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Sorption of Neptunium in the Highest Oxidation States from Alkaline Solutions with Complexing Fibrous "Filled" Sorbents

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Abstract—Sorption of Np(VII), Np(VI), and Np(V) from 1 M NaOH by complexing fibrous "filled" sorbents was examined. POLIORGS 33-n and 34-n sorbents containing amidoxime and hydrazidine groups efficiently recover Np in the highest oxidation states and exhibit good kinetic properties. During sorption, Np(VII) is reduced with the sorbent to Np(VI) having a higher, under the actual conditions, distribution coefficient. The distribution coefficients, ml g^{-1}, were estimated at 4.6×10^3 for Np(VII), 1.4×10^4 for Np(VI), and 3.6×10^2 for Np(V).

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In recent years, nuclear fuel reprocessing generated huge amounts of alkaline slurries, whose precipitates and mother liquors are abundant in various radionuclides, including Np, which require reprocessing and further disposal. The most promising way to solve this urgent problem is sorption recovery using fibrous "filled" complexing sorbents comprised of thin porous polyacrylonitrile fibers with finely dispersed filler strongly fixed in their pores. Various sorption materials are suitable as filler: polymeric and mineral ion exchangers, complexing sorbents, natural tuffs, etc. Advantages offered by fibrous "filled" sorbents are high sorption capacity, fast sorption kinetics ensured by the porous structure, and selectivity of recovery, determined by the filler properties [1]. We examined previously the sorption of actinides, including Np(V), with fibrous "filled" sorbents containing amidoxime and hydrazidine groups from aqueous media and multicomponent salt-containing alkaline solutions [2–4]. Depending on the conditions, the oxidation state of neptunium in solutions varies from III to VII. In alkaline solutions, Np occurs in the highest oxidation states only, and compounds of Np(VII) are the most readily soluble in alkalis [5]. Sorption recovery of Np(VII) and Np(VI) from alkaline solutions is studied inadequately. Examination of sorption of Np in the highest oxidation states from strongly alkaline solutions is of both scientific and practical importance.

EXPERIMENTAL

In our experiments we used ^{237}Np containing 0.03 wt % ^{241}Am. A solution of Np(V) in 1 M NaOH was prepared by the following procedure: 0.3 ml of a 48.1 mg ml^{-1} Np(IV) solution in 4 M HCl was diluted to 2 ml with distilled water; the resulting solution was heated on a water bath to 90°C, after which several $NaNO_2$ crystals were added. The solution acquired an emerald-green color typical for solutions of Np(V) in acidic media. Then 1 M NaOH was added in small portions to the resulting solutions to precipitate NpO_2OH. To achieve complete precipitation, the NaOH solution was added in a small excess. The precipitate was separated from the mother liquor by centrifugation and washed with NaOH solution, after which 10 ml of 1 M NaOH was added. The resulting suspension was stirred for 3 days using a shaker. Then the solution containing soluble neptunium hydroxide was separated from the precipitate by centrifugation. The Np(V) concentration in the resulting solution was 5.49×10^{-5} M.

The solution of Np(VI) in 1 M NaOH was prepared by evaporating virtually to dryness 0.5 ml of a Np(IV) solution with 3 ml of concentrated HNO_3 added. The dry residue was dissolved in 3 ml of concentrated HNO_3, and the resulting solution was again evaporated to wet salts. This yielded a red-brown salt, to which 1 M NaOH was added. The resulting light pink

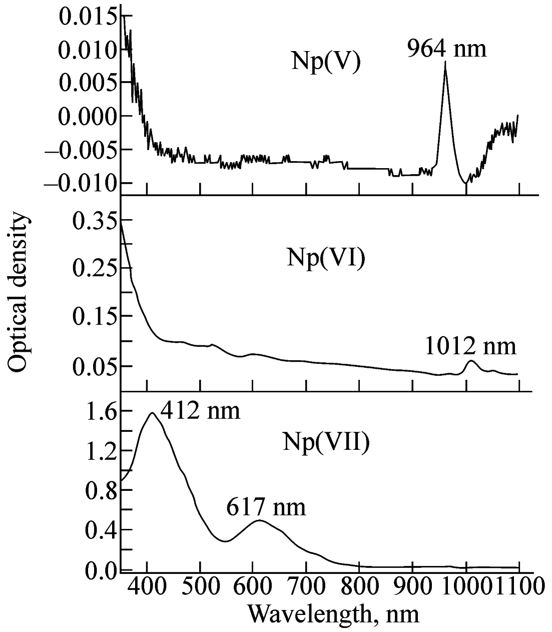

Fig. 1. Electronic absorption spectra of solutions of Np(V), Np(VI), and Np(VII). [NaOH] = 1, [Np(V)] = 5.49×10^{-5}, [Np(VI)] = 3.87×10^{-4}, and [Np(VII)] = 8.64×10^{-4} M.

solution was separated from a scanty precipitate by centrifugation. The Np(VI) concentration in the solution was 3.87×10^{-4} M.

A solution of Np(VII) in 1 M NaOH was prepared by electrochemical oxidation of Np(VI) solution. To this end, the solution of Np(VI) in 1 M NaOH, prepared by the above-described technique, was electrolyzed for 40–60 min in an electrochemical cell at the anode potential of +1.094 V vs. standard hydrogen electrode. A platinum grid served as anode, and a platinum wire, as cathode. The cathode space was separated from the anode space by a glass frit. A mercury oxide electrode served as reference electrode; its potential in 1 M NaOH is +0.0984 V vs. standard hydrogen electrode. The degree of oxidation of Np was monitored spectrophotometrically from the optical density D at $\lambda = 412$ nm. Electrolysis was carried out until a maximal D was achieved. The Np(VII) concentration in solution was 8.64×10^{-4} M.

Table 1. Sorption of Np(VII), %, with "filled" complexing sorbents in relation to the phase contact time (V/m = 100 ml g^{-1}, [NaOH] = 1 M)

Time, min	POLIORGS 34-n	POLIORGS 33-n	AV 17-n
5	86	84	0
10	89	87	4
30	98	98	18
60	99	98	18

The electronic absorption spectra of the Np solutions were taken on Cary 100 (Varian) and UV300 (Unicam Instruments) spectrophotometers.

Figure 1 shows the absorption spectra of the solutions of Np in different oxidation states. The spectra contain absorption bands characteristic only for Np(V), Np(VI), and Np(VII).

We used the following fibrous "filled" sorbents: POLIORGS 34-n with amidoxime groups, POLIORGS 33-n with amidoxime and hydrazidine groups, and AV-17-n with AV-17 anion exchanger as filler. The degree of filling of the fiber with sorbents was 50%. Sorption was run under static conditions with stirring of the Np(V), Np(VI), and Np(VII) solutions in 1 M NaOH with sorbents on a LAB-PU-02 stirring device for 1–60 min. The solution volume to the sorbent mass ratio (V/m) was 100 ml g^{-1}.

The Np concentration in the solutions was determined by α-ray spectrometry. To this end, aliquots of the solution under study were applied to stainless-steel targets. The targets were dried under an IR lamp, calcined over an alcoholic burner flame to red heat, and analyzed on an Alpha Analyst (Canberra) α-ray spectrometer. The latter was preliminarily calibrated using ^{239}Pu (5155 keV), ^{243}Am (5275 keV), and ^{242}Cm (6112 keV). The background of the α-ray spectrometer at energies within 3–7 MeV is 5×10^{-5} Bq.

The degree of recovery, %, of Np was determined from its content in the solution before and after sorption; the distribution coefficients K_d of Np were calculated by the standard formula.

The reagents were of no less than analytically pure grade.

RESULTS AND DISCUSSION

The focus of this study was sorption of Np(VII) from alkaline solutions, which was studied to the least extent compared to Np in other oxidation states. The most probable species of Np(VII) and Np(VI) ions in strongly alkaline solutions are $NpO_4(OH)_2^{3-}$ and $NpO_2(OH)_4^{2-}$, respectively [6, 7]. Presumably, Np(V) also forms a similar anionic hydroxo complex $NpO_2(OH)_2^{-}$. It was of interest to examine the sorption recovery of Np in the highest oxidation states from alkaline solutions with POLIORGS 34-n and 33-n complexing sorbents, as well as with AV-17-n highly basic anion-exchanging sorbent.

Table 2. Stability of Np(VII) in contact with the polyacrylonitrile matrix

Parameter	Phase contact time, min						
	0	5	10	20	30	60	120
Np concentration, mM	1.76	1.74	1.73	1.76	1.74	1.78	1.73
Optical density at λ = 412 nm	2.078	1.892	1.731	1.539	1.378	0.927	0.333
Np(VII) content in solution, rel. %	100	89.3	80.1	69.1	59.9	34.0	0

Table 3. Distribution coefficients, ml g^{-1}, of Np(VII), Np(VI), and Np(V) in sorption on POLIORGS 34-n from 1 M NaOH in relation to the phase contact time. *V*/*m* = 100 ml g^{-1}

Phase contact time, min	Np(VII)	Np(VI)	Np(V)
1	102	180	33
2	225	500	39
3	372	680	42
5	596	2550	50
10	807	4600	130
30	4220	10470	252
60	4621	13970	361

Table 1 presents the results of sorption of Np(VII) from 1 M NaOH on POLIORGS 34-n, POLIORGS 33-n, and AV-17-n polymeric sorbents. It is seen that high degrees of recovery of Np(VII) by sorption with the complexing sorbents were achieved within 5–10 min, whereas the Np(VII) sorption by AV-17-n anion-exchanging sorbent in this period is negligible. In the case of sorption on POLIORGS 34-n sorbent, a green color of the solution and the sorbent, typical for Np(VII) in 1 M NaOH, is preserved during 5–10 min, whereas in the case of POLIORGS 33-n containing hydrazidine groups the green color of the solution and sorbent disappears virtually immediately after the phases are brought into contact. This suggests rapid reduction of Np(VII) on the sorbent. Therefore, in subsequent experiments we used POLIORGS 34-n. Also, we examined how the stability of Np(VII) is influenced by the polyacrylonitrile matrix of the sorbent without filler. Table 2 presents the data characterizing the stability of Np(VII) in 1 M NaOH in the presence of polyacrylonitrile fiber. We found that the latter reduces Np(VII) to Np(VI), but much more slowly in the case of the fiber without filler compared to the filled fiber, and the green color of the solutions is preserved for 1 h. As seen form Table 2, Np is not sorbed by the polyarcylonitrile fiber (the Np concentration in solution remains unchanged), and the optical density of the solution at λ = 412 nm tends to monotonically decrease, which suggests reduction of Np(VII) to Np(VI).

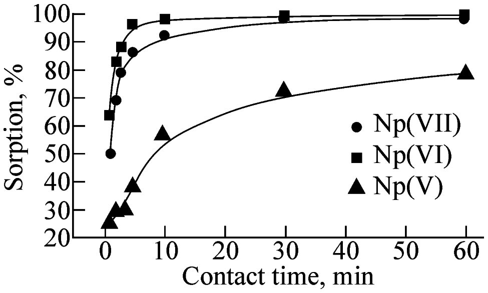

Fig. 2. Sorption, %, of Np in different oxidation states in relation to the phase contact time. [NaOH] = 1 M, *V*/*m* = 100 ml g^{-1}.

We examined the degree of recovery of Np(VII), Np(VI), and Np(V) with POLIORGS 34-n sorbent from 1 M NaOH as influenced by the phase contact time. Figure 2 and Table 3 show that, under the actual conditions, Np(VI) is sorbed most efficiently. This suggests that, under these conditions, POLIORGS 34-n sorbs Np(VI) preferably to Np(VII) and especially to Np(V). This is also confirmed by the fact that, after a 10-min contact of the solutions with the sorbent, the distribution coefficient, ml g^{-1}, of Np(VI), 4.6×10^3, is higher than those of Np(VII) and Np(V): 8.1×10^2 and 1.3×10^2, respectively (Table 3).

The experiments on sorption of Np in the highest oxidation states from 1 M NaOH with fibrous "filled" sorbents POLIORGS 34-n and 33-n showed that high distribution coefficients of Np can be achieved within the phase contact time of 5–10 min. Sorption of Np(VII) under identical conditions with highly basic anion exchanger AV-17-n is insignificant. During sorption, Np(VII) is reduced to Np(VI) with the filler and the polyacrylonitrile matrix simultaneously. The reduction with the unfilled matrix is much slower than that with the filled matrix, and no sorption of Np with the unfilled matrix is observed.

Our data indicate that complexing fibrous "filled" sorbents with amidoxime and hydrazidine groups show promise for sorption recovery of Np in the highest oxidation states from strongly alkaline solutions.

REFERENCES

1. Myasoedova, G.V., *Ross. Khim. Zh.*, 2005, vol. 49, no. 2, pp. 72–75.
2. Medvedeva, I.B., Rovnyi, S.I., Myasoedova, G.V., and Molochnikova, N.P., *Radiokhimiya*, 2001, vol. 43, no. 4, pp. 359–362.
3. Myasoedova, G.V., Nikashina, V.A., Molochnikova, N.P., and Lileeva, L.V., *Zh. Anal. Khim.*, 2000, vol. 55, no. 6, pp. 611–615.
4. Molochnikova, N.P., Tananaev, I.G., Myasoedova, G.V., and Myasoedov, B.F., *Radiokhimiya*, 2007, vol. 49, no. 1, pp. 58–60.
5. Krot, N.N., Gel'man, A.D., Mefod'eva, M.P., et al., *Semivalentnoe sostoyanie neptuniya, plutoniya, ameritsiya* (Heptavalent State of Neptunium, Plutonium, and Americium), Moscow: Nauka, 1977.
6. Chaikhorskii, A.A., *Khimiya neptuniya* (Chemistry of Neptunium), Moscow: Atomizdat, 1978.
7. Bolvin, H., Walhgren, U., Moll, H., et al., *J. Phys. Chem. A*, 2001, vol. 105, no. 51, pp. 11441–11445.