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## 論 文 内 容 要 旨

### 1. Introduction

The safety assessment of geological disposal for high level radio active waste requires knowledge of migration of actinides in the geological environment because actinides have usually long half lives and most actinides are  $\alpha$  emitters. These nuclides migrate mainly with groundwater but the sorption of nuclides onto rocks and soils retards migration of nuclides. On the other hand, interaction (or complexation) with dissolved organic colloids raises the concentration of nuclides in groundwater and impedes the retardation.

In this study, the complexation mechanism of metal ions with the organic colloids (humic substances) and the effect of complexation on the migration of nuclides have been examined.

As humic substances are made by decomposition and condensation of organic colloids in nature, the following two effects affect complexation of metal ion:

- (1) Polyelectrolyte effect due to the crowded negative charges of the dissociated functional groups (complex sites) which are fixed on macro molecule skeleton.
- (2) Heterogeneous structure effect that is derived from the heterogeneous composition of humic substances and nonuniform distribution of the binding strength and capacity of complexing site.

To discuss these two effects separately, complex formation of humic acid has been compared with polyacrylic acid

( $[-\text{CH}_2\text{CH}(\text{COOH})-]_n$ ) which is macro molecule and has homogeneous structure.

Complex formation constant,  $\beta$ , which indicates the intensity of complexation, is described as

$$\beta = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \quad (1)$$

where [L] is the complexing ligand concentration, [M] the free metal ion concentration and [ML] the complex concentration. In the case of monomeric ligand, the value of [L] can be clearly defined and obtained. For polymeric acids such as polyacrylic acid and humic acid, however, it is difficult to describe complexing ligand concentration, because the number and speciation of complexing site changes with pcH, which is defined as  $-\log [\text{H}]$ , and ionic strength since the functional groups are fixed on their macro molecule. Therefore, the values of the apparent complex formation constant,  $\beta_\alpha$ , were obtained by using the definition as

$$\beta_\alpha = \frac{[\text{MR}_m]}{[\text{M}][\text{R}]} \quad (2)$$

where [R] denotes the concentration of dissociated functional group, [M] and  $[\text{MR}_m]$  denote the concentration of free and bound metal and  $m$  denotes the number of dissociated functional group bound to a metal ion.

To clarify the existence of different types of complex sites, the apparent complex formation constants were determined by the solvent extraction technique with using the wide range of the actinide ion concentration. The concentration of neptunium was controlled by using  $^{237}\text{Np}$  and  $^{239}\text{Np}$ . Since it is experimentally impossible to vary the americium concentration, europium was used instead of americium, because chemical behavior of europium is similar to americium. The concentration of europium was controlled by using  $^{152}\text{Eu}$  and non-radioactive europium.

The apparent complex formation constant was evaluated from the values of distribution ratio. The distribution ratio  $D_0$  or  $D$ , which is with or without ligand, respectively, was expressed as,

$$D_0 = \frac{[\text{MT}_n\text{B}_l]_o}{[\text{M}]} \quad (3)$$

$$D = \frac{[\text{MT}_n\text{B}_l]_o}{[\text{M}] + [\text{MR}_m]} \quad (4)$$

where  $[MT_nB_l]_o$  is the concentration of metal ion extracted into organic phase and  $[M]$  and  $[MR_m]$  is the concentration of free and bound metal ion. With using  $\beta_\alpha$ , the relation between  $D_0$  and  $D$  is,

$$\log D = \log D_0 - \log \left( 1 + 10^{(\log \beta_\alpha + \log[R])} \right) \quad (5)$$

To evaluate  $\log D_0$  and  $\log \beta_\alpha$ , a non-linear least-squares fitting was conducted to minimize following equation:  $S = \sum (\log D_{\text{observed}} - \log D)^2$  where  $\log D_{\text{observed}}$  denotes distribution ratio observed. Since the values of  $\log \beta_\alpha$  of Eu(III)-humate could not be obtained by using the above fitting, they were directly calculated by eq. (2) where  $[MR_m]$ ,  $[M]$  and  $[R]$  were evaluated from distribution ratio and the mass balance of metal ion and functional group.

## 2. Outline

### (1) Acid dissociation of polymeric weak acid:

Titration of polyacrylic acid and humic acid was conducted to investigate the acid dissociation properties of functional groups that regulate complex formation.

### (2) Complexation of metal ion with polymeric weak acid:

The results of titration enabled the evaluation of the concentration of dissociated functional group at a given pH and ionic strength. To obtain the apparent complex formation constant of Np(V) or Eu(III) with polyacrylic acid or humic acid, solvent extraction was conducted at ionic strength of 0.02 M through 1.0 M NaClO<sub>4</sub>. To extract Np(V), thenoyltrifluoroacetone(TTA) and 1,10-phenanthroline (phen) in isoamylalcohol was used. To extract Eu(III), TTA and tributyl phosphate(TBP) in xylene was used.

### (3) Complexation with humic acid under groundwater system:

The effect of Ca(II) on the complexation of Np(V) or Eu(III) with humic acid was examined to evaluate humate concentration under a model groundwater.

## 3. Results

### (1) Acid dissociation of polymeric weak acid.

Titration has been carefully conducted considering the slow kinetics of dissociation and protonation of polyacrylic acid and humic acid due to their polymeric structure. The titration curves of polyacrylic acid and humic acid revealed a different characteristic from those of monomeric acids in the point that pCH buffer region does not exist and the increase of pCH with added alkali is steeper than monomeric acids. That is, as compared with monobasic

acid, polyacrylic acid and humic acid act as stronger acid at lower pcH and as weaker acid at higher pcH. The analysis of their titration curves indicated that polyacrylic acid and humic acid can be regarded as tribasic acid. This means that the dissociation of its certain functional group on macro molecule skeleton is affected by the dissociation, protonation status of its adjacent functional groups on both sides. The titration also indicated that the acid dissociation of polyacrylic acid and humic acid strongly depends on ionic strength. Since there is a competition between  $H^+$  and  $Na^+$  (controlling the ionic strength of the solution) in their electrostatic condensation to the zone immediately around the polyanion, the increase in ionic strength, the increase in sodium ion concentration, drives hydrogen ion, out of the polyanionic region thus enhancing the dissociation of the acid. The value of proton exchange capacity (PEC) of humic acid was dependent on ionic strength, while that of polyacrylic acid was independent of ionic strength. Possibly, with increase in ionic strength, sodium ion promotes the dissociation of more weakly acidic functional groups contained in the humic acid of heterogeneous composition, this giving higher value of PEC for humic acid.

## (2) Complexation of metal ion with polymeric weak acid.

The synergistic extraction systems of Np(V) and Eu(III) were confirmed to be reliable for the determination of apparent complex formation constant,  $\log \beta_\alpha$ .

By using these extraction systems, the apparent complex formation constants of polyacrylate and humate of Np(V) and Eu(III) have been obtained at different pcH, ionic strength and metal ion concentrations.

The values of  $\log \beta_\alpha$  of polyacrylates and humates depended on the degree of ionization,  $\alpha$ , differently from monomeric complexation. The results indicated that the value of  $\log \beta_\alpha$  increases against  $\log \alpha$  with a slope of 6. This increment suggests that a set of three adjacent dissociated functional groups on macro molecule binds to a metal ion.

The values of  $\log \beta_\alpha$  of polyacrylates were independent of free metal ion concentration, while those of humates decreased with free metal ion concentration. The binding strength of complexing sites on polyacrylic acid are the same independent of the site due to homogeneous structure, while for humic acid, the binding strength of complexing sites are different depending on the site due to its heterogeneous structure. Under the condition of low metal ion concentrations, the strong complexing sites on humic acid regulate complexation. At higher metal ion concentrations the strong sites are occupied by metal ion and the remaining weaker sites regulate complexation.

As a result, the values of  $\log \beta_\alpha$  of humates decrease with the metal ion concentration.

The values of  $\log \beta_\alpha$  of polyacrylates and humates were also dependent on ionic strength. As compared with Np(V) and Eu(III), the value of  $\log \beta_\alpha$  of Ca(II) was strongly dependent on ionic strength decreased with ionic strength. This is perhaps due to the nature of the bonding in complexation. The property of Eu(III) and Np(V) complexation is covalent rather than ion-association in Ca(II) complexation so that the values of  $\log \beta_\alpha$  are less independent on ionic strength than Ca(II). These strong complexing ions bind to strong complexing site on humic acid, therefore, the values of  $\log \beta_\alpha$  of Np(V) and Eu(III) humates are higher than those of Ca(II) humates.

### (3) Complexation with humic acid under groundwater system.

It was examined whether the values of  $\log \beta_\alpha$  evaluated individually can reproduce the distribution ratios of Eu(III) and Np(V) in the coexistence of Ca(II). For polyacrylates, the distribution ratios of metal ions are reproduced. While for humates those of Eu(III) are not reproduced at lower free Eu(III) concentrations and the degree of complexation decreases. As Eu(III) is stronger complexing ion than Ca(II), Eu(III) usually precedes Ca(II) in complexation. But if Eu(III) concentration decreases, relative to Ca(II) concentration, Ca(II) competes with Eu(III) for stronger complexing sites on humic acid so that complexation regulated by weaker complexing sites leads to the lower values of  $\log \beta_\alpha$  of Eu(III)-humate. As the complexing sites of polyacrylic acid is homogeneous, complexation with polyacrylic acid is independent of coexistence of Ca(II). This leads to the constant value of  $\log \beta_\alpha$  of polyacrylate.

The effect of coexistence of several ions, lanthanides(III) and Ca(II), to Am(III)-humate was estimated in a weakly acidic to a weakly alkaline region. The humate complex concentration is highest in the weakly acidic region. The humate concentration decreases with increasing alkalinity from the neutral region because free metal ion concentration decreases with a formation of carbonate. With coexistence of Ca(II), Am(III)-humate concentration decreases. In the weakly alkaline region where Am(III) free ion concentration is low due to the formation of carbonate, the coexistence of Ca(II) particularly affects the formation of humate so that Am(III)-humate concentration decreases. The examination of coexistence effect concludes that the evaluation of actinide-humate concentration in groundwater requires the consideration for competition of metal ions which originate from groundwater or high level radio active waste.

#### 4. Conclusions

For complexation of metal ions with organic colloids (humic acid), the following results were obtained:

(1) The values of  $\log \beta_{\alpha}$  of Np(V) and Eu(III) with polyacrylic acid and humic acid are dependent on the degree of ionization and ionic strength due to the polyelectrolyte effect of organic colloids.

(2) The values of  $\log \beta_{\alpha}$  of Np(V) and Eu(III) with humic acid are dependent on the concentration of the metal ion due to heterogeneous structure effect of humic acid. Therefore description of humate complexation of actinides in groundwater requires knowledge about the concentrations of competing metal ions in groundwater as well as the understanding of the two effects, polyelectrolyte effect and heterogeneous structure effect, of humic acid. The result of this study on the interaction of metal ions with organic colloids is useful to understand and estimate the migration behavior of metal ions in groundwaters, which is important not only for the safety assessment of geological disposal of high level radio active waste but also for the assessment of the behavior of heavy metal ions in the polluted environment.

# 審査結果の要旨

使用済核燃料の再処理工程より発生する高レベル放射性廃棄物中には、毒性が強く半減期の長いアクチノイド核種が含まれる。高レベル放射性廃棄物の地層処分の安全評価には、地層中におけるこれらの核種の移行挙動を把握することが重要となる。金属イオンは主として地下水を媒体として移行拡散するが、その際、地下水中の溶存する有機コロイドの影響を受けると考えられている。そのため、地層中の有機コロイドとアクチノイドの相互作用についての知見を得る必要がある。

有機コロイド(フミン酸)はその起源より考えて、金属イオンとの相互作用において「高分子電解質」である効果と「組成不均一」である効果の2つが影響する。これまでの研究においては、この2つの効果を分けて議論されることがほとんど無かった。これに対して本論文では組成が均一な高分子電解質のポリアクリル酸と比較することで、フミン酸の持つ2つの効果を分けて考察を行っている。本論文は、これらの研究成果についてまとめたものであり、全編6章からなる。

第1章は序論であり、本研究の背景および目的を述べている。

第2章では、実験方法について述べている。

第3章では、ポリアクリル酸とフミン酸との酸解離挙動の違いについて述べている。ポリアクリル酸およびフミン酸は高分子電解質であるため、その酸解離挙動は低分子量の酸とは異なることを示しており、高分子電解質としての性質を考慮してその酸解離挙動を三塩基酸として記述することを提案している。また、フミン酸は組成不均一性により酸性官能基容量が溶液のイオン強度の影響を受けることを見出している。

第4章では、ポリアクリル酸とフミン酸の錯生成挙動を比較することで、フミン酸の「高分子電解質」の効果と「組成不均一」の効果について述べている。この中で、フミン酸の組成不均一性により、錯生成力は金属イオン濃度の影響を受けることを見出し、地下水中に含まれる金属イオンがアクチノイドと有機コロイドの錯体生成に対して競争反応を起こすことを示唆している。これは重要な成果である。

第5章では、第4章で得られた錯生成定数を用いて、地下水中で多量に存在するカルシウムおよび廃棄物に含まれるランタノイドの共存下におけるフミン酸とアクチノイドの錯生成について考察している。

第6章は総括である。

以上要するに本論文は有機コロイドと金属イオンの相互作用において「高分子電解質」の効果と「組成不均一」の効果を明らかにしたものであり、放射性廃棄物処分工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。