

Sorption Behavior of Neptunium onto Smectite under Reducing Conditions in Carbonate Media

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Sorption Behavior of Neptunium onto Smectite under Reducing Conditions in Carbonate Media

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Abstract

Sorption behavior of neptunium onto smectite was investigated under reducing conditions in carbonate media. Distribution coefficient (K_d) of neptunium on smectite was determined by a batch method as a function of total carbonate concentration (C_T) in a weak alkaline solution. The C_T value ranged from 0.09 M ($M \equiv \text{mol} \cdot \text{dm}^{-3}$) to 1.0 M. The obtained K_d value decreased with increase the total carbonate concentration. It was found that both Np(IV) and Np(V) coexisted in the solution by a TTA-extraction method. In the present experimental conditions, contribution of neptunyl ion, NpO_2^+ , carbonate complexes of Np(V), $\text{NpO}_2(\text{CO}_3)_n^{(2n-1)-}$ ($n=1, 2$ and 3), and a carbonatohydroxo complex of Np(IV), $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$, to the sorption onto smectite was expected. The K_d values of respective species of neptunium were estimated by a least-squares fit to the experimental data. From the obtained K_d values of respective species, sorption behavior of neptunium onto smectite was discussed.

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還元条件・炭酸共存下におけるスメクタイトに対する ネプツニウムの収着挙動

(研究報告)

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要 旨

還元条件・炭酸共存下におけるネプツニウムの収着挙動を調べた。バッチ法を用いて、スメクタイトに対するネプツニウムの分配係数の全炭酸濃度の関数を求めた。全炭酸濃度は、0.09 M ($M \equiv \text{mol} \cdot \text{dm}^{-3}$)から 1.0 M の範囲で変化させた。得られた分配係数は、全炭酸濃度の増加とともに減少した。水溶液は Np(IV) と Np(V)の共存系であることが、TTA 抽出法により明らかになった。本研究の試験条件では、水溶液中において、ネプツニルイオン NpO_2^+ 、Np(V)の 3 種の炭酸錯体 $\text{NpO}_2(\text{CO}_3)_n^{(2n-1)-}$ ($n=1, 2$ および 3) と、Np(IV)の 1 種のヒドロキソ炭酸錯体 $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ の収着への寄与が予想された。試験で得られた分配係数を最小二乗法により解析することで、各化学種の分配係数を推定した。各化学種の分配係数の値から、スメクタイトに対するネプツニウムの収着挙動を論じた。

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1. INTRODUCTION

Understanding the radionuclide migration behavior is important for safety assessment of a geological disposal of high-level radioactive wastes (HLW). Chemical compositions and pH value of a groundwater around the repository of HLW will affect the migration behavior of cationic radionuclides due to the complexation with anionic ligands when the radionuclides dissolve to the groundwater. In the report of "H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan" [1], five types of hypothetical groundwater are summarized. Among five types, four types of hypothetical groundwater, which are FRHP (fresh-reducing-high pH), FRLP (fresh-reducing-low pH), SRHP (saline-reducing-high pH) and SRLP (saline-reducing-low pH), have been defined and modeled as generic groundwater compositions for the performance assessment for HLW disposal in the "H-3" first progress report [2]. In some special locations in Japan, however, middle salinity, reducing, neutral pH waters which contain high concentration of HCO_3^- have been found. Thus, a new type of hypothetical groundwater "MRNP" (mixing-reducing-neutral pH) [3] has been defined as an additional generic groundwater compositions in the "H-12" report [1]. The MRNP groundwater contains high concentration of HCO_3^- (5×10^3 ppm) and Cl^- (1×10^4 ppm).

Thus, investigation of migration behavior of radionuclides in buffer materials and rocks in highly carbonate media is important for the performance assessment for HLW disposal. Especially, Np-237, which is an α -emitter and has the long half-life of 2.14×10^6 years, is regarded as one of the most hazardous radionuclides for HLW disposal. In a deep geological environment which is expected to be reducing conditions, a tetravalent neptunium will be dominant, while a pentavalent neptunium is dominant in the near-neutral solutions contact with air. Expected dominant aqueous species of neptunium in a deep geological environment are $\text{Np}(\text{OH})_4(\text{aq})$ and $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ in the "H-12" report [1]. Consequently, it is important to understand the migration behavior of Np(IV). Extensive studies have been performed to obtain the data to elucidate the sorption and diffusion behavior of neptunium. The previous studies on neptunium sorption onto bentonites under reducing conditions, however, are insufficient to evaluate the sorption behavior of Np(IV), especially in highly carbonate media.

In the present study, sorption of neptunium onto smectite under reducing

conditions in highly carbonate media has been investigated. Distribution coefficient (K_d) of neptunium onto smectite, which is a major component of bentonite, is determined in a weak alkaline solution as a function of total carbonate concentration (C_T). Considering the redox state speciation of neptunium, the K_d values of respective aqueous neptunium species are obtained. The sorption behavior of neptunium carbonate complexes is discussed.

2. EXPERIMENTAL

2.1 Preparation of Smectite

The bentonite sample of Kunipia-F® (Kunimine Industries Co.), which was commercially purified from Kunigel-V1® (Kunimine Industries Co.), was used as a starting material for purification of smectite. Before purification, Kunipia-F® contains 99 wt.% of Na-type smectite and some impurities, for example, quartz and calcite. A counter ion of Na⁺ on the smectite may be replaced with other counter ions such as Ca²⁺. Thus, further purification was required for the present study.

The dried Kunipia-F® of 20 g and 1 M ($M \equiv \text{mol} \cdot \text{dm}^{-3}$) NaCl of 1 dm³ was mixed in a glass beaker and was shaken for 3 hours. After 1 hour leaving, the coagulated suspension was obtained by a decantation method. After adding an aliquot of distilled water to the suspension, the suspension was centrifuged at 3×10^3 rpm for 15 min for removal of the mineral impurities and large particles above 5×10^{-7} m. The centrifuged suspension was washed with a HNO₃ and NaCl mixed solution as a pH around 3.1, re-centrifuged and decanted for several times. For removal of NaCl, a dialysis method was performed by using a semipermeable membrane. The remained suspension was finally evaporated to dryness.

The detail of the above procedure is described in the literature [4].

2.2 Sorption Procedure

Distribution coefficient (K_d) of neptunium onto smectite was determined by a batch method. A stock solution of ²³⁷NpO₂Cl in an 1.4 M HCl solution was obtained from Amersham Co., and used without further purification. In a polypropylene tube, 0.2 g of smectite powder was added into 20 ml of an 1 M NaCl and 0.01 M Na₂S₂O₄ mixed solution. Reagent of NaHCO₃ powder was also added into the tube for ranging a total carbonate concentration (C_T) from 0.09 M to 1.0 M. The initial concentration of Np-237 was set at 1×10^{-6} M. The sample was gently contacted with shaking at 22 ± 3 °C to attain sorption equilibrium. The pH value was measured by using a pH/ion meter, IM-55G (DKK-TOA Co.), with a glass electrode, GST-5421C (DKK-TOA Co.), and the pH of the solution was adjusted around 9. The redox potential E_h (vs. SHE) in the solution was monitored during the experimental procedure by using a glass electrode,

PST-5421C (DKK-TOA Co.).

After shaking time of 16 d and 42 d, the solution of the sample was filtered by using an ultrafilter with the molecular weight cut-off (MWCO) of 10^4 (Advantec USY-1, Toyo Roshi Kaisha Ltd.), and the total neptunium concentration in the solution was determined. After shaking time of 42 d, a TTA-extraction method [5, 6] was applied to the determination of the oxidation state of neptunium. The method was performed as follows. The concentration of HNO_3 in the filtrate was adjusted around 1 M by adding 10 M HNO_3 . The filtrate and 0.5 M TTA (thenoyltrifluoroacetone) in a xylene solvent was vigorously shaken for 10 min for extraction of Np(IV) to the organic phase. After removal of aqueous phase, 10 M HNO_3 was added to the organic phase and vigorously shaken again for 10 min for back-extraction of Np(IV) to the aqueous phase. The Np(IV) and Np(V) concentrations were defined as the concentration in 10 M HNO_3 after back-extraction and that remained in the aqueous phase after the first extraction, respectively. The α -ray counting of Np-237 was performed by using either the alpha spectrometer Octète PCTM (EG&G ORTEC Co.) or the liquid scintillation counter, 2770TR/SL (Packard Instruments Co.) with the scintillator Ultima GoldTM XR (Packard Instruments Co.).

All the procedures except α -ray counting were performed in a glove box filled with N_2 gas ($\text{O}_2 < 1$ ppm) to avoid the contamination of O_2 and CO_2 gas in air.

2.3 Desorption Procedure

A desorption experiment was performed after the sorption procedure. After equilibration of sorption experiment, a mixed solution containing 1 M KCl and 0.01 M $\text{Na}_2\text{S}_2\text{O}_4$ was added to the suspension which was containing the neptunium-sorbed smectite. After a shaking time of 3 d, an aliquot of the solution was filtered by using the ultrafilter with the MWCO of 10^4 , and the α -ray of Np-237 in the filtrate was detected by either the alpha spectrometer or the liquid scintillation counter. A HCl solution was added to the suspension adjusting the HCl concentration to 1 M after the desorption procedure with KCl. The same procedures for the filtration and α -ray counting was performed after shaking time of 3 d.

Finally, sorption of neptunium onto the vessel wall of polypropylene tube was investigated. After removal of the smectite and the solution which was not used to the above desorption experiment, the polypropylene tube was washed by distilled water.

A concentrated HCl solution (around 11.4 M) was introduced to the tube, and the neptunium concentration in the concentrated HCl solution was determined.

Similar to the previous procedure (see section 2.2), all the procedures except α -ray counting were performed in a glove box filled with N_2 gas ($O_2 < 1$ ppm) to avoid the contamination of O_2 and CO_2 gas in air.

3. RESULTS AND DISCUSSION

3.1 Distribution Coefficient by the Batch Experiment

Experimental K_d ($\text{m}^3 \cdot \text{kg}^{-1}$) of neptunium onto smectite is calculated by the following equation:

$$K_d = \frac{(C_0 - C_f)V}{C_f W}, \quad (1)$$

where C_0 (M) and C_f (M) denote the concentrations of the neptunium before and after equilibration, respectively, V (m^3) the volume of the solutions and W (g) the weight of the dried smectite sample.

The obtained K_d values are shown as a function of C_T in Fig. 1 and listed in Table 1. The final pH value of the samples was 8.6 ± 0.3 as shown in Table 1. It is found that the K_d values decrease with increasing C_T . As shown in Fig. 1, little difference in the K_d values between the shaking time of 16 d and that of 42 d is found. Based on this, it is judged that the sorption of neptunium onto smectite approximately equilibrated. Under C_T of 0.08 M, it was presumed that the concentration of neptunium in solution steeply decreased with decreasing C_T due to the precipitation of Np(IV). Thus, only the K_d values equal or larger than C_T of 0.09 M are adopted as reliable data in the present study. The K_d values were not determined for several samples due to a weak sorption of neptunium onto smectite, especially in high C_T solutions.

3.2 Speciation of Redox States of Neptunium in Solution

Experimental results for the ratio between the concentration of Np(IV) ($[\text{Np(IV)}]$) and the total neptunium concentration ($[\text{Np}]_{\text{total}}$) in the solution are shown as a function of C_T in Fig. 2 and listed in Table 1. As shown in Table 1, the E_h (vs. SHE) values have been held around -0.4 V. It is found, however, that a major oxidation state below C_T of 0.5 M is pentavalent. According to the thermodynamic database developed by the Nuclear Energy Agency in the Organization for Economic Co-operation and Development (OECD/NEA) [7], a major oxidation state is tetravalent in the present experimental conditions. The dominant aqueous species of Np(IV), on the other hand,

only $\text{Np}(\text{OH})_4$ (aq.), $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ are accepted to the thermodynamic database by OECD/NEA [7]. Considering the two aqueous species of Np(IV), however, the solubility of Np(IV) is calculated to be much lower than the concentration of Np(IV) experimentally obtained from the present study. Several researchers have been determined an equilibrium constant of a carbonatohydroxo complex of tetravalent actinides, $\text{An}(\text{CO}_3)_2(\text{OH})_2^{2-}$ (An: U [8, 9], Np [9-11] or Pu [12, 13]), which is considered to be a dominant species of An(IV) in a weak alkaline solution containing carbonate or hydrogencarbonate ions. The solubility of Np(IV), including the carbonatohydroxo complex of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$, in an 1 M NaCl solution as a function of C_T at pH 8.6 is calculated as shown in Fig. 3. The ionic strength correction is performed by a “specific ion interaction theory (SIT)” model [14]. The thermodynamic data for the calculation of the solubility of Np(IV) are listed in Table 2.

It is also found that the ratio of $[\text{Np(IV)}]/[\text{Np}]_{\text{total}}$ increases with increasing C_T . The present result shows that the steady-state/equilibrium is reached rapidly in high hydrogencarbonate solutions and that high hydrogencarbonate solutions appear to stabilize the tetravalent state, similar to the results by Rai et al. [10].

3.3 Analytical Procedure

As mentioned above, result of the TTA-extraction method shows that both Np(IV) and Np(V) coexist in the solution for the sorption experiments. Based on the result, it is considered that K_d values shown in Fig. 1 result in sorption by several species of Np(IV) and Np(V). Thus, the experimental K_d value is expressed as

$$K_d = \sum_i K_{di} X_i, \quad (2)$$

where K_{di} and X_i denote the distribution coefficient and the molar fraction of species i in solution, respectively.

According to the thermodynamic data by OECD/NEA [7] as listed in Table 3, several hydrolysis species and carbonate complexes are considered to be formed in a weak alkaline solution containing carbonate or hydrogencarbonate ions. The fractions of the species of Np(V) at pH 8.6 in an 1 M NaCl solution are shown as a function of C_T in Fig. 4. In the present experimental conditions (C_T from 0.09 to 1.0 M), three

carbonate complexes, $\text{NpO}_2(\text{CO}_3)_n^{(2n-1)-}$, are considered to be the dominant species. Neptunyl ion (NpO_2^+) is also considered to remain in the present conditions. On the other hand, the dominant species of Np(IV) is considered to be $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ as shown in Fig. 3. Thus, equation (2) can be represented as

$$K_d = \frac{1}{C_f} (K_{d1}[\text{NpO}_2^+] + K_{d2}[\text{NpO}_2\text{CO}_3^-] + K_{d3}[\text{NpO}_2(\text{CO}_3)_2^{3-}] + K_{d4}[\text{NpO}_2(\text{CO}_3)_3^{5-}] + K_{d5}[\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}]), \quad (3)$$

where K_{d1} , K_{d2} , K_{d3} , K_{d4} and K_{d5} denote the distribution coefficient of NpO_2^+ , $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2(\text{CO}_3)_3^{5-}$ and $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$, respectively.

Respective concentrations of Np(V) are calculated as multiplying the molar fraction with $[\text{Np(V)}]$ which is obtained from a TTA-extraction method. The concentration of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ is considered to be equal to $[\text{Np(IV)}]$ of experimental results as shown in Fig. 3. For the K_d values after 16 d, the concentration ratio between $[\text{Np(IV)}]$ and $[\text{Np(V)}]$ is assumed to be same as that after 42 d. Then, a least-squares fitting analysis with equation (3) is performed to the experimental data shown in Fig. 1. In the analysis, distribution coefficients of respective species, K_{dn} ($n = 1 - 5$), are treated as a free parameter. The analytical result is shown in Fig. 5, and the obtained K_{dn} values are listed in Table 4. The obtained K_{d1} (for NpO_2^+) and K_{d2} (for $\text{NpO}_2\text{CO}_3^-$) values are similar to the previously reported K_d values in weak alkaline groundwaters at aerobic conditions [15-18]. It is considered to be reasonable that the obtained K_d values of respective species are decreasing with increasing the number of negative charge of the species, because the surface of the smectite is considered to be negatively charged in alkaline solutions [4, 19]. The obtained K_{d5} (for $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$) value will be discussed later.

3.4 Desorption Results

The fractions of neptunium desorbed by 1 M KCl and the residual completely desorbed by 1 M HCl solution are shown as a function of C_T in Fig. 6. It is reported that neptunium desorbed by 1 M KCl solution is probably located ion-exchangeably on the outer surface of the mineral, while specifically sorbed neptunium was fixed in the interlayer of smectite [20]. At low C_T values below 0.2 M, it is observed that most of

neptunium is not desorbed by KCl but desorbed by only HCl. At high C_T values above 0.3 M, on the other hand, it is observed that all neptunium is desorbed by KCl. The present result is considered to be due to the contribution of different neptunium species for the different C_T values. Considering the results shown in Figs. 2 and 4, the dominant species of neptunium contributed to the sorption onto smectite is expected to be NpO_2^+ at low C_T solutions. At high C_T solutions, on the other hand, that is expected to be $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$. As mentioned previously, the surface of the smectite is considered to be negatively charged in alkaline solutions [4, 19]. Thus, NpO_2^+ is expected to be sorbed onto negatively charged smectite surface as an electrostatic sorption, while $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ is expected to be sorbed as a weaker sorption than NpO_2^+ . Further investigation may be required to elucidate the desorption behavior.

3.5 Discussion of Mechanism of Sorption of Neptunium onto Smectite

Despite the low E_h values around -0.4 V measured in the present study, it is found that the dominant redox states of neptunium for the sorption onto smectite is pentavalent in carbonate media below C_T of 0.5 M, as shown in Fig. 2. As mentioned above, the obtained K_d dependency on C_T has been well explained by considering the major contribution of NpO_2^+ . The K_d value for $\text{Np}(\text{IV})$ (K_{d5}) also has been determined.

There are a few studies on the sorption of $\text{Np}(\text{IV})$ onto mineral surfaces considering with the aqueous neptunium species. Pratopo et al. study on $\text{Np}(\text{IV})$ sorption onto quartz [21] and Ca-type bentonite [22] under reducing conditions in carbonate media with pH ranged from 4.5 to 13. As shown in Table 5, Pratopo et al. have determined the K_d of $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ (K_{d5}) onto quartz and Ca-type bentonite, which are much larger than that of NpO_2^+ . There is a large discrepancy between the K_{d5} value by the present study and those by Pratopo et al. A reason of the discrepancy may be due to the calculation of molar fraction of aqueous neptunium species, even the distribution coefficient is dependent on pH in general. The studies of Pratopo et al. have no information for the speciation of neptunium in the experimental results. Thermodynamic calculation of the redox states and molar fractions of neptunium may provide the major contribution of $\text{Np}(\text{IV})$ under reducing conditions in alkaline solutions. The experimental results, however, the contribution of $\text{Np}(\text{IV})$ is smaller than the thermodynamic calculation, such as the present study and the solubility study on $\text{Np}(\text{IV})$ by Rai et al. [10]. Furthermore, it is difficult to describe the experimental

K_d value which decreases with increasing C_T , without the contribution of $Np(V)$, especially of NpO_2^+ . Thus, the K_{d5} value (for $Np(CO_3)_2(OH)_2^{2-}$) of the present study is considered to be more reasonable.

As shown in Table 4, it is found that the K_{dn} value of the respective species decreases with increasing the number of negative charge of the species independent of the redox state of neptunium. Considering with the desorption results as mentioned above, carbonate and carbonatohydroxo complexes of neptunium are expected to be sorbed onto smectite as a weak electrostatic interaction (it may be at ion-exchangeable sites). The neptunyl ion (NpO_2^+), on the other hand, may be sorbed onto smectite as a formation of surface complex. Further experiments will be required to elucidate the mechanism of sorption of neptunium onto smectite under reducing conditions in carbonate media.

4. CONCLUSIONS

Distribution coefficient of neptunium onto smectite was determined under reducing conditions in carbonate media by a batch method. The experimentally determined distribution coefficient decreased with increasing the total carbonate concentration. Considering the molar fractions of Np(IV) and Np(V), distribution coefficients of respective species of neptunyl ions, carbonate complexes of Np(V) and carbonatohydroxo complex of Np(IV) were determined by a least-squares fitting analysis. It was found that the distribution coefficients of respective species decreased with increasing the number of negative charge. Considering the desorption results, carbonate and carbonatohydroxo complexes of neptunium are expected to be sorbed onto smectite as a weak electrostatic interaction.

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REFERENCES

1. Japan Nuclear Cycle Development Institute (JNC): "H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan – Second Progress Report on Research and Development for the Geological Disposal of HLW in Japan", JNC TN1410 2000-001(2000).
2. Power Reactor and Nuclear Fuel Development Corporation (PNC): "Research and Development on Geological Disposal of High-Level Radioactive Waste: First Progress Report", PNC TN1410 93-059(1993).
3. M. Yui et al.: "Groundwater Evolution Modeling for the Second Progress Performance Assessment (PA) Project", JNC TN8400 99-030(1999).
4. T. Shibutani et al.: "Physico-Chemical Characteristics of Purified Na-Smectite and Protonation/Desorption Behavior of Smectite Surface", JNC TN8400 99-066(1999) (in Japanese).
5. A. M. Poskanzer, B. M. Foreman Jr.: "A Summary of TTA Extraction Coefficients", J. Inorg. Nucl. Chem., vol. 16, pp. 323-336(1961).
6. S. C. Foti, E. C. Freiling: "The Determination of the Oxidation States of Tracer Uranium, Neptunium and Plutonium in Aqueous Media", Talanta, vol. 11, pp. 385-392(1964).
7. R. J. Lemire et al.: "Chemical Thermodynamics of Neptunium and Plutonium", North-Holland, Amsterdam(2001).
8. D. Rai, A. R. Felmy, N. J. Hess, D. A. Moore, M. Yui: "A Thermodynamic Model for the Solubility of $\text{UO}_2(\text{am})$ in the Aqueous $\text{K}^+\text{-Na}^+\text{-HCO}_3^-\text{-CO}_3^{2-}\text{-OH}^-\text{-H}_2\text{O}$ System", Radiochim. Acta, vol. 82, pp. 17-25(1998).
9. M. I. Pratopo, H. Moriyama, K. Higashi: "Carbonate Complexation of Neptunium(IV) and Analogues Complexation of Ground-Water Uranium", Radiochim. Acta, vol. 51, pp. 27-31(1990).
10. D. Rai et al.: "A Thermodynamic Model for the Solubility of $\text{NpO}_2(\text{am})$ in the Aqueous $\text{K}^+\text{-HCO}_3^-\text{-CO}_3^{2-}\text{-OH}^-\text{-H}_2\text{O}$ System", Radiochim. Acta, vol. 84, pp. 159-169(1999).
11. A. Kitamura, Y. Kohara: "Solubility of Np(IV) under Carbonate Conditions", JNC TN8400 2001-006(2001).
12. D. Rai, N. J. Hess, A. R. Felmy, D. A. Moore, M. Yui, P. Vitorge: "A Thermodynamic Model for the Solubility of $\text{PuO}_2(\text{am})$ in the Aqueous $\text{K}^+\text{-HCO}_3^-$

- $\text{CO}_3^{2-}\text{-OH}^-\text{-H}_2\text{O}$ System”, *Radiochim. Acta*, vol. 86, pp. 89-99(1999).
13. T. Yamaguchi, Y. Sakamoto, T. Ohnuki: “Effect of the Complexation on Solubility of Pu(IV) in Aqueous Carbonate System”, *Radiochim. Acta*, vol. 66/67, pp. 9-14(1994).
 14. I. Grenthe et al.: “Modelling in Aquatic Chemistry”, OECD, Paris(1997).
 15. L. L. Ames et al.: “Basalt-Radionuclide Reactions: FY-1981 Annual Report – Prepared for Rockwell Hanford Operations”, RHO-BW-CR-127-P/PNL-3992(1981).
 16. B. Torstenfelt et al.: “Actinide Sorption on Granites and Minerals as a Function of pH and Colloids/Pseudocolloids”, *Radiochim. Acta*, vol. 44/45, pp. 111-117(1988).
 17. D. Stumm et al.: “Sorption Mechanisms of Three Actinides on a Clayey Mineral”, *Appl. Clay Sci.*, vol. 7, pp. 225-238(1992).
 18. J. F. Relyea et al.: “Batch Kd Determinations with Common Minerals and Representative Groundwaters”, in: “Waste Isolation Safety Assessment Program Task 4: Second Contractor Information Meeting”, PNL-SA-7352, vol. 2(1978).
 19. W. Stumm, J. J. Morgan: “Aquatic Chemistry”, 3rd ed., John Wiley & Sons Inc., New York(1996).
 20. N. Kozai et al.: “Sorption Characteristics of Neptunium by Sodium-Smectite”, *J. Nucl. Sci. Technol.*, vol. 30, pp. 1153-1159(1993).
 21. M. I. Pratopo et al.: “Adsorption of Np(IV) on Quartz in Carbonate Solutions”, *Radiochim. Acta*, vol. 55, pp. 209-213(1991).
 22. M. I. Pratopo et al.: “Sorption and Colloidal Behavior of Np(IV) in a Bentonite-Carbonate Solution System”, *J. Nucl. Sci. Technol.*, vol. 30, pp. 560-566(1993).

Table 1 Experimental data for the determination of K_d of neptunium onto smectite

C_T (M)	final pH	final E_h (V)	K_d ($m^3 \cdot kg^{-1}$)		$\frac{[Np(IV)]}{[Np]_{total}}$
			16 d	42 d	
9.0×10^{-2}	8.41	-0.405	1.48×10^{-1}	8.47×10^{-2}	0.151
9.0×10^{-2}	8.41 *		1.94×10^{-1}	8.44×10^{-2}	0.189
1.0×10^{-1}	8.31	-0.409	1.35×10^{-1}	8.98×10^{-2}	0.178
1.0×10^{-1}	8.31 *		1.98×10^{-1}	7.06×10^{-2}	0.174
1.1×10^{-1}	8.40	-0.409	1.07×10^{-1}	9.07×10^{-2}	0.180
1.1×10^{-1}	8.40 *		6.73×10^{-2}	1.40×10^{-1}	0.253
1.2×10^{-1}	8.58	-0.413	1.83×10^{-1}	1.30×10^{-1}	0.354
1.2×10^{-1}	8.58 *		9.59×10^{-2}	2.69×10^{-1}	0.368
1.5×10^{-1}	8.65	-0.416	7.64×10^{-2}	2.31×10^{-1}	0.319
1.5×10^{-1}	8.65 *		1.01×10^{-1}	2.01×10^{-2}	0.207
2.0×10^{-1}	8.60	-0.413	2.50×10^{-2}	7.26×10^{-3}	0.237
2.0×10^{-1}	8.60 *		1.86×10^{-2}	1.97×10^{-2}	0.344
3.0×10^{-1}	8.42	-0.416	9.53×10^{-2}	1.28×10^{-3}	0.378
3.0×10^{-1}	8.42 *		3.83×10^{-2}	3.53×10^{-2}	0.322
5.0×10^{-1}	8.71	-0.425	3.13×10^{-2}	n. d.**	0.364
5.0×10^{-1}	8.71 *		5.90×10^{-2}	n. d.**	0.419
7.0×10^{-1}	8.89	-0.418	4.71×10^{-3}	n. d.**	0.772
7.0×10^{-1}	8.89 *		3.25×10^{-2}	n. d.**	0.760
1.0×10^0	8.33	-0.414	4.69×10^{-3}	6.94×10^{-3}	0.871
1.0×10^0	8.33 *		n. d.**	5.48×10^{-3}	0.933

* The pH value were measured only one of the same condition samples. Those of the other sample were assumed to be same as the ones.

** n.d. = not determined

Table 2 Thermodynamic data of Np(IV) for the calculation of solubility in an 1 M NaCl solution

species	reactions	$\log K^0$	$\log K'^*$	ref.
$\text{Np(OH)}_4(\text{am})$	$\text{Np(OH)}_4(\text{am}) \rightleftharpoons \text{Np}^{4+} + 4 \text{OH}^-$	-54.47	-55.08	[7]
$\text{Np(OH)}_4(\text{aq})$	$\text{Np}^{4+} + 4 \text{OH}^- \rightleftharpoons \text{Np(OH)}_4(\text{aq})$	46.17	43.10	[7]
$\text{Np(CO}_3)_4^{4-}$	$\text{Np}^{4+} + 4 \text{CO}_3^{2-} \rightleftharpoons \text{Np(CO}_3)_4^{4-}$	36.68	34.03	[7]
$\text{Np(CO}_3)_5^{6-}$	$\text{Np}^{4+} + 5 \text{CO}_3^{2-} \rightleftharpoons \text{Np(CO}_3)_5^{6-}$	35.61	36.81	[7]
$\text{Np(CO}_3)_2(\text{OH})_2^{2-}$	$\text{Np}^{4+} + 2 \text{CO}_3^{2-} + 2 \text{OH}^- \rightleftharpoons \text{Np(CO}_3)_2(\text{OH})_2^{2-}$	43.35	43.86	[11]

*At ionic strength of $1.05 \text{ mol}\cdot\text{kg}^{-1}$ ($\equiv 1 \text{ M NaCl}$)

Table 3 Thermodynamic data of Np(V) for the calculation of molar fractions in an 1 M NaCl solution [7]

species	reactions	$\log K^0$	$\log K'^*$
$\text{NpO}_2\text{OH(aq)}$	$\text{NpO}_2^+ + \text{OH}^- \rightleftharpoons \text{NpO}_2\text{OH(aq)}$	2.70	2.42
$\text{NpO}_2(\text{OH})_2^-$	$\text{NpO}_2^+ + 2 \text{OH}^- \rightleftharpoons \text{NpO}_2(\text{OH})_2^-$	4.40	4.18
$\text{NpO}_2\text{CO}_3^-$	$\text{NpO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2\text{CO}_3^-$	4.96	4.56
$\text{NpO}_2(\text{CO}_3)_2^{3-}$	$\text{NpO}_2^+ + 2 \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{3-}$	6.53	6.80
$\text{NpO}_2(\text{CO}_3)_3^{5-}$	$\text{NpO}_2^+ + 3 \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$	5.50	8.34

*At ionic strength of $1.05 \text{ mol}\cdot\text{kg}^{-1}$ ($\equiv 1 \text{ M NaCl}$)

Table 4 Distribution coefficient of respective species (K_{dn} ($n = 1 - 5$)) onto smectite obtained from a least-squares fitting analysis

species	$K_{dn} (m^3 \cdot kg^{-1})$	
NpO_2^+	K_{d1}	4.8×10^{-1}
$NpO_2CO_3^-$	K_{d2}	1.8×10^{-1}
$NpO_2(CO_3)_2^{3-}$	K_{d3}	$< 5.3 \times 10^{-4}$
$NpO_2(CO_3)_3^{5-}$	K_{d4}	$< 7.0 \times 10^{-5}$
$Np(CO_3)_2(OH)_2^{2-}$	K_{d5}	1.4×10^{-2}

Table 5 Distribution coefficient of respective species onto smectite, quartz and Ca-type bentonite obtained from a least-squares fitting analysis

species	$K_{dn} (m^3 \cdot kg^{-1})$		
	smectite	quartz*	Ca-type bentonite
NpO_2^+	4.8×10^{-1}	$(1.31 \sim 13.1) \times 10^{-3}$	$10^{-2.10 \pm 0.01}$
$NpO_2(OH)_2^-$			$10^{2.82 \pm 0.39}$
$NpO_2CO_3^-$	1.8×10^{-1}	$< 3.93 \times 10^{-4}$	
$NpO_2(CO_3)_2^{3-}$	$< 5.3 \times 10^{-4}$	$< 3.93 \times 10^{-4}$	
$NpO_2(CO_3)_3^{5-}$	$< 7.0 \times 10^{-5}$		
$Np(CO_3)_2(OH)_2^{2-}$	1.4×10^{-2}	6.56×10^{-1}	$10^{1.01 \pm 0.24}$
$Np(CO_3)_2(OH)_4^{4-}$		6.13×10^{-2}	$10^{0.93 \pm 0.37}$
$Np(OH)_5^-$		$> 1.04 \times 10^4$	
reference	present	[21]	[22]

*Converting the surface-based distribution coefficient with the specific surface area of $1.31 \times 10^2 m^2 \cdot kg^{-1}$ in the literature [21].

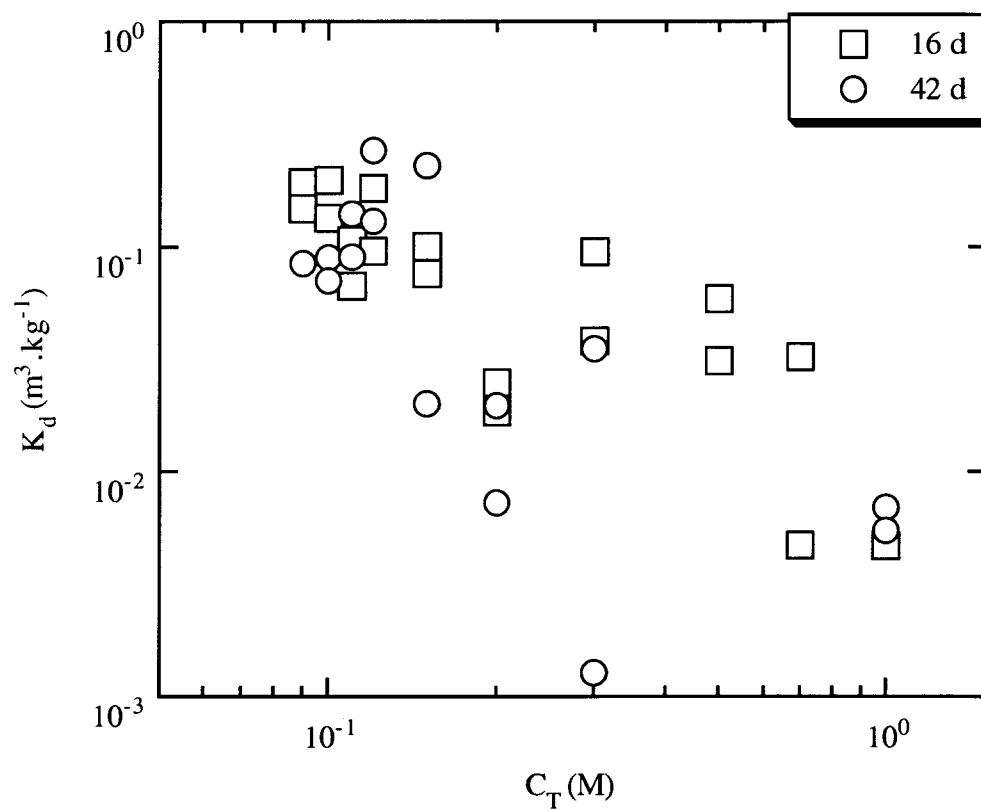


Fig. 1 Distribution coefficient (K_d) of neptunium onto smectite as a function of total carbonate concentration (C_T)

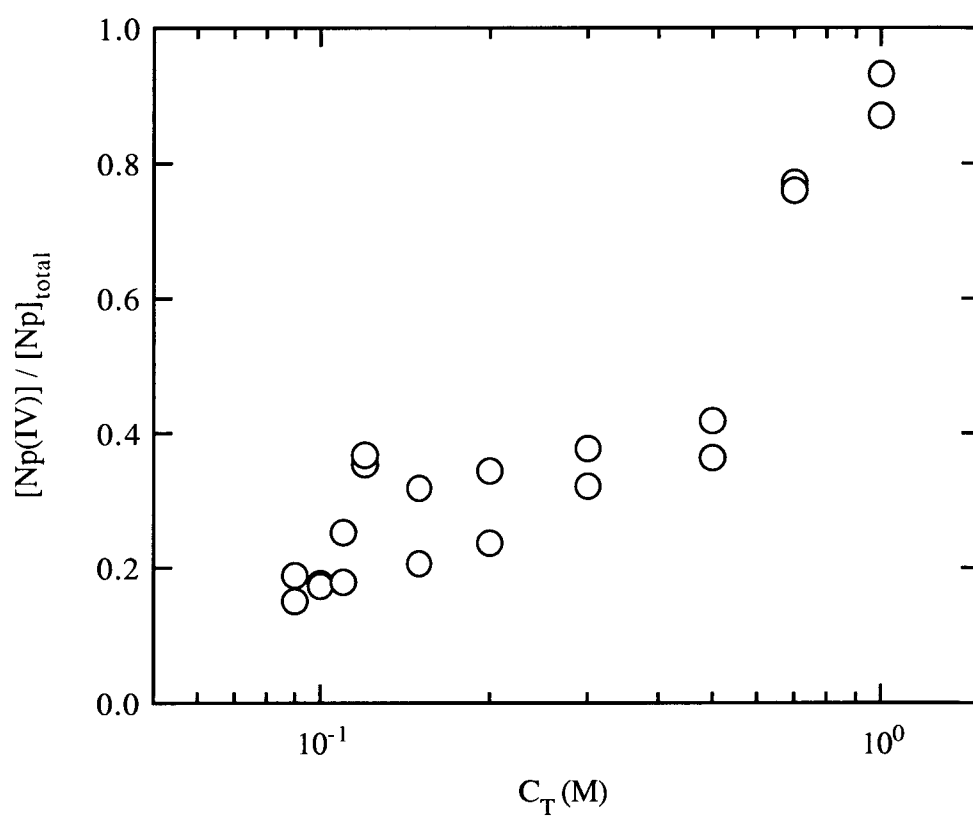


Fig. 2 Ratio between aqueous concentration of Np(IV) and that of total neptunium determined by a TTA-extraction method

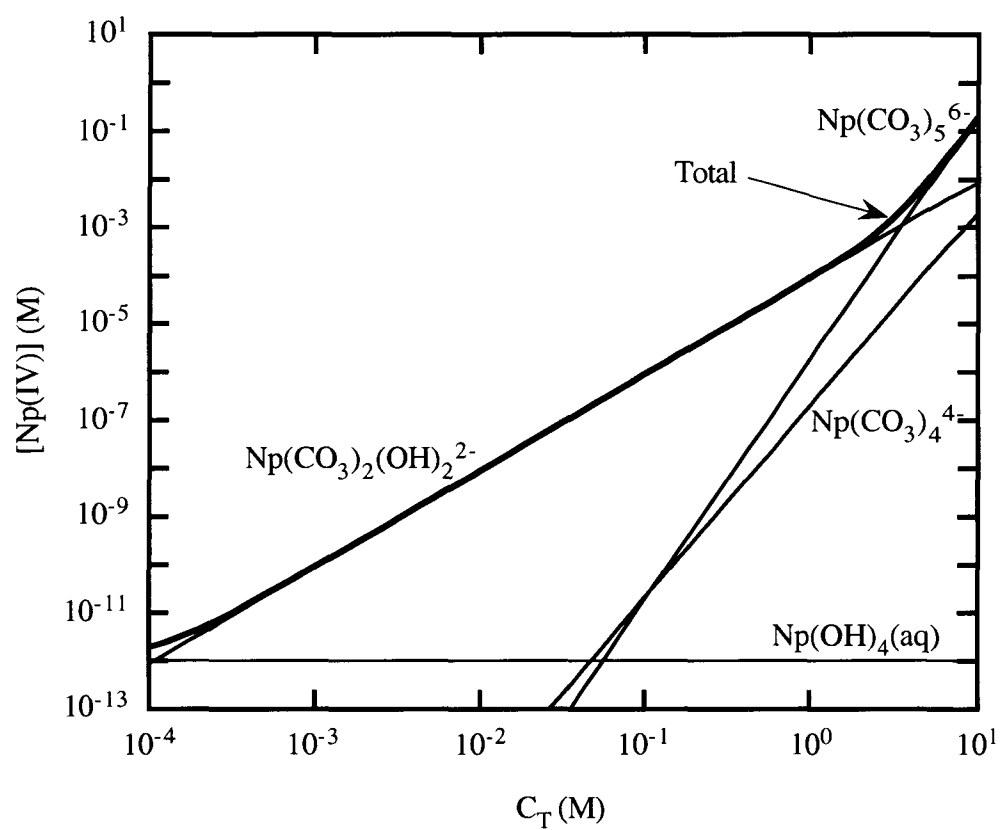


Fig. 3 Solubility of Np(IV) as a function of C_T
in an 1 M NaCl solution at pH 8.6

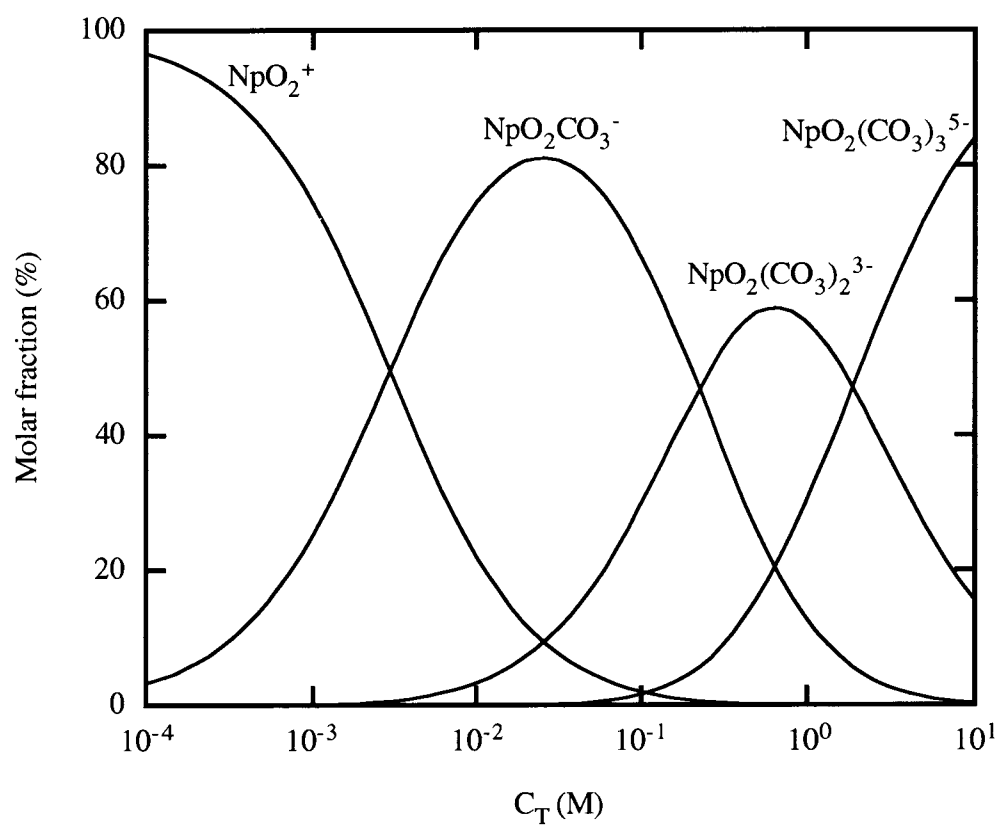


Fig. 4 Fraction of Np(V) species as a function of C_T in an 1 M NaCl solution at pH 8.6

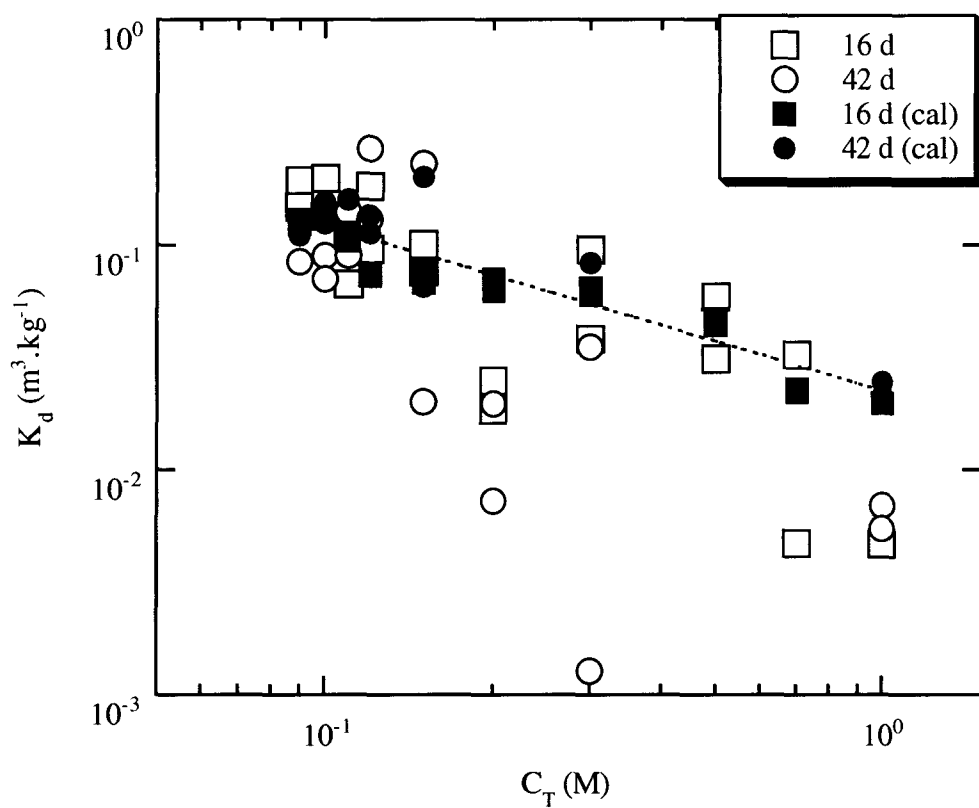


Fig. 5 Experimental and calculated K_d values of neptunium onto smectites as a function of C_T

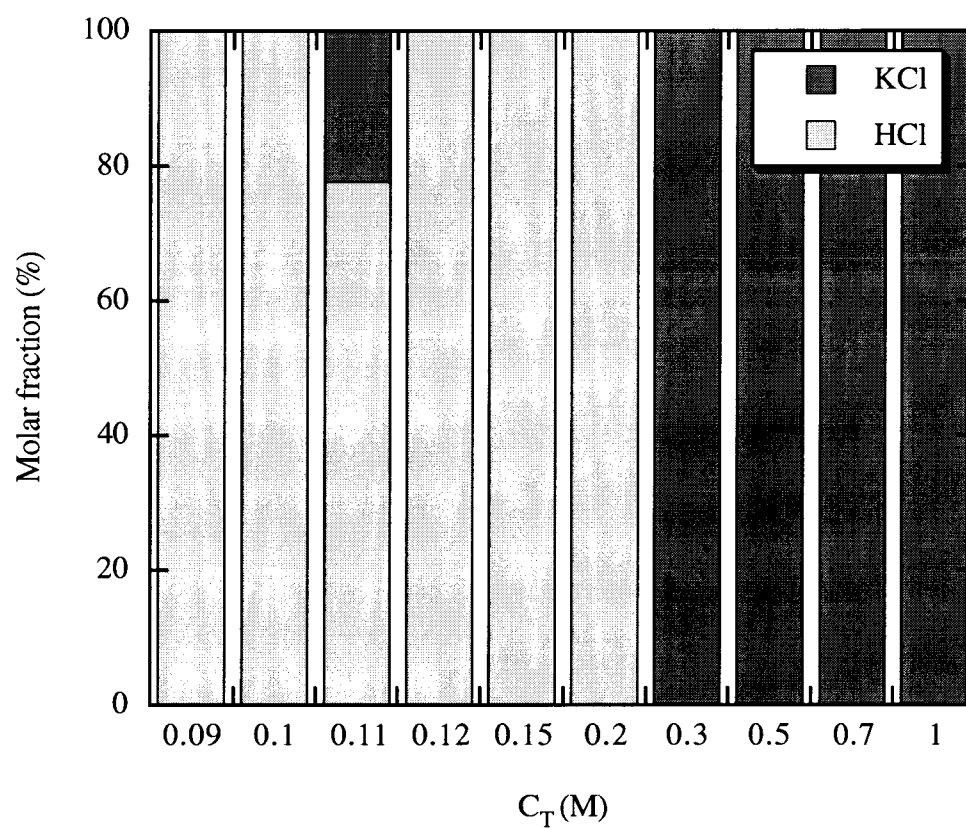


Fig. 6 Fraction of neptunium sorbed ion-exchangeably and specifically onto smectite by the desorption experiments with 1 M KCl and 1 M HCl, respectively