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The interaction of Np(V), Pu(VI) and Tc(VII) with metal in alkaline solutions

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Abstract

The interaction of Np(V), Pu(VI) and Tc(VII) with metal reductants Zn, Cr, Sn and their alloys was investigated in 0.5–4 mol l^{-1} NaOH solutions in static and dynamic conditions (by filtration of solutions through the column filled with grains of metal). In this paper, it was found that the reduction and succeeding precipitation hydroxides of these elements, on the surface of metal grains from 0.5 to 4 mol l^{-1} NaOH solutions, gives a decontamination factor (DF) from 1.1 to 67. The best result was achieved for Pu (DF=67) on Cr grains after 2.5 h contact at 60°C with 0.5 mol l^{-1} NaOH solution containing Pu(VI). Increasing the NaOH concentration, and the addition of chromate ions and complex-forming agents to alkaline solution results in a decrease of the decontamination factor (DF). A better result for Np sorption from 1 mol l^{-1} NaOH solutions was achieved after longer contact, than for Pu, with Cr and Zn grains. The maximum DF=8.9 was achieved for Tc on a column with Zn grains after filtration with a 3.5 mol l^{-1} NaOH solution containing Tc(VII). Washing out of Np and Pu, sorbed on the Cr grain surfaces, was achieved using an acid solution (1 mol l^{-1} HNO_3). The technetium was desorbed from metal surface by 10% H_2O_2 solution. © 1998 Elsevier Science S.A.

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1. Introduction

The interaction of metals (Zn, Cr, Sn and others) on alkaline solutions of Np(V), Pu(VI), Tc(VII) can, as in electrolysis, result in their reduction to the tetravalent state and in the adhesion of hydroxides on the surface of metals. The application of this technique for the recovery of Np(V), Pu(VI) and Tc(VII) from alkaline solutions has been rarely studied, in contrast to other methods, e.g. ion exchange, solvent extraction and electrochemistry, being elaborated more intensely, for example, in the US for the treatment of alkaline wastes [1].

The decontamination of water solutions from technetium by its reductive sorption on metallic zinc and aluminium is described in the work by Fletcher et al. [2]. The decontamination factors from technetium (DF=3.3–18.6) were obtained in solution with initial pH of 1–2 by action of granulated or powder zinc, and for the action of powder aluminium on solutions at pH 13–14, the DF was found to be 2.1–7.8. At the Tomsk radiochemical plant, Volk et al. [3] have studied the recovery of technetium from the raffinates of the first-extraction Purex process cycle by action of granulated zinc or iron on the low acidity solution. They obtained a recovery of more than 90% of technetium on zinc, and about 61% on iron; the decontamination factor from fission products being about 30. Electrodeposition of technetium from acid and alkaline water solutions, as well as from non-water solvents, is described in Ref. [4]. The reduction of Tc(VII) to Tc(IV) and electrodeposition of $TcO_2 \cdot nH_2O$ has been shown to be effective in alkaline solutions in the presence of nitrate and nitrite ions [2,5]. It has been shown that the solubility of the electrodeposited $TcO_2 \cdot nH_2O$ in 4.0 mol l^{-1} NaOH solution, not containing dissolved oxygen, is $(5–7)\times10^{-7}$ mol l^{-1}, being about 50 times lower, than the solubility of this compound, obtained by chemical reduction of Tc(VII) or by hydrolysis of K_2TcCl_6 [6].

The present work is devoted to the study of neptunium, plutonium and technetium recovery from alkaline solutions by interaction and sorption of the reduced forms of their hydroxides on some metal reductants.

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2. Reductive sorption of Np(V), Pu(VI) and Tc(VII) from alkaline solutions under interaction with the metals Pb, Sn, Sb, Cr and Zn

2.1. Selection of metals

It was important for our study to select metals which have a redox potential sufficient for the reduction of Np(V), Pu(VI) and Tc(VII) to $MeO_2 \cdot nH_2O$ in alkaline solutions. The other requirement is the absence of metal passivation in alkaline solution, that is, there must be no formation of oxide film, insoluble in alkali, that would break contact of solution with metal. On the base of the described criteria, Zn, Cr, Sn, Pb and Sb metals have been selected for the study of the reductive sorption of plutonium, neptunium and technetium from alkaline solutions. Associated sorption of Np and Pu from alkaline solutions, by reduction and creation of their respective AnO_2 films, was also studied. The redox potentials of these metals are presented in Table 1. The alloys Pb–1.5%Sb and Sn(63.5%), Pb(34%), Sb(2.5%) were also used for the study.

The redox potential of the Tc(VII)/Tc(IV) pair was about −0.6 V/N.H.E. in alkaline solutions [4,5].

Table 1

Redox potentials (V/N.H.E.) of metals, chosen for reductive sorption experiments, in 1 mol l^{-1} NaOH [7]

	Metal				
	Zn	Cr	Sn	Sb	Pb
E° Me^{2+}/Me°	−1.2	−(1.2–1.48)	−0.91	−0.59	−0.58

2.2. Experimental procedures

The metals were used in the form of grains, 3–3.5 mm in radius, washed with acetone, 0.5 mol l^{-1} HCl and water. The reductive sorption was studied under static conditions, shaking 5 ml of alkaline solution, containing $(0.1–7)\times 10^{-6}$ mol l^{-1} of neptunium(V), plutonium(VI), or $(3–9)\times 10^{-5}$ mol l^{-1} of technetium(VII) with some metal grains, their total visible surface being 5.6–7.7 cm^2. In addition, the sorption was studied also in dynamic conditions, by passing an alkaline solution of radionuclide through a column, 150 mm high and 10 mm I.D., filled with metal grains (column experiments). The concentrations of alkaline solutions were 0.5–4 mol l^{-1} NaOH, and alkaline solutions were also prepared, containing different inorganic and organic complex-forming agents, simulating alkali radwastes.

For the determination of the completeness of the isolation of these radioelements from solution into the precipitate, samples were taken from the solution before sorption (0.1 ml) and after every 30 min of contact with grains of metal (0.2 ml) during 2.5 h (static experiments). The samples withdrawn were acidified by adding 0.1–0.2 ml of 2 mol l^{-1} HNO_3, then 7 ml of Beckman Ready Gel cocktail was added, and the radioactivity was measured on a Beckman LS-6500 liquid scintillation analyzer.

The decontamination factor (DF) of solution from the radioelement was calculated as the ratio: $DF = I_0V_0/I_fV_f$, where I_0, I_f is the specific radioactivity of solution before (0) and after (f) sorption on metal (Bq ml^{-1}), V_0, V_f is the volume of the alkaline solution before (0) and after (f) sorption on metal (ml).

The sorption on metals has been studied both in oxic conditions, that is in presence of oxygen, dissolved in alkaline solutions, and in anoxic conditions after the removal of dissolved oxygen by sparging with argon for 15–20 min. After the contact with metal grains, the solution was centrifuged for 10 min at a speed of 8000 r.p.m., samples for analysis were then taken. For measurements of the radioactivity of neptunium-237 solutions, on a Beckman LS-6500 instrument, in which daughter protactinium-233 is present, the narrow peak, corresponding to α-emission of neptunium-237, was cut out from the total spectra using the program installed in the instrument.

2.3. Results

2.3.1. Reductive sorption of neptunium(V) and plutonium(VI) in alkaline solution on metals

It follows from the data in Table 2, that sorption on the studied metals gives rather high decontamination factors for neptunium and plutonium in (0.5–1.0) mol l^{-1} NaOH (variation of DF is from 11 to 67). The reductive sorption of neptunium(V) and plutonium(VI) on metals becomes less effective when alkali concentration increases to 4.0 mol l^{-1} NaOH (DF from 1.1 to 9.2), as well as in simulant solutions, containing 3.2 mol l^{-1} NaOH, 0.04 mol l^{-1} Na_2CrO_4 and 12 complex-forming agents (DF is from 1.8 to 3.7).

Reductive sorption of Pu on metals from 1 mol l^{-1} NaOH is shown also on Fig. 1. The rate of plutonium sorption from alkaline solutions on the studied metals is significantly higher than that of neptunium. Decontamination factors >10 are being reached for plutonium(VI) after 1–2 h, and for neptunium(V), under analogous conditions, after 10–20 h of contact with alkaline solution. This is in accordance with literature information, that reduction of plutonium(VI) to plutonium(IV) in alkalis proceeds easier and under milder conditions, than reduction of neptunium(V) to the tetravalent state [8].

High decontamination factors from neptunium (DF = 12–22) and from plutonium (DF = 34–67) have been obtained by sorption on chromium grains in 0.5–1.0 mol l^{-1} NaOH. Double passing of a deaerated solution $(1.5\times 10^{-5}$ mol l^{-1} Pu, 1 mol l^{-1} NaOH) through the column

Table 2
Reductive sorption of Np(V) and Pu(VI) from alkaline solutions on metals and alloys

No.	Metal or alloy	[NaOH] (M)	DF			
			Np(V)		Pu(VI)	
			20°	60°	20°	60°
1	Cr	0.5	12	19	53	67
		1.0	15	22	34	40
		2.0	—	7.2	11	14
		4.0	3.2	3.7	3.7	4.3
		3.2 (simulant)	2.1	2.7	3.5	2.8
		1.6 (diluted simulant)	—	8	10,6	4.3
2	Zn	1.0	47	64	32	37
		4.0	2.3	2.5	8.4	9.2
		3.2 (simulant)	1.8	1.9	3.8	3.7
3	Sn	1.0	35	42	15	18
		4.0	2.0	2.2	4.3	6.4
		3.2 (simulant)	2.5	2.7	1.4	1.5
4	Pb-1.5%Sb	1	13	18	21	27
		4	1.1	1.7	4.2	1.7
5	Sn–Pb–Sb	1	22	24	11	16
		4	2.7	2.5	4.0	2.1
		3.2 (simulant)	1.9	2.2	3.9	3.5

[Pu],[Np]=$(0.1–7.0)\times10^{-6}$ mol l^{-1}. Surface/volume ratio=1.3 cm^{-1}.

(150 mm high, 10 mm I.D.; free column volume, 4.5 cm^3; flow rate 8 ml h^{-1}; T=60°c), filled with chromium grains, decreased plutonium concentration up to 3.4×10^{-7} mol l^{-1} Pu. (Fig. 2). More than 2 h contact of the filtrate with a fresh portion of chromium grains decreased plutonium concentration from 3.4×10^{-7} to 8.7×10^{-8} mol l^{-1}, which is close to the solubility of $PuO_2{\cdot}nH_2O$ in 1 mol l^{-1} NaOH.

The stripping of neptunium and plutonium, sorbed on chromium, has been investigated. Nitric and hydrochloric

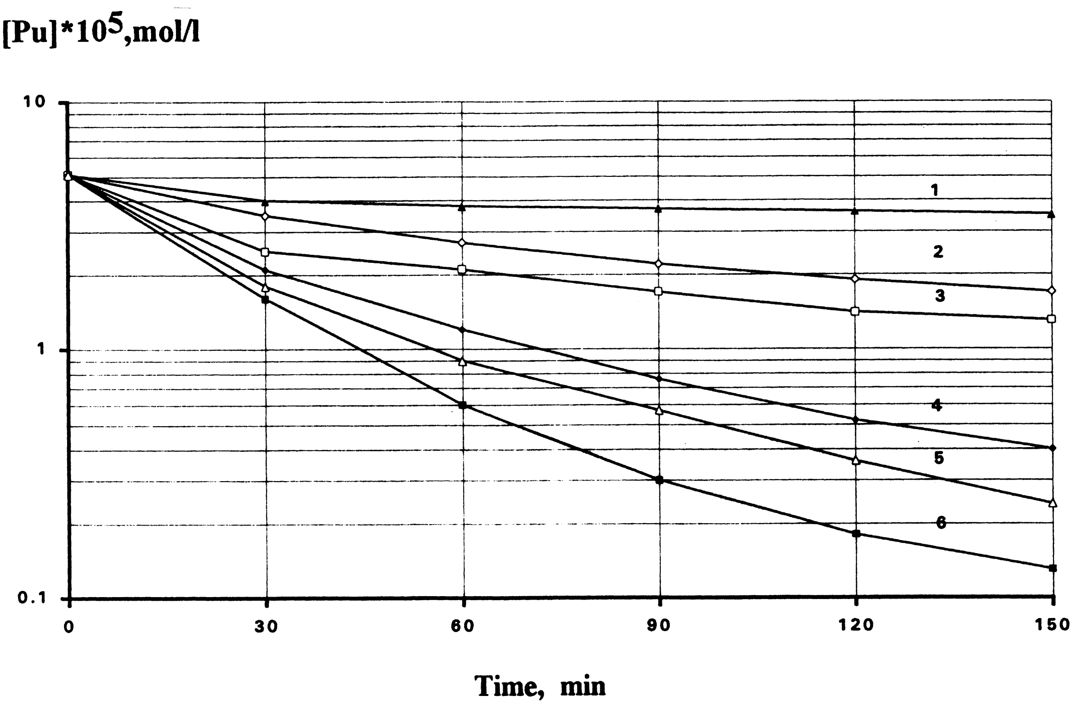

Fig. 1. Reductive sorption of Pu from 1.0 mol l^{-1} NaOH solution on metals and alloys at 60°C. (1) Pb; (2) Pb–Sn; (3) Zn; (4) Sn; (5) Sn–Pb–Sb; (6) Cr.

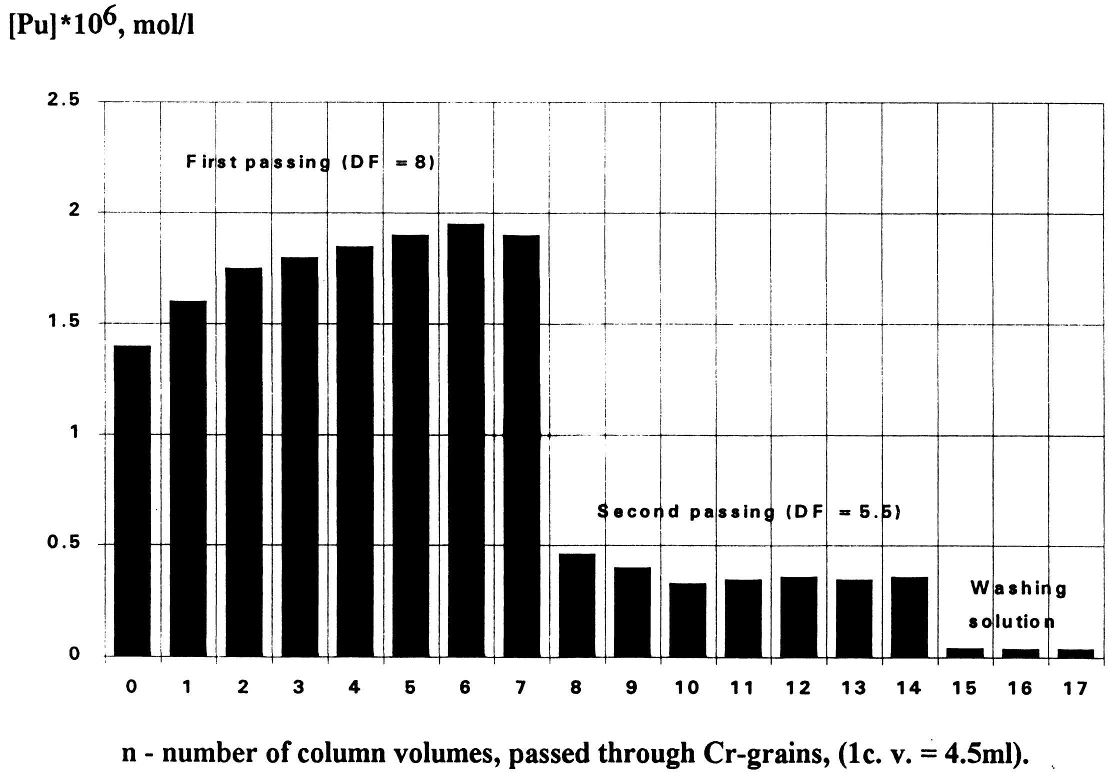

Fig. 2. Reductive sorption of Pu on Cr grains from 1 mol l^{-1} NaOH solution at 60°C. The initial Pu concentration=1.5×10^{-5} mol l^{-1}. (column experiment).

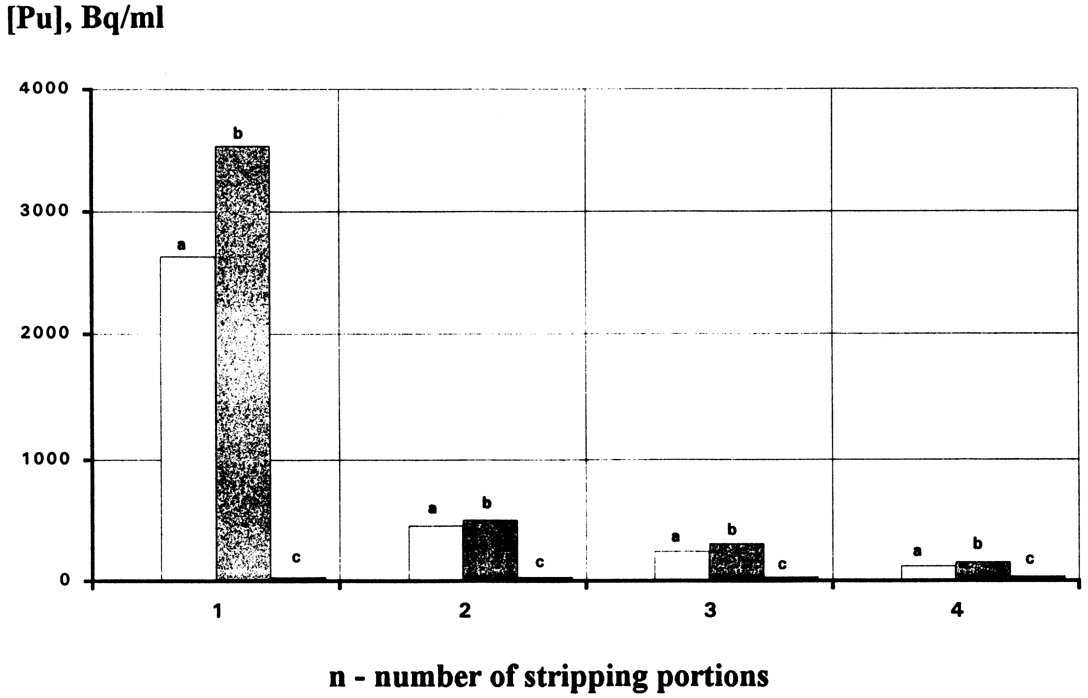

Fig. 3. The washing out of Pu from 5Cr grains; every stripping fraction (2 ml) was stirred with grains for 30 min: (a) 1 mol l^{-1} HNO_3; (b) 2 mol l^{-1} HCl; (c) 5% H_2O_2.

Table 3
Reductive sorption of technetium by metals from alkaline solutions and simulants, containing (3–9)$\times 10^{-5}$ M Tc(VII)

No.	[NaOH] (M)	Additions	DF[a]				
			Zn	Cr	Sn	Pb+1.5%Sb	Sn63.5+Pb34+Sb2.5%
1	0.5	—	1.4/1.9	1.07/1.15	1.15/2.8	1.2/2.9	1.5/4.3
2	1.0	—	1.46/3.6	1.09/1.23	1.23/3.9	1.3/3.5	1.9/5.4
3	2.0	—	3.9/4.7	1.3/1.4	1.27/4.1	1.4/3.8	1.8/5.3
4	2.0	Simulant-1	6.0/5.8	1.23/1.32	1.21/3.5	1.8/6.0	1.7/5.1
5	3.5	—	5.7/8.9	1.3/1.5	1.4/4.6	1.8/5.1	1.8/3.5
6	3.5	Simulant-2	—	1.03/1.05	1.1/1.2	1.6/3.7	1.4/1.8
7	3.2	Simulant-2	1.7/2.3	1.01/1.03	1.03/1.1	1.5/3.2	1.2/1.5

Simulant-1 contained only five additions of complex-forming agents, while simulant-2 contained 12 complex-forming agents, including chromate ions.
[a] Numerator is DF, obtained under shaking conditions; denominator is DF in the experiments on the column with metal grains.

acids of (1–2) mol l^{-1} concentration effectively strip plutonium from metal grains (Fig. 3). Hydrogen peroxide solution (5% concentration) has little effect on stripping plutonium sorbed on metals. The ratio of the visible surface of solid phase to the solution volume was close to 3 cm^{-1}.

2.3.2. Reductive sorption of technetium(VII) on metals in alkaline solutions

The decontamination factor of alkaline solutions and simulants from technetium by sorption on zinc, chromium, tin, lead and their alloys are presented in Table 3. The DF values for technetium in 0.5–3.5 mol l^{-1} NaOH solutions, obtained by sorption under conditions where the metal grains were in contact with solution for 2.5 h, for a ratio of metal surface to solution volume of 1.3 cm^{-1}, lie in the range from 1.01 to 6.0. Under dynamic conditions, when alkaline solution or simulant was passed through the column (free column volume, 3.5 cm^3; flow rate, 7 ml h^{-1}; T=20°C) filled with metal grains, the highest decontamination factors, 8.9, were obtained for sorption on zinc from 3.5 mol l^{-1} NaOH. The reductive sorption of Tc on Zn grains from alkaline solutions at 20°C is shown in Fig. 4.

As follows from the data in Table 3, tin, lead and their alloys with antimony proved to be less effective than zinc, in accordance with their lower redox potential compared to zinc. The decontamination factor from technetium by sorption on the studied metals, in contrast to actinide elements, increases with growth of alkali concentration from 0.5 to 4 mol l^{-1} NaOH. In waste simulant solutions,

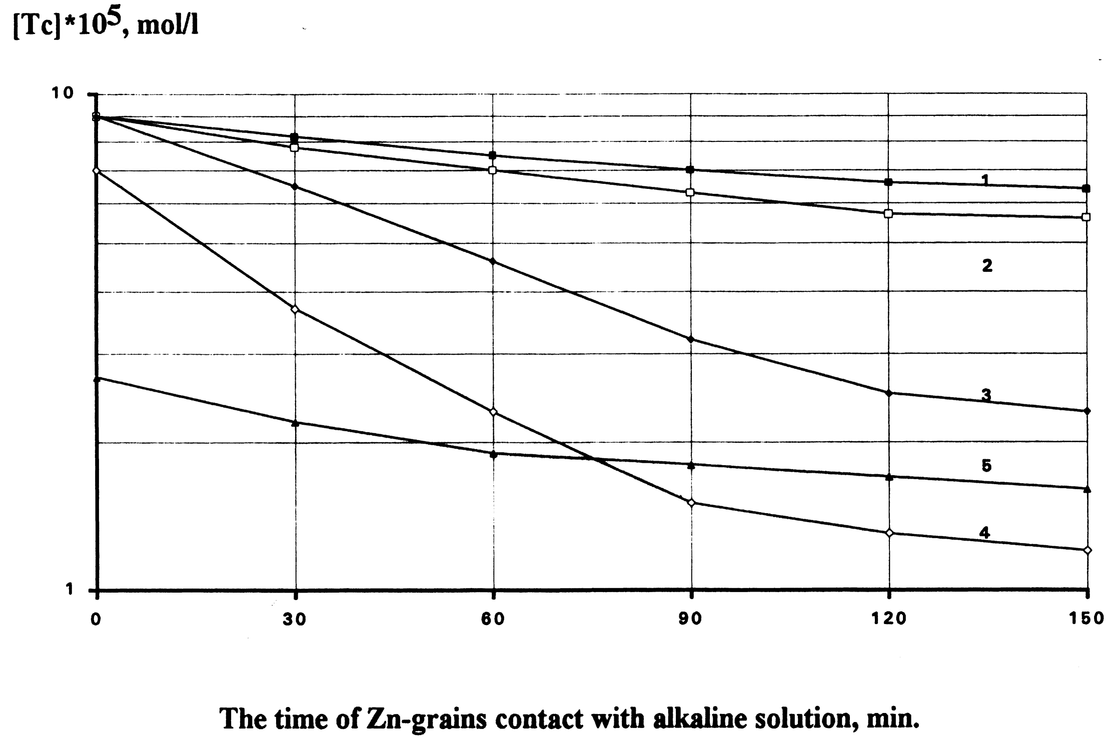

Fig. 4. Reductive sorption of Tc on Zn grains from alkaline solutions at 20°C. (1) 0.5 M NaOH; (2) 1.0 M; (3) 2.0 M; (4) 4.0 M; (5) 3.2 M (simulant; 3.2 M NaOH plus 12 complex-forming agents.

containing 0.04 mol l^{-1} CrO_4^- and a number of organic and inorganic complex-forming agents, the decontamination factors under investigation are lower than in pure alkalis. The increase in temperature from 20 to 60°C, and the removal of dissolved oxygen, gave no significant effect. It is important to note that double passing of the same solution through the column with zinc leads to decontamination of alkaline solution from technetium up to 1.2×10^{-6} mol l^{-1}, it is close to the solubility of electrodeposited technetium dioxide in 4 mol l^{-1} NaOH solutions [6].

The stripping of technetium, sorbed on metal grains, has been carried out with 10% solution of hydrogen peroxide. The 30-min shaking of 5 ml of 10% H_2O_2 solution with five grains of chromium has resulted in ~90% washing out of technetium. Repeated shaking with a fresh portion of this solution gave almost total technetium recovery from the surface of metals: up to 98–99%.

3. Conclusions

(1) The reductive sorption of plutonium(VI) and neptunium(V) on the above-mentioned metal reductants is more effective on chromium grains, where the sorption of plutonium reaches more than 98% and DF=67 in 0.5 mol l^{-1} NaOH at 60°C (static conditions, with the ratio metal surface to solution volume, 1.3 cm^{-1}).

(2) The contact Tc(VII) alkaline solutions (0.5–4 mol l^{-1} NaOH) with grains of Zn, Cr, Sn, Pb metals and their alloys, results in an incomplete precipitation $TcO_2 \cdot nH_2O$ on the surface of the metals. The best decontamination of 3.5 mol l^{-1} NaOH solutions from technetium was increased to 8.9 for the granulated Zn in the column experiment.

(3) The dilution of the waste simulant solution leads to an increase of the decontamination factor from Pu to 2–3 times that of its interaction with the studied metals and alloys.

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