromichi, OGAWA[1], Tomozo, SASAKI[5]

1.Japan Atomic Energy Research Institute, Department of Fuel Cycle Safety Research, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195 Japan

2.Nuclear Fuel Industries, LTD., Environmental and Safety Management Department, 3135-41, Muramatu, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1196 Japan

3.Nuclear Fuel Industries, LTD., Technical Development Department, 950, Noda, Kumatori-cho, Sennan-gun, Osaka-fu, 590-1195 Japan

4. Japan Atomic Energy Research Institute, Office of Radioactive Waste Management, 14-1, Suehiro-cho, Kashiwa-shi, Chiba-ken, 277-0842 Japan

5.Radioactive Waste Management Funding and Research Center, Research Division of Shallow land Disposal, 2-8-10, Toranomon, Minato-ku, Tokyo, 105-0001 Japan

Sorption behavior of ^{227}Ac and ^{233}Pa onto several kinds of soil has been studied by a batch sorption experiment and a sequential extraction technique. The sorbed form of ^{227}Ac was mainly fractionated into a lattice-bound form in the soils, which suggests strong binding with a crystalline phase in the soils. On the other hand, most of ^{233}Pa was fractionated into an association with amorphous Fe+Mn oxides in the soils. In addition, a linear relationship between the Kd values of ^{233}Pa and the content of iron oxides in the soils was found. From these results, it was concluded that ^{227}Ac and ^{233}Pa are irreversibly sorbed to the crystalline phase and amorphous Fe+Mn oxide in the soils, respectively. Carbonate concentration dependence of the Kd values of ^{227}Ac and ^{233}Pa on soil was also studied to evaluate the influence of groundwater composition on the sorption behavior. The Kd values of ^{237}Ac and ^{233}Pa increased with increasing carbonate concentration because of the formation of carbonate complexes of ^{237}Ac and ^{233}Pa to be irreversibly sorbed on the soil surface.

Keywords: sorption/actinium/protactinium/soil/sequential extraction/irreversible sorption/

I. Introduction

Most of uranium bearing waste arising from uranium fuel fabrication plants will be disposed of into a shallow land disposal facility in Japan[1]. For safety assessment of the disposal system of the uranium bearing wastes, it must be considered that groundwater can penetrate the repository through time and uranium series radionuclides released from the repository to the biosphere. For this reason, sorption/migration behavior of uranium series radionuclides under the shallow land condition is important. In previous works[2,3,4], the basic sorption behavior of Pb, Ra, Ac, Th, Pa, U on Japanese soils have been studied to obtain the distribution coefficients(Kd values). In these studies, the complex sorption behavior of Ac and Pa on soils has been pointed out because of the complex chemical behavior in the groundwater.

The sorption behavior of Ac was investigated by Lieser et al. who showed cation exchange reaction to be important at low pH and chemi-sorption reaction at neutral pH[5]. The sorption behavior of Pa was studied from the point of view of colloidal formation of Pa by Berry et al.[6]. However, detailed information about the sorbed forms of Ac and Pa is needed to obtain reliable Kd values for Japanese soils to be used for the safety assessment of the disposed uranium bearing waste.

Groundwater composition is influencing the sorption behavior of Ac and Pa, because pH and anions in groundwater will affect the sorption/migration behavior in the geosphere due to changes of chemical forms of transuranium elements by complexiation and hydrolysis reactions. The pH dependence of Ac and Pa sorption on loam and sand have been studied in previous work to show the relationship between the Kd values and chemical forms in solution[3,4]. However, the influence of anion ligands, such as carbonate, in groundwater on the sorption behavior of Ac and Pa on soils has not been described yet.

In this work, the Kd values of ^{227}Ac and ^{233}Pa on five kinds of soils have been measured by a batch method. At the end of the sorption experiment, the sorbed forms of ^{227}Ac and ^{233}Pa have been studied by a sequential extraction technique of the soils. The Kd values of ^{227}Ac and ^{233}Pa on soil were also measured as a function of carbonate concentration to study the influence of carbonate on the sorption behavior of ^{227}Ac and ^{233}Pa.

II. Experimental

1. Radionuclides

Radionuclides, ^{227}Ac and ^{233}Pa, were used in this study. One mega Bq of ^{227}Ac in $1cm^3$ of 1N hydrochloric acid solution was purchased from AEA Technology. The actinium-227 solution was diluted into 0.5N hydrochloric acid stock solution for using in the sorption experiments.

Protactinium-233 was separated from a ^{237}Np stock solution purchased from CEA. Neptunium-237 stock solution in 7N nitric acid was contacted with silica gel for adsorption of ^{233}Pa on the silica gel surface. After that, the silica gel was contacted with 0.5N nitric acid with 0.01M fluoric acids to remove ^{233}Pa[7]. The separation of ^{233}Pa and ^{237}Np was con-

* Corresponding author:Tel.81-29-282-5543
Fax.81-29-282-5934
E-mail:sakamoto@sparclt.tokai.jaeri.go.jp

Table 1 Characteristics of soil samples

Soil Samples	Specific surface area (m^2/g)	CEC (meq/100g)	Chemical composition(wt%)					
			SiO_2	Na_2O	K_2O	CaO	Fe_{Total}	P_2O_5
Loam	99.5	15.6	79.7	0.06	0.17	0.22	5.35	<0.01
Yellowish Soil	26.0	10.7	57.8	1.27	0.07	0.64	5.44	0.03
Sand-A	6.3	4.3	86.2	0.30	0.24	0.97	2.34	<0.01
Sand-B	20.9	3.0	68.1	0.29	0.14	--	1.75	0.02
Tuff	20.8	5.7	58.6	0.52	0.40	--	2.95	0.02

Fe_{total} :Sum of Fe(II) and Fe(III)

Table 2 Chemical composition of water samples

Water samples	pH	Mg^{2+}	Ca^{2+}	Na^+	K^+	Fe_{total}	SiO_2	SO_4^{2-}	Cl^-	HCO_3^-	Organic carbon
GW-1	7.0	2.55	3.31	10.6	1.12	0.25	4.83	2.5	16.0	25.7	<0.1
GW-2	8.2	13.9	31.1	24.9	1.55	0.64	23.4	60.3	29.5	110.0	1.9

Unit: mg/dm^3(except pH)

firmed by measurement of alpha and beta counting with liquid scintillation counter (PACKARD TRI-CURVE 2000). Interference with alpha decay of ^{237}Np was eliminated using pulse decay analysis method of discrimination separate alpha and beta energies. After the separation treatment, the radioactivity concentration of ^{233}Pa was $500Bq/cm^3$ with coexisting ^{237}Np of $6Bq/cm^3$.

2. Soil and water samples

Loam, yellowish soil, two kinds of sand (sand-A and sand-B) and tuff, which were sampled in Japan, have been used in this study. The loam and sands and yellowish soil were dried in air, and were sieved with a 2mm sieve to remove coarse particles. The tuff was crushed and sieved into a particle size smaller than 2mm. The characteristics of each sample are listed in **Table 1**[2,3,4].

Two kinds of natural groundwater (GW-1, GW-2) were used for sorption experiments. They were sampled at Tohoku area (GW-1) and Kanto area (GW-2) in Japan. The groundwater was filtered with 10μm, 1μm and 0.45μm membrane filters to eliminate suspended particles. The chemical composition of these groundwaters is listed in **Table 2**[2,3,4].

3. Batch sorption experiment

Eight cm^3 water sample, which included ^{227}Ac or ^{233}Pa, were contacted with 0.8g soil in Teflon vessel. The sorption experiment was carried out under aerobic conditions at 15℃ for 14 days. Concentrations of ^{227}Ac and ^{233}Pa were 6.7×10^{-13} mol/dm^3 (=10Bq/cm^3) and 5.6×10^{-14}mol/dm^3 (=10Bq/cm^3), respectively. At the end of the sorption period, the solid and liquid was separated with a 0.45μm membrane filter (MILLIPORE Ultrafree-CL). The Kd values were obtained from the difference in the radioactivity concentration before and after the sorption experiment as follows;

$$Kd\ (m^3/Kg) = \frac{C_0 - C}{C} \cdot \frac{V}{W} \quad (1)$$

where C_0 is a initial radioactivity concentration of radionuclides (Bq/m^3), C is a final radioactivity concentration of radionuclides (Bq/m^3), V is volume of the water samples (m^3) and W is weight of the soil samples (Kg).

The GW-1 was used for the sorption experiment with the sand-B and tuff samples. The GW-2 water sample was used for the sorption experiment with the loam, sand-A, and yellowish soil. The combination of GW-1 and sand-B or tuff simulates an aerated zone environment. That of the GW-2 and loam, sand-A or yellowish soil simulates an aquifer environment

4. Sequential extraction

A sequential extraction of the sorbed ^{227}Ac and ^{233}Pa on the soils was carried out with a three step chemical extraction to study their dominant sorbed forms on the soils[8].

Step1: 0.5 mol/dm^3 $CaCl_2$ + 0.5 mol/dm^3 KCl solution for 24 hours to remove the fraction exchangeable by Ca^{2+} and K^+ (cation exchange fraction).

Step2: 0.1 mol/dm^3 NH_2OH-HCl + 0.1 mol/dm^3 K-Oxalate solution for 24 hours to remove the fraction adsorbed on amorphous Fe and Mn oxyhydroxides/oxides (amorphous Fe and Mn fraction).

Step3: 30wt% H_2O_2 at 60℃ for 3hours to digest a fraction interacting with organic substances (organic fraction).

The residual fraction that was not extracted by any of these chemicals was called "Lattice-bound fraction".

5. Carbonate concentration dependence

The Kd values of ^{227}Ac and ^{233}Pa on the loam sample were measured as a function of carbonate concentration. The basic sorption experimental procedure was the same for the batch sorption experiments. In this experiment, 0.1 mol/dm^3 sodium perchlorate solution was used to eliminate the influence of the increasing in ionic strength by the addition of sodium carbonate used for changing of carbonate concentration. Carbonate concentration range was chosen from 1.6×10^{-4}mol/dm^3 (=10mg/dm^3) to 2.5×10^{-3} mol/dm^3 (=150mg/dm^3) for simulation of a typical groundwater composition in Japan[9].

III. Results and discussion

1. Kd values and sorbed form of Ac

The Kd values of ^{227}Ac are shown in **Fig.1**. The Kd values of ^{227}Ac on the soils in the pH range from 6.5 to 7.9 were from $6m^3/kg$ for loam to $18m^3/kg$ for tuff. This result

indicates that Kd values of ^{227}Ac show little dependence on the kinds of soil.

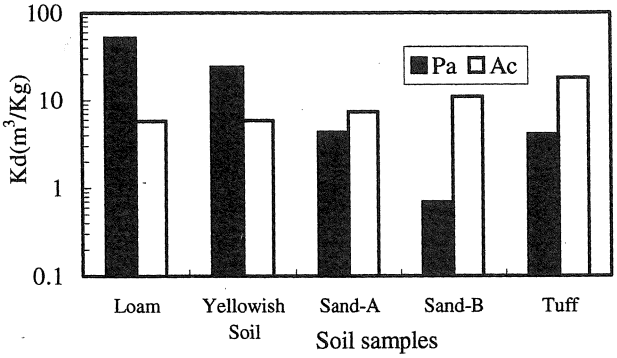

Fig. 1 Distribution coefficients of ^{227}Ac and ^{233}Pa on soils

The result of the sequential extraction of ^{227}Ac from the each soil is shown in **Fig.2**. The percentage of ^{227}Ac that was extracted in the cation exchange fraction raged from 20% for sand-B to 25% for tuff, and in the amorphous Fe and Mn fraction from 5% for sand-B to 20% for yellowish soil. The percentage of ^{227}Ac in the organic fraction was small for all soils. About 60-70% of ^{227}Ac was in a lattice-bound fraction. Because the lattice-bound fraction is considered to be caused by the interactions with crystalline phases in soil[8], most of the sorption of ^{227}Ac is supposed to be caused by the strong binding with crystalline phase, which is irreversible sorption reaction on soil surface. Then, it is likely that the sorption reaction of ^{227}Ac is based on the irreversible sorption reaction with the any crystalline phase in the soils to indicate the Kd values in the same range among the soils as shown in Fig.1.

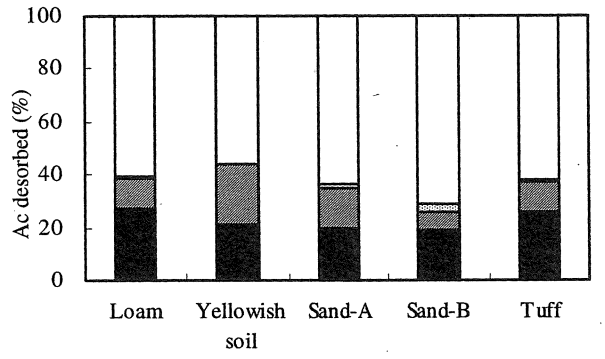

Fig.2 Percentage of ^{227}Ac desorbed from soils by the sequential extraction

Under the chemical conditions of the GW-1 and GW-2 in the Table 2, the main chemical species of ^{227}Ac were estimated to be Ac^{3+}, $Ac(OH)_2^+$, $AcCO_3^+$ by calculation with geochemical code CHESS[3]. From this speciation, it is likely that the irreversible sorption of ^{227}Ac on soil surface is cause by the formation of surface complexes of a $Ac(OH)_2^+$, $AcCO_3^+$, because Lieser et al. previously pointed out chemi-sorption of ^{227}Ac in a hydrolyzed form[5]. On the other hand, a small percentage of the cation exchange fraction was observed as shown in Fig.2. The cation exchange reaction could have been caused by cation exchange of ^{227}Ac in cationic form, Ac^{3+}.

2. Kd values and sorbed form of Pa

The Kd values of ^{233}Pa are shown in Fig.1. The Kd values of ^{222}Pa on the soils in the pH range from 6.2 to 8.9 ranged from $0.7m^3/kg$ to $52m^3$. The Kd values of ^{233}Pa varied widely depending on the kinds of soil.

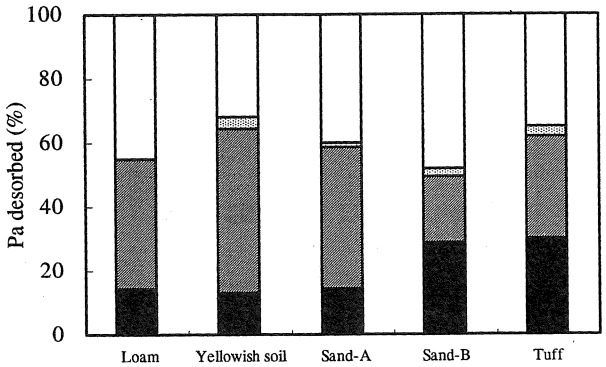

Fig.3 Percentage of ^{233}Pa desorbed from soils by the sequential extraction

□Lattice-bound fraction
▨Organic fraction
▨Amorphous Fe and Mn fraction
■Cation exchange fraction

The result of the sequential extraction of ^{233}Pa from each soil is shown in **Fig.3**. The protactinium-233 that was extracted in the cation exchange fraction ranged from about 15% for yellowish soil to 30% for tuff, and in the amorphous Fe and Mn fraction from 20% for sand-B to 50% for yellowish soil. The percentage of ^{233}Pa in the organic fraction was small for all soils. About 30-45% of ^{233}Pa could not be desorbed by each chemical extraction step. This result shows that most of ^{233}Pa was associated with the amorphous Fe and Mn oxides in the soils. In addition, a relationship between the Kd values of ^{233}Pa on the soils and the amount of iron oxides in soils (wt%) is plotted in **Fig.4**. The Kd

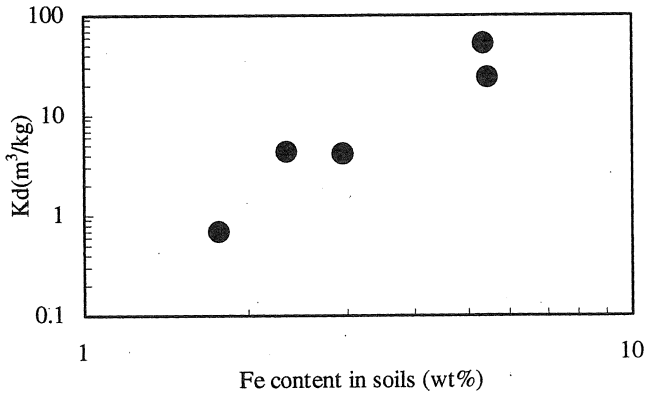

Fig.4 Relationship between Kd values of ^{233}Pa and the Fe content in the soils

values of ^{233}Pa on the soils were in linear proportion to the amount of iron oxides in soils. Then, it is likely that the major part of the sorption reaction is based on irreversible uptake on the iron oxides in the soils.

As shown in Fig.1, a large difference in the Kd values of ^{233}Pa among the soil samples was found. This difference in the Kd values among the soils may have been caused by the difference in the amount of the sorbed ^{233}Pa on the specific portion in the soils, such as the iron oxide surface.

3. Influence of carbonate on the sorption of Ac and Pa

The carbonate concentration dependence of the Kd values of ^{227}Ac and ^{233}Pa on the loam is shown in **Fig.5** and **Fig.6**, respectively.

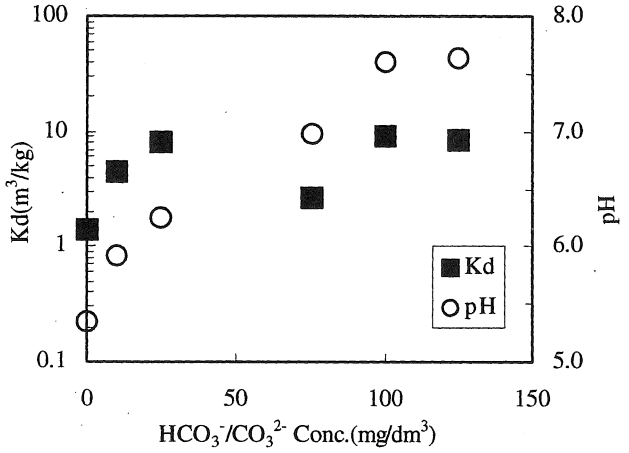

Fig.5 Carbonate concentration dependence of the Kd values of ^{227}Ac

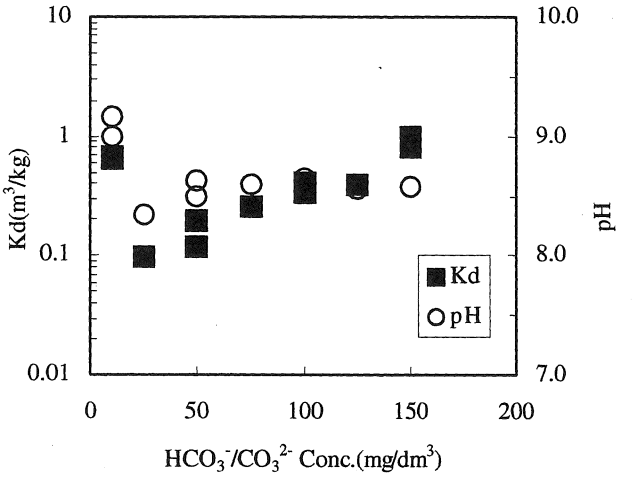

Fig.6 Carbonate concentration dependence of the Kd values of ^{233}Pa

The Kd values of ^{227}Ac increased with the carbonate concentration and achieved to maximum value beyond the carbonate concentration of 30mg/dm^3. The chemical form of ^{227}Ac is estimated to change from Ac^{3+}, $Ac(OH)_2^+$ and $AcCO_3^+$ to $AcCO_3^+$ with increasing carbonate concentration. In the previous work, the sorbed form of ^{227}Ac on the loam in the pH range from 6 to 8 was estimated to be as surface complexed form of $AcCO_3^+$ [3]. If true, the increase in the Kd values of ^{227}Ac after the addition of sodium carbonate to the solution could be caused by the sorption of carbonate complex to the loam.

Kd values of ^{233}Pa increased with the carbonate concentration as well. In the case of ^{233}Pa, the thermodynamic data to estimate the chemical forms in solution is limited. Formation of $Pa(CO_3)_5^{6-}$ has been reported[10], however, the exact chemical form under this condition cannot be estimated. From the result in Fig.6, the formation of carbonate complexes of ^{233}Pa may also be the cause for the increases in its Kd values. Furthermore, polymerization of Pa hydrolysis species is well known to result in high Kd values on geological materials[6,10]. One possibility is that higher molecular weight polymerized species are formed by the addition of sodium carbonate.

IV. Conclusion

The Kd values of ^{227}Ac on the five kinds of soils were in the same range among the soils. The sorption of ^{227}Ac was shown to be based on an irreversible sorption reaction with the crystalline phase and a cation exchange reaction.

The Kd values of ^{233}Pa varied widely among different kinds of soils, because the sorption of the ^{233}Pa was mainly based on irreversible sorption on amorphous Fe and Mn oxides surfaces.

The Kd values of ^{227}Ac and ^{233}Pa on loam increased with increasing carbonate concentrations. This phenomenon is assumed to be based on sorption of the carbonate complex on the loam.

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