

Acquisitions of Effective Diffusion Coefficients
(De) for Ni(II), Am(III), Sm(III) and Se(IV)
in Bentonite by Through-Diffusion Method

October, 1999

TOKAI WORKS
JAPAN NUCLEAR CYCLE
DEVELOPMENT INSTITUTE

本資料の全部または一部を複写・複製・転写する場合は、下記にお問い合わせください。

〒319-1184 茨城県那珂郡東海村村松4番地49

核燃料サイクル開発機構

技術展開部 技術協力課

Inquiries about copyright and reproduction should be addressed to :
Technical Cooperation Section,
Technology Management Division,
Japan Nuclear Cycle Development Institute
4-49 Muramatsu, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1184
Japan

© 核燃料サイクル開発機構 (Japan Nuclear Cycle Development Institute)
1999

透過拡散法によるベントナイト中の Ni(II), Am(III), Sm(III), Se(IV) の実効拡散係数 (De) の取得

(研究報告)

佐藤治夫*

要 旨

圧縮ベントナイト中でのイオン電荷の影響を定量的に評価するため、 Ni^{2+} , Am^{3+} , Sm^{3+} , SeO_3^{2-} の実効拡散係数(De)を拡散化学種の電荷をパラメータとして取得した。 Ni^{2+} , Sm^{3+} に対しては、乾燥密度 $1.8\text{Mg}\cdot\text{m}^{-3}$, pH5~6 の模擬間隙水条件にて透過拡散法により測定した。 SeO_3^{2-} に対しては、乾燥密度 $1.8\text{Mg}\cdot\text{m}^{-3}$, pH11 の模擬間隙水条件にて測定した。 Am^{3+} に対しては、陽イオン排除の効果を確認する目的で、乾燥密度 0.8, 1.4, $1.8\text{Mg}\cdot\text{m}^{-3}$, pH2 の間隙水条件で測定した。測定では、Na 型ベントナイト(クニゲル VI) を用いた。 Am の測定においては、低 pH 領域で行うため、予め層間イオンの Na^+ を H^+ と置換した H 型クニゲル VI を用いた。得られた De は、 $\text{Sm}^{3+} > \text{Ni}^{2+} > \text{Am}^{3+} > \text{SeO}_3^{2-}$ の順で小さくなった。得られた De をこれまでに報告されているデータと比較した結果、De は、 $\text{Cs}^+ > \text{Sm}^{3+} > \text{HTO} > \text{Ni}^{2+} > \text{陰イオン}(\text{I}^-, \text{Cl}^-, \text{CO}_3^{2-}, \text{SeO}_3^{2-}, \text{TcO}_4^-, \text{NpO}_2\text{CO}_3^-, \text{UO}_2(\text{CO}_3)_3^{4-})$ の順で小さくなり、陽イオン $>$ HTO $>$ 陰イオンの傾向を示した。 Am^{3+} の De のみは陰イオンと同程度であった。 Ni^{2+} の De が HTO より小さかった原因は、 Ni^{2+} の自由水中の拡散係数(Do)が HTO のその約 1/3 と遅いことによると考えられる。また、 Am^{3+} の De が陰イオンと同程度であった原因は、 Am^{3+} の Do も HTO の約 1/3 であったこと、及び陽イオン排除によるベントナイト表面からの静電的反発によると考えられる。そこで、各イオンの Do で規格化して求めた形状因子(FF)で比較した結果、 $\text{Sm}^{3+} > \text{Cs}^+ > \text{Ni}^{2+} > \text{HTO} > \text{Am}^{3+} > \text{陰イオン}$ の順で小さくなり、 Cs^+ , Ni^{2+} , Sm^{3+} に対しては表面拡散、 Am^{3+} に対しては陽イオン排除、 SeO_3^{2-} を含む陰イオンに対しては陰イオン排除の可能性が示された。FF の計算結果から、乾燥密度 $1.8\text{Mg}\cdot\text{m}^{-3}$ に対する表面拡散の程度は、HTO を基準として Sm^{3+} に対しては 5 倍程度、 Cs^+ に対しては 3 倍程度、 Ni^{2+} に対しては 1.3 倍程度であった。また、同条件における陰イオン排除の程度は、 TcO_4^- で 1/7 程度、 $\text{NpO}_2\text{CO}_3^-$ で 1/16 程度、 SeO_3^{2-} で 1/5 程度と見積もられた。さらに同密度における Am^{3+} に対する陽イオン排除の程度は、HTO を基準として 0.85 倍程度とそれ程 De の減少は認められなかった。しかしながら、最も表面拡散の効果が見られた Sm^{3+} の Do でも HTO の 1/3 程度あることから、De の値は HTO よりも若干高い程度であったものと考えられる。このことから、ベントナイト中の De に与える表面拡散の影響はそれ程大きくないものと考えられる。

*核燃料サイクル開発機構 東海事業所 環境保全・研究開発センター
処分研究部 放射化学研究グループ

Acquisitions of Effective Diffusion Coefficients (D_e) for Ni(II), Am(III), Sm(III) and Se(IV) in Bentonite by Through-Diffusion Method

Haruo Sato*

Abstract

Effective diffusion coefficients (D_e) for Ni^{2+} , Sm^{3+} , Am^{3+} and SeO_3^{2-} were measured as a function of the ionic charge of diffusion species to quantitatively evaluate the effect of ionic charge in compacted bentonite. The D_e measurements for Ni^{2+} and Sm^{3+} were carried out for a bentonite dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ with a simulated porewater condition of pH5~6 by through-diffusion method. The D_e values for SeO_3^{2-} were measured for a bentonite dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ with a simulated porewater condition of pH11. The D_e measurements for Am^{3+} were carried out for the dry densities of 0.8, 1.4 and $1.8 \text{ Mg}\cdot\text{m}^{-3}$ with a porewater condition of pH2 in order to check cation exclusion. Sodium bentonite, Kunigel-V1® was used for those measurements. For the measurements of Am, H-typed Kunigel-V1® which interlayer ion (Na^+) was exchanged with H^+ , was used, because the experiments are carried out for a low pH range. The order of obtained D_e values was $\text{Sm}^{3+} > \text{Ni}^{2+} > \text{Am}^{3+} > \text{SeO}_3^{2-}$. These D_e values were compared to those reported to date. Consequently, the order of D_e values was $\text{Cs}^+ > \text{Sm}^{3+} > \text{HTO} > \text{Ni}^{2+} > \text{anions} (\text{I}^-, \text{Cl}^-, \text{CO}_3^{2-}, \text{SeO}_3^{2-}, \text{TcO}_4^-, \text{NpO}_2\text{CO}_3^-, \text{UO}_2(\text{CO}_3)_3^{4-})$, showing a tendency of cations $>$ HTO $>$ anions. Only the D_e values of Am^{3+} were approximately the same degree as those of anions. The reason that the D_e of Ni^{2+} was lower than that of HTO may be because the free water diffusion coefficient (D_o) of Ni^{2+} is about 1/3 of that of HTO. The cause that the D_e of Am^{3+} was approximately the same degree as those of anions may be because the D_o of Am^{3+} is about 1/3 of that of HTO and that Am^{3+} was electrostatically repulsed from the surface of bentonite by cation exclusion. The formation factors (FF), calculated normalizing D_o , were in the order, $\text{Sm}^{3+} > \text{Cs}^+ > \text{Ni}^{2+} > \text{HTO} > \text{Am}^{3+} > \text{anions}$, indicating a possibility of surface diffusion for Cs^+ , Ni^{2+} and Sm^{3+} , cation exclusion for Am^{3+} and anion exclusion for anion exclusion including SeO_3^{2-} . From the calculations of FF values, the degree of surface diffusive effect for a dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ was approximately estimated to be 5 times for Sm^{3+} , 3 times for Cs^+ and 1.3 times for Ni^{2+} as much assuming that FF of HTO is the standard. The degree of anion exclusive effect for the same condition was approximately estimated to be 1/7 for TcO_4^- , 1/16 for $\text{NpO}_2\text{CO}_3^-$ and 1/5 for SeO_3^{2-} as much. The degree of cation exclusive effect for Am^{3+} for the same density was approximately calculated to be 0.85 times as much as that of HTO and not so much effect on D_e was recognized. However, since the D_o of Sm^{3+} is also about 1/3 of that of HTO, the D_e values of Sm^{3+} may have been only a little higher than those of HTO. Based on this, it is presumed that surface diffusive effect on D_e in bentonite is insignificant.

* Radiochemistry Group, Waste Isolation Research Division,
Waste Management and Fuel Cycle Research Center, Tokai Works,
Japan Nuclear Cycle Development Institute

Contents

1. INTRODUCTION	1
2. EXPERIMENTAL	2
2.1 Material and Experimental Conditions	2
2.2 Sorption Tests of Am onto Diffusion Cell Materials to Determine Experimental Conditions	2
2.3 Preparation of H-Typed Kunigel-V1	3
2.4 Experimental Procedure for Diffusion Experiments	4
3. DIFFUSION THEORY AND ANALYTICAL METHODS	6
3.1 Diffusion Equation	6
3.2 Correction of Concentration Gradient in Filter for De	7
4. RESULTS AND DISCUSSION	8
4.1 Diffusion Coefficients	8
4.2 Ionic Charge and Bentonite Density Dependencies for De	11
4.3 Bentonite Density and Ionic Charge Dependencies for FF	13
5. CONCLUSIONS	14
6. FUTURE WORK	14
7. ACKNOWLEDGMENTS	15
8. REFERENCES	15

Figures

Figure 1 Sectional view of a diffusion cell and a tracer tank connected with the diffusion cell	4
Figure 2 An image of concentration profiles in bentonite and filters for steady state	7
Figure 3 Changes in concentrations of Ni, Sm and Se in the tracer and measurement cells as a function of time in through-diffusion experiments (left) and the concentration profiles of these elements in bentonite (right)	9

Figure 4 Changes in concentrations of Am in the tracer and measurement cells as a function of time for the dry densities of 0.8, 1.4 and 1.8 Mg•m⁻³ ----- 10

Figure 5 De values of Ni²⁺, Sm³⁺, Am³⁺ and SeO₃²⁻ plotted as a function of ionic charge for a dry density of 1.8 Mg•m⁻³ ----- 11

Figure 6 De values of various ions as a function of bentonite dry density reported to date ----- 12

Figure 7 FF values of various ions as a function of bentonite dry density calculated from De and Do values ----- 13

Tables

Table I Experimental conditions for the Diffusion Experiments ----- 3

Table II Chemical Composition of the Simulated Porewater for the Diffusion Experiments of Ni, Sm and Se ----- 3

Table III Def, Det and De Values for Ni, Sm, Am and Se Obtained ----- 11

1. INTRODUCTION

Effective diffusion coefficient (D_e) in compacted bentonite is one of the key parameters for performance assessment of the geological disposal of high-level radioactive waste (HLW)[1], because it controls the release rates of nuclides from buffer material. Sodium bentonite has been considered as a candidate of the buffer material so far and much data concerning diffusion have been reported. It is known that D_e values of nuclides in bentonite depend on the diffusion species particularly on the charge of the species[2]. It is therefore ideal that D_e is determined every species, but D_e values of nuclides obtained under repository in relevant conditions are quite limited. In particular, no D_e in bentonite obtained under reducing conditions has been reported.

The surface of bentonite is negatively charged in the porewater for compacted bentonite. This is because the zero point of charge (ZPC) of the bentonite is lower than the pH of the porewater. The ZPC of montmorillonite which is major clay mineral is 2.5 and that for SiO_2 which is the major impurity of the bentonite is 2.0[3]. The ZPC values for goethite and feldspars which are respectively weathering and minor minerals composing the bentonite are respectively 7.2[4] and 2~2.4[3]. In this case, cations are electrostatically attracted near the surface of bentonite and the concentrations of cations near the surface of bentonite become high.

On the other hand, anionic species are repulsed from the surface of bentonite. In the case of the former, electrostatically attracted cations diffuse on the surface of bentonite due to concentration gradient. This is generally called surface diffusion. For the latter, since the migration pore is limited, it is called ion exclusion. This case is particularly called anion exclusion, because anionic species are excluded. If the surface of bentonite is positively charged, cationic species are excluded from the surface of the bentonite. In this case, it is called cation exclusion. In this case, surface diffusion is possible to occur for anionic species. Thus surface diffusion and ion exclusion depend on both the surface charge condition of solid and species, and surface diffusion and ion exclusion do not necessarily occur only for cations and anions, respectively.

For measurement of D_e in bentonite, some studies have been reported so far and they have discussed for surface diffusion in cations and anion exclusion in anions. Muurinen et al.[5] have measured the D_e values of Cs^+ and Sr^{2+} for a Na-bentonite, MX80 (density $1.75 \text{ Mg}\cdot\text{m}^{-3}$), pointing out a possibility of surface diffusion. Chueng and Gray [6] have also measured the D_e values of Cs^+ , I^- and Cl^- for a Na-bentonite, Avonlea bentonite (densities 1.25 and $1.75 \text{ Mg}\cdot\text{m}^{-3}$), discussing on surface diffusion for Cs^+ and on anion exclusion for I^- and Cl^- . However, neither the degree of surface diffusion nor anion exclusion can be quantitatively estimated in their study, because there is no datum for neutral species such as tritiated water (HTO) to be compared. For this bentonite, Oscarson and Gray [7] and Choi et al.[8] have also treated and discussed on surface diffusion based on obtained D_e values (HTO, Sr^{2+} , Na^+ , I^- and Ca^{2+} for [5] and HTO, I^- and Sr^{2+} for [6]), concluding that surface diffusion in cations is unimportant for performance assessment. This conclusion came from that apparent diffusion coefficients (D_a) predicted by geometric factors calculated from D_e values of HTO, distribution coefficients (K_d) obtained from batch experiments and free water diffusion coefficients (D_o) were approximately in good agreement with actually measured D_a values. However, no detailed discussion is made.

Muurinen et al.[9] have discussed a possibility of anion exclusion from the effect of ionic strength and bentonite density on D_e values of U and Cl. Eriksen and Jansson[10] have also obtained the D_e values of Cs^+ , Sr^{2+} and I^- for MX80, discussing on both surface diffusion of

cations and anion exclusion of Γ^- , and have calculated the surface diffusivities (D_s) of both cations. Furthermore, some other reports for surface diffusion in cations and anion exclusion in anions have been found.

For Japanese bentonite, Kato et al.[11, 12], and Sato and Shibutani[2] have reported D_e values of HTO, ^{137}Cs (Cs^+), ^{99}Tc (TcO_4^-), ^{237}Np ($\text{NpO}_2\text{CO}_3^-$), U ($\text{UO}_2(\text{CO}_3)_3^{4-}$), ^{125}I (I^-), ^{36}Cl (Cl^-) and ^{14}C (CO_3^{2-}) for a Na-bentonite, Kunigel-V1[®] obtained as a function of dry density of the bentonite and the obtained D_e values show a tendency of cations > neutral species (HTO) > anionic species. It is generally familiar that D_e values of cations are higher than those of anions. However, no quantitative discussion for the effect of the ionic charge of diffusion species on D_e in compacted bentonite has been carried out so far.

In this study, D_e in compacted bentonite was measured as a function of the ionic charge of diffusion species to quantitatively evaluate the degree of surface diffusion and cation and anion exclusion based on obtained data.

2. EXPERIMENTAL

2.1 Material and Experimental Conditions

Sodium bentonite, Kunigel-V1[®], which is a crude bentonite and was treated in the reference case of performance assessment in the second progress report[13], was used. Major clay mineral of the bentonite is Na-montmorillonite, which mode is 46–49wt% and chalcedony, quartz, plagioclase, calcite, dolomite, analcite and pyrite are contained as impurities. The detailed mineralogy is described in the literatures of Ito et al.[14, 15]. A simulated porewater, prepared to obtain certain concentration by dissolving NaCl, Na_2CO_3 and Na_2SO_4 in distilled water, was used in all diffusion experiments for Ni, Sm and Se. For Am, an HCl solution adjusted at pH2 was used to prevent sorption onto the wall of diffusion cell. The concentration and chemical composition was determined based on the results of bentonite leaching tests for various liquid-solid ratios. Tables I and II show the experimental conditions and the chemical composition of the simulated porewater, respectively.

2.2 Sorption Tests of Am onto Diffusion Cell Materials to Determine Experimental Conditions

Batch sorption tests of Am onto materials (acrylic resin and stainless steel) composing diffusion cell were carried out to determine experimental condition for diffusion, because sorption of Am onto diffusion cell is significant and it is difficult to carry out diffusion experiment. The simulated porewater shown in Table II was used and initial concentration of Am-241 was $160 \text{ Bq}\cdot\text{ml}^{-1}$. Consequently, sorption ratios of Am onto both materials increased with time and almost all Am in the solutions was sorbed onto the materials.

Next, surface active agent was painted on the wall of the acrylic bottle to reduce sorption quantity of Am. Although sorption quantity was a little reduced, about 60 % of initial quantity was adsorbed. Furthermore, Eu (europium) was added as a carrier. However, about 25 % of initial quantity was adsorbed. From this, it is considered to be difficult to carry out through-diffusion experiment for simulated porewater condition.

Additionally, sorption tests onto polyethylene, polypropylene, Teflon[®] and glass materials were also carried out. Although sorption quantity onto polyethylene material was the lowest, much Am was sorbed. Therefore, it can not be expected to improve by modification of material. Finally, sorption tests onto acrylic resin and stainless steel were carried out for a low pH condition. Consequently, no sorption was found for pH2. Based on this result, only diffusion experiments for Am were determined to carry out for pH2.

Table I Experimental Conditions for Diffusion Experiments

Bentonite	Ni, Sm, Se: Na-bentonite, Kunigel-V1 [®] (Kunimine Industries Co. Ltd.) Am: H-typed Kunigel-V1 [®]
Dry density	Ni, Sm, Se: 1.8 Mg•m ⁻³ Am: 0.8, 1.4, 1.8 Mg•m ⁻³
Sample size	Ni, Sm, Se: ϕ 20x3 mm, Am: ϕ 20x1 mm
Tracer	Sm (SmCl ₃), Se (Na ₂ SeO ₃), Ni (Ni-63+NiCl ₂ (carrier)) Am (Am-241)
Concentration	Sm: 0.01 M, Se: 0.001 M, Ni: 2 kBq•ml ⁻¹ (Ni-63)+0.001 M Am: 160 Bq•ml ⁻¹ (Am-241)
Porewater	Ni, Sm, Se: simulated porewater (see Table II) Am: HCl solution adjusted at pH2
pH	Ni, Sm: 5 ~ 6, Se: not adjusted (monitoring), Am: 2
Temperature	room temperature
Atmosphere	Se: Ar-atmosphere (O ₂ concentration < 1ppm) Ni, Sm, Am: aerobic condition
Producibility	Ni, Sm, Se: n = 2, Am: n = 1
Test period	30 ~ 130 d

2.3 Preparation of H-Typed Kunigel-V1

Since Kunigel-V1[®] contains much buffering materials, the pH of solution rises when the bentonite contacted with the solution. To reduce this, Kunigel-V1[®], which is the Na-bentonite, was treated with HCl in advance to prepare for H-typed bentonite. The treatment was carried out by the following procedure.

- (1) Kunigel-V1[®] contacted with 0.1 M HCl with a liquid-solid ratio of 10 ml•g⁻¹ and was filtered with a 5 C filter. This operation was repeated 3 times.
- (2) The treated bentonite was washed with ionized water with a liquid-solid ratio of 10 ml•g⁻¹.
- (3) The bentonite was dried at 110 °C for 24 hours and the grain size was prepared in a range of

Table II Chemical Composition of the Simulated Porewater for the Diffusion Experiments of Ni, Sm and Se

Ion	Concentration (M)
Na ⁺	0.83
Cl ⁻	0.0071
SO ₄ ²⁻	0.12
CO ₃ ²⁻	0.29

Ionic Strength: 1.2

200 to 350 mesh (42~74 μm).

When the bentonite was washed with ionized water, the pH of the water was 2.0 and leaching cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were little recognized. Therefore, it is presumed that the treated bentonite is H-type.

2.4 Experimental Procedure for Diffusion Experiments

The diffusion experiments were carried out by through-diffusion method[e.g 5]. Figure 1 shows the schematic view of a diffusion cell. The diffusion cell consists of a tracer cell, a measurement cell and a sample holder. The sample holder is set between both cells and bentonite is also filled in this holder. The tracer cell is additionally connected with a tracer tank with a volume of 1 dm^3 to keep the concentration of the tracer in the tracer cell constant and the solution is circulated by a pump. This tank is not constantly connected with the diffusion cell and was connected and circulated if necessary. Bentonite was dried at $105 \text{ }^\circ\text{C}$ for over night and filled in the sample holder with the size of 20 mm in diameter and 3 mm in thickness with a dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ for Ni, Sm and Se. For Am, the bentonite was filled in the sample holder with the size of 20 mm in diameter and 1 mm in thickness with the dry densities of 0.8, 1.4 and

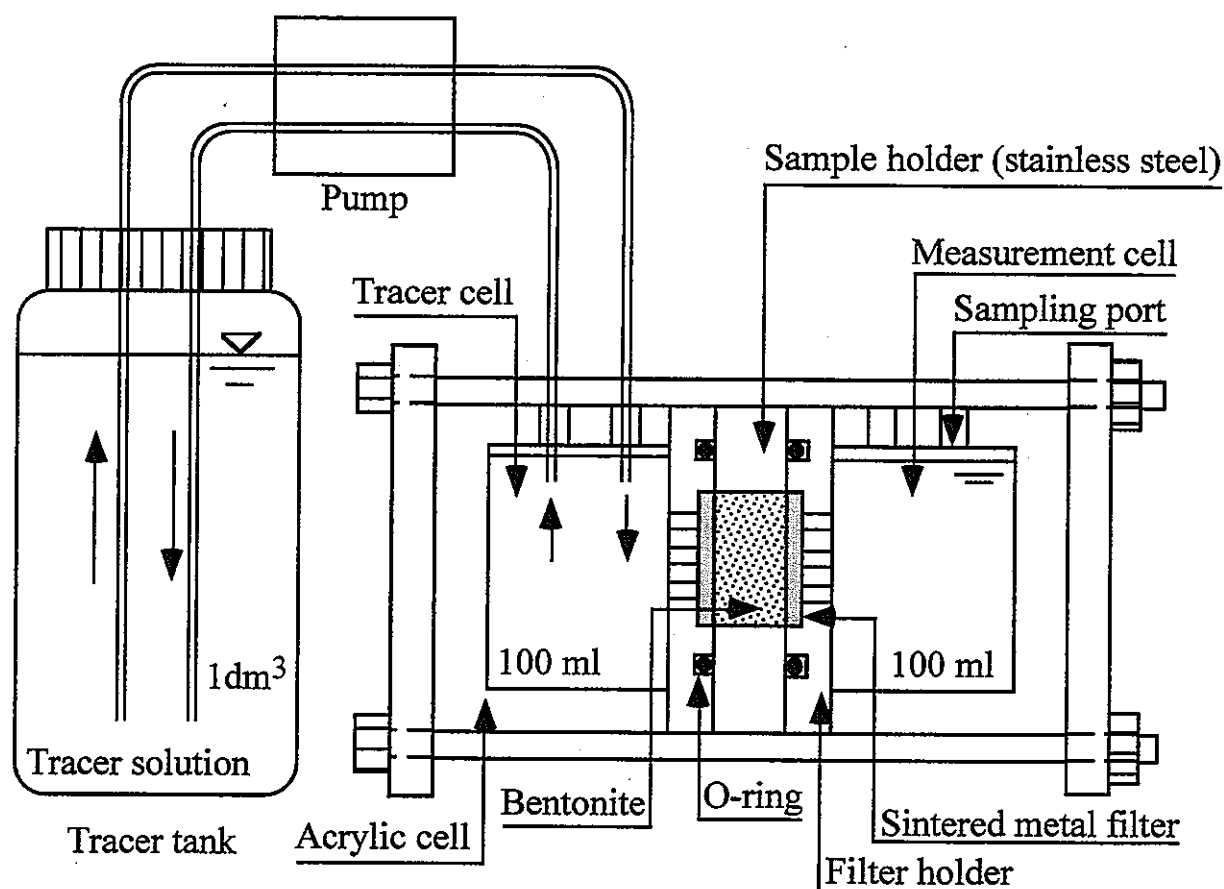


Figure 1 Sectional view of a diffusion cell and a tracer tank connected with the diffusion cell

1.8 Mg·m⁻³. The bentonite in the holder was saturated with simulated porewater before diffusion experiment for Ni, Sm and Se. For Ni and Sm, the bentonite was saturated with the simulated porewater adjusted at pH5-6. For Am, the bentonite was saturated with a HCl solution adjusted at pH2. The saturation was carried out in a vacuum chamber for a week after degassed an hour. The pH of the simulated porewater was monitored and adjusted using HCl if necessary.

All experiments for Se were conducted under Ar atmosphere (O₂ concentration < 1ppm). The operations for Se were performed in an atmospheric controled glove-box. The simulated porewater, degassed for over night, was injected into both cells to saturate the bentonite.

Each tracer solution was prepared by dissolving Na₂SeO₃, NiCl₂ and SmCl₃ in the simulated porewater so as to obtain certain concentrations. The tracer for Am was prepared by diluting a stock solution with the HCl solution adjusted at pH2. The tracer solution for Se was prepared by dissolving Na₂SeO₃ with degassed simulated porewater in the glove box. The tracer solution for Ni was prepared by dissolving a ⁶³Ni stock solution and NiCl₂ as a carrier in the simulated porewater so as to obtain a concentration of 2 MBq·l⁻¹ (10⁻³ M for carrier). In this case, since the concentration of ⁶³Ni is equivalent to 1.5x10⁻⁸ M, total concentration of Ni can be regarded as the concentration of carrier. All tracer solutions excepting Am were checked that no colloidal formation was all found from the results of filtration tests for 4 filters: 0.45 μm membrane filter, 300,000, 30,000 and 10,000 MWCO (Molecular Weight Cut Off) ultrafilters. For Am, it is presumed that no colloidal formation occurs, because the solution pH is quite low.

After the saturation of bentonite, the porewater in the tracer cell was exchanged with the tracer solution and then the experiment was started. Samples (0.5 ml for Ni and Am, 10 ml for Se and Sm) were periodically taken from the measurement cell and an identical volume of the porewater was added excepting Ni and Am. Since sampling volume was small for Ni and Am, no addition of the porewater was carried out. A small fraction of samples were also extracted from the tracer cell. The pH and ORP of the solution were monitored. Furthermore, through-diffusion tests for sintered metal filters were carried out for each element to correct concentration gradients in the filters when De values are calculated. The samples were analyzed for Se and Sm concentrations with ICP-AES (detection limit: 0.5 ppm for both). Those for Ni were analyzed for β activity (65.9keV) emitted from ⁶³Ni with a liquid scintillation counter (detection limit: 0.2 Bq·ml⁻¹). Those for Am were analyzed for α (5.4 MeV) and γ (64 keV) activities emitted from ²⁴¹Am with a liquid scintillation counter.

The accumulative quantities of Ni, Sm, Am and Se permeated through bentonite from the tracer cell were obtained with time based on these analyzed data. For Ni and Am, no addition of porewater was carried out after sampling. In this case, the accumulative quantities of Ni and Am permeated through bentonite were calculated from the following equation.

$$Q_n = C_n \cdot \{V - (n-1) \cdot v\} + \sum_{i=1}^{n-1} (C_i \cdot v) \quad (n = 1, 2, 3, 4, \dots) \quad (1)$$

Where Q_n is the accumulative quantity of the tracer permeated through bentonite up to the n-th sampling (cpm), C_n is the analyzed concentration in the n-th sample (cpm·ml⁻¹), V is the solution volume in the measurement cell (ml) and v is the sampling volume (ml)(0.5 ml for Ni and Am).

On the other hand, the accumulative quantities of Sm and Se permeated through bentonite were calculated from the following equation.

$$Q_n = C_n \cdot V + \sum_{i=1}^{n-1} (C_i \cdot v) \quad (n = 1, 2, 3, 4, \dots) \quad (2)$$

Where Q_n is the accumulative quantity of the tracer permeated through bentonite up to the n -th sampling (μg) and C_n is the analyzed concentration in the n -th sample (ppm).

At the end of diffusion experiment, bentonite in the holder was pushed out and cut with a knife into 0.3 mm pitched slices for Ni, Sm and Se. Each slice was immediately weighed and dried at 105 °C for over night to obtain water content. The slices for Se were immersed in 10 ml distilled water for several hours to remove Se from the slices. The slices for Ni and Sm were immersed in a 10 ml HCl solution (0.1 M) to extract these elements from the slices. The concentrations of Ni, Sm and Se were then analyzed and the concentration profiles in the bentonite were determined.

3. DIFFUSION THEORY AND ANALYTICAL METHODS

3.1 Diffusion Equation

The calculations of D_e values were based on Fickian law[16]. The diffusion equation for a one-dimensional non-steady state is generally expressed by the following equation[17].

$$\frac{\partial C}{\partial t} = \left(\frac{\phi \cdot D_p}{\alpha} \right) \cdot \frac{\partial^2 C}{\partial x^2} \quad (3)$$

Where C is the concentration of the tracer in the bentonite ($\text{kg} \cdot \text{m}^{-3}$), t is the diffusing time (s), D_p is the diffusion coefficient in the porewater ($\text{m}^2 \cdot \text{s}^{-1}$), ϕ is the porosity (-), α is the rock capacity factor ($\alpha = \phi + \rho \cdot K_d$), ρ is the dry density of the sample ($\text{Mg} \cdot \text{m}^{-3}$), K_d is the distribution coefficient ($\text{m}^3 \cdot \text{Mg}^{-1}$) and x is the distance from the source (m).

The $\phi \cdot D_p / \alpha$ is equal to apparent diffusion coefficient (D_a). The accumulative quantity of tracer permeated through bentonite up to an arbitrary time for equation (3), based on initial and boundary conditions, is written as follows:

Initial condition

$$C(t, x) = 0, t = 0, 0 \leq x \leq L$$

Boundary condition

$$C(t, x) = C_0 \cdot \alpha, t > 0, x = 0$$

$$C(t, x) = 0, t > 0, x = L$$

$$\frac{Q(t)}{A \cdot L \cdot C_0} = \frac{D_e}{L^2} t - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \left\{ \frac{(-1)^n}{n^2} \exp\left(\frac{D_e \cdot n^2 \cdot \pi^2 \cdot t}{L^2 \cdot \alpha} \right) \right\} \quad (4)$$

Where $Q(t)$ is the accumulative quantity of the tracer permeated through bentonite (cpm for Ni and Am, μg for Sm and Se), A is the cross-section area of the sample (m^2), L is the thickness of the sample (m), C_0 is the concentration of the tracer in the tracer cell ($\text{cpm}\cdot\text{ml}^{-1}$ for Ni and Am, ppm for Sm and Se) and D_e is the effective diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$).

At long time such as steady state, the exponentials fall away to zero. Therefore, equation (4) is approximately written by the following equation for steady state.

$$\frac{Q(t)}{A \cdot L \cdot C_0} = \frac{D_e}{L^2} t - \frac{\alpha}{6} \quad (5)$$

The D_e is calculated from the slope of $Q(t)/(A \cdot L \cdot C_0)$ with time in steady state based on equation (5). If surface diffusion does not occur, D_e is expressed by the following parameters[1, 17, 18].

$$D_e = \phi \cdot \left(\frac{\delta}{\tau^2} \right) \cdot D_0 = \phi \cdot G \cdot D_0 = FF \cdot D_0 \quad (6)$$

Where δ is the constrictivity (-), τ^2 is the tortuosity (-), D_0 is the free water diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$), G is the geometric factor (or tortuosity factor)(-) and FF is the formation factor (-).

It is familiar that D_0 depends on species. The D_0 is calculated by the Nernst expression[19].

$$D_0 = \frac{R \cdot T \cdot \lambda}{F^2 \cdot Z} \quad (7)$$

Where R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), λ is the limiting ionic equivalent conductivity ($\text{m}^2\cdot\text{S}\cdot\text{mol}^{-1}$), F is the Faraday constant ($96,493 \text{ C}\cdot\text{mol}^{-1}$) and Z is the absolute value of the ionic charge (-).

The D_0 values of Ni^{2+} , Sm^{3+} , Am^{3+} and SeO_3^{2-} are calculated to be 6.61×10^{-10} , 6.08×10^{-10} , 6.24×10^{-10} and $8.13 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ (25°C)[20], respectively, using equation (7).

3.2 Correction of Concentration Gradient in Filter for D_e

The effect of the concentration gradient of tracer in the filter

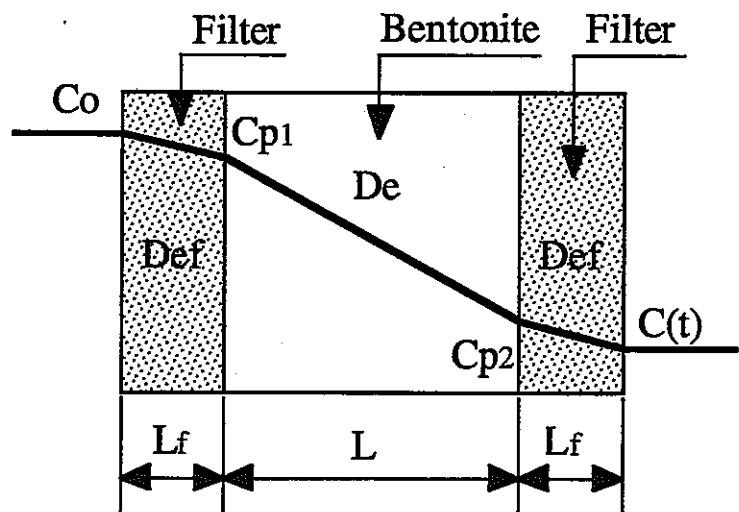


Figure 2 An image of concentration profiles in bentonite and filters for steady state

which was used to constrict the swelling of bentonite is also included in De calculated based on equation (5) and this concentration gradient in the filter must be corrected to determine true De in bentonite. **Figure 2** shows an image of the concentration profiles in the bentonite and filters for steady state. As shown in **Figure 2**, actual concentration gradient in bentonite is between C_{p1} and C_{p2} . However, the concentrations of the tracer in the porewater at the border between bentonite and filter, C_{p1} and C_{p2} , can not be directly measured. In this study, De was corrected by the following equation derived for steady state.

$$De = \frac{L}{\left(\frac{L + 2L_f}{De_t}\right) - \left(\frac{2L_f}{De_f}\right)} \quad (8)$$

Where De_t is the effective diffusion coefficient before correction ($m^2 \cdot s^{-1}$), De_f is the effective diffusion coefficient in the filter ($m^2 \cdot s^{-1}$) and L_f is the thickness of the filter (m)(1 mm).

The detailed derivation method for the correction of De is described in [21].

4. RESULTS AND DISCUSSION

4.1 Diffusion Coefficients

Figure 3 shows the changes in concentrations of Ni, Sm and Se in both cells as a function of time in through-diffusion experiments and the concentration profiles in bentonite. The concentrations of Ni and Sm in the measurement cell show non-linear curves in transient state and increase in a straight line as a function of time in steady state. For Se, no non-linear curve, shows transient state like Ni and Sm, is found. This may be because Se is little sorptive onto bentonite[22]. Each through-diffusion experiment was carried out in duplicate and good reproducibility was obtained. The concentration profiles of Ni, Sm and Se in the bentonite approximately linearly decrease from the tracer cell side to the other side in all cases. This indicates that the diffusion in all cases is in steady state. The concentrations of Ni, Sm and Se in the tracer cell are approximately kept constant, although some variation in the plots is found.

Figure 4 shows the changes in concentrations of Am in both cells as a function of time for the dry densities of 0.8, 1.4 and 1.8 $Mg \cdot m^{-3}$. Since no slicing of bentonite was carried out for Am, no concentration profile in bentonite is shown. The concentrations of Am in the measurement cell also show non-linear curves in transient state and increase in a straight line as a function of time in steady state.

Table III shows obtained De_f , De_t and De values for Ni, Sm, Am and Se together with pH, Eh and temperature. Both pH and Eh were approximately stable during the experiments. Although Sm is possible to form carbonate complexes such as $SmCO_3^+$ and $Sm(CO_3)_2^-$ in a high pH region[24], since the pH values were kept around 5.5, Sm^{3+} is predominant in this case. Also for Ni, hydroxide such as $Ni(OH)_2(aq)$ is formed in a high pH region[25], but Ni^{2+} is predominant in this pH condition. Similarly the dominant species of Se is estimated to be SeO_3^{2-} from Eh-pH diagrams[25]. Although Am is also possible to take similar behaviour to that of Sm, since the pH values of solutions were kept around 2, Am^{3+} is predominant in this case.

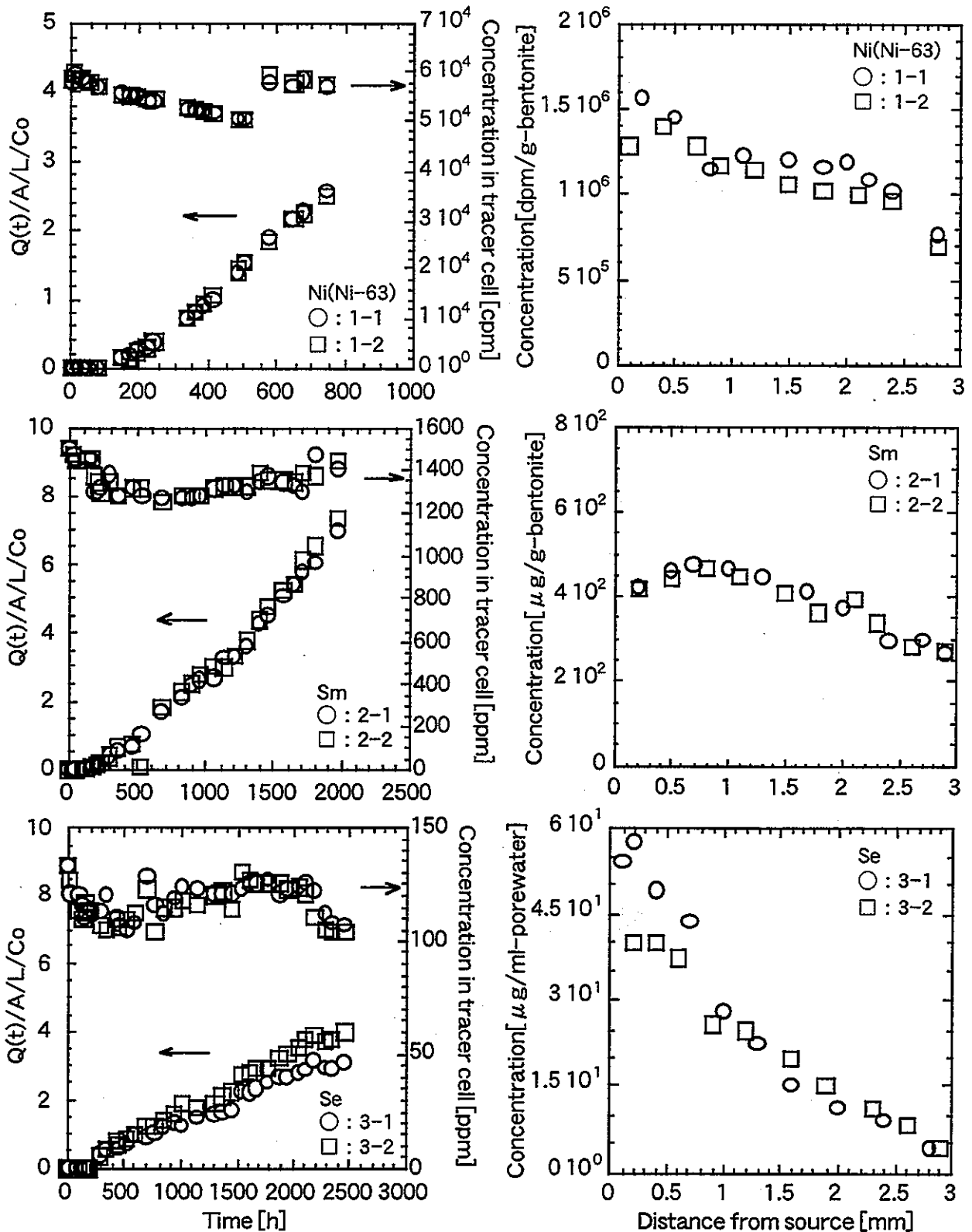


Figure 3 Changes in concentrations of Ni, Sm and Se in the tracer and measurement cells as a function of time in through-diffusion experiments (left) and the concentration profiles of these elements in bentonite (right)

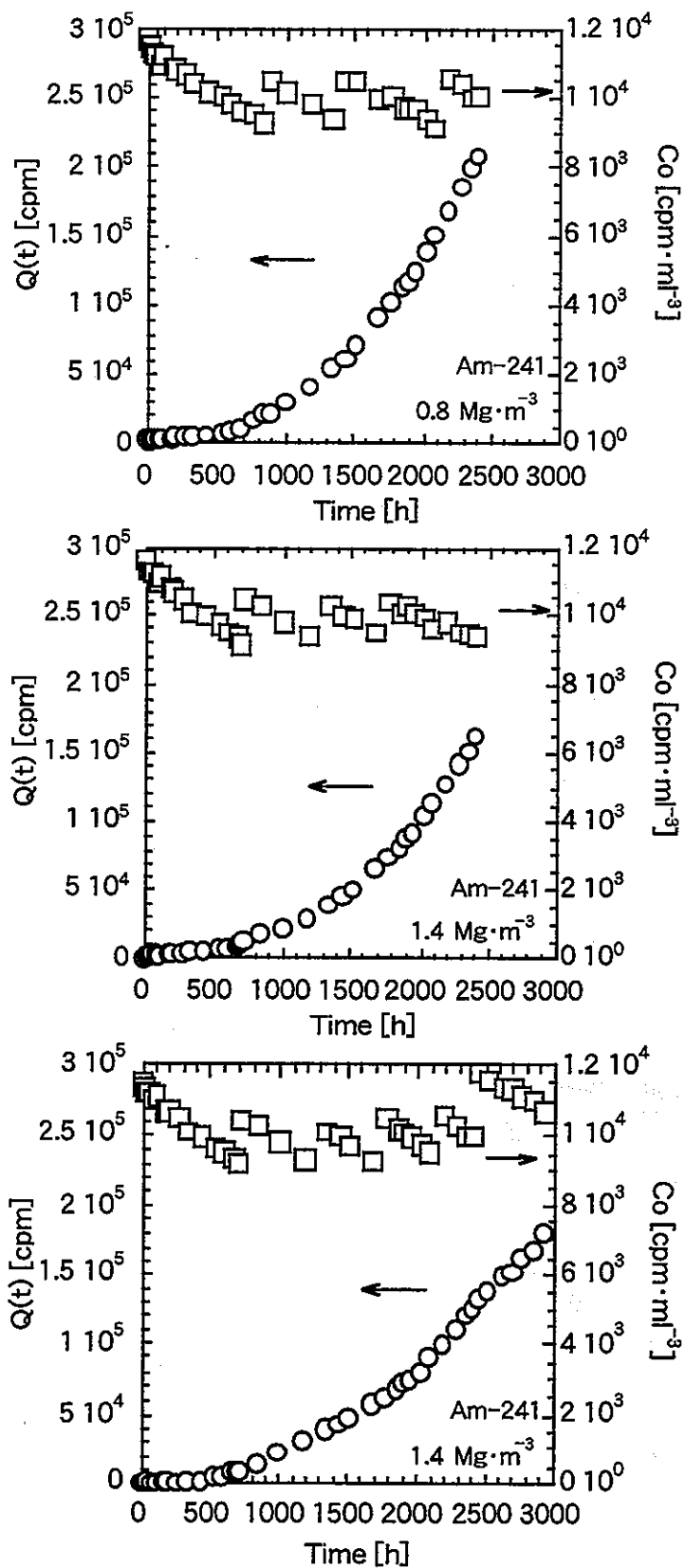


Figure 4 Changes in concentrations of Am in the tracer and measurement cells as a function of time for the dry densities of 0.8, 1.4 and 1.8 Mg·m⁻³

Table III De_f , De_t and De Values for Ni, Sm, Am and Se Obtained

No.	Element (Nuclide)	Species	Dry density [Mg/m ³]	Effective diffusion coefficient [m ² /s]			pH	Eh [mV]*	Temperature [°C]
				De_f	De_t	De			
1-1	Ni (Ni-63)	Ni ²⁺	1.8	5.0x10 ⁻¹¹	3.2x10 ⁻¹¹	2.6x10 ⁻¹¹	5.6±0.1	23.3±0.8	
1-2				3.3x10 ⁻¹¹	3.1x10 ⁻¹¹	2.9x10 ⁻¹¹	5.6±0.1	23.3±0.7	
2-1	Sm	Sm ³⁺	1.8	1.4x10 ⁻¹¹	3.0x10 ⁻¹¹	1.3x10 ⁻¹⁰	5.3±0.3	23.5±0.5	
2-2				1.5x10 ⁻¹¹	2.9x10 ⁻¹¹	7.3x10 ⁻¹¹	5.4±0.2	23.5±0.5	
3-1	Se	SeO ₃ ²⁻	1.8	4.2x10 ⁻¹¹	9.2x10 ⁻¹²	6.1x10 ⁻¹²	11.4±0.2	65±30	
3-2				6.2x10 ⁻¹¹	1.2x10 ⁻¹¹	8.1x10 ⁻¹²	11.3±0.5	68.1±23.3	
4-1		Am ³⁺	0.8	4.2x10 ⁻¹¹		7.4x10 ⁻¹¹	2 (not monitored)	room	
4-2			1.4	3.7x10 ⁻¹¹		5.2x10 ⁻¹¹	2 (not monitored)	room	
4-3			1.8	3.3x10 ⁻¹¹		1.8x10 ⁻¹¹	2 (not monitored)	room	

De_f : effective diffusion coefficient in the filter

De_t : effective diffusion coefficient in the filter plus bentonite

De : effective diffusion coefficient in bentonite

*Eh vs. SCE, Eh vs. SHE can be calculated based on equation proposed by Ostwald;

Eh = ORP + 0.2415 - 0.00079 (Tc-25)[23], where Eh is the Eh vs. SHE (V), ORP is the Eh vs. SCE (V) and Tc is the temperature(°C).

4.2 Ionic Charge and Bentonite Density Dependencies for De

Figure 5 shows the De values of Ni²⁺, Sm³⁺, Am³⁺ and SeO₃²⁻ as a function of ionic charge. The De values increase with increasing ionic charge excepting Am³⁺. The authors[2] have measured De values of HTO, ¹³⁷Cs (Cs⁺), ⁹⁹Tc (TcO₄⁻), ²³⁷Np (NpO₂CO₃⁻) and U (UO₂(CO₃)₃⁴⁻) as a function of dry density and reported that the De values were in the order, Cs⁺ > HTO > anions. Kato et al.[11] have obtained De values of HTO, ¹³⁷Cs (Cs⁺) and ⁹⁹Tc (TcO₄⁻) as a function of dry density and reported the same result. Moreover, Kato et al.[12] have obtained De values of ¹²⁵I (I⁻), ³⁶Cl (Cl⁻) and ¹⁴C (CO₃²⁻) as a function of dry density and reported that the De values were in the order, I⁻ ≥ Cl⁻ > CO₃²⁻. As clear also in

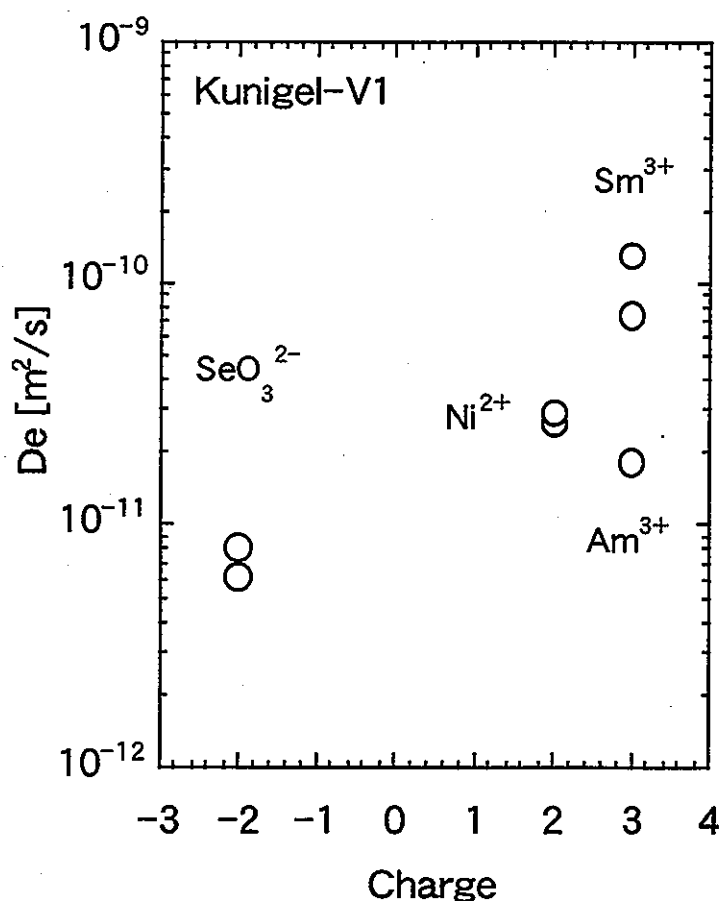


Figure 5 De values of Ni²⁺, Sm³⁺, Am³⁺ and SeO₃²⁻ plotted as a function of ionic charge for a dry density of 1.8 Mg·m⁻³

studies to date, De values for cations tend to be higher than those of HTO and De values for anions tend to be lower than those of HTO. This cause is generally interpreted to be due to electrostatic interaction. The surface of bentonite is negatively charged and cations are electrostatically attracted, while anions are repulsed. The retardation effect by the latter is called anion exclusion. However, detailed mechanism for surface diffusion on solid-liquid interface has not been made clear. The concentration distributions of cations and anions from the surface of solid can be calculated based on electric double layer theory and some studies for the modelling of De based on this theory have been reported[2, 11, 12, 26]. Here the degree of surface diffusion and anion exclusion is quantitatively evaluated based on De data obtained in this study and data reported to date.

For Am³⁺, not so high De was obtained. Only diffusion experiments for Am were carried out for H-typed bentonite and pH2. The surface of bentonite in this condition is presumed to be positively charged, because the ZPC of the bentonite is predicted to be higher than 2 at least. This is clear because the ZPC values of minerals such as montmorillonite, SiO₂ and feldspars composing the bentonite. Therefore, it is presumed to be due to cation exclusion that the De of Am³⁺ was lower about one order of magnitude than that of Sm³⁺.

The obtained De values were compared with those[2, 11, 12] reported to date. The order of De values was consequently Cs⁺ > Sm³⁺ > HTO > Ni²⁺ > anions (I⁻, Cl⁻, CO₃²⁻, SeO₃²⁻, TcO₄⁻, NpO₂CO₃⁻ and UO₂(CO₃)₃⁴⁻), showing a tendency of cations > neutral species > anions excepting Am³⁺. Figure 6 shows De values as a function of dry density reported to date. The order of De values does not necessarily agree to the number of ionic charge. This reason may be because the Do of Ni²⁺ (6.61x10⁻¹⁰ m²·s⁻¹ (25°C)) is about 1/3 of that of HTO (2.28x10⁻⁹ m²·s⁻¹ (25°C)[27]). Similarly, since the Do of Sm³⁺ (6.08x10⁻¹⁰ m²·s⁻¹ (25°C)) is also about 1/3 of that of Cs⁺ (2.06x10⁻⁹

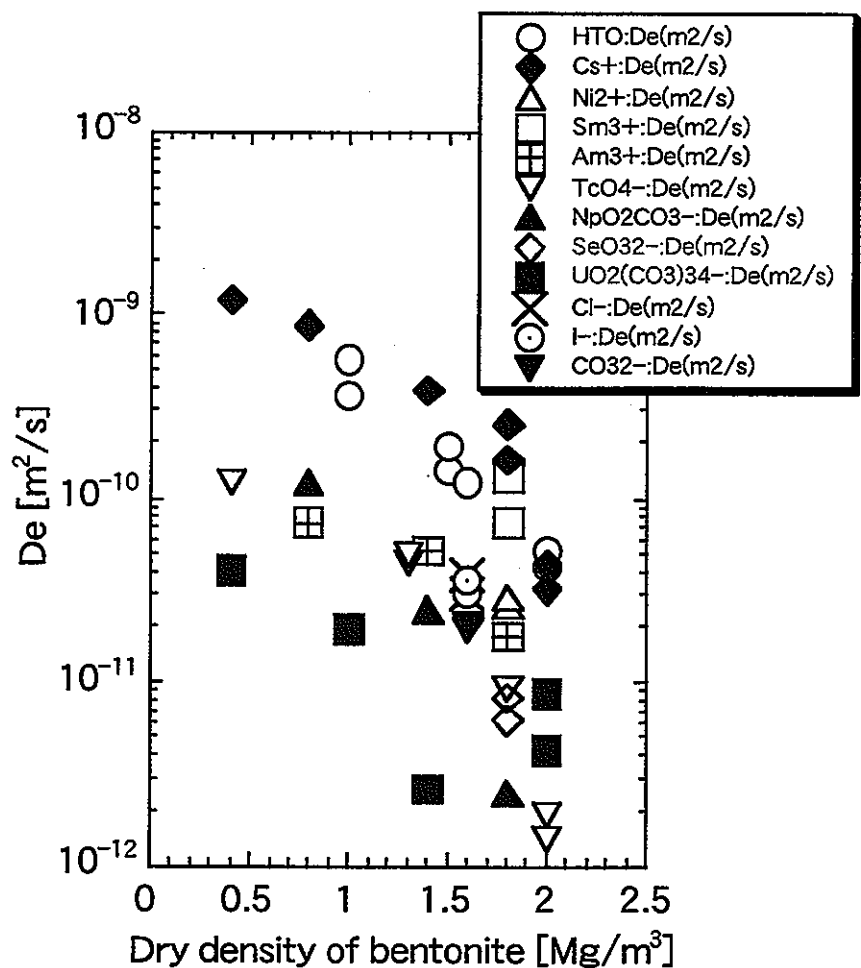


Figure 6 De values of various ions as a function of bentonite dry density reported to date
Ni²⁺ and Sm³⁺: pH5~6, Am³⁺: pH2

$\text{m}^2\cdot\text{s}^{-1}$ (25°C)[20], it is presumed that the D_e values of Sm^{3+} were a little lower than those of Cs^+ .

For Am^{3+} , the D_e values of Am^{3+} decreased with increasing the dry density of bentonite as shown in Figure 6. The D_e values of Am^{3+} were approximately the same degree as those of anions. Since the D_o of Am^{3+} is also approximately the same ($6.24 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ at 25 °C) as that of Sm^{3+} , the correction or normalization of D_o for each species is essential to evaluate in detail the degree of surface diffusion, anion exclusion and cation exclusion.

4.3 Bentonite Density and Ionic Charge Dependencies for FF

The FF values were calculated normalizing D_e values by D_o values. Figure 7 shows the FF values as a function of the dry density of bentonite. The D_o values of I^- , Cl^- , CO_3^{2-} [20] and TcO_4^- [28] are calculated 2.05×10^{-9} , 2.03×10^{-9} , 9.23×10^{-10} and $1.95 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ (25°C), respectively. Although the D_o values of $\text{NpO}_2\text{CO}_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ have not been measured, that of $\text{UO}_2(\text{CO}_3)_3^{4-}$ has been estimated $7.2 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ (25°C)[29] based on the Stokes equation[19] by the ionic radius calculated from the molecular structure. Since the hydrous radius of ion generally increases with increasing the absolute value of ionic charge, D_o decreases with increasing the absolute value of ionic charge, meaning that the

D_o of $\text{NpO}_2\text{CO}_3^-$ is similar values to those of ions which take the same absolute value of ionic charge. The D_o of HCO_3^- ($1.19 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ (25°C)[20]) was thereupon used as the analogue of $\text{NpO}_2\text{CO}_3^-$.

The FF values showed a tendency to be in the order, $\text{Sm}^{3+} > \text{Cs}^+ > \text{Ni}^{2+} > \text{HTO} > \text{Am}^{3+} > \text{SeO}_3^{2-} > \text{NpO}_2\text{CO}_3^-$ for a dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ and those for cations wholly showed a

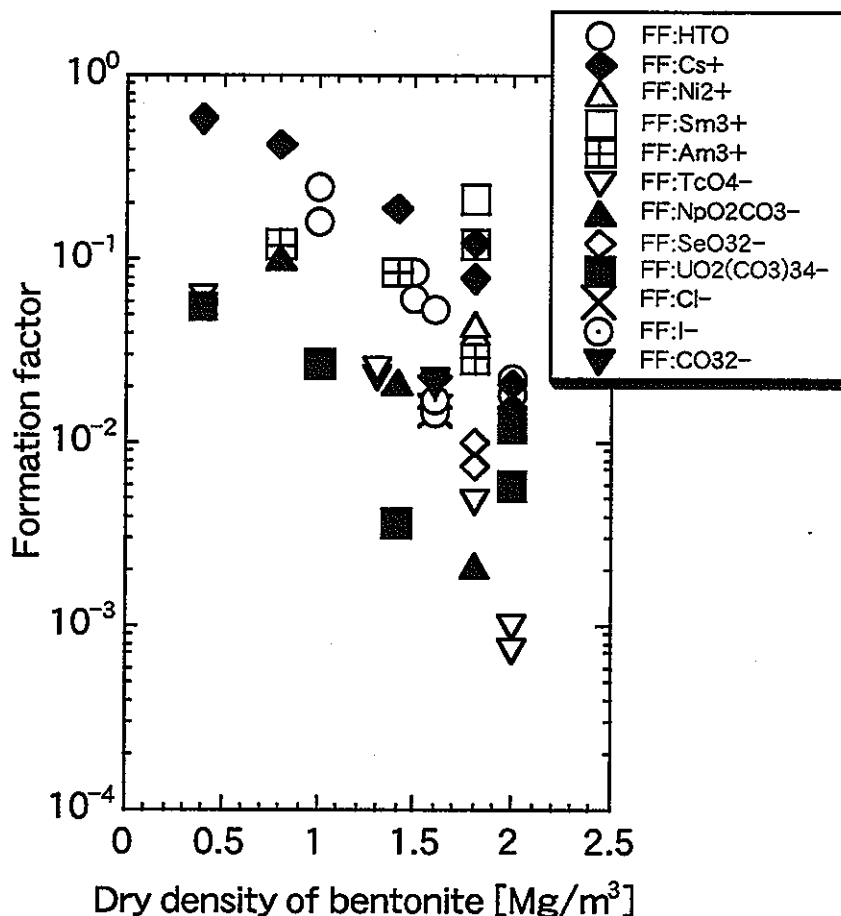


Figure 7 FF values of various ions as a function of bentonite dry density calculated from D_e and D_o values

Ni^{2+} and Sm^{3+} : pH5~6, Am^{3+} : pH2

tendency to be high for overall density. This indicates a possibility of surface diffusion in cations excepting Am^{3+} . While, the FF values for all anions were wholly lower than those of HTO for overall density and the effect of ionic charge on De was clearly found. This indicates a possibility of anion exclusion in anions.

The FF values of Am^{3+} are also relatively high compared with those of anions, although it is possible that cation exclusion occurs. This is presumed because the ZPC of the bentonite is low and near pH2. In this case, the charge (positively charged) is not so high and repulsion from the surface of bentonite is presumed to be small.

The degree of surface diffusion, anion exclusion and cation exclusion was estimated for a bentonite dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ based on De values reported to date. The FF values of Sm^{3+} , Cs^+ and Ni^{2+} were approximately 5, 3 and 1.3 times greater than that of HTO, respectively. While, those of TcO_4^- , $\text{NpO}_2\text{CO}_3^-$ and SeO_3^{2-} were approximately 1/7, 1/16 and 1/5 of that of HTO, respectively. The FF of Am^{3+} was approximately 85 % of that of HTO and was only a little low compared to that of HTO. If these effect is caused by electrostatic interaction, this is affected by the ionic strength of porewater. In this study, simulated porewater with an ionic strength of approximately 1.2 was used excepting Am^{3+} . For Am^{3+} , a HCl solution adjusted at pH2 was used. Therefore, there is a possibility that more significant surface diffusive and anion exclusive effect is found for porewater with lower ionic strength.

5. CONCLUSIONS

- (1) The De values of Ni^{2+} , Sm^{3+} and SeO_3^{2-} in bentonite for a bentonite dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ were obtained. Additionally, the De values of Am^{3+} in bentonite for the dry densities of 0.8, 1.4 and $1.8 \text{ Mg}\cdot\text{m}^{-3}$ were also obtained for a porewater condition of pH2. The De values, including De data reported to date, were in the order, $\text{Cs}^+ > \text{Sm}^{3+} > \text{HTO} > \text{Ni}^{2+} >$ anions for overall density, showing a tendency to be approximately in the order, cations $>$ neutral species $>$ anions excepting Am^{3+} . Only the De values of Am^{3+} were approximately the same degree as those of anions. This reason may be because the Do of Am^{3+} is about 1/3 of that of HTO and Am^{3+} was electrostatically repulsed from the surface of bentonite by cation exclusion.
- (2) The FF values for the same density, calculated normalizing Do, were in the order, $\text{Sm}^{3+} > \text{Cs}^+ > \text{Ni}^{2+} > \text{HTO} > \text{Am}^{3+} > \text{SeO}_3^{2-} > \text{NpO}_2\text{CO}_3^-$, showing a tendency to be in the order, cations $>$ neutral species $>$ anions. The degree of surface diffusive effect for a dry density of $1.8 \text{ Mg}\cdot\text{m}^{-3}$ was approximately estimated to be 5 times for Sm^{3+} , 3 times for Cs^+ and 1.3 times for Ni^{2+} as much assuming that FF of HTO is the standard. The degree of anion exclusive effect for the same condition was approximately calculated to be 1/7 for TcO_4^- , 1/16 for $\text{NpO}_2\text{CO}_3^-$ and 1/5 for SeO_3^{2-} as much. The degree of cation exclusive effect for the same density was approximately calculated to be 85 % for Am^{3+} as much and not so much effect was recognized.

6. FUTURE WORK

In this study, although the degree of surface diffusion, anion exclusion and cation exclusion was estimated based on experimental data, theoretical discussion is not carried out. Discussion from theoretical viewpoint, especially from the viewpoint of electrostatic interaction, will be

carried out.

7. ACKNOWLEDGMENTS

The author would like to thank Messrs. S. Ueta and H. Kato of Mitsubishi Materials Corporation for the performance of diffusion experiments.

8. REFERENCES

1. H. Sato, Data Setting for Effective Diffusion Coefficients (De) of Nuclides in the Buffer for Reference Case in Performance Assessment of the Geological Disposal of High-Level Radioactive Waste (I), PNC TN8410 98-097, 1998.
2. H. Sato and T. Shibutani, Study on Adsorption and Diffusion Mechanism of Nuclides in Buffer Material and Geosphere, PNC Technical Review No.91, PNC TN8410 94-284, 1994 (in Japanese).
3. W. Stumm and J. J. Morgan, *Aquatic Chemistry: An Introduction Emphasising Chemical Equilibria in Natural Waters*, 2nd ed. (John Wiley and Sons, Inc., New York, 1981). p. 631.
4. T. Shibutani, Y. Nishikawa, S. Inui, N. Uchidate, M. Yui, and T. Mano, A Study on Sorption Behaviour for Se onto Rocks and Minerals, PNC TN8410 94-395, 1994 (in Japanese).
5. A. Muurinen, P. Pentilä-Hiltunen, and J. Rantanen, Diffusion Mechanisms of Strontium and Cesium in Compacted Sodium Bentonite, in *Scientific Basis for Nuclear Waste Management X*, edited by J. K. Bates and W. B. Seefeldt (Mater. Res. Soc. Proc. **84**, Pittsburgh, PA, 1987) pp. 803-811.
6. S. C. Chung and M. N. Gray, Mechanism of Ionic Diffusion in Dense Bentonite, in *Scientific Basis for Nuclear Waste Management XII*, edited by W. Lutze and R. C. Ewing (Mater. Res. Soc. Proc. **127**, Pittsburgh, PA, 1989) pp. 677-681.
7. D. W. Oscarson and M. N. Gray, Surface Diffusion: Is It an Important Transport Mechanism in Compacted Clay ?, *Clay and Clay Minerals* **42**, 534 (1994).
8. J. W. Choi, D. W. Oscarson, and M. N. Gray, Diffusion Transport Through Compacted Na- and Ca-Bentonite, *J. Contaminant Hydrology* **22**, 189 (1996).
9. A. Muurinen, P. Pentilä-Hiltunen, and K. Uusheimo, Diffusion of Chloride and Uranium in Compacted Sodium Bentonite, in *Scientific Basis for Nuclear Waste Management XII*, edited by W. Lutze and R. C. Ewing (Mater. Res. Soc. Proc. **127**, Pittsburgh, PA, 1989) pp. 743-748.
10. T. E. Eriksen and M. Jansson, Diffusion of I^- , Cs^+ and Sr^{2+} in Compacted Bentonite - Anion Exclusion and Surface Diffusion, SKB 96-16, 1996.
11. H. Kato, M. Muroi, N. Yamada, H. Ishida, and H. Sato, Estimation of Effective Diffusivity in Compacted Bentonite, in *Scientific Basis for Nuclear Waste Management XVIII*, edited by T. Murakami and R. C. Ewing (Mater. Res. Soc. Proc. **353**, Pittsburgh, PA, 1995) pp. 277-284.
12. H. Kato, T. Nakazawa, and S. Ueta, Effective Diffusivities of Iodine, Chlorine, and Carbon in Bentonite Buffer Material, in *Scientific Basis for Nuclear Waste Management XXII* (Mater. Res. Soc. Proc. **556**, in press).
13. Japan Nuclear Cycle Development Institute, H12 Project to Establish Technical Basis for HLW Disposal in Japan: Project Overview Report, JNC TN1400 99-010, 1999.

14. M. Ito, M. Okamoto, M. Shibata, Y. Sasaki, T. Danbara, K. Suzuki, and T. Watanabe, Mineral Composition Analysis of Bentonite, PNC TN8430 93-003, 1993 (in Japanese).
15. M. Ito, M. Okamoto, K. Suzuki, M. Shibata, and Y. Sasaki, Mineral Composition Analysis of Bentonite, J. Atomic Energy Soc. Japan, **36** (11), 1055-1058 (1994)(in Japanese).
16. J. Crank, *The Mathematics of Diffusion*, 2nd ed. (Pergamon Press, Oxford, 1975).
17. K. Skagius and I. Neretnieks, Diffusion in Crystalline Rocks of Some Sorbing and Nonsorbing Species, KBS TR82-12, 1982.
18. H. Sato, T. Shibutani, and M. Yui, Experimental and Modelling Studies on Diffusion of Cs, Ni and Sm in Granodiorite, Basalt and Mudstone, J. Contaminant Hydrology **26**, 119 (1997).
19. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. (Butterworths, London, 1959). p. 317.
20. Y. Marcus, *Ion Properties* (Marcel Dekker, Inc., New York, 1997), pp. 168-170.
21. H. Sato, Diffusivity Database (DDB) for Major Rocks: Database for the Second Progress Report, JNC TN8400 99-065, 1999.
22. T. Shibutani, M. Yui, and H. Yoshikawa, Diffusion in Crystalline Rocks of Some Sorbing and Nonsorbing Species, in *Scientific Basis for Nuclear Waste Management XVII*, edited by A. Barkatt and R. A. Van Konynenburg (Mater. Res. Soc. Proc. **333**, Pittsburgh, PA, 1994) pp. 725-730.
23. S. Tajima, *An Introduction to Electrochemistry*, 3rd ed. (Kyoritsu, Tokyo, 1986), p.102 (in Japanese).
24. S. Shibutani, PNC Technical Review, Solubility Measurement of Trivalent Lanthanide for Performance Assessment, No.97, PNC TN8410 96-011, 1996 (in Japanese).
25. D. G. Brookins, *Eh-pH Diagrams for Geochemistry* (Springer-Verlag, Berlin, 1988).
26. H. Sato and M. Yui, Diffusion Behaviour for Se and Zr in Sodium Bentonite, in *Scientific Basis for Nuclear Waste Management XVIII*, edited by T. Murakami and R. C. Ewing (Mater. Res. Soc. Proc. **353**, Pittsburgh, PA, 1995) pp. 269-276.
27. Chemical Society of Japan, *Chemical Handbook*, 4th ed. (Maruzen, Tokyo, 1993), p. II-61 (in Japanese).
28. H. Sato, M. Yui, and H. Yoshikawa, Ionic Diffusion Coefficientts of Cs^+ , Pb^{2+} , Sm^{3+} , Ni^{2+} , SeO_4^{2-} and TcO_4^- in Free Water Determined from Conductivity Measurements, J. Nucl. Sci. Tech., **33** (12), 950-955 (1996).
29. T. Yamaguchi, Diffusivity of Actinides in a Granite from Inada, Ibaraki, Japan, PNC TN1100 96-010, 156-160, 1996 (in Japanese).