

INTERACTION OF Pu(VI) AND Np(VI) WITH CARBOHYDRAZIDE IN NITRIC ACID SOLUTIONS

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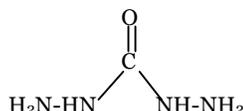
Abstract. The kinetics of Pu(VI) and Np(VI) recovery by carbohydrazide in an aqueous nitric acid solution was researched spectrophotometrically. Regarding to Pu(VI) it was established that in the interval of $[HNO_3] = 0.75-3.0 M$ and $[CO(N_2H_3)_2] = 0.1-0.4 M$, the reaction rate was proportional to the concentration of Pu(VI). The reaction order with respect to carbohydrazide was determined to be 2.3, and -3 to nitric acid. The found activation energy of the reaction was $111 kJ \cdot mol^{-1}$. Regarding Np(VI), it was found that in the interval of $[HNO_3] = 0.75-3.0 M$ and $[CO(N_2H_3)_2] = 0.03-0.12 M$, the reaction rate was proportional to the Np(VI) concentration. Reaction order with respect to carbohydrazide was determined to be 1.15, and -1.35 with respect to nitric acid. The found activation energy of the reaction was $85 kJ \cdot mol^{-1}$. Based on this kinetic data, a possible fundamental reaction mechanism was theorized.

Key words: Spent nuclear fuel, recovery, plutonium, neptunium, reduction, carbohydrazide, nitric acid

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INTRODUCTION

In the development of a new hydrometallurgical technology of spent nuclear fuel reprocessing use of various organic reducing agents (substituted hydrazine, hydroxylamine and urea, oxime, etc.) was suggested to extract plutonium and neptunium and for their subsequent purification. The most promising reducing agents were carbohydrazide, $CO(N_2H_3)_2$, hydrazine and urea derivative:



In one of the options for mixed nitride uranium plutonium fuel processing, the fuel was dissolved in the concentrated nitric acid (8-10 mol/l). In the solution obtained, plutonium was in the form of a mixture of Pu (IV, VI) [1], and neptunium was oxidized to Np (VI). These valent forms were well-extractable by tributylphosphate. In order to control the plutonium and neptunium reducing back-extraction process, it was necessary to know the nitric acid concentration influence and the reducing agent concentration influence on the interaction rate of Pu(VI) and Np(VI) with carbohydrazide.

EXPERIMENTAL PART

The study of the Pu(VI) and Np(VI) interaction was carried out by the spectrophotometry on $\lambda = 830.5$

(Perkin-Elmer) by fixing changes in optical spectra at specified intervals. In the work a disposable optical cells with a path length of 10 mm were used. Nitric acid of 1 mol/l was used as a blank solution.

The technique was as follows. A predetermined amount of nitric acid, plutonium(VI) nitrate and neptunium(VI) stock solutions was added to the optical cell. A cell with the solution was placed in a thermostatic cell holder, held for 10 minutes at the certain temperature and then an aliquot of the carbohydrazide stock solution was added. The spectra recording started after the 10 seconds of the solution stirring.

To study the kinetics of Pu(VI) and carbohydrazide interaction the optical spectra were recorded in a wavelength range from 450 to 950 nm. The concentration of Pu(VI) was determined from the optical peak density at 830.5 nm.

Since the NpO_2^{2+} ions had no clear characteristic peaks in the spectrophotometer operating range (190-1100 nm), the kinetics of Np(VI) and carbohydrazide interaction was studied by the NpO_2^+ ions formation, which had a characteristic peak at 980 nm.

To convert an optical density to the components concentration value the corresponding extinction coefficients depending on the nitric acid concentration were used.

RESULTS AND DISCUSSION

The interaction of the Pu(VI) with carbohydrazide. Observations for the spectrum changes in time showed Pu(VI) stepwise reducing. In Fig. 1 are shown the

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changes in the optical spectra that occur during the reaction of plutonium ions with carbohydrazide. Peak optical density at 830.5 nm decreases, which corresponds to a decrease in the Pu(VI) concentration and simultaneously increasing the optical density peak at 570 nm, which is characteristic of the Pu(V). Pu(V) was initially formed at low acidity (less than 2 mol/l) and at the temperature below 30°C, and only after the long-term holding Pu(III) was formed in the solution. In this case, peaks of absorbance appear at the spectra at 560 and 602 nm, that is typical for Pu(III), and the peak at 570 nm decreases. With the increase of the temperature, nitric acid concentration or holding time (more than 7 hours), further reduction to Pu(III) happens. Pu(III) is the finite form of Pu(VI) and carbohydrazide interaction. The formation of tetravalent forms in conditions of the spectrophotometric study was not detected.

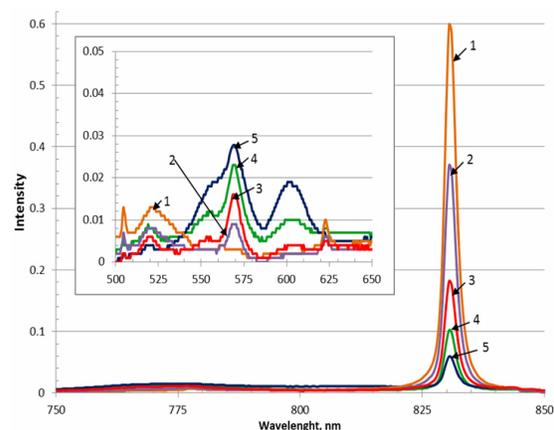


Figure 1. Changes in optical spectra after the carbohydrazide addition at $[HNO_3]=1.57$ mol/l, $[Pu(VI)]_0=0.001$ mol/l, $[CO(N_2H_3)_2]=0.2$ mol/l and 20°C. 1 – 0.5 min; 2 – 30 min; 3 – 84 min; 4 – 144 min; 5 – 239 min

The processing of experimental data was performed assuming that the reaction proceeds according to the first order equation with respect to plutonium

$$-\frac{d[Pu(VI)]}{dt} = k \cdot [Pu(VI)], \quad (1)$$

where k - first-order rate constant, min^{-1} .

By means of a graphic method in “ $\ln[Pu(VI)]$ – time” coordinates, the first order rate constants were determined for all studied conditions (Fig.2). According to the calculations, the increase of the solution acidity decreased the Pu(VI) reduction rate and growth of carbohydrazide concentration increased the reaction rate. Using the calculated rate constants, the reaction orders with respect to nitric acid and carbohydrazide were determined. The orders were equal to -3 and 2.3 respectively. The constancy of the reaction orders occurs if the nitric acid concentration was between 0.75 and 3.0 mol/l and the reductant concentration was between 0.1 and 0.3 mol/l.

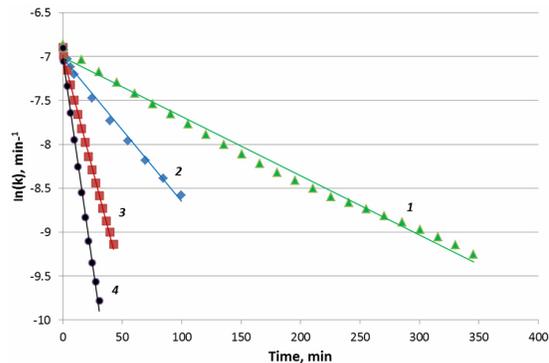


Figure 2. Plot of $\ln(k)$ vs. time in reduction of Pu(VI) with carbohydrazide. $[Pu] = 1 \times 10^{-3}$, $[HNO_3] = 1$ mol/l, 20 °C and $[CO(N_2H_3)_2]$, mol/l: 1 - 0.1; 2 - 0.15; 3 - 0.25; 4 - 0.3

Based on the calculations of the reaction orders with respect to all components of the reaction system the general Pu(VI) and carbohydrazide interaction rate equation took the form

$$-\frac{d[Pu(VI)]}{dt} = k_2 \cdot [Pu(VI)] \cdot [HNO_3]^{-3} \cdot [CO(N_2H_3)_2]^{2.3}, \quad (2)$$

where $k_2=(1.41 \pm 0.11) \text{ mol}^{0.7}/(\text{l}^{0.7} \cdot \text{min})$ under 20 °C.

The activation energy of the Pu(VI) reduction to the Pu(V) by carbohydrazide was calculated from the $\ln(k)$ and the inverse temperature ($1/T$) dependence was found to be $(111 \pm 11) \text{ kJ/mol}$.

The interaction of the Np(VI) with carbohydrazide

In the observation of the Np absorption spectra in time, it was revealed that the Np(VI) reduction process by carbohydrazide was going on until Np(V) formation.

It is noteworthy that during all the experiments the formation of Np(IV) was not observed for 4 hours after the carbohydrazide addition.

As it was found, an earlier [2] Np(IV) formation from the Np(V) was observed at $[HNO_3] \geq 3$ mol/l and relatively high concentration of $CO(N_2H_3)_2$ (more than 0.2 mol/l).

Similarly to Pu(VI), the processing of experimental data was performed, assuming the first reaction order with respect to the metal

$$-\frac{d[Np(VI)]}{dt} = k_1 \cdot [Np(VI)], \quad (3)$$

The kinetic curves were transformed into straight lines in semi-logarithmic coordinates, the values of the rate constants k_i were calculated from their slope. An example of the kinetic curves transformation is shown in Fig. 3. It was found that the order of the reaction with respect to nitric acid was -1.35, and with respect to reductant 1.15, if the nitric acid concentration was between 0.75 and 3.0 mol/l and the reductant concentration between 0.03 and 0.12 mol/l.

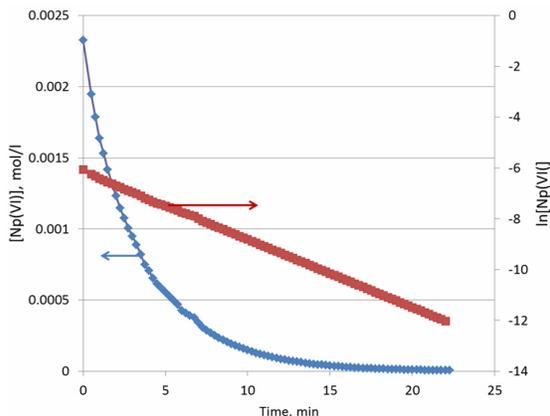


Figure 3. Kinetic curve of Np(VI) reduction and its linearization in semilog coordinates. $[Np(VI)] = 0.003$, $[HNO_3] = 2$, and $[CO(N_2H_3)_2] = 0.03$ mol/l and $15^\circ C$

Based on the calculations of the reaction orders with respect to all components of the reaction system, the general Np(VI) and $CO(N_2H_3)_2$ interaction rate equation took the form

$$-\frac{d[Np(VI)]}{dt} = k_3 \cdot [Np(VI)] \cdot [HNO_3]^{-1.35} \cdot [CO(N_2H_3)_2]^{1.15}, \quad (4)$$

where $k_3 = (39.7 \pm 2.7) \text{ mol}^{0.2} / (l^{0.2} \cdot \text{min})$ under $15^\circ C$.

The activation energy of the Np(VI) reduction to the Np(V) by the carbonylhydrazide was equal to $(85 \pm 20) \text{ kJ/mol}$.

DISCUSSION OF THE REACTION SCHEME

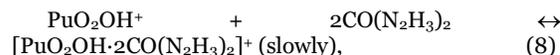
As one can see, the obtained kinetic equations (2) and (4) were similar: they had the first order with respect to the metal, the negative order with respect to the acid and fractional positive order with respect to the reductant. The found values of the carbonylhydrazide reaction orders differed from the data of the other studies on Pu(VI) and Np(VI) reduction with various organic hydrazine derivatives [3-6]. In most cases, the order of the reaction with respect to reducing agent was less than 1. According to the author's opinion [4,5], the reaction of Pu(VI) and Np(VI) with substituted hydrazine occurred by a mechanism in a slow stage at which Pu^{4+} and NpO_2^{2+} ions interact with neutral molecules of the reducing agent. Hydrazine derivatives are weak bases and therefore there was an equilibrium between the protonated and molecular form of the reducing agent in the presence of acid.



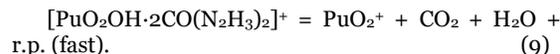
One can assume that this mechanism applied in the case of carbonylhydrazide:



More negative order with respect to the hydrogen in the reaction of Pu(VI) with $CO(N_2H_3)_2$, and the fact that Pu(VI) was more hydrolysis-prone, unlike neptunium(VI), allowed to consider the hypothesis of PuO_2OH^+ hydrolyzed forms interaction in slow reaction stages with carbonylhydrazide, which reacts in the form of uncharged molecules.



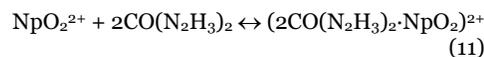
Then a fast inner-sphere electron transition occurred in the $[PuO_2OH \cdot 2CO(N_2H_3)_2]^+$ complex, leading to the PuO_2^+ formation.



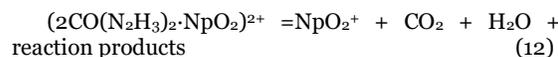
It is known [7] that the uranyl ion formed complexes with carbonylhydrazide molecules and it was obtained in a solid form. It could be suggested that in the solutions with low acidity such complex can be formed with plutonyl and neptunyl ions. Since the rate-determining stage in this mechanism was stage (8), the reduction rate was expressed by the ratio:

$$-\frac{d[Pu(VI)]}{dt} = k' \cdot [PuO_2OH^+] \cdot [CO(N_2H_3)_2]^2, \quad (10)$$

Similarly to the Pu(VI), it is possible to assume that NpO_2^{2+} ion reacts with carbonylhydrazide through the complex formation by the reaction (11)



and during the reaction (11) or after the complex formation, an inner-sphere electron transfer occurs in the complex $(2CO(N_2H_3)_2 \cdot NpO_2)^{2+}$ leading to the NpO_2^+ formation.



Fractional reaction orders for the reducing agent obtained in this study suggest that there was another parallel path of the Pu(VI) and Np(VI) interaction with carbonylhydrazide.

CONCLUSION

The kinetic equations that consider the effect of the nitric acid and carbonylhydrazide concentration on the reaction rate of Pu(VI) and Np(VI) reduction were determined. Based on the data obtained, the kinetic coefficient of the reactions and their activation energy were calculated. The resulting equations will be used in the development of mathematical models of the extraction processes based on oxidation-reduction processes.

The general dependences of the reducing agent and nitric acid effect for both metals are similar. There is a difference in the reaction orders with respect to both components. This observation can be explained in terms of the formation of complexes of CG with metal ions. It is possible that PuO_2^{2+} forms a more stable complex with at least two molecules of CG. To verify this assumption, it is required to determine the CG complexation constants with PuO_2^{2+} and NpO_2^{2+} .

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