Reduction rate of neptunium(V) in heterogeneous solution with magnetite

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Summary. The sorption kinetics of neptunium on magnetite was investigated under both aerobic and anaerobic conditions in $0.1 \, mol \, L^{-1}$ $NaNO_3$ at pH $= 5.7$ to 5.9. It was found that the sorption of neptunium on magnetite reaches an equilibrium in 1 h under aerobic conditions, while it takes 10 h or more to reach the equilibrium under anaerobic conditions. The difference in sorption kinetics between aerobic and anaerobic conditions took place because sorption kinetics under the anaerobic condition involved the reduction of Np(V) to Np(IV), confirmed by an extraction technique using $0.5 \, mol \, L^{-1}$ TTA in xylene and $2.0 \, mol \, L^{-1}$ HNO_3 solution. The reduction rate of Np(V) by Fe(II) in magnetite was calculated in solution with magnetite. It was found that Np(V) was reduced 1000 or more times faster in solution with magnetite than the Np(V) reduction by Fe(II) ions in homogeneous solution. It was revealed that the reduction of Np(V) in solution with magnetite took place on the surface of magnetite.

1. Introduction

Neptunium-237 is one of the most radiologically important radionuclides because of its long half-life, toxicity and high chemical stability of its pentavalent state, NpO_2^+ [1, 2]. The oxidation state of neptunium is reported to have a dramatic effect on its speciation, solubility and sorption behavior [3], and understanding of the redox reaction of neptunium is crucial to describing the mobility of neptunium in natural water. The Fe(II) and Fe(III) system is considered to be one of the pairs that control redox conditions in groundwater environments. Iron oxides and iron-containing minerals also play an important role in controlling the redox condition and reactions in natural groundwater.

Previous studies revealed the possibility that Fe(II)-bearing minerals act as catalysts for redox reactions [4, 5].

The redox reaction in a single solution phase (homogeneous solution) may differ completely from that in a mixture of solution and solid phases (heterogeneous solution with magnetite). Therefore, a comparative study of the difference in redox reactions between homogeneous solution and heterogeneous solution with magnetite is important for understanding the migration behavior of neptunium in the subsurface.

In the present work, sorption kinetics experiments of Np(V) on magnetite (Fe_3O_4) under anaerobic and aerobic conditions were carried out in order to investigate the reduction of Np(V) to Np(IV) by Fe(II) in heterogeneous solution contacting magnetite. Comparing the different sorption kinetics between anaerobic and aerobic conditions, we calculated the reduction rate of Np(V) in the heterogeneous solution. Through a comparison of the reduction rate in heterogeneous solution contacting magnetite with that in homogeneous solution, the reduction mechanism in heterogeneous neptunium solution contacting magnetite is discussed.

2. Experimental

2.1 Chemicals

Magnetite powder was obtained from Rare Metallic Co.. The magnetite powder was sieved to a particle size smaller than $250 \, \mu m$, washed with deionized water and air-dried before the sorption experiment. The specific surface area of magnetite powder was $1.0 \, m^2 \, g^{-1}$, as measured by the BET method with N_2 gas.

Neptunium of $9.2 \times 10^{-2} \, mol \, L^{-1}$ in $2.2 \, mol \, L^{-1}$ HNO_3 was obtained from CERCA, and diluted with deionized water to obtain $2.0 \times 10^{-3} \, mol \, L^{-1}$ neptunium stock solution. The oxidation state of neptunium was confirmed to be pentavalent because no evidence of the presence of Np(IV) was obtained by solvent extraction using $0.5 \, mol \, L^{-1}$ thenoyltrifluoroacetone (TTA) in xylene [6].

2.2 Procedures

All experiments under the anaerobic condition were carried out in an atmospherically controlled chamber ($O_2 < 1 \, ppm$)

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with high-purity Ar gas. All of the solutions and samples used for experiments under the anaerobic condition were deaerated by bubbling them with high-purity Ar and placing them in an atmospherically controlled chamber after bubbling for at least 7 d to remove the oxygen before the experiment.

2.2.1 Sorption kinetics

Three series of batch experiments were conducted to investigate neptunium sorption kinetics. In the first series of experiments, sorption kinetics over a period of 10 d was investigated under the anaerobic condition. In the second series of experiments, rapid sorption kinetics that occurred within 6 h was investigated under the anaerobic condition. The intervals of measurement were set to 1 h. In the third series of experiments, sorption kinetics under the aerobic condition was investigated.

Batch experiments were conducted at room temperature by mixing 3 g of magnetite with 150 mL solution for the first and third series, and 0.15 g of magnetite in 7.5 mL solution for the second series using a 50 mL polytetrafluoroethylene centrifuge tube and a 150 mL polytetrafluoroethylene vessel. The pH of solution was adjusted to 5.7 to 5.9 with HNO_3 and NaOH. Neptunium solution was added so that the initial concentration of neptunium was 1.8×10^{-5} mol L^{-1} in each series. The initial valence state of neptunium was Np(V), confirmed by extraction with TTA/xylene solution. After adding neptunium solution, pH was immediately adjusted to 5.7 to 5.9 and the samples were well shaken manually, and then the samples were placed at room temperature. After a prescribed time had elapsed, 1.0 mL of the suspension was taken from each vessel and filtrated with a 0.45 μm pore-size membrane filter to separate the solids from the solution. Blank tests with 0.1 mol L^{-1} $NaNO_3$ solutions were carried out in parallel with the sorption experiments in order to measure the neptunium sorption onto the vessel wall. During the sorption experiment, pH was repeatedly adjusted to carry out the experiment at the defined pH.

2.2.2 Determination of valence state of sorbed neptunium as a function of time in contact with neptunium solution with magnetite

To investigate the oxidation state of neptunium sorbed on magnetite as a function of the time in contact with neptunium solution, the following extraction technique was applied [7]. First, the sorption experiment was carried out at room temperature by mixing 1 g of magnetite with 50 mL solution using polytetrafluoroethylene centrifugal tubes. The procedure of the sorption experiment is the same as that described in sorption kinetics experiments. After the prescribed time (5 h, 1 d, 2 d and 4 d) had elapsed, solid and liquid phases were separated, and the solid phase was used in the extraction experiment. Twenty milliliters of 0.5 mol L^{-1} TTA in xylene and 20 mL of 2.0 mol L^{-1} HNO_3 solution were added to the solid phase after the sorption experiment. The samples were well shaken for 3 min, and then water and xylene phases were separated and the concentration of neptunium in each phase was measured after filtration with

a 0.45 μm pore-size membrane filter. To determine the effect of Fe(II), sorption and extraction experiments on hematite (Fe_2O_3) were also carried out in the same way as that for magnetite.

In this work, the concentration of neptunium was measured using an α–β discriminating liquid scintillation analyzer (TRI-Curve, Packard Institute).

3. Results and discussion

3.1 Sorption kinetics and calculation of reduction rate

In the previous study [7], we carried out sorption and desorption experiments involving neptunium on magnetite and hematite under aerobic and anaerobic conditions to investigate the possibility of the reduction of Np(V) to Np(IV) at pH 4 to 8 within 7 d. After the sorption experiment, the dominant valence state of sorbed Np was confirmed by extraction with TTA in xylene and 2.0 mol L^{-1} HNO_3 solution. The sorption behavior of neptunium on magnetite under the anaerobic condition was completely different from that under the aerobic condition. The amount of neptunium sorbed on magnetite under anaerobic conditions was about 2 to 3 times greater than that under aerobic conditions. This suggests that the dominant valence state of neptunium sorbed on magnetite under anaerobic conditions is Np(IV), while that under aerobic conditions is Np(V). The Np(IV) ion in a liquid phase was not found under either aerobic or anaerobic conditions.

These results indicate a possibility that the reduction rate of Np(V) in heterogeneous solution with magnetite is calculated by comparing the sorption kinetics between anaerobic and aerobic conditions. The amount of neptunium sorbed under anaerobic conditions includes the species sorbed as Np(IV) and Np(V), while the amount of Np sorbed under aerobic conditions can be regarded to consist almost solely of Np(V). Therefore the value $([Np_{mag}(t)]_{anaerobic} - [Np_{mag}(t)]_{aerobic})$ shows the amount of Np(IV) sorbed on magnetite at time t, where $[Np_{mag}(t)]_{anaerobic}$ and $[Np_{mag}(t)]_{aerobic}$ (mol g^{-1}) are the amounts of Np sorbed on 1 g of magnetite under anaerobic and aerobic conditions at time t. In line with this consideration, sorption kinetics under anaerobic and aerobic conditions was investigated to calculate the reduction rate in heterogeneous solution contacting magnetite. Furthermore, this consideration was confirmed by investigating a change in the oxidation state of neptunium sorbed on magnetite as a function of its time in contact with neptunium solution using the extraction technique.

The results of sorption kinetics experiments on magnetite for 10 d and 6 h are summarized in Fig. 1. It was found that the sorption of neptunium on magnetite reaches an equilibrium in 1 h under the aerobic condition, while it takes 10 h or more to reach the equilibrium under the anaerobic condition. It was conjectured that the different sorption kinetics between the aerobic and anaerobic conditions was due to the reduction of Np(V) to Np(IV) and its sorption on magnetite under the anaerobic condition.

If the reduction rate of Np(V) in heterogeneous solution contacting magnetite under the anaerobic condition follows
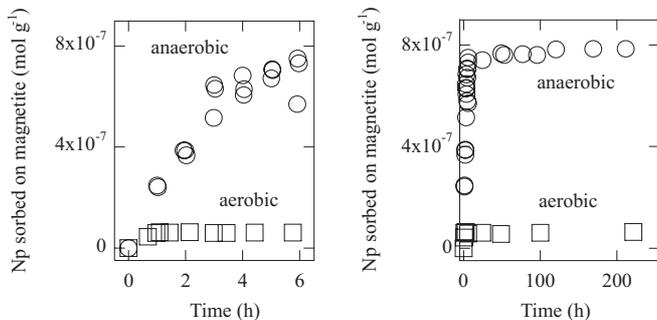
Fig. 1. The amount of sorbed neptunium on magnetite as a function of time at $pH = 5.7$ to 5.9 in $0.1 \, mol \, L^{-1}$ $NaNO_3$ solution under aerobic and anaerobic conditions. The initial concentration of Np(V) is $1.8 \times 10^{-5} \, mol \, L^{-1}$. The amount of magnetite is 1 g and volume of liquid phase is 50 mL.

the pseudo-first order, the reduction rate is described as

$$-\frac{d[Np(V)]}{dt} = \frac{d([Np_{mag}(t)]_{anaerobic} - [Np_{mag}(t)]_{aerobic})}{dt}$$
$$= k[Np(V)] \quad (mol \, L^{-1} \, s^{-1}), \qquad (1)$$

where k is the reduction rate constant. We can obtain Eq. (2), by integrating Eq. (1)

$$1 - \frac{([Np_{mag}(t)]_{anaerobic} - [Np_{mag}(t)]_{anaerobic})}{[Np_{total}]} = \exp(-kt), \qquad (2)$$

where $[Np_{total}]$ $(mol \, g^{-1})$ is the amount of neptunium sorbed on 1 g magnetite in the case where all of the added neptunium is sorbed on magnetite. Under the experimental condition described above, Np_{total} is calculated as $9.0 \times 10^{-7} \, mol \, g^{-1}$.

Fig. 2 shows $\ln\{1 - ([Np_{mag}(t)]_{anaerobic} - [Np_{mag}(t)]_{aerobic}) / 9.0 \times 10^{-7}\}$ versus time. In Fig. 2, it is clearly indicated that the value $\{1 - ([Np_{mag}(t)]_{anaerobic} - [Np_{mag}(t)]_{aerobic}) / 9.0 \times 10^{-7}\}$ follows the pseudo-first order. As indicated in Eq. (2), the slope of the line in Fig. 2 represents the reduction rate constant of Np(V) in heterogeneous solution with magnetite under the anaerobic condition. From the least squares fit of the experimental data to Eq. (2), the reduction rate constant k was determined to be $1 \times 10^{-4} \, s^{-1}$. Therefore, under this experimental condition, the reduction rate of Np(V) in heterogeneous solution with magnetite under anaerobic con-
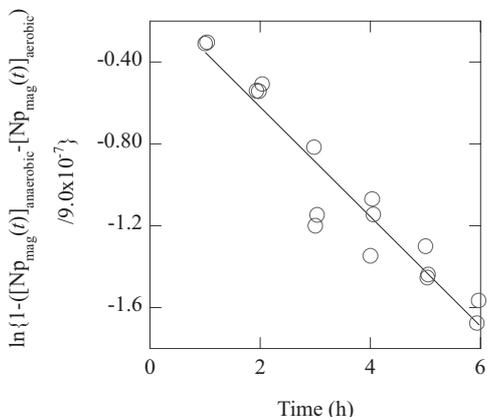

Fig. 2. $\ln(([Np_{mag}(t)]_{anaerobic} - [Np_{mag}(t)]_{aerobic}) / 9.0 \times 10^{-7})$ versus time under anaerobic condition. Initial concentration is $1.8 \times 10^{-5} \, mol \, L^{-1}$

dition can be described as

$$-\frac{d[Np(V)]}{dt} = 1.0 \times 10^{-4} \, [Np(V)] \, (mol \, L^{-1} \, s^{-1}) . \qquad (3)$$

The kinetics of the reduction of Np(V) by Fe(II) in the homogeneous solution phase has been reported [8, 9]. Huizenga [8] investigated this reaction under the following conditions: the temperature of $25\,°C$; ionic strength of $0.1 \, mol \, L^{-1}$ (NaClO$_4$); and initial concentrations of $[Np(V)] = 3.79 \times 10^{-3} \, mol \, L^{-1}$, $[Fe(II)] = 2.40 \times 10^{-3} \, mol \, L^{-1}$ and $[H^+] = 3.29 \times 10^{-3} \, mol \, L^{-1}$. The kinetics of this reaction in acidic solutions is described as

$$-\frac{d[Np(V)]}{dt} = 7.8 \times 10^{-2} \, [Fe(II)][H^+][Np(V)]$$
$$(mol \, L^{-1} \, s^{-1}), \qquad (4)$$

the equation obtained by considering the rate-determining step involving hydrolyzed species of neptunium. Although it is applicable under relatively acidic conditions, Eq. (4) can be used to obtain the reaction rate even at $pH = 6.0$. The reaction rate obtained from Eq. (4) with $[H^+] = 1 \times 10^{-5.7} \, mol \, L^{-1}$ was

$$-\frac{d[Np(V)]}{dt} = 7.8 \times 10^{-8} \, [Fe(II)][Np(V)] \, (mol \, L^{-1} \, s^{-1}). \qquad (5)$$

Furthermore, we investigated the kinetics of the reduction of Np(V) by Fe(II) in a homogeneous solution phase under the following conditions: the temperature of $25\,°C$; ionic strength of $0.1 \, mol \, l^{-1}$ (NaNO$_3$); and initial concentrations of $[Np(V)] = 2.2 \times 10^{-6} \, mol \, L^{-1}$, $[Fe(II)] = 2.2 \times 10^{-6} \, mol \, L^{-1}$ and $[H^+] = 1.0 \times 10^{-6} \, mol \, L^{-1}$. From Eq. (4), only $2 \times 10^{-13} \, mol \, L^{-1}$ of Np(V) would be reduced even after 7 d, since Np(V) was in contact with Fe(II) under the conditions of this experiment. The Np(V)–Np(IV) and Fe(II)–Fe(III) concentrations as a function of time are shown in Fig. 3(a) and (b). No obvious change in the concentrations of Np(V) and Fe(II) was observed. Furthermore, the concentrations of Np(IV) and Fe(III) were under the detection limit even after 7 d. These results indicate that even at $pH = 6.0$ in $0.1 \, mol \, L^{-1}$ NaNO$_3$ solution, the reduction rate of Np(V) by Fe(II) in the homogeneous solution phase is low. Therefore, no changes in the concentrations of Np(V) or Fe(II) were detected, as predicted by Eq. (5).

Comparing Eqs. (3) and (5), the reduction rate of Np(V) in heterogeneous solution contacting a magnetite was 1000 times higher than that in the homogeneous solution phase. The k value, $1.0 \times 10^{-4} \, s^{-1}$, in Eq. (3) includes an effect of the Fe(II) concentration on the surface of magnetite. However, the amount of Fe(II) on the surface of magnetite was $2 \times 10^{-7} \, mol \, m^{-2}$ from the surface sorption site density [10], which is equivalent to $4 \times 10^{-6} \, mol \, L^{-1}$ under experimental conditions in which the mass of the solid phase was 3 g and the volume of the liquid phase was 150 mL. Therefore, even if the effect of Fe(II) concentration is taken into consideration, the reduction rate of Np(V) in solution contacting magnetite was 1000 or more times higher than that in the homogeneous solution. Previous investigations revealed a possibility that Fe(II)-bearing minerals acted as catalysts for redox reactions [4, 11]. Therefore, this higher rate in
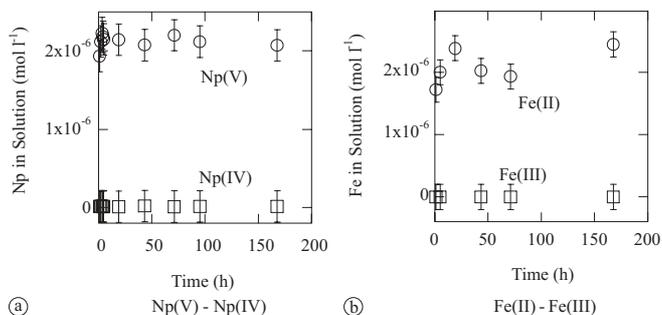
Fig. 3. Concentration of Np and Fe ions as a function of time at pH = 6.0 in 0.1 mol L^{-1} NaNO$_3$ solution under aerobic condition. The initial concentration of both Np(V) and Fe(II) are 2.2×10^{-6} mol L^{-1}. (**a**) Concentration of Np(V)–Np(IV), (**b**) Concentration of Fe(II)–Fe(III).

the heterogeneous solution contacting a magnetite than in homogeneous solution indicates that Np(V) is reduced by Fe(II), not in the homogeneous solution but at the interface between the magnetite and the solution.

To examine whether Np(V) is reduced by Fe(II) ions released from the magnetite into the solution or by Fe(II) on the surface of the magnetite, two experiments were carried out. One was the sorption experiment using two kinds of magnetite with different surface areas (1.0 and 2.0 m^2 g^{-1}) under the anaerobic condition. The other was the dissolution experiment of Fe(II) ion from magnetite at pH = 6.0 in 0.1 mol L^{-1} NaNO$_3$ solution under the anaerobic condition. The results of the sorption and dissolution experiments are summarized in Figs. 4 and 5. As shown in Fig. 4, the sorption kinetics of Np(V) on magnetite under the anaerobic condition were influenced by the surface area of the magnetite. The reduction rate of Np(V) in heterogeneous solution contacting magnetite calculated from Fig. 4 increased with increasing surface area of magnetite as follows:

$$-\frac{d[\mathrm{Np(V)}]}{dt} = 1.6 \times 10^{-4}\,[\mathrm{Np(V)}]\,(\mathrm{mol\,L^{-1}\,s^{-1}})$$
$$(\text{surface area} = 2.0\,\mathrm{m^2\,g^{-1}}). \qquad (6)$$
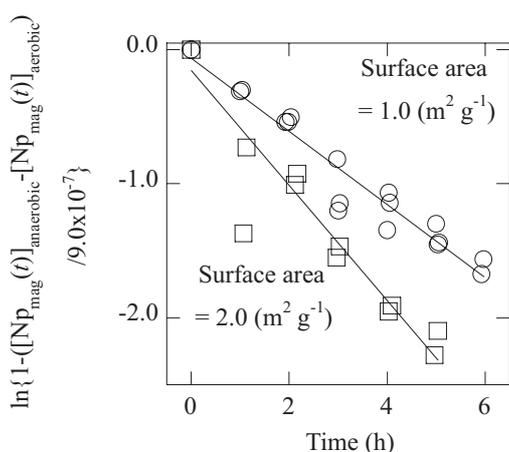

Fig. 4. The amount of sorbed neptunium on magnetite (surface area was 1.0 and 2.0 m^2 g^{-1}) as a function of time at pH = 5.7 to 5.9 in 0.1 mol L^{-1} NaNO$_3$ solution under anaerobic condition showed by ln$\{1 - ([\mathrm{Np_{mag}}(t)]_{\text{anaerobic}} - [\mathrm{Np_{mag}}(t)]_{\text{anaerobic}})/9.0 \times 10^{-7}\}$ *versus* time. The initial concentration of Np(V) is 1.8×10^{-5} mol L^{-1}. The amount of magnetite is 1 g and volume of liquid phase is 50 mL.
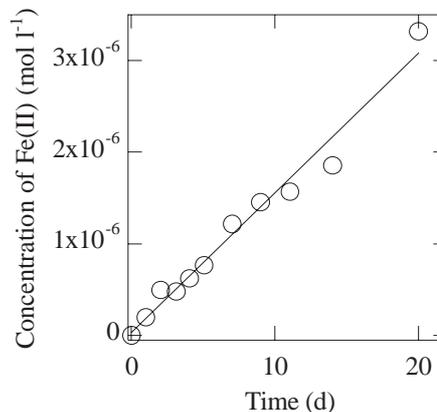

Fig. 5. The concentration of Fe(II) ion dissolved from magnetite (surface area was 1.0 m^2 g^{-1}) as a function of time at pH = 6.0 in 0.1 mol L^{-1} NaNO$_3$ solution under anaerobic condition. The amount of magnetite is 2 g and volume of liquid phase is 100 mL.

As shown in Fig. 5, the concentration of Fe(II) was, at most, 2.0×10^{-6} mol L^{-1} even after 14 d. As indicated by Eq. (5), the concentration of Fe(II) ions dissolved from magnetite after 14 d is as low as 2.0×10^{-6} mol L^{-1}, and no significant amount of Np(V) would be reduced by the Fe(II) ions dissolved from magnetite alone. These results indicate that the reduction of Np(V) proceeds on the surface of magnetite.

3.2 Determination of the change of the oxidation state of sorbed neptunium

The change in the oxidation state of neptunium sorbed on magnetite was investigated as a function of the time in contact with neptunium solution and magnetite using the extraction technique. Table 1 shows the fraction of Np(IV) extracted from magnetite as a function of the time. Fig. 6 shows the fraction of Np(IV) extracted from magnetite under the anaerobic condition. The neptunium extracted in the xylene phase was regarded as Np(IV) in this experiment. The fractions of Np(IV) were calculated by

$$\mathrm{Np(IV)\ fraction} =$$
$$\frac{[\mathrm{Np\ in\ xylene\ phase}]}{[\mathrm{Np\ in\ xylene\ phase}] + [\mathrm{Np\ in\ aqueous\ phase}]} \times 100. \qquad (7)$$

As shown in Table 1, the fractions of Np(IV) and Np(V) extracted from magnetite were completely different between

Table 1. The fraction of Np(IV) and Np(V) extracted from magnetite and hematite *versus* the time in contact with Np solution in 0.1 mol L^{-1} NaNO$_3$ solution under aerobic and anaerobic conditions.

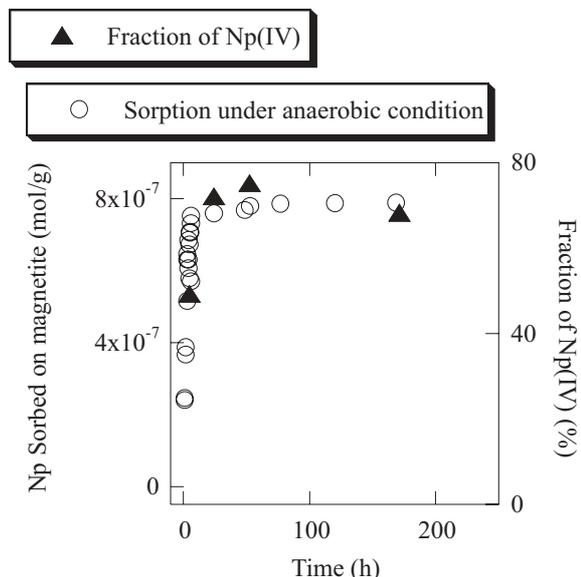| Condition	Time in contact	Np(IV) (%)	Np(V) (%)
Anaerobic	5 h	49.3	50.7
Anaerobic	1 d	72.1	27.9
Anaerobic	2 d	75.1	24.9
Anaerobic	7 d	68.3	31.7
Aerobic	7 d	10.0	90.0
Hematite anaerobic	7 d	2.0	98.0

Fig. 6. The fraction of Np(IV) extracted from magnetite as a function of time and amount of sorbed neptunium as a function of time at pH = 5.7 to 5.9 under aerobic condition. Initial concentration of Np(V) is 1.8×10^{-5} mol L^{-1}. The amount of magnetite is 1 g and volume of liquid phase is 50 mL.

the aerobic and anaerobic conditions. The results of these extraction experiments indicate that the dominant oxidation state of Np sorbed on magnetite under anaerobic conditions was Np(IV), while that of Np sorbed on magnetite under aerobic conditions was Np(V). The dominant oxidation state of Np sorbed on hematite was Np(V), even under anaerobic conditions after 7 d. Therefore, the different sorption kinetics between aerobic and anaerobic conditions can be considered to be due to the reduction of Np(V) to Np(IV) by Fe(II) in magnetite under anaerobic conditions. As shown in Fig. 6, the amount of neptunium sorbed on magnetite and the fraction of Np(IV) extracted from magnetite under anaerobic conditions have a similar dependence on the time. This result indicates qualitatively that the sorption kinetics of Np(V) on magnetite under anaerobic conditions reflects the rate of reduction of Np(V) by magnetite. It is impossible to estimate the total amount of Np(IV) and Np(V) by this extraction technique, because 2.0 mol L^{-1} HNO$_3$ dissolved only the surface of the magnetite and hematite. However, the present results clearly showed that sorption kinetics under the anaerobic condition reflects the reduction rate of Np(V) contacting magnetite. Therefore, it is possible to calculate the reduction rate of Np(V) in heterogeneous solution with magnetite by comparing the sorption kinetics under aerobic and anaerobic conditions.

4. Conclusions

In this study, sorption kinetics under anaerobic and aerobic conditions was investigated to calculate the reduction rate in heterogeneous solution contacting magnetite in 0.1 mol L^{-1} NaNO$_3$ at pH = 5.7 to 5.9. The sorption came to an equilibrium in 1 h under anaerobic condition. On the other hand, it took 10 h or more to reach the equilibrium under the anaerobic condition. From the results of extraction by HNO$_3$ and TTA solution, it was shown that the different sorption kinetics between the aerobic and anaerobic conditions were due to the reduction of Np(V) to Np(IV) that occured under the anaerobic condition.

Considering the difference in sorption kinetics under the aerobic and anaerobic conditions, the reduction rate of Np(V) by Fe(II) in magnetite was calculated in a heterogeneous solution contacting magnetite with 1.0 m^2 g^{-1} of the surface area.

The reduction rate of Np(V) in heterogeneous solution contacting magnetite was 1000 or more times higher than that in homogeneous solution. This higher rate in the heterogeneous solution contacting a magnetite than in homogeneous solution indicates that Np(V) is reduced by Fe(II), not in the homogeneous solution but at the interface between the magnetite and the solution.

References

1. Thompson, R. C.: Neptunium – the neglected actinide: a review of the biological and environmental literature. Radiat. Res. **90**, 1 (1982).
2. Annals of the ICRP, ICRP Publication 30. Limits for Intakes of Radionuclides by Workers. Vol. 5, Pergamon Press, Oxford (1981).
3. Silva, R. J., Nitsche, H.: Actinid environmental chemistry. Radiochim. Acta **70**/**71**, 377 (1995).
4. Stumm, W.: *Chemistry of the Solid-Water Interface*. John Wiley & Sons, Inc., New York (1992).
5. Cui, D., Eriksen, T. E.: Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological mineral. Environ. Sci. Technol. **30**, 2263 (1996).
6. Moore, F. L., Hudgens, J. E. Jr.: Separation and determination of plutonium by liquid–liquid extraction. Anal. Chem. **29**, 1767 (1957).
7. Nakata, K., Nagasaki, S., Tanaka, S., Sakamoto, Y., Tanaka, T., Ogawa, H.: Sorption and reduction of neptunium(V) on the surface of iron oxides. Radiochim. Acta **90**, 665 (2002).
8. Huizenga, R. J., Magnusson, L. B.: Oxidation-reduction reactions of neptunium(IV) and (V). J. Am. Chem. Soc. **73**, 3202 (1951).
9. Gourisse, D.: Report CEA-N-1441 (1971).
10. Fujita, T., Tsukamoto, M., Ohe, T., Nakayama, S., Sakamoto, Y.: Modeling of neptunium(V) sorption behavior onto iron-containing minerals. Mat. Res. Soc. Symp. Proc. **353**, 965 (1995).
11. Bidoglio, G., Avofadro, A., Plano, A. D.: Influence of redox environment on the geochemical behavior of radionuclides. Mat. Res. Soc. Symp. Proc. **50**, 709 (1995).