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# On the Highest Oxidation States of Plutonium in Alkali Solutions in the Presence of Ozone

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**Abstract**—During ozonation of Pu(VI) alkaline solutions, the highest oxidation state of Pu is formed in an oscillatory reaction. This plutonium species is reduced with Pu(VI) or Fe(III). Ferrate ion is also reduced with Pu(VI). It was assumed that in alkali solution plutonium is partially oxidized with ozone to Pu(VIII).

Ozonation of a Pu(VI) hydroxide suspension or Pu(VI) solution in 1–3 M NaOH is the best known method for preparing Pu(VII) [1, 2]. In this process, blue-black solutions having a characteristic absorption spectrum with a maximum at 635 nm are formed. In accordance with [1–4], the extinction coefficient $\varepsilon_{635}$ varies from 530 to 600 $\text{l mol}^{-1}\text{ cm}^{-1}$.

In this work, we performed experiments on plutonium(VI) oxidation in NaOH solutions with ozone (Tekhnozon high-frequency ozonizer, Russia; the $O_3$ content in $O_2$ was about 3.5%, flow rate 5–7 $\text{l h}^{-1}$ at 20°C). Ultrapure grade NaOH was used. Its solutions were ozonized just before the experiment to eliminate possible reducing impurities. The Pu(VI) alkaline solutions were prepared by the known method of ozonation of freshly precipitated Pu(IV) hydroxide to $\text{Pu(VI)O}_3 \cdot n\text{H}_2\text{O}$, followed by dissolution in ozonized alkali with preset concentration, which excluded the presence of reducing impurities in them.

We found that, during oxidation of 2.9 mM Pu(VI) in 3.5 M NaOH with ozone for more than 30 min, the optical density of the ozonized solution undergoes oscillations, their amplitude reaching 30% of the maximal value (Fig. 1), which substantially exceeded the probable error in optical density determination (on a Shimadzu UV-160 spectrophotometer). Similar results were obtained also during ozonation of Pu(VI) hydroxide suspension at [NaOH] 0.7 and 1.5 M.

Similar effect was observed also during prolonged ozonation of Am(III) hydroxide in bicarbonate solutions, in which [Am(VI)]–[Am(V)] oscillations were observed [5]. In both cases, the effect found is probably the result of ozone decomposition in the systems studied, followed by formation of hydroperoxy radicals and hydrogen peroxide, which partially reduce the highest valence forms of Pu and Am in the solution.

The fact of oscillations of the plutonium solution optical density during oxidation with ozone (with the amplitude reaching 30% of the maximal value) was not noted earlier and casts doubt on the kinetic parameters of this reaction reported in [3] and, first of all, on data on 100% yield of oxidized Pu form in the above process. To clarify the nature of this phenomenon, we performed a series of additional experiments.

**Reaction of plutonium obtained by ozonation in NaOH solutions with Pu(VI).** Aliquots of 1.3 mM Pu(VI) in 1.5 M NaOH (0.05 ml) were added in succession to a 2.9 mM Pu(VI) solution in 1.5 M NaOH (1 ml), through which ozone was preliminarily bubbled for 60 min at room temperature to obtain blue-black color, and then the absorption spectrum of the solution was recorded within the 400–800 nm range (Fig. 2). Another part of the blue-black solution was left as a reference.

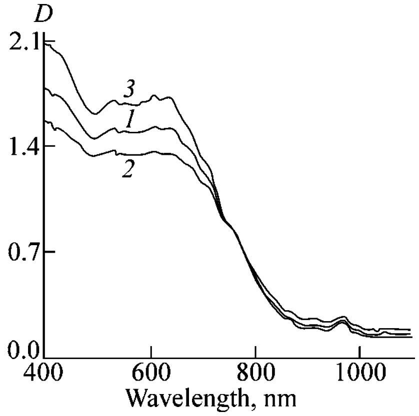

**Fig. 1.** Absorption spectra of Pu(VI) solution in 3.5 M NaOH ozonated for (*1*) 42, (*2*) 45, and (*3*) 47 min.

It was found that the optical density of the Pu solution decreases in proportion to the amount of the Pu(VI) added (with regard to dilution of the initial volume). The results obtained (Fig. 2) show that the Pu oxidized with ozone in NaOH solution reacts with the added Pu(VI). At the same time, the spectral characteristics of the reference solution remained constant in time.

Similar results were obtained in experiments on reaction of the Pu(VI) solution (~$10^{-3}$ M) in 1–3 M NaOH, oxidized with ozone, with freshly precipitated Pu(VI) hydroxide taken in excess. At contact of this solution with the precipitate, the blue-black color rapidly becomes grayish-blue with a sharp decrease in the solution optical density within the 500–700 nm range.

It should be noted that, during ozonation for more than 5 h of the Pu(VI) hydroxide suspension taken in substantial excess as compared to its solubility in 1–3 M NaOH, neither the solution nor the precipitate acquire a blue-black color. The spectra of both liquid and solid ozonation products are “smooth,” similar to the spectrum of Pu(VI), and do not show oxidized plutonium species.

**Reaction of Pu(VI) with Fe(VI) in 1 M NaOH.** We found that on adding of 0.2 ml of 2 mM Pu(VI) in 1 M NaOH to 1 ml of 0.3 mM Fe(VI) in 1 M NaOH at room temperature, the optical density of the solution decreases by ~50% within the time of mixing (Fig. 3, spectra *1*, *2*). Addition of the second aliquot of 2 mM Pu(VI) solution in 1 M NaOH (0.2 ml) leads to a further decrease in the optical density of the solution (spectrum *3*), and the solution becomes colorless. Addition of the next portion of Pu(VI) (0.2 ml) does not further change the absorption spectrum of the solution (spectrum *4*), which obviously indicates complete reduction of the ferrate ions. No changes in the spectrum of a reference Fe(VI) solution were observed within the same time. These results suggest that in 1 M NaOH Pu(VI) is oxidized with $FeO_4^{2-}$ ions, which follows from decrease in the optical density of Fe(VI) solution. This fact contradicts the known data [1] that the redox potential of the Pu(VII)/Pu(VI) couple in 1 M NaOH amounts to 0.85 V, which is substantially higher than the potential of the Fe(VI)/Fe(III) couple, 0.72 V (relative to standard hydrogen electrode) under the same conditions [6, 7].

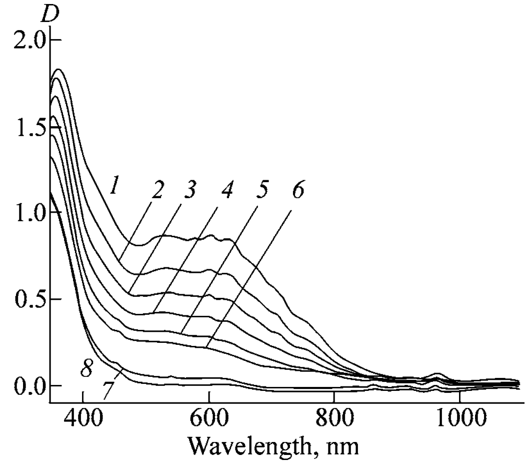

**Fig. 2.** Absorption spectra of (*1*) 2.9 mM Pu(VI) solution in 1.5 M NaOH (1 ml) ozonized for 60 min and (*2–8*) its mixtures with 1.3 mM Pu(VI) solution in 1.5 M NaOH. Additions of Pu(VI) solution, ml: (*2*) 0.05, (*3*) 0.1, (*4*) 0.15, (*5*) 0.2, and (*6*) 0.25; (*7*, *8*) the same as (*6*), after storage for 30 and 90 min, respectively.

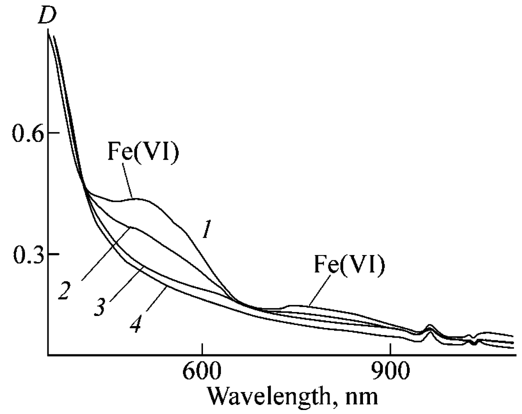

**Fig. 3.** Absorption spectra of (*1*) 0.3 mM Fe(VI) solution in 1 M NaOH (1 ml) and its mixtures with 2 mM Pu(VI) solution in 1 M NaOH. Additions of Pu(VI) solution, ml: (*2*) 0.2, (*3*) 0.4, and (*4*) 0.6.

**Reaction of Fe(III) with Pu ozonized in 1 M NaOH.** Ozonation of Pu(VI) in 1 M NaOH was performed for 40 min up to formation of a blue-black solution with the well-known absorption spectrum [1] (Fig. 4, spectrum *1*). Then, to this solution, aliquots (0.05 ml) of weakly acidic 1 mM Fe(III) solution were added in succession. On adding the very first Fe(III) aliquot, the optical density of the solution decreases (spectrum *2*). Addition of the next Fe(III) aliquot leads to a further decrease in the solution optical density. At the same time, the band characteristic of ferrate ion appears (spectrum *3*). This solution after storage for 40 min at room temperature becomes colorless, obviously due to Fe(VI) reduction with water molecules.

If during ozonation of Pu(VI) alkaline solution plutonium is oxidized to Pu(VII) only, we should expect the following reaction with Fe(III):

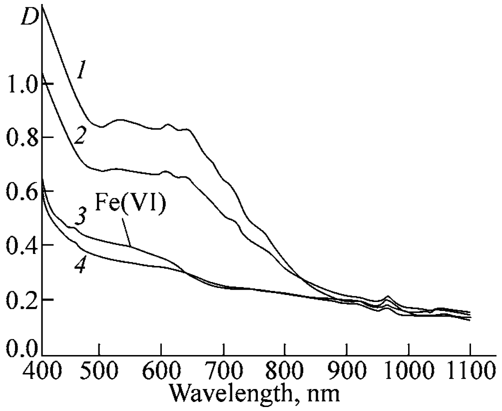

**Fig. 4.** Absorption spectra of (*1*) Pu(VI) solution in 1 M NaOH and (*2–4*) its mixtures with 1 mM Fe(III) solution. Addition of Fe(III) solution, ml: (*2*) 0.05 and (*3*) 0.10; (*4*) the same as (*3*), after storage for 40 min.

$$3\mathrm{Pu(VII)} + \mathrm{Fe(III)} = 3\mathrm{Pu(VI)} + \mathrm{Fe(VI)}. \quad (1)$$

However, our above data (Fig. 3) show that Pu(VI) is readily oxidized with ferrate ion.

Thus, the following conclusions arise from our study.

During oxidation of Pu(VI) with ozone (> 30 min) in 0.7–3.5 M NaOH, oscillations of the optical density with the amplitude reaching 30% of the maximal density are observed. Therefore, discrepancies in the extinction coefficient $\varepsilon_{635}$, which ranges from 530 to 600 $\mathrm{l\,mol^{-1}\,cm^{-1}}$ according to different papers [1–4], may be caused by this phenomenon.

Plutonium oxidized with ozone in alkaline solutions reacts with the added Pu(VI). Since in our experiments only ozonized solutions were used (which excludes the presence of any reductants), the phenomenon observed can be explained by the formation of Pu(VIII) upon oxidation with ozone. In this case, the Pu(VI) added reacts with Pu(VIII) (reproportionation reaction). In addition, it follows from Fig. 2 that approximately equimolar amount of Pu(VI) reacts with Pu(VIII). Hence, taking into account the consumption of Pu oxidized with ozone in the experiment, the content of probable reducing impurities (if they are the reason of this fact) should be close to the Pu(VI) content, which is hardly possible.

In addition, we noted that Pu(VI) is oxidized by ferrate ion in 1.5 M NaOH, and, on the other hand, plutonium oxidized by ozone is reduced by Fe(III) with formation of Pu(VI). These results cannot be explained by formation of Pu(VII) as the only species in ozonation of Pu(VI) in alkaline solutions, as it was assumed in earlier works.

Thus, it follows from the experimental data obtained that, during Pu(VI) oxidation with ozone in alkali solutions, not only Pu(VII) but also (partially) Pu(VIII) is formed. We estimated the extinction coefficient of Pu(VIII) $\varepsilon_{635}$ at $2600 \pm 400\ \mathrm{l\,mol^{-1}\,cm^{-1}}$ and the Pu(VIII) content under the experimental conditions, at ~12% from the amount of Pu(VI) introduced ($0.5\ \mathrm{ml} \times 1.3\ \mathrm{mM} = 6.5 \times 10^{-5}$ mmol) into the solution of ozonized plutonium (Fig. 2, spectra *1*, *2*) and taking into account a decrease in the optical density at 635 nm (~0.180).

Further studies aimed to confirm more reliably the possibility of Pu(VI) oxidation with ozone to Pu(VIII) in alkali solutions are now in progress.

## ACKNOWLEDGMENTS

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