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Capture of Pu(V), Np(V) and Pu(VI) from alkaline solutions by hydroxides of Pu(IV), Th(IV) and La(III)

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Abstract

In systematic studies of actinide chemistry in alkaline solution, it was found that Pu(IV) hydrous oxide can remove significant amounts of plutonium present in higher oxidation states from solution. By spectrophotometry it was found that the capture of Pu(VI) by Pu(IV) hydrous oxide is negligible whereas Pu(V) and Np(V) are highly adsorbed. Quantitative characterization of the process was investigated by a radiometric method based on ^{239}Np-labeled neptunium. The influence of temperature, alkali concentration, and the Pu/Np molar ratio on the extent of capture of Np(V) by PuO_2xH_2O was investigated. © 1998 Elsevier Science S.A.

Keywords: Neptunium; Plutonium; Alkaline solution; Capture

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1. Introduction

Much of the high-level waste accumulated in Russia and the USA in the production of plutonium for weapons is alkaline. Processing of these wastes for long-term storage has caused recent increased interest in the alkaline chemistry of the actinides. Despite the recent research, works on this subject are few and the research often exposes new problems.

One issue is the stability of pentavalent plutonium in alkaline media. In recent work, the stability of Pu(V) with respect to disproportionation was studied in 1 to 10 M NaOH at −12 to 40°C [1]. It was found that Pu(V) disproportionates in alkaline solutions with hydroxide concentration less than 8 M according to the reaction:

$$2\mathrm{Pu(V)} \Rightarrow \mathrm{Pu(VI)} + \mathrm{Pu(IV)O_2}x\mathrm{H_2O(s)}. \qquad (1)$$

The extent and rate of disproportionation increases with temperature and decreases with increasing hydroxide concentration.

However, determination of the thermodynamic and kinetic characteristics of reaction (1) is complicated by parallel reactions. Among them are reduction of Pu(VI), formed by reaction (1), by water α-radiolysis products:

$$\mathrm{Pu(VI)} \Rightarrow \mathrm{Pu(V)}, \qquad (2)$$

reproportionation of reaction (1) products in strong alkali:

$$\mathrm{Pu(VI)} + \mathrm{PuO_2}x\mathrm{H_2O} \Rightarrow 2\mathrm{Pu(V)}, \qquad (3)$$

and oxidation of Pu(V) by dissolved oxygen:

$$2\mathrm{Pu(V)} + \mathrm{O_2} \Rightarrow 2\mathrm{Pu(VI)}\,. \qquad (4)$$

Because the disproportionation of Pu(V) produces PuO_2xH_2O precipitate, reactions (1) to (4) proceed in a multicomponent heterogeneous system. Plutonium(IV) hydrous oxide formed by reaction (1) may sorb plutonium in other valence states from the alkaline solution.

The extent of sorption and the fate of the sorbed plutonium depends on the coprecipitation mechanism. It is likely that eventually, as the precipitates age, part of the captured Pu(V) will return to solution and participate in reactions (1 to 4). It is unclear whether the captured Pu(V) can disproportionate in the solid phase. Experimental study of these questions was undertaken to help describe the disproportionation process.

2. Experimental techniques

The ^{239}Pu, ^{237}Np and ^{239}Np test solutions were purified by standard anion exchange and oxalate precipitation techniques. The ^{239}Np tracer was separated from ^{243}Am stored over one month to achieve secular equilibrium with ^{239}Np. Standardized 1 to 10 M NaOH solutions were

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prepared just before experiment from 17.7 M NaOH stored in a sealed plastic vessel to prevent carbonate contamination. All solutions were prepared from distilled water acidified to pH 4 and boiled to remove dissolved CO_2. All reagents were pure and extra pure grades. Spectrophotometry was used to determine neptunium and plutonium valence (Shimadzu UV-3100 spectrophotometer, Japan). Radiometric measurements were performed on a liquid scintillation counter (Beckman LS6500, USA).

3. Results and discussion

Plutonium(IV) hydrous oxide precipitates obtained by Pu(V) disproportionation in NaOH solution have a different color than precipitates obtained by adding acidic Pu(IV) solution to alkali. The color difference may indicate sorption of Pu(V) or Pu(VI) onto PuO_2xH_2O precipitate. Spectrophotometric tests in the Pu(V)–Pu(IV) system were performed. A Pu(V) solution in 6 M NaOH ($[Pu(V)]=2\times10^{-3}$ M) was added to freshly precipitated PuO_2xH_2O obtained by treating a carbonate Pu(IV) solution with strong alkali and washing the precipitate with 6 M NaOH. The Pu(IV)/Pu(V) suspension was stirred intensively at 40°C. Periodically, aliquots were taken and spectra obtained of the clarified supernatant. The only observed change was decrease in the Pu(V) absorption band at 809 nm (molar extinction coefficient is 8 l mol^{-1} cm^{-1}). More than half the Pu(V) sorbed from the solution in the first 5 min (Fig. 1).

The amount of Pu(VI) capture by Pu(IV) hydrous oxide was evaluated at 1 M NaOH where the disproportionation of Pu(V) goes essentially to completion. The amount of Pu(VI) was determined by spectrophotometry using the 631 nm band (10 l mol^{-1} cm^{-1}) for the alkaline supernate and the Pu(VI) absorption at 830 nm for the acid-dissolved and $HClO_4$-oxidized deposit. The amounts of plutonium in the deposit and in the supernatant were identical, within experimental error. Thus, at the conditions studied, sorption of Pu(VI) on Pu(IV) hydrous oxide is negligible in Pu(V) disproportionation by reaction (1).

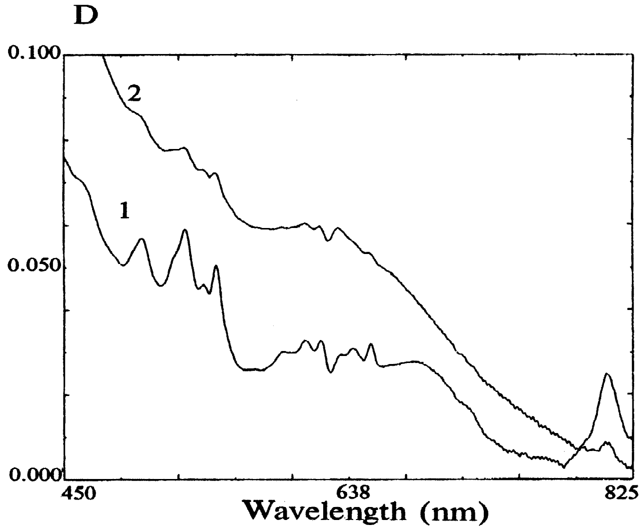

Fig. 1. The sorption of Pu(V) on Pu(IV) hydrous oxide at 50°C. [NaOH]=6 M; molar ratio Pu(V):Pu(IV)=1:2; $[Pu(V)]=2\times10^{-3}$ M; (1) the optical spectrum of Pu(V) initial solution; (2) the optical spectrum of Pu(V) solution 5 min after contact with Pu(IV) hydrous oxide.

More thorough experiments were conducted using ^{237}Np(V), labeled with ^{239}Np, to model Pu(V). The neptunium concentration was chosen to exclude the formation of a separate solid phase [2]. To simplify the experiments, the Pu(IV) hydrous oxide deposit was formed at thermostated temperatures (40, 60, 80°C) in 2, 4, 6 and 8 M NaOH by reduction of Pu(VI) with a stoichiometric amount of hydroxylamine; Np(V) is not reduced in these conditions [3]. Initial Np(V) and Pu(VI) concentrations were 2×10^{-5} M. Experiments were also conducted at 1:10 and 1:20 Np/Pu ratios. At selected times, 0.1 ml samples were taken, clarified and analyzed.

The sorption of Np(V) by PuO_2xH_2O was evaluated by analyzing ^{239}Np β activities in the sampled and initial solutions. Kinetic curves illustrating the process of Np(V) capture by PuO_2xH_2O are presented in Fig. 2. The sorption behavior is similar to that shown by selfprecipitating components with one component in macroconcentration and the other in microconcentration. In this case, however, both components are in microconcentration. Therefore, in some experiments, the concentrations of plutonium in solution and the concentrations of neptunium in the acidified precipitate were determined to obtain additional information. Results are presented in Table 1 as the Np(V) distribution coefficient, K_c ($=[Np(V)]_c/[Np(V)]_s$, where $[Np(V)]_c$ and $[Np(V)]_s$ are neptunium concentration in the deposit and solution, respectively).

The results show that much of the Np(V) is adsorbed by the forming PuO_2xH_2O. The distribution coefficient decreases with increasing NaOH concentration because particle velocity decreases. The experimental condition was dynamic, with precipitate being formed to give a changing surface and possibly a changing surface charge and the state of the element being absorbed.

It is unlikely that a mixed neptunium and plutonium compound is formed though isomorphous coprecipitation in amorphous systems is postulated [4]. Because the system is not stirred, the interphase distribution of Np(V) following from layer-by-layer formation of PuO_2xH_2O must obey the law of logarithmic adsorption [5–7] described by the Doerner–Hoskins formula:

$$\ln\{(x_0-x)/x_0\} = Q\ \ln(y_0-y)/y_0, \tag{5}$$

where x and x_0, and y and y_0, are the amounts of neptunium and plutonium in the solution and in the whole system, respectively, and the quotients represent the frac-

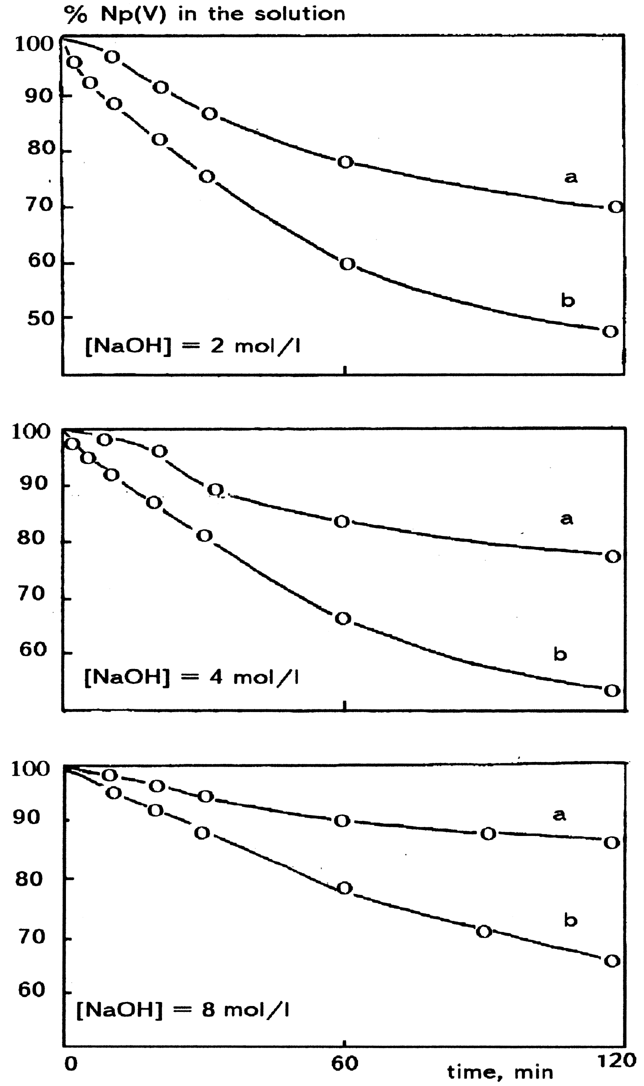

Fig. 2. The kinetic curves of Np(V) capture by Pu(IV) hydrous oxide. (a) 40°C; (b) 80°C; $[Np]_{total} = [Pu]_{total} = 2 \times 10^{-5}$ M.

Table 1
Np(V) partition coefficient between solution and precipitating Pu(IV) hydrous oxide at 60°C, 120 min, as a function of NaOH concentration

[NaOH] (M)	$[Np_s]$, solution (M)	$[Np_c]$, in solids (M)	K_c
2	1.15×10^{-5}	9.28×10^{-6}	0.807
4	1.09×10^{-5}	8.44×10^{-6}	0.774
6	1.21×10^{-5}	8.10×10^{-6}	0.669
8	1.32×10^{-5}	6.96×10^{-6}	0.527

tion of Np or Pu in the solid phase. Results of Doerner–Hoskins analysis of the data appear in Table 2.

As shown in Table 2, at times below 60 min, Q is practically constant. However, with increased time, the ratio Q changes and the even Np(V) distribution in the deposit is changed. In experiments having initial [Pu(VI)]:[Np(V)] ratios greater than 1, the Np(V) sorption shows a minimum with time (Fig. 3). The minimum may be caused by ordering of the solid phase, desorbing a part of the Np into the solution. Change in the heterogeneous distribution coefficient Q also may be determined by change in the active concentration of ions of the admixture being precipitated [8,9].

Sorption of Pu(V) by oxides/hydroxides of elements which do not form oxygenated cations [Th(IV) and La(III)] was also investigated. The experiments were conducted in a stirred thermostatted cell at 8 M NaOH where Pu(V) disproportionation does not occur. Decrease in Pu(V) concentration was monitored using the Pu(V) band at 809 nm. Optical spectra of Pu(V) solutions in contact with Th and La precipitates are presented in Figs. 4 and 5.

Evidently, the capture of Pu(V) by hydroxide deposits, especially at high $[Me(OH)_n]$:[Pu(V)] ratios, can signifi-

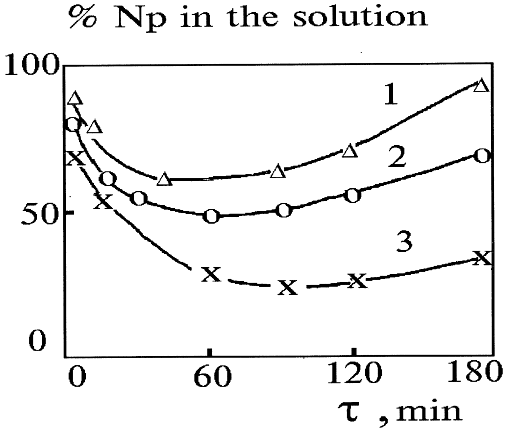

Fig. 3. Neptunium(V) capture on Pu(IV) hydrous oxide at various [Np(V)]:[(Pu(VI)] ratio in initial solution; $[Np(V)] = 2 \times 10^{-5}$ M; (1) [Np(V)]/[Pu(VI)] = 1:1; (2) [Np(V)]/[Pu(VI)] = 1:10; (3) [Np(V)]/[Pu(VI)] = 1:20.

Table 2
Np(V) coprecipitation characteristics with Pu(IV) hydrous oxide (40°C, 4 M NaOH, 2×10^{-5} M Np(V), [Np(V)]:[Pu(VI)] = 1:1)

Time (min)	[Np] (M)	[Pu] (M)	$\log[(Np_o - Np)/Np_0]$	$\log[(Pu_o - Pu)/Pu_o]$	Q
10	1.85×10^{-5}	1.83×10^{-5}	−0.034	−0.039	0.88
30	1.65×10^{-5}	1.55×10^{-5}	−0.084	−0.111	0.75
60	1.49×10^{-5}	1.36×10^{-5}	−0.129	−0.167	0.76
90	1.33×10^{-5}	0.44×10^{-5}	−0.177	−0.658	0.27
120	1.13×10^{-5}	0.12×10^{-5}	−0.248	−1.222	0.20

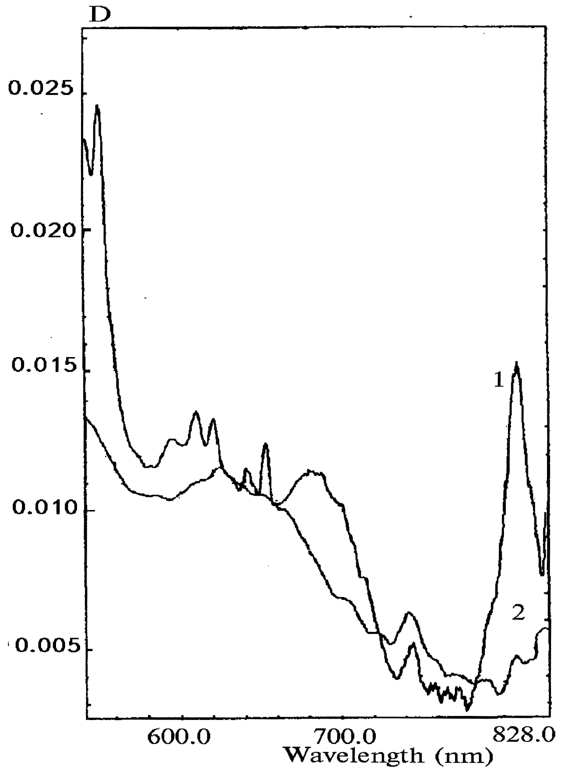

Fig. 4. The sorption of Pu(V) on Th(IV) hydroxide frrom 8 mol l^{-1} NaOH at 50°C; [Th(IV)]:Pu(V)]=30:1; $[Pu(V)_0]=2\times10^{-3}$ M; (1) the optical spectrum of the initial solution; (2) the optical spectrum of the solution after 60 min contact.

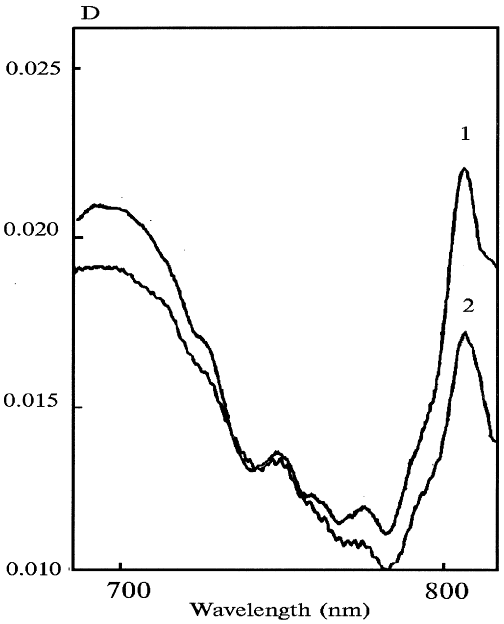

Fig. 5. The sorption of Pu(V) on La(III) hydroxide from 8 mol l^{-1} NaOH at 50°C; [La(III)]:[Pu(V)]=2:1; $[Pu(V)_0]=2\times10^{-3}$ M; (1) the optical spectrum of initial solution of Pu(V); (2) the optical spectrum of the same solution after 120 min contact.

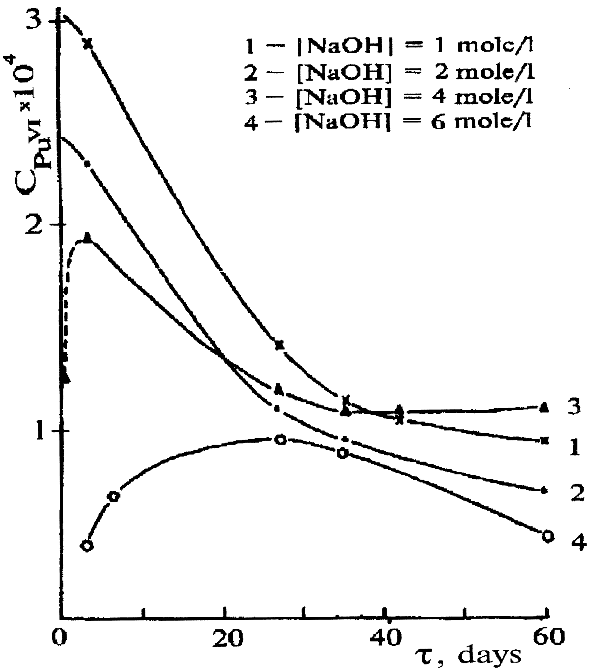

Fig. 6. Variation of plutonium(VI) concentration from Pu(V) disproportionation as a function of NaOH concentration and time. $[Pu(V)_0]=2\times10^{-3}$ M. (1) 1 M NaOH; (2) 2 M NaOH; (3) 4 M NaOH; (4) 6 M NaOH.

cantly influence the existence of the plutonium valence in both the precipitate and mother solution. Experiments on long-term storage of solid Pu(V) carbonate in NaOH solutions of various concentrations have shown that, in the absence of stirring, Pu(V) undergoes a number of transformations exhibited as nonmonotonous changes in the solution composition (Fig. 6).

These initial experiments confirm that the capture of Pu(V) by PuO_2xH_2O is influenced by aging of the deposit and leads to the return of part of the Pu(V) to solution. This phenomenon, and others, help various plutonium valence forms to exist simultaneously in concentrated alkali.

Acknowledgements

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