

Influence of Molecular Size of Humic Acid on the Sorption of Radionuclides onto Ando Soil †

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Sorption experiments of ^{60}Co , ^{85}Sr and ^{241}Am on an ando soil were performed by a batch method. The effects of humic acid (HA) on the interaction of the radionuclides with the ando soil have been examined with respect to different molecular size fractions of HA, which were fractionated from the Aldrich Chemical's HA into <5,000, 5,000-30,000, 30,000-100,000 and >100,000 in molecular weight range (MW). Distribution coefficient (K_d) in the sorption of ^{60}Co on the ando soil was little affected by the presence of HA. The K_d of ^{85}Sr increased with the HA concentration. The K_d of ^{241}Am decreased with increasing HA concentration, as well as the K_d of HA. In the solution, ^{241}Am selectively forms stable compounds with HA of 30,000-100,000 MW, whereas ^{60}Co and ^{85}Sr preferentially but weakly interact with the HA fractions smaller than 100,000 MW. These results suggest that the K_d of ^{60}Co and ^{85}Sr is mainly controlled by sorption of both cationic species and humic compounds, while the K_d of ^{241}Am is dependent on the sorption ability of HA due to a large complexing stability of ^{241}Am with HA.

Key words: Humic acid, Sorption, Distribution coefficient, Molecular size, Ando soil, Complexation

クロボク土への ^{60}Co 、 ^{85}Sr および ^{241}Am の収着実験をバッチ法で実施し、クロボク土とこれら核種間の相互作用に及ぼすフミン酸の影響について、フミン酸の分子サイズに着目して調べた。 ^{60}Co の分配係数(K_d)はフミン酸の存在によってほとんど影響を受けなかったが、 ^{85}Sr の K_d は共存するフミン酸の濃度が高くなるに従って大きくなった。一方、 ^{241}Am の K_d は、クロボク土に対するフミン酸の K_d と同様に、共存するフミン酸の濃度が高くなるに従って小さくなった。水溶液中で、 ^{241}Am は分画分子量30,000~100,000のサイズのフミン酸と安定な結合体を選択的に形成したが、 ^{60}Co および ^{85}Sr は100,000以下のサイズのフミン酸と ^{241}Am に比べて弱く結合することが分かった。これらの結果から、フミン酸との相互作用が小さな ^{60}Co や ^{85}Sr の K_d は陽イオンとフミン酸結合体の両化学種の収着によって主に支配されるが、フミン酸との錯形成能が高い ^{241}Am の K_d はクロボク土に対するフミン酸の収着特性に依存することが示された。

キーワード：フミン酸、収着、分配係数、分子サイズ、クロボク土、錯形成

1. Introduction

Understanding the process of radionuclide migration in hydrogeologic environments is important in the assessment of radioactive waste disposal. Many radionuclides are readily sorbed on immobile geologic media and therefore are considered to be virtually immobile in the subsurface and to cause little effects to groundwater supplies. McCarthy *et al.*, however, have described that colloids in the geologic media may be mobile in subsurface environments, so that, the colloids act as a third

phase that can increase the amount of radionuclide transported with groundwater[1].

Much of the dissolved organic matter in natural water consists of humic substances, which are formed during microbial degradation of biomass in soil and water. The generic humic substance "humic acid (HA)" is very stable to further degradation. Humic acid has substantial chelation properties for metals, especially the transition metals. The resulting product "humic complexes" acts as a pseudocolloid of radionuclides[1,2]. From a geochemical point of view, it is important to know the stability of humic complexes with radionuclides released from a radioactive-waste repository.

Various research results have been reported dealing with the elucidation of the physico-chemical sorption of humic complexes onto geologic media[3-8]. Davis *et*

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al. have found that HA with different molecular sizes influences its sorption ability onto soils[3]. Alberts *et al.*[5] and the authors[6] have reported that the complexation between HA and metal ions is influenced by the molecular size of the HA. These molecular size effects of HA on the sorption ability and the complexation affinity is assumed to significantly affect the migration behavior of radionuclides.

We have performed sorption experiments of ^{60}Co , ^{85}Sr and ^{241}Am on an ando soil in the presence of humic acid, in order to clarify the effects of concentration and molecular size of HA on sorption behavior of the radionuclides onto the ando soil. The ando soil, which was known to be a soil having a high content of humic substances, will sorb also humic complexes, so it is available to study on influence of sorption ability of HA on the sorption behavior of the radionuclides.

2. Experimental

The ando soil collected in Ibaraki prefecture, Japan was used in this experiment. Physico-chemical properties of the ando soil are presented in Table 1. The ando soil contains clay minerals, such as gibbsite, kaolinite and chlorite, and it contains considerable amounts of organic carbon. Before use for the experiments, the ando soil was sieved and a grain size fraction between 37 and 1000 μm was collected by washing out with deionized water, and then air-dried.

Humic acid purchased from Aldrich Chemical Co. was further purified to remove insoluble humin, fulvic acid and ash following the procedure described by Nash *et al.*[7]. Nash *et al.* described, however, the final product of this purification contained 2 ~ 4 % ash, mainly Fe(III) compounds[9]. The purified HA was dissolved in a small amount of 0.1 M NaOH, and the HA solutions with predetermined concentrations were prepared by diluting with 0.01 M NaNO_3 .

The 2.5 g ando soil samples were contacted with 50 ml of HA solutions spiked with ^{60}Co , ^{85}Sr or ^{241}Am , yielding a final activity of about 1×10^3 Bq/ml (chemical concentrations: Co, 4×10^{-9} ; Sr, 4×10^{-8} ; and Am, 8×10^{-8} mol/L). The ionic strength of the solutions was

adjusted to 0.01 M with NaNO_3 , the pH to 5.5 with 0.1 M HCl and NaOH, and the temperature was controlled at 25 $^\circ\text{C}$ by using a water jacket. The solutions with the ando soil were gently agitated on a reciprocal shaker at 60 rpm for 7 days when equilibrium was roughly established (Fig. 1). The pH of the solutions was kept at 5.5 ~ 6.0 throughout the experiments. Blank tests not containing the ando soil were also carried out.

The supernatant was sampled and ultrafiltered using Millipore filters of 5,000, 30,000 and 100,000 molecular weight cutoff (MW)[10]. Concentrations of the radionuclide in each filtrate were measured by using an ORTEC γ -ray detector, and those of the HA were determined as dissolved organic carbon concentration by using a Shimadzu UV-240 spectrophotometer[10].

Sorption of radionuclide, M, onto the ando soil can be described by the equilibrium reaction:



Table 1 Physico-chemical properties of ando soil

Bulk density	0.69 g/cm ³
Cation exchange capacity(CEC)	17.2 meq/100g
Anion exchange capacity(AEC)	1.9 meq/100g
Organic carbon	3200 mgC/100g
Chemical composition	
SiO ₂	51.59 %
Al ₂ O ₃	21.28 %
TiO ₂	1.23 %
Fe ₂ O ₃	3.66 %
CaO	1.15 %
MgO	1.71 %
FeO	6.54 %
Na ₂ O	0.59 %
K ₂ O	0.59 %
P ₂ O ₅	0.32 %
MnO	0.15 %
H ₂ O	11.24 %
Mineral composition	
Quartz	Major
Plagioclase	Minor
Gibbsite	Minor
Cristobalite	Trace
Kaolinite	Trace
Sericite	Trace
Chlorite	Trace
K-feldspar	Trace

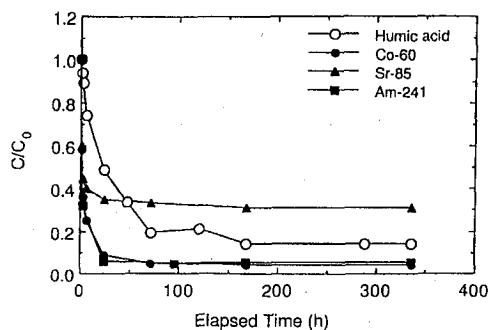


Fig.1 Time course of concentration (C) of humic acid and radionuclides in solution through the sorption experiments; C_0 represents initial concentration.

and

$$\frac{[M]_{solid}}{[M]_{liquid}} = K_d \quad (2)$$

where K_d is distribution coefficient of M between liquid and solid phases (ml/g).

3. Results and Discussion

3.1 Influence of humic acid concentration on the distribution coefficient of radionuclides

In the case without any ultrafiltrations, the influence of HA concentration on the distribution coefficient K_d of the radionuclides is shown in Fig.2 together with that of HA. The HA was well sorbed onto the ando soil as was expected due to its chemical properties. The K_d values of HA decreased with increasing HA concentration. No organic substance dissolved from the ando soil to the solution at a background test not adding HA, though the ando soil contains considerable amounts of organic carbon (Table 1). The K_d of ^{60}Co was constant at 580 ml/g, that is the K_d at the absence of HA, except for 131 mg/L where the K_d decreased from 580 to 340 ml/g. The K_d of ^{241}Am was 350 ml/g at the absence of HA, and decreased with increasing HA concentration, similar to that of HA. On the other hand, the K_d of ^{85}Sr was 52 ml/g at the absence of HA, and gradually increased with the HA concentration. These results suggest that the effects of HA

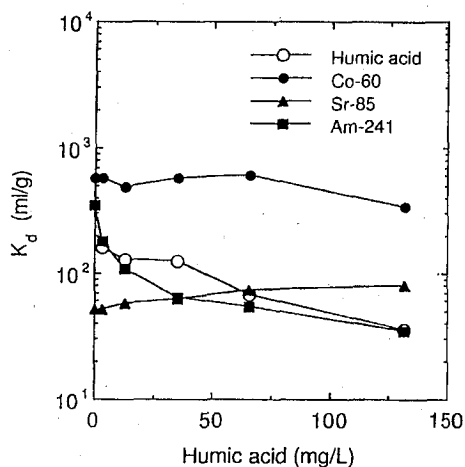


Fig.2 The dependence of the distribution coefficient K_d of radionuclides and humic acid as a function of the initial humic acid concentration.

on the K_d are different among the three radionuclides.

3.2 Size distribution of humic acid in solutions

Concentration of HA in each size fraction at the blank tests and after the sorption experiments is shown in Fig.3. As to the blank test at 3.5 mg/L of HA concentration and the sorption experiments at 3.5 and 13 mg/L, the HA concentration in some filtrates was lower than detection limit and it was not enough to obtain the size distribution of HA. At the blank tests, in the fraction larger than 100,000 MW (>100,000 MW), approximately 20 % of the HA were detected. About half of the HA was present in the molecular size range from 30,000 to 100,000 MW (30,000-100,000 MW). The amounts of HA detected in the fraction from 5,000 to 30,000 MW (5,000-30,000 MW) and that less than 5,000 MW (<5,000 MW), were 20 and 10 %, respectively. The size distribution profile of HA was independent of the HA concentration.

After the sorption, the HA of >100,000 MW remained in the solutions, while that smaller than 30,000 MW was little. This shows that the ando soil preferably sorbs the HA of smaller sizes. The HA of 30,000-100,000 MW increased with HA concentration. This increase reduced the K_d of HA in Fig.2.

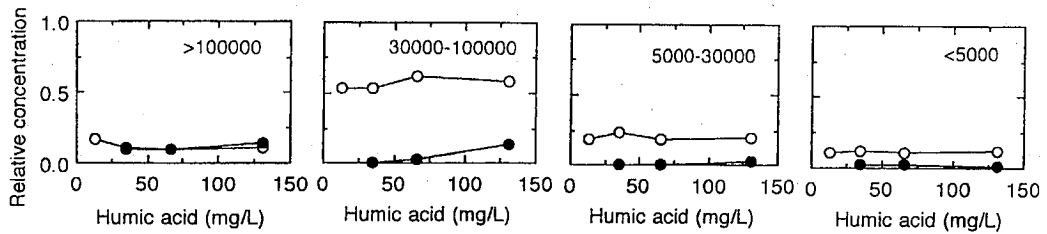


Fig.3 Concentration of humic acid in each size fraction at blank tests and after the sorption experiments; relative concentration is normalized to the initial one in the solution at the blank tests, ○: blank test, ●: after sorption.

3.3 Effects of molecular size of humic acid on the sorption of ^{60}Co

Concentration of ^{60}Co in each size fraction at the blank tests and after the sorption experiments is shown in Fig.4(a). At the absence of HA, all ^{60}Co in the solutions was present in the fraction of <5,000 MW. In the solutions at the blank tests, the ^{60}Co concentration in the fraction of 30,000-100,000 MW increased with the HA concentration. This indicates that the HA of 30,000-100,000 MW effectively contributes to an interaction with ^{60}Co . The ^{60}Co in the fraction of 5,000-30,000 MW was measured to be 20 %, and was independent of the HA concentration. This suggests that ^{60}Co also interacted with HA of 5,000-30,000 MW.

The ^{60}Co concentration in all fractions was reduced to near 0 after the sorption at different HA concentrations. Hence the K_d of ^{60}Co in Fig.2 is not apparently affected by the HA concentration. Additionally, the fact that the concentration of ^{60}Co associated with the HA of >100,000 MW was reduced after the sorption in spite that the HA was not sorbed on the ando soil, suggests that most of ^{60}Co in the fraction of >100,000 MW is dissociated from HA and the resulting cationic ^{60}Co is sorbed on the ando soil. The cationic ^{60}Co is very strongly sorbed on the ando soil, as indicated by the highest K_d value among the three radionuclides at the absence of HA (in Fig.2). The sorption process of ^{60}Co seems to be dominated by the sorption of cationic ^{60}Co on the ando soil. Though the HA is sorbed onto the ando soil or is dissolved, the influence of HA on the sorption of ^{60}Co will therefore be of minor importance.

3.4 Effects of molecular size of humic acid on the sorption of ^{85}Sr

In the solution at the blank tests, the concentration of ^{85}Sr in the fraction of <5,000 MW significantly decreased with increasing HA concentration, while that in the fraction of 30,000-100,000 MW increased similar to that of ^{60}Co (Fig.4(b)). This shows that a portion of the ^{85}Sr in the solution can be attracted by the HA of 30,000-100,000 MW. However, the authors have previously found that a binding between ^{85}Sr and the HA of 30,000-100,000 MW is broken so easily, and such a binding is not based on coordination bond, but on a binding such as electrostatic force[11]. The fraction of <5,000 MW contains not only the humic compounds but also the cationic species. Since the ^{85}Sr in the solutions at different HA concentrations was not trapped by any ultrafilters from 5,000 to 30,000 MW, the ^{85}Sr in the fraction of <5,000 MW had not formed humic compounds and was present as a cationic species Sr^{2+} [12,13].

The concentration of ^{85}Sr in the fraction of 30,000-100,000 MW significantly reduced after the sorption, whereas considerable amounts of the cationic ^{85}Sr in the fraction of <5,000 MW remained after the sorption. The cationic ^{85}Sr should be removed by the sorption from the fraction of <5,000 MW onto the ando soil. When the cationic ^{85}Sr is removed from the solution, it might be mainly supplied again by dissociating the humic compounds in the fraction of 30,000-100,000 MW, because the binding between ^{85}Sr and the HA of 30,000-100,000 MW is easily broken. The dissociation of the humic compounds proceeds until the equilibrium in the solution achieves. Hence it seems that the humic com-

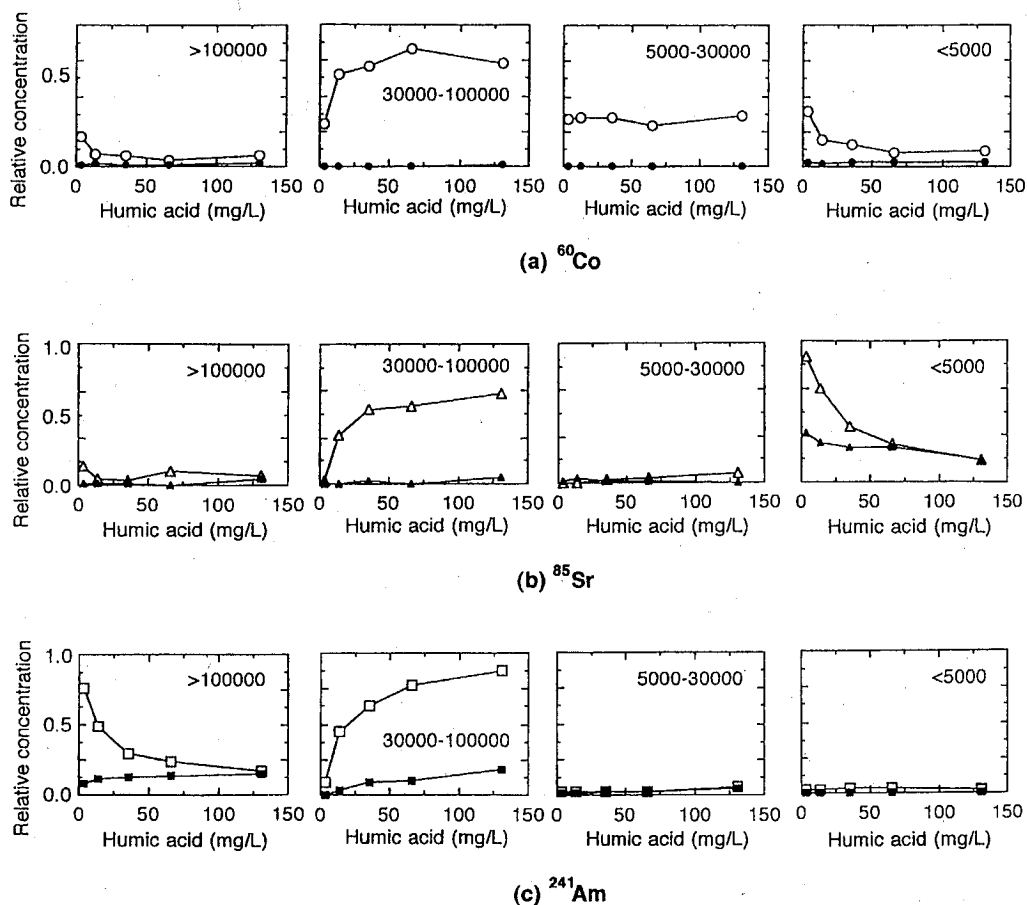


Fig. 4 Concentration of radionuclides in each size fraction at blank tests and after the sorption experiments; relative concentration is normalized to the initial one in the solution at the blank tests, \circ, Δ, \square : blank test, $\bullet, \blacktriangle, \blacksquare$: after sorption.

pounds of ^{85}Sr in the fraction of 30,000-100,000 MW are apparently sorbed on the ando soil. However, the cationic ^{85}Sr is weakly sorbed on the ando soil, as indicated by the small K_d value at the absence of HA, so that it remained in the solution after the sorption. The cationic ^{85}Sr remaining in solution can associate with the HA which either is sorbed onto the ando soil or is dissolved. Such a sorption process possibly causes the increase in the K_d of ^{85}Sr with increasing HA concentration, as shown in Fig. 2.

3.5 Effects of molecular size of humic acid on the sorption of ^{241}Am

In the solution at the blank tests, most ^{241}Am formed

humic compounds even in extremely low HA concentration region, since ^{241}Am , that is a trivalent element, has a large complexing stability with HA and other organic ligands [14, 15] (Fig. 4(c)). The ^{241}Am selectively interacted with the HA in size range larger than 30,000 MW. This indicates that ^{60}Co and ^{85}Sr preferentially form smaller humic compounds but ^{241}Am forms larger ones. The concentration of ^{241}Am in the fraction of 30,000-100,000 MW increased with the HA concentration. Thus the ^{241}Am effectively interacts with the HA of 30,000-100,000 MW. Contrary to this, the concentration of ^{241}Am in the fraction of $>100,000$ MW decreased gradually with increasing HA concentration. This suggests that ^{241}Am interacts more strongly with the HA of

30,000-100,000 MW than that of >100,000 MW. The differences in the effects of molecular size of the HA on the interaction with ^{241}Am were considerably influenced by the variation of structure and/or steric hindrance around functional groups of HA at different molecular size[6].

The concentration of ^{241}Am in the fraction of 30,000-100,000 MW was significantly reduced by the sorption, but it slightly increased with the HA concentration after the sorption. This increase means a decrease of sorption amounts of ^{241}Am on the ando soil, so that the K_d of ^{241}Am decreased with increasing HA concentration, as shown in Fig.2. The size distribution profile of ^{241}Am remaining in the solution after the sorption (in Fig.4(c)) was similar to that of HA (in Fig.3). This indicates that the sorption behavior of ^{241}Am is dominated by the sorption of HA which involves ^{241}Am . Therefore, the agreement in the K_d values between ^{241}Am and HA in the presence of HA (in Fig.2) is probably attributable to the strong complexation of ^{241}Am with HA.

4. Conclusions

Values of distribution coefficient K_d in the sorption of ^{241}Am , which forms stable compounds with HA of 30,000-100,000 MW in the solutions, on the ando soil decreased with increasing HA concentration, as well as the K_d of HA. On the other hand, the K_d of ^{60}Co was little affected by the presence of HA and that of ^{85}Sr increased with the HA concentration, because ^{60}Co and ^{85}Sr preferentially but weakly interact with the HA fractions smaller than 100,000 MW. These results suggest that the migration of cationic radionuclide in geologic media in the presence of HA can be partly accelerated by formation of the humic compounds and/or partly retarded by sorption of the humic compounds.

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6. References

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