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Interaction of Np(V), (VI), and (VII) with Aluminosilicates in Alkaline Medium

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Abstract—The behavior of Np in higher oxidation states in alkaline solution containing silicate and aluminate ions was studied. In formation of a crystalline aluminosilicate in a solution, Np(V), (VI), and (VII) are not incorporated into its crystal structure but hamper formation of the solid phase. The possibility of sorption of Np on various aluminosilicates is primarily governed by its oxidation state. Np(V) and Np(VII) are not sorbed from strong alkali. Np(VI) is retained by aluminosilicate materials to various extents depending on the surface characteristics and surface area of these materials. On heating, the degree of Np(VI) sorption decreases, which suggests the physical nature of the process.

We studied previously [1] the Pu(VI) sorption on aluminosilicates of the zeolite type, whose spontaneous formation is possible in prolonged storage of alkaline radioactive wastes containing silicate and aluminate ions at elevated temperature. It was shown that Pu(VI) existing in strong alkalis in the form of anionic hydroxo complexes hampers crystallization of aluminosilicate, but in the case of formation of a solid phase it is partially sorbed on its surface. The sorption capacity of crystalline aluminosilicates is low (approximately 6 mg per gram of the sorbent), which apparently reflects the ratio of neutral hydroxo complexes $PuO_2(OH)_2(H_2O)_2$ and negatively charged complexes $[PuO_2(OH)_n(H_2O)_{4-n}]^{2-n}$ existing in alkaline solution, among which $PuO_2(OH)_4^{2-}$ predominates at $[OH^-] > 1$ M. Highly charged ionic species are less sorbable because of electrostatic repulsion from the negatively charged aluminosilicate surface [2]. Almost quantitative sorption of Pu(VI) with natural montmorillonite is caused by reduction of Pu(VI) to Pu(IV), which is well retained by many materials.

No less interesting is the behavior of long-lived radionuclide ^{237}Np, which can be present in alkaline wastes in oxidation state +5 and, under certain conditions, +6, since Np(IV) under these conditions is unstable and is oxidized to Np(V) even with atmospheric oxygen. The hydrolytic behavior of Np(V) and Np(VI) is different. Np(VI) can be expected to be similar to Pu(VI) in the hydrolytic behavior, although there are no published data on the speciation of Np(VI) in strong alkalis. Pentavalent neptunium is subject to hydrolysis to a lesser extent than Np(VI); in addition, it shows a weaker tendency to form polymeric species [3, 4]. It was assumed [5, 6] that, at relatively high concentration of hydroxide ions in a solution, the major ionic Np(V) species are $[NpO_2(OH)_2]^-$, $[NpO_2(OH)_3]^{2-}$, and $[NpO_2(OH)_3(H_2O)]^{2-}$.

In this study we examined the reaction of Np(V) and Np(VI) with various aluminosilicates at $[OH^-]$ of approximately 2 M. Under the same conditions, we also studied the behavior of Np(VII), which, as known, exists in alkaline solutions as a highly charged anion $NpO_4(OH)_2^{3-}$ [7, 8] and is highly soluble in alkalis. In addition, attention should be given to the possibility of disproportionation of Np(VI) in alkaline solutions with formation of Np(VII) and Np(V) [9].

EXPERIMENTAL

The experimental conditions were the same as in [1]. A solution of Np(VI) purified by anion exchange was used as the initial solution. The Np(VI) concentration in this solution was determined by complexometric titration after its reduction to Np(IV) with hydroxylamine in 4 M HCl [10].

The working solutions were prepared by two procedures. The hydroxides were carefully precipitated with ammonia from neutral Np(VI) or Np(V) solutions conditioned by the standard procedures. After washing to remove excess ammonia, these hydroxides were dissolved in 2 M tetramethylammonium hydroxide (TMA). In the second procedure, Np(VI) and Np(V) solutions were directly mixed with the calculated amount of TMA. In the case of both Np(VI) and Np(V), the spectra of alkaline solutions prepared by different methods were identical. Preliminary experiments showed that these solutions were stable in

storage: the Lambert–Beer law was obeyed for these solutions, and the intensity of the analytical absorption bands [530 and 1020 nm for Np(VI) and Np(V), respectively] remained practically unchanged for 2 weeks. Np(VII) was obtained by ozonation of a Np(VI) solution in 1–2 M NaOH of ultrapure grade.

To prepare the zeolite phase, we used aqueous solutions of sodium metasilicate $Na_2SiO_3 \cdot 9H_2O$ of chemically pure grade and sodium aluminate prepared by dissolving in NaOH a calculated amount of $Al(OH)_3$ freshly precipitated with ammonia.

All experiments with alkaline solutions were performed in plastic vessels.

The powder X-ray patterns of solid samples were recorded on a Philips diffractometer (PW1140/00/60 generator) in a 100-mm XDC-700 Guinier camera (Jungner Instrument, Sweden), using CuK_α radiation and Si powder as an internal reference.

The IR absorption spectra of solid samples in a matrix from melted NaCl were recorded on a Specord M80 spectrophotometer in the range $4000–400$ cm^{-1}. The electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer in the range 600–900 nm.

RESULTS AND DISCUSSION

We examined the possibility of incorporation of NpO_2^+ and NpO_2^{2+} ions into the aluminosilicate crystal lattice directly in the course of the synthesis. As shown previously [1], crystalline phases of the zeolite type with the composition $(AlO_2)_2(SiO_2)_4 \cdot 7H_2O$ similar to faujasite mineral (as judged from the X-ray diffraction patterns) are formed at 80–100°C from alkaline solutions with $[OH^-]$ of approximately 2 M at the Si : Al molar ratio varied from 2 to 6. Np(V) or Np(VI) was added to the initial reaction mixture in the form of a 1×10^{-3} M solution in TMA, in which the solubility of Np is higher than that in sodium alkali.

As in the case of Pu(VI), during the low-temperature synthesis Np(V) or Np(VI) is not incorporated into the skeleton of the aluminosilicate formed. At the Np content in the initial mixture exceeding 5 mol %, the solid phase is formed more slowly and in a smaller amount than in the absence of NpO_2^+ and NpO_2^{2+} ions. The finely dispersed precipitate formed can capture some amount of Np(VI), which is suggested by weakly pronounced color of the solid phase and a decrease in the Np content in the mother liquor, registered spectrophotometrically. However, Np is retained very weakly and is easily washed out with water.

Aluminosilicate in the presence of Np(VII) was synthesized as follows. Freshly prepared Np(VII) $\{[Np(VII)] = 2.7 \times 10^{-7}$ M, $[OH^-] = 2$ M$\}$ was added to a 2 M NaOH solution preliminarily ozonized for 40 min and containing AlO_2^- ions; then, a preliminarily ozonized solution of sodium metasilicate was added. Two runs were performed in parallel. In the first run, ozonation was continued after mixing the reactants, and in the other run, the gelation proceeded in air. Within 2 h, after consolidation of the gel and phase separation, aliquots of the mother liquor were withdrawn and the Np(VII) content in these samples was determined spectrophotometrically from the absorption at 412 and 618 nm. It was found that, without ozonation, the Np(VII) concentration in the solution decreased, apparently owing to the reduction of Np(VII) to Np(VI); with ozonation, the Np(VII) concentration did not change.

We studied the sorption of Np(V), Np(VI), and Np(VII) on synthetic faujasite and some natural aluminosilicates under static conditions. A weighed portion of the sorbent and 5 ml of alkaline solution with the given concentration of Np were placed in a covered plastic vessel equipped with a magnetic stirrer. At regular intervals, 1.5 ml of the suspension was withdrawn, and after centrifugation the alkaline solution was analyzed spectrophotometrically in a plastic cell to monitor the valence state of Np. Then, a 0.1-ml sample was withdrawn from this solution and evaporated with concentrated perchloric acid. The residue was dissolved in 1 ml of water, and a drop of 2 M $NaNO_2$ was added to convert Np into the pentavalent state. The solution was transferred into a cell, the absorption spectrum of the solution was measured, and the current concentration of Np was determined from the absorption at 980 nm. Then, the degree of sorption was evaluated by the formula $R_s = \{([Np^{n+}]_0 - [Np^{n+}]_\tau)/[Np^{n+}]_0\}(V/m)$, where $[Np^{n+}]_\tau$ is the concentration of Np(V), Np(VI), or Np(VII) at time τ and V/m is the ratio of solution volume (ml) to the sorbent amount (g).

As natural sorbents we used montmorillonite, kaolinite, and phlogopite. These layered aluminosilicates widely occur in the nature. It is well known that, depending on the conditions of hydrolysis and accumulation of deposits, silicate rocks inevitably transform into clay materials of various types. For example, in a silica-rich medium with high pH, rocks of the montmorillonite type are formed [11].

Sorption of Np(V). We performed two series of experiments in which synthetic faujasite, montmorillonite (Krym deposit, Bakhchisarai raion), kaolinite
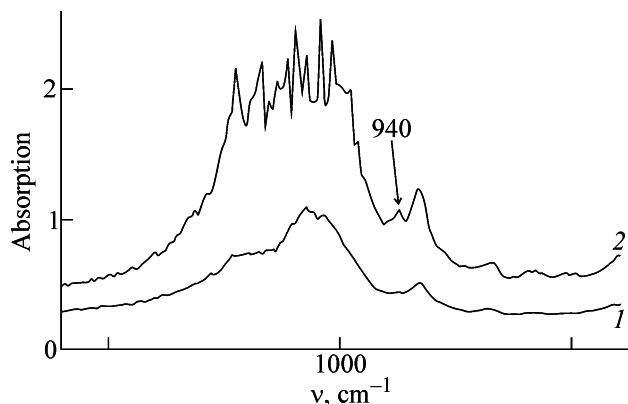
Fig. 1. Fragments of IR spectra: (*1*) initial sample of montmorillonite and (*2*) the sample after contact with a Np(VI) solution for 15 days.
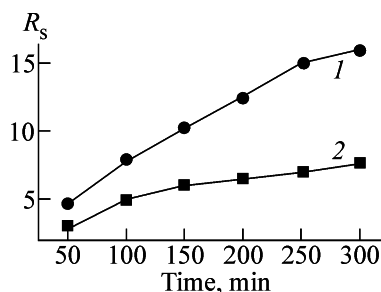

Fig. 2. Sorption curves of Np(VI) on montmorillonite at (*1*) 20 and (*2*) 60°C.

(Prosyanov deposit, Ukraine), and phlogopite (Kovdor deposit, Kola Peninsula) were used as sorbents. In the first series, the maximum contact time of the solution ([Np(V)] = 1×10^{-3} M, [OH$^-$] = 2 M) and sorbent was 6 h, and in the second, 15 days; in addition, in the experiments the ratio of the Np(V) amount to the sorbent weight was varied. Irrespective of the experimental conditions, Np(V) is not noticeably sorbed with the examined materials from alkaline solution. At the same time, it is known that, from neutral solutions (pH 6), Np(V) is sorbed with montmorillonite in the form of NpO_2^+ ion by the mechanism of ion exchange [12].

Sorption of Np(VI). The capability of Np(VI) to interact with aluminosilicates depends on their kind. Synthetic faujasite and phlogopite are poor sorbents for Np(VI). Sorption of Np(VI) with kaolinite proceeds slowly and reaches 2–3 mg g^{-1} after 15-day contact of the solution with the sorbent.

Under the same conditions, Np(VI) is sorbed with montmorillonite more completely (approximately 7 mg g^{-1}); in this case, sorption is irreversible and Np is not desorbed upon treatment of the precipitate with a fresh portion of alkali. It was found spectrophoto-

metrically that, unlike Pu(VI), Np(VI) is not reduced in contact with montmorillonite and is sorbed in the form of the dioxo cation, as confirmed by the IR spectra of montmorillonite precipitates after the sorption completion. The fragments of the IR spectra of the initial sample (spectrum *1*) and the sample after contact with Np(VI) solution (spectrum *2*) are shown in Fig. 1. In spectrum *2*, there is a weak absorption band with a maximum at 940 cm^{-1}, assigned to the stretching vibrations of the NpO_2^{2+} group. In the spectrum of the initial sample this band is absent. An increase in the sample weight results in increased intensity of absorption bands corresponding to vibrations of aluminosilicate tetrahedra; however, the $\nu(NpO_2^{2+})$ band is not manifested.

With increasing ratio of the sorbent weight to the volume of the Np(VI) solution, the degree of sorption increases practically linearly. Heating results in a decrease in the degree of sorption (Fig. 2), which is not typical for chemisorption.

Sorption of Np(VII). In the presence of ozone, Np(VII) is stable for a long time in 2 M alkali. Therefore, in the experiments on sorption under static conditions, the Np(VII) solution was stirred by bubbling of ozonized oxygen through the solution. Spectrophotometric study of the solution with its subsequent control deoxidation showed that Np(VII) is not sorbed on faujasite and montmorillonite.

In air (stirring of the solution with a magnetic stirrer), the content of Np(VII) in the solution in contact with aluminosilicate decreased by approximately 1/3 in 2 h; in this case, the solution color changed from bright green to brown-green. In contact with natural montmorillonite, the Np(VII) content decreased at a higher rate, by 30% in 60 min. It is evident that Np(VII) is reduced to the hexavalent state, in which it can be fixed with the sorbent as mentioned above.

Thus, the possibility of sorption of Np with aluminosilicates from a strong alkali is mainly governed by its oxidation state. As expected, Np(VII) occurring in the solution in the form of an anionic complex with a high negative charge is not fixed on the surface of aluminosilicate layers, which are negatively charged or neutral.

Np(V) does not interact with aluminosilicates under the examined conditions either, even by the mechanism of physical sorption. Since Np(V) hydroxo complexes occurring in strong alkali have a lower negative charge than the Np(VII) complexes, it can be suggested that the absence of apparent sorption of Np(V) is caused by its weak tendency to polymerize in alkaline solution.

In its sorption characteristics Np(VI) is similar to Pu(VI). The degree of its sorption strongly depends on the kind of the sorbent: it is minimal for phlogopite containing negatively charged layers with the interlayer spacing of approximately 10 Å and specific surface area of approximately 70 $m^2 g^{-1}$, and is maximal for montmorillonite containing neutral layers with the interlayer spacing of 15 Å and specific surface area exceeding 300 $m^2 g^{-1}$. The dependence of the sorption on the surface area of the sorbent was noted in a study of sorption of uranyl ion with natural materials at pH typical for natural water, i.e., pH 6–9 [13]. However, the possibility of Np sorption from strong alkali is apparently governed by the surface charge rather than surface area. In any case, kaolinite containing neutral structural layers sorbs Np(VI) better than does phlogopite, although the specific surface area of kaolinite is smaller (less than 40 $m^2 g^{-1}$).

The results obtained show that Np in higher oxidation states, present in alkaline wastes with $[OH^-] = 2$ M, hampers formation of the aluminosilicate phase; however, Np(VI) can be sorbed by the forming precipitate. In a hypothetical contact of neptunium-containing alkaline wastes with natural clay materials, these minerals are weak barriers for Np migration and can fix only small amounts of Np(VI).

ACKNOWLEDGMENTS

REFERENCES

1. Budantseva, N.A., Lapitskaya, T.S., and Fedoseev, A.M., *Radiokhimiya*, 2003, vol. 45, no. 5, pp. 445–448.

2. Schmeide, K., Pompe, S., Bubner, K., *et al.*, *Radiochim. Acta*, 2000, vol. 88, p. 723.

3. Liersne, C., Treiber, W., and Kim, J.I., *Radiochim. Acta*, 1985, vol. 38, p. 27.

4. Sevost'yanova, E.P. and Khalturin, G.V., *Radiokhimiya*, 1976, vol. 18, no. 6, p. 870.

5. Tananaev, I.G., *Radiokhimiya*, 1994, vol. 36, no. 1, p. 15.

6. Neck, V., Kim, J.I., and Kanallakopulos, B., *Radiochim. Acta*, 1992, vol. 56, p. 25.

7. Krot, N.N., Mefod'eva, M.P., and Gel'man, A.D., *Radiokhimiya*, 1968, vol. 10, no. 4, p. 412.

8. Krot, N.N., Mefod'eva, M.P., and Gel'man, A.D., *Radiokhimiya*, 1968, vol. 10, no. 6, p. 634.

9. Krot, N.N., Mefod'eva, M.P., Shilov, V.P., and Gel'man, A.D., *Radiokhimiya*, 1970, vol. 12, no. 3, p. 471.

10. Smirnov-Averin, A.P., Kovalenko, A.P., Ermolaev, N.P., and Krot, N.N., *Zh. Anal. Khim.*, 1966, vol. 21, no. 1, p. 76.

11. Millot, G., *Geologie des argiles. Alterations. Sedimentologie. Geochimie*, Paris: Masson, 1964.

12. Nagasaky, Sh., and Tanaka, S., *Radiochim. Acta*, 2000, vol. 88, p. 705.

13. Pabalan, R.T. and Turner, D.R., *Aquatic Geochem.*, 1997, vol. 2, p. 203.