

SORPTION OF NEPTUNIUM ON CLAYS

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Batch sorption experiments with ^{237}Np using kaolinite and molasse clays were carried out under oxic conditions. The sorption kinetics and the effects of particle size of clay samples, concentration of neptunium in the solutions and the pH below and above the point of zero charge of the clays on the sorption coefficients were studied. The sorption coefficients of neptunium, on kaolinite were between 23 and 1100 ml/g at pH 1.5 and 7.6, respectively, whereas, sorption on the molasse clay was not affected significantly by pH ($R_d \sim 600$ ml/g).

Introduction

Neptunium is one of the most important elements from the safety point of view due to its hazardous nuclide ^{237}Np with a half-life of $2.1 \cdot 10^6$ years. It exists in five oxidation states in aqueous solutions and the most stable species under oxidizing conditions is the pentavalent one ($\text{NpO}_2^+ \cdot \text{aq}$).¹ On the other hand, Np(IV) dominates under reducing conditions.

Sorption of neptunium was widely studied on different solids like basalt, bentonite and granitic rocks under oxic and anoxic conditions.^{2–4} This paper presents the results of batch sorption experiments with ^{237}Np using two different types of clays under oxic conditions.

Materials and methods

Molasse clay used in the experiments was taken from the clay horizon of North-East Switzerland. It consisted of 65–70% montmorillonite, 5–10% illite and small amounts of quartz. Kaolinite test material from Zettlitz (Czechoslovakia) contained 90% kaolinite, 2–5% illite and 2–5% quartz. Both samples were separated into 2 particle size ranges as 5–10 μm and 10–20 μm by the Andreasen pipette method.⁵

The neptunium solutions were prepared by diluting a standard ^{237}Np solution with Säkingen ground water.⁶ This water was strongly mineralized and had a pH of 8. The concentrations of Np in the solutions were between 10^{-6} and 10^{-9} M. The oxidation states of neptunium in the solutions were checked by thenoyltrifluor-

acetone (TTA) extraction method.⁷ The pH of the solutions were adjusted by HNO_3 . Solid/liquid ratio was kept constant for all the experiments as 1/100.

The experiments were carried out in polyallomer centrifuge tubes. Before sorption, the clay samples were equilibrated with groundwater for four days. The samples were shaken at 200 rpm and phase separation was performed by centrifuging at 10 000 rpm. The α -activity of ^{237}Np was measured by a surface barrier silicon detector. Desorption tests were performed after the sorption procedures, by replacing the solutions with the groundwater.

Results and discussion

The extraction with TTA showed that about 98% of neptunium in the solutions was in the 5+ oxidation state. The solubility calculations with the geochemical code PHREEQE⁸ indicated that the precipitation of NpO_2 was likely at the highest Np concentration (10^{-6}M). The speciation calculations with the same code suggested that the main species in the neutral solutions were NpO_2^+ and $\text{NpO}_2\text{CO}_3^-$, whereas, in the solution with low pH, the dominant species was NpO_2^+ .

The isoelectric points, the pH at which the net charge on the surface is zero, is around 3.5 and less than 2.5 for kaolinite and montmorillonite type of clays respectively.⁹⁻¹¹ At pH 1.5, therefore, the surface of both kaolinite and molasse clays are supposed to be positively charged.

The change in sorption coefficients (R_d) with time for both of the clays (5–10 μm) at pH 1.5 and pH 7.6 is shown in Fig. 1. It is seen that the sorption of neptunium on molasse clay is nearly pH independent (except the kinetics of sorption), whereas

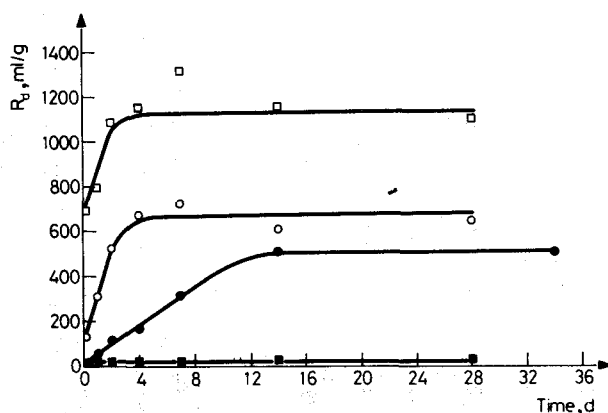


Fig. 1. Change of R_d of Np with time for kaolinite and molasse clays: ● molasse pH 1.5, ○ molasse pH 7.6, ■ kaolinite pH 1.5, □ kaolinite pH 7.6

sorption on kaolinite displays a strong dependence on pH. The explanation of this fact can be the tightly bound layers in kaolinite, therefore, the reactions occur mainly on the surfaces of the outer layers which are positively charged at low pH. On the other hand, since the interlayers in the expandable smectite type clays are also available for sorption, the effect of surface charge is less than in the case of kaolinite. Presumably, diffusion into the interlayers caused the slow kinetics at low pH.

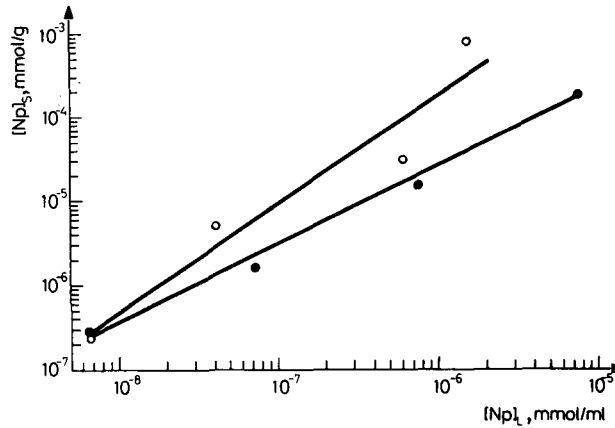


Fig. 2. Freundlich isotherms for Np sorption on kaolinite and molasse clays: ● kaolinite, ○ molasse

The sorption coefficients of neptunium on molasse clay were measured as 600 and 450 ml/g for the particle sizes 5–10 and 10–20 μm , respectively. On the other hand, on kaolinite clay, R_d were 1100 and 550 ml/g respectively, for the same size ranges as above. The higher R_d for smaller particle sizes observed especially in the case of kaolinite clay suggests also, as pH dependency, a surface adsorption on this clay. The desorption tests suggested a clear irreversibility for both clays.

The experimental data was fitted to Freundlich isotherm.^{1,2} In Fig. 2, isotherms for both of the clays with 5–10 μm particle sizes are shown. The Freundlich constants are given in Table 1.

Table 1.
Freundlich constants for sorption
of Np (equation: $[\text{Np}]_{\text{solid}} = K \cdot [\text{Np}]_{\text{liquid}}^N$)

Clay	K	N	r
Kaolinite	6.92	0.91	0.996
Molasse	15 488	1.32	0.965

Isotherm for Np sorption on molasse clay suggests some precipitation at Np concentrations higher than 10^{-6} M ($N > 1$ is also an indication of precipitation). On the other hand, the isotherm for Np sorption on kaolinite is nearly linear.

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References

1. S. AHRLAND, J. O. LILJENZIN, J. RYDBERG, *Solution Chemistry*, Vol. 5, Actinides, J. C. Bailar, New York, 1973.
2. B. ALLARD, H. KIPATSI, J. RYDBERG, KBS Technical Report, 55 (1977).
3. G. BIDOGLIO, A. DE PLANO, *Nucl. Technol.*, 74 (1986) 307.
4. B. TORSTENFELT, *Radiochim. Acta*, 39 (1986) 105.
5. B. A. WILLS, *Mineral Processing Technology*, Pergamon Press, 1979.
6. S. AKSOYOGLU, *J. Radioanal. Nucl. Chem.*, 134 (1989) 393.
7. P. A. BERTRAND, G. R. CHOPPIN, *Radiochim. Acta*, 31 (1982) 135.
8. D. L. PARKHURST, D. C. THORSTENSON, L. N. PLUMMER, NTIS Techn. Report PB 81-167801, 1980.
9. G. A. PARKS, *Chem. Rev.*, 65 (1965) 177.
10. J. O. LECKIE, R. O. JAMES, *Aqueous Environmental Chemistry of Metals*, A. J. RUBIN (Ed.), Ann Arbor Science Publishers, Ann Arbor, Mich., 1974, p. 1.
11. R. O. JAMES, M. G. MacNAUGHTON, *Geochim. Cosmochim. Acta*, 41 (1977) 1549.
12. H. FREUNDLICH, *Colloid and Capillary Chemistry*, Methuen, London, 1926.