

## **SORPTION OF NEPTUNIUM ON IRON-CONTAINING MINERALS**

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The sorption of neptunium on magnetite, hematite and biotite in 0.05, 0.1 and 0.2 M NaNO<sub>3</sub> was investigated at 25 °C for pH values between 1 and 8. The pH dependence of the sorption was different for the three minerals. However, there were no or a little (biotite) dependence of the sorption on ionic strength. After the sorption experiment, desorption with water of which pH was adjusted to corresponding value, 1M KCl and 0.1M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was also carried out to investigate the Np sorption form. It was found that for magnetite 50% of sorbed Np were sorbed by ion exchange and 25% were sorbed on the crystalline part, and that for biotite 35% of Np were sorbed by ion exchange and 30% were sorbed on the crystalline part. The sorption on crystalline part was a dominant mechanism together with ion exchange in magnetite and biotite systems. For hematite system, the sorption mechanism changed from ion exchange to the sorption on non-crystalline and crystalline parts, especially on the crystalline part, around pH6. This phenomenon is considered because surface of hematite changed with increase of pH.

### **1 Introduction**

According to the performance allocation analysis on multi-barrier system for high-level radioactive waste disposal, it was found that Np-237 dominates the hazard at the exit of the natural barrier[1], namely at the inlet of the biosphere. Neptunium-237 is present in the high-level radioactive wastes, although in comparison to other radionuclides its amount is small [2]. However, because of its long half-life and its mobile nature under aerobic conditions due to the high chemical stability of its pentavalent state, NpO<sub>2</sub><sup>+</sup>, Np-237 is considered as a possible long-term pollutant of the ecosystem. The understanding of the Np sorption behavior is required in order to describe quantitatively its transport in surface and groundwater systems.

Under aerobic conditions, iron-containing minerals are expected to play an important role in regulating the migration of radionuclides[3] because of their widespread existence, and high sorption capacity. Therefore, Np sorption data on iron-containing minerals are required to describe the mobility of Np in natural waters. Neptunium sorption on iron-containing minerals has been investigated in some studies. Nakayama et al.[4] studied the pH dependence of Np(V) sorption on magnetite, goethite, hematite and biotite. Tochiyama et al.[5] clarified the effect of crystallinity of various iron oxides on the Np(V) sorption. Fujita et al.[6] interpreted the sorption behavior of Np(V) on magnetite and goethite using a surface complexation model. However, mechanism of the sorption of Np(V) needs further elucidation and the dependence of Np(V) sorption on ionic strength, which can yield an important information about

sorption mechanism, is not well known. Furthermore, although there is a possibility of reduction of Np(V) to Np(IV) at the surface of Fe(II)-containing minerals[7], the reduction of Np(V) to Np(IV) and the sorption/precipitation of Np(IV) has been investigated only in a few works[7,8] and a clear evidence of reduction of Np(IV) has not been obtained. In the present study, we carried out sorption and desorption experiments with Np(V) on hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and biotite (K(Mg,Fe)<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>) using a batch method and a sequential extraction method, and obtained information on the Np sorption mechanism as well as on the possibility of reduction of Np(V) to Np(IV).

## 2 Experimental

### *Chemicals*

Magnetite and hematite powders were obtained from Rare Metallic Co., Ltd.(Tokyo, Japan). Biotite was obtained from Nihon Chikagakusha Co.(Kyoto, Japan) and was crushed with a tungsten-carbide mill. All the minerals were sieved to particle size of less than 250  $\mu$ m before sorption experiments. Specific surface areas of the magnetite, hematite and biotite, measured by BET method with N<sub>2</sub> gas, were 5.4, 5.8 and 7.3 m<sup>2</sup>/g, respectively.

1.3x10<sup>-5</sup>M Np in 0.1M HNO<sub>3</sub> was obtained from LMRI, France and diluted by deionized water in order to obtain a 6.5x10<sup>-8</sup> M solution. The pH was adjusted to between 4.0 and 5.0 with HNO<sub>3</sub>. The pentavalent oxidation state of Np was confirmed by a solvent extraction technique with 0.5M thenoyltrifluoroacetone (TTA) in xylene[9] and by measuring UV-VIS absorption spectra.

### *Procedure*

All experimental procedures were carried out under ambient aerobic conditions. Batch experiments were conducted to investigate Np sorption as follows. 1g of the individual mineral was placed in 50 ml polyethylene centrifuge tube with 20 ml of solution. The solution pH was adjusted to the required value (between 1 and 8) using HNO<sub>3</sub> and NaOH while the ionic strength was set to 0.05, 0.1 or 2.0 M by NaNO<sub>3</sub>. The tubes were placed in a shaker bath at 25°C for 7 days to allow equilibration of the pH. Then, 100  $\mu$ l Np solution was added and the tube was again placed in a shaker bath at 25°C for 7 days in order to achieve a sorption equilibrium. After 7 days, the pH was measured and 5 ml aqueous samples were taken from each mixture after filtration with a 0.45  $\mu$ m-pore size membrane filter. The Np concentration in the aqueous samples was measured using a Ge-detector (ORTEC). Blank tests with Np in 0.1 M NaNO<sub>3</sub> solutions without a mineral were carried out in parallel with the sorption experiments in order to measure the Np sorption onto the polyethylene wall.

The desorption of Np from the individual samples was investigated after the end of the sorption experiments using a sequential extraction technique utilizing 20 ml of distilled water (pH was adjusted to the corresponding value), 1M KCl[3] and 0.1M potassium oxalate[10] in order to investigate the sorption forms of Np.

### 3 Results and discussion

#### Sorption results

The results of sorption experiments are summarized in Fig. 1. The uptake,  $K$  (%), was calculated using the following equation

$$K = \frac{C_b - C_f}{C_b} \times 100$$

where  $C_b$  and  $C_f$  represent the blank and final concentration of Np, respectively. The results show that the Np sorption onto magnetite, hematite and biotite was strongly influenced by pH, differently for each mineral. Neptunium sorption on magnetite began around pH 5 and sharply increased at pH values between 6 and 7. The sorption on biotite began at pH values between 4 and 5, and sharply increased at pH between 6 and 7. The sorption on hematite began at about pH 3, sharply increased at pH between 4 and 5, and its value reached 100% at pH 7. These results are in a good agreement with earlier data [7]. The differences in the Np sorption on the individual minerals are most probably due to differences in their structural characteristics. From the hydrolysis and complexation constants of Np(V) [6,11,12] it follows, that a dominant species in the solution at pH 1-8 is  $\text{NpO}_2^+$  and carbonate complexes are not of major concern. According to the literature [13], the points of zero charge (pzc) of magnetite and hematite are pH=6.5 and pH=8.3, respectively. There is no correlation between pzc and the pH of the beginning of sorption in these experiments. We will study this relationship in detail in future. The surface sorption coefficients,  $K_a$  [ $\text{mol/ml m}^2$ ] of magnetite, hematite and biotite calculated using the BET surface areas are plotted in Fig. 2.

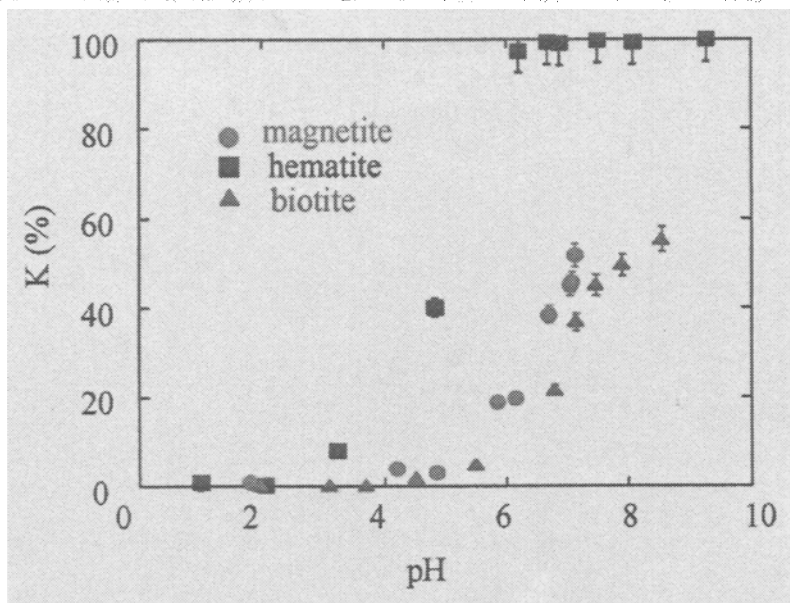


Fig. 1. Neptunium sorption by magnetite, hematite and biotite in 0.1M  $\text{NaNO}_3$  solution at 25°C as a function of pH

One of the aims of this work was to study the possibility of reduction of Np(V) to Np(IV) at the surface of the Fe(II)-containing minerals, but from a quantitative point of view, Np sorption enhancement on Fe(II)-containing minerals was not observed in this study. A check for Np(IV) in the aqueous phase by solvent extraction technique with 0.5M TTA in xylene did not provide an evidence of presence of Np(IV) in our systems. This suggested that the reduction of Np(V) to Np(IV) by Fe(II) did not take place in the aqueous phase under our aerobic experimental conditions. However, there is a possibility of reduction of Np(V) to Np(IV) at the surface of Fe(II)-containing minerals under anaerobic conditions. We will study the possibility of reduction under anaerobic conditions and the effect of surface properties on Np sorption and Np(V) reduction in detail in future.

The dependence of Np sorption on the ionic strength is presented in Fig. 3. The sorption on magnetite and hematite was independent of ionic strength. According to Girvin et al. [14], the sorption which depends on ionic strength is of an outer-sphere complexation type and the sorption which is independent of ionic strength is of an inner-sphere complexation type. In agreement with this proposal, we conclude that the sorption of Np both on magnetite and hematite is of an inner-sphere complexation type. Similar results for biotite (Fig. 3c) do not allow drawing any conclusion in this respect, although they seem to indicate a slight effect of ionic strength on the Np sorption. Mechanism of Np sorption on biotite will be investigated again in future.

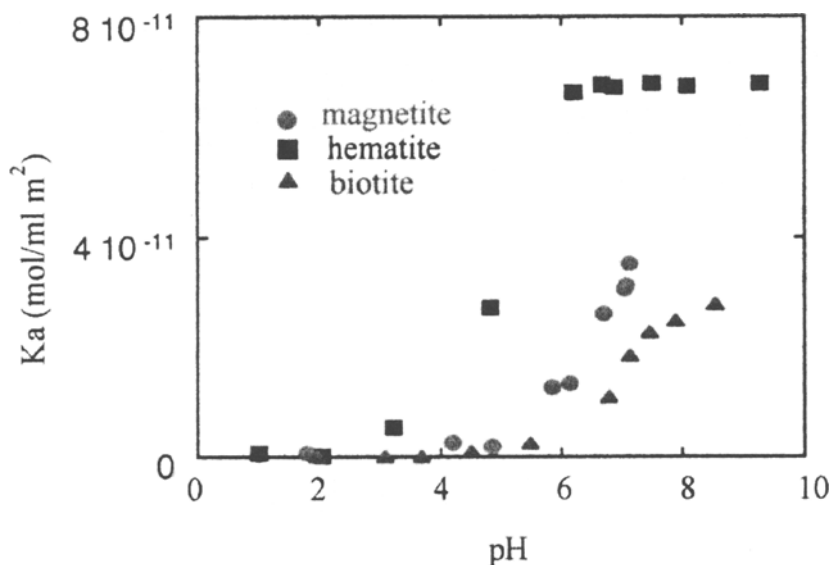


Fig. 2. Neptunium sorption normalized to BET surface area on magnetite, hematite and biotite at 25°C

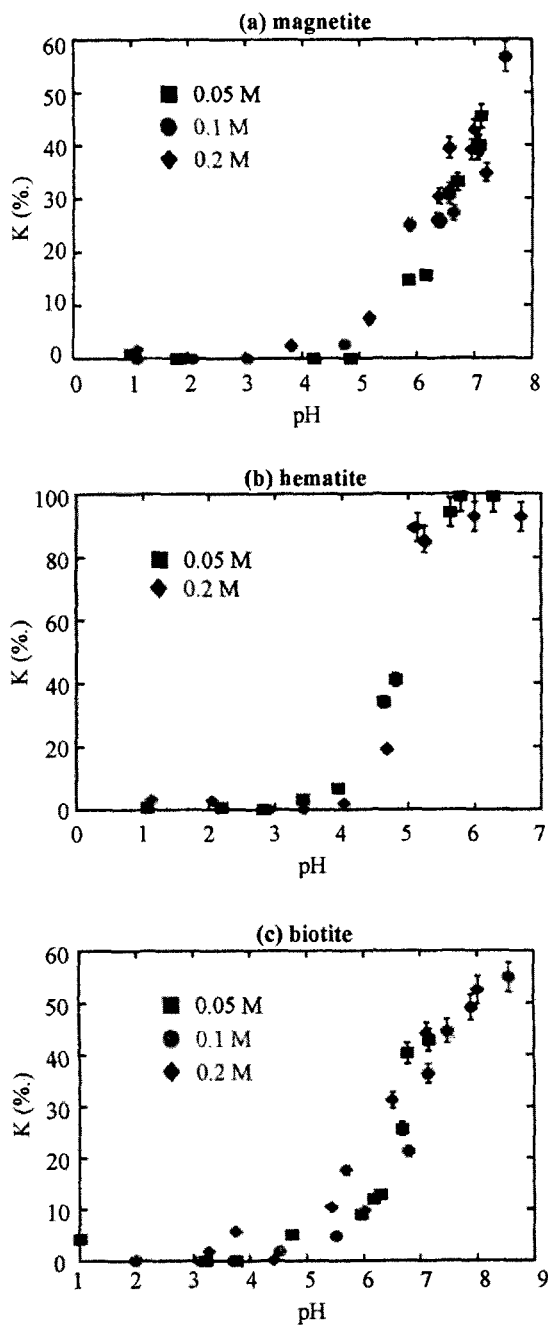


Fig. 3. Dependence of neptunium sorption on ionic strength at 0.05, 0.1 and 0.2M NaNO<sub>3</sub> solution at 25°C. (a) magnetite, (b) hematite, (c) biotite.

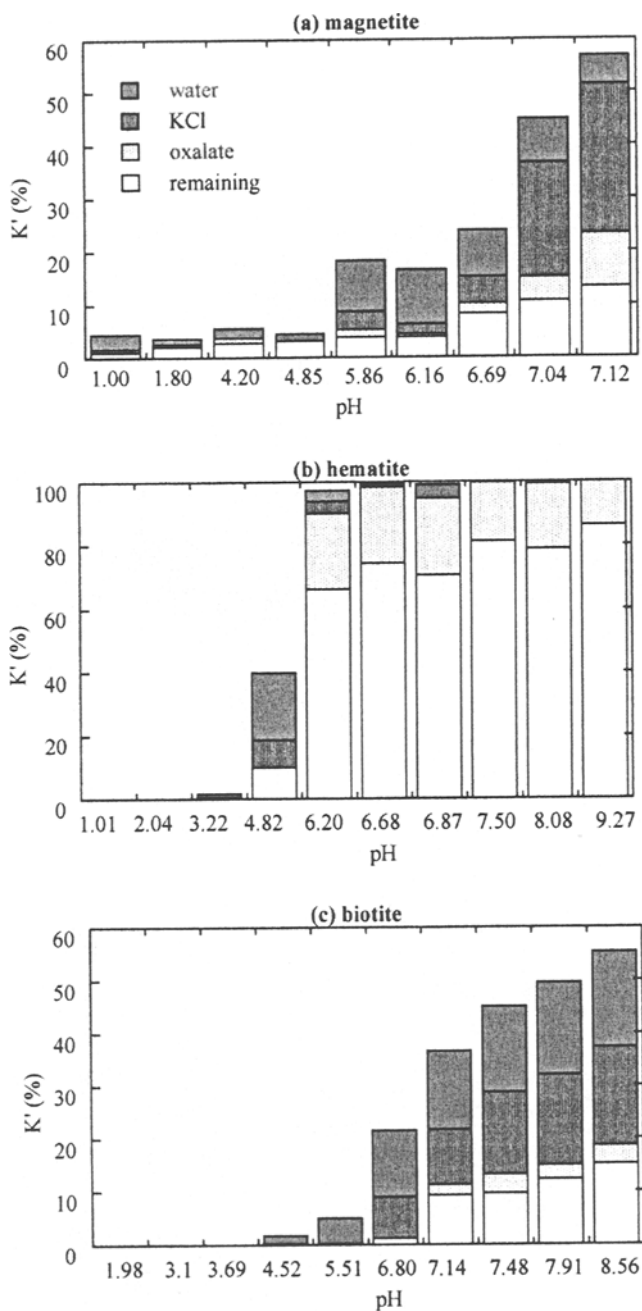


Fig. 4. Desorption of Np by water(pH adjusted), 1M KCl and 0.1M potassium oxalate at 25 °C from: (a) magnetite, (b) hematite, (c) biotite.

*Desorption results*

The results of desorption experiment are summarized in Fig. 4. Desorption ratio,  $K'$  (%), was calculated using the following equation,

$$K = \frac{C_b - C_f'}{C_b} \times 100$$

where  $C_f'$  represents the final concentration of Np in desorption solution.

The use of sequential desorption in this work is based on the assumption, that Np sorbed as an exchangeable ion can be desorbed by KCl while the Np sorbed on a non-crystalline part of iron-containing minerals is released by  $K_2C_2O_4$  (cf. [15,16]). The remaining sorbed Np which cannot be extracted by water, 1M KCl and 0.1M potassium oxalate, is considered to be sorbed on a crystalline part of iron-containing minerals. Therefore, in this paper, we defined the Np desorbed by water as "Np sorbed loosely", that desorbed by KCl as "Np sorbed by ion exchange", that released by  $K_2C_2O_4$  as "Np sorbed on non-crystalline part" and remaining Np as "Np sorbed on crystalline part". A similar definition was described by Idemitsu et al. for explanation of U sorption [3].

*magnetite*

The first extractant, the pH-adjusted water, could extract a small fraction of Np in the whole pH range studied, with highest desorption around pH 6. This suggests that a small fraction of Np was sorbed loosely on magnetite, especially around pH6. The second solution, 1M KCl, could extract a great deal ( about 50%) of Np sorbed at pH>7. Therefore, at pH>7, the sorption is mainly controlled by ion exchange. The third solution, 0.1M  $K_2C_2O_4$ , could also extract a small fraction of Np. The fractions of Np sorbed on a non-crystalline part and on a crystalline part of magnetite increased with pH at pH>6.16. The fraction of Np sorbed on the crystalline part was about 25% in this pH range. Therefore, the sorption on the crystalline part was also a major mechanism of the Np sorption.

*hematite*

The pH-adjusted water and 1M KCl could extract a significant part of Np at pH 4.82 but very little at pH>6.20. This suggests that Np was sorbed loosely or by ion exchange on hematite in the acidic solution. On the other hand, at pH>6.20, 0.1M  $K_2C_2O_4$  extracted some fraction (about 20%) of Np. The total fractions of Np sorbed on a non-crystalline part and on a crystalline part of hematite reached nearly 100% at pH>6.20. These results indicate that the sorption mechanism changed around pH6 from the loose sorption and ion exchange to the sorption on the non-crystalline and (predominantly) crystalline parts.

*biotite*

The pH-adjusted water and 1M KCl could extract a great deal of Np in the whole pH range studied. Thus ion exchange as well as the loose sorption seems to be dominant. At pH>6.80, Np sorption on a crystalline part of biotite increased with pH and became one of major mechanisms of Np sorption. Little Np was desorbed with  $K_2C_2O_4$ , suggesting that its sorption on a non-crystalline part of biotite was small.

The desorption behavior of the studied systems is different. In the future work, we will study the relationship between the sorption behavior (effect of ionic strength etc.)

and desorption behavior, and elucidate the sorption mechanism in more detail by investigation of structural characteristics and surface alteration by pH. Furthermore, we intend to study the possibility of Np(V) reduction at the surface of iron(II)-containing oxides under anaerobic conditions.

#### 4 Conclusions

1. The pH dependence of Np sorption on magnetite, hematite and biotite was different.
2. The sorption of Np on magnetite and hematite was independent of ionic strength. This indicates that the sorption is of an inner-sphere complexation type. No such conclusion can be drawn for the sorption of Np on biotite.
3. Prevailing mechanisms of the sorption of Np on magnetite and biotite are the sorption on a crystalline part of the minerals and the ion exchange.
4. The mechanism of Np sorption on hematite changes at pH around 6 from the ion exchange to the sorption on a non-crystalline and a crystalline parts of the mineral, especially on the crystalline part.

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