Irradiation Effects on Neptunium Oxidation States

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Abstract – Preliminary results describing the spectroscopic observation of neptunium valence state changes in irradiated aqueous nitric acid are presented. The reduction of Np(VI) to Np(V) is attributed to radiolytically-produced nitrous acid. No evidence was found for the catalyzed oxidation of Np(V) at nitric acid concentrations of 0.09 – 4.0 M.

A. INTRODUCTION

The successful implementation of hydrometallurgical separations requires the preparation and maintenance of metal ions in known oxidation states. Trivalent metals such as the lanthanides or americium, for example, are not extracted in the PUREX process, while hexavalent uranium and tetravalent plutonium are complexed. In some cases, such as the separation of uranium in the PUREX process, the TBP complexation of U(VI) does not require heroic efforts to maintain the necessary oxidation state. Other elements have multiple oxidation states that occur within the range of acidities and redox potentials found in the process and the relative abundance of these may be an artefact of process conditions, including irradiation. Neptunium is especially problematic in this regard.

Although neptunium has been recovered in various PUREX processes [2] its complicated redox reactions under PUREX conditions are still being studied worldwide to improve process efficiency. A number of studies have attempted to define the parameters under which neptunium extraction is adversely affected and to create models which can be used to predict neptunium valence states under various process conditions. [3] In this paper, the initial results for an experimental program investigating the change in neptunium redox speciation in nitric acid solution as a function of absorbed γ-ray dose are presented.

B. EXPERIMENTAL METHODS

Samples of 237-neptunium in nitric acid solution from on-hand stock at the Idaho National Lab were irradiated in sealable cuvettes (Helma USA, Plainville, NY). These cuvettes contain supracil optical windows that do not darken upon γ-irradiation. Once the cuvettes were loaded they were irradiated in sealed fashion, at a location in the irradiator with a well-characterized dose rate. This dose rate was determined using standard Fricke dosimetry, and the absorbed doses to the samples were then calculated based on the duration of the irradiation. The irradiator was a Nordion Gammacell 220E (Nordion Corporation, Ottawa, Canada) containing a 20,000 Ci 60-cobalt source. The sample cell base-line dose rate was 0.151 kGy min⁻¹, and the temperature during irradiation was 48°C, due to heating of the irradiator shielding.

Immediately following irradiation the sample absorbance was measured using a Cary 50 UV/Vis absorption spectrophotometer (Varian Inc., Palo Alto, CA, USA), over the range 400-1100 nm.
The absorbance of Np(V) was measured using the sharp absorbance peak at 981 nm. The absorbance of Np(VI) was observed as a broad absorbance at < 450 nm. Neptunium(VI) also has a sharp absorbance feature at ~ 1200 nm. However, this wavelength is not observable with the Cary 50.

C. RESULTS AND DISCUSSION

Samples of $5.5 \times 10^{-3}$ M neptunium were prepared by repetitive metathesis with nitric acid, and finally dissolved in varying concentrations of HNO$_3$. The resulting solutions were observed spectroscopically and contained a mixture of Np(V) and Np(VI). No Np(IV) was found in these experiments.

These samples were then irradiated with $\gamma$-rays in a series of absorbed doses over the range 0—50 kGy, with spectroscopic measurements made at selected intervals. A steady decrease in Np(VI) occurred, as measured by the reduction in the absorbance below 450 nm. The decrease in Np(VI) was accompanied by an increase in Np(V), as measured at 980 nm. This is shown in Figure 1 using the 0.9 M HNO$_3$ solution as an example. The increase in peak height at 980 nm versus absorbed dose is shown in Figure 2, for 0.09 M, 0.9 M and 4 M HNO$_3$ solutions. The increase in Np(V) absorbance occurred in all irradiated acid concentrations, and is clearly faster at the lower acid concentrations. The maximum absorbance at 980 nm for an unirradiated 100% Np(V) solution in 0.9 M HNO$_3$ was $1.60 \pm 0.06$, corresponding to $\varepsilon = 291$ L mol$^{-1}$ cm$^{-1}$. Assuming this $\varepsilon$ holds for all acid concentrations, approximate $G_0$ values for the reduction of Np(VI) may be calculated as 0.84, 0.35, and 0.11 $\mu$mol Gy$^{-1}$, in 0.09, 0.9, and 4 M HNO$_3$, respectively.

![Figure 1: The production of Np(V) in an irradiated solution of 1.3 mg mL$^{-1}$ neptunium in 0.9 M HNO$_3$. The sharp peaks at 981 and 617 nm show the increase in Np(V) concentration, while the decrease in broad absorbance below 450 nm shows the decrease in Np(VI) concentration.](image)
The valence state of neptunium in aqueous nitric acid is generally considered to depend on the concentration of nitrate, acidity and nitrous acid according to Equation 1: [5]

\[
\text{NpO}_2^+ + \frac{3}{2}H^+ + \frac{1}{2}\text{NO}_3^- \rightleftharpoons \text{NpO}_2^{2+} + \frac{1}{2}\text{HNO}_2 + \text{H}_2\text{O} \quad (1)
\]

For our unirradiated samples, preparation at higher concentrations of nitric acid favored higher initial concentrations of Np(VI), in agreement with Equation 1. It can also be seen that nitrous acid favors the reduction of Np(VI) to Np(V). Nitrous acid is a product of direct nitric acid radiolysis: [6]

\[
\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_2 + \text{H}_2\text{O} \quad (2)
\]

We irradiated various concentrations of nitric acid and measured the production of nitrous acid by HPLC. These results are shown in Figure 3. It can be seen that nitrous acid production is greater for higher concentrations of nitric acid. As much as 3 mM HNO₂ was produced in 4 M HNO₃ at 40 kGy absorbed dose. The initial fast production of nitrous acid begins to level off with increasing dose, with a maximum of < 4 mM for 4 M HNO₃. Similarly, the reduction of Np(VI) in 4 M HNO₃ appears to level off at absorbed doses > 50 kGy. This plateau in nitrous acid production has been attributed to the reaction of nitrous acid with radiolytically-produced hydrogen peroxide, which oxidizes nitrous acid back to nitric acid via a peroxynitrous acid intermediate as shown in Equation 3: [7, 8]

\[
\text{H}_2\text{O}_2 + \text{HNO}_2 \rightarrow \text{HOONO} \rightarrow \text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O} \quad (3)
\]

Further evidence that Np(VI) reduction is due to reaction with nitrous acid is provided by the fact that reduction continues for a short time (~ 1 h) when sample irradiation is terminated. This implicates a relatively long-lived radiolytically-produced reducing agent. Thus, we conclude that the generation of nitrous acid in irradiated nitric acid promotes Np(VI) reduction. In contrast to this expectation it is frequently reported that small amounts of nitrous acid promote catalytic oxidation of Np(V) to Np(VI). [2, 5, 9] However, we found no evidence of neptunium oxidation in these preliminary experiments.
Excess amounts of nitrite are reported to reduce neptunium to Np(V), as expected from Equation 1. [10]

![Figure 3: The radiolytic generation of nitrous acid in varying concentrations of nitric acid.](image)

**D. CONCLUSION**

Experiments were designed to monitor the valence state of neptunium in irradiated nitric acid solution using UV/Vis spectroscopy. In preliminary results we have shown that Np(VI) is reduced to Np(V) by irradiation, at a rate that depends on the nitric acid concentration. This coupled with the finding that reduction continues for a short time after the completion of the irradiation suggests that the long-lived radiolysis product nitrous acid is responsible for this reduction. We have also reported yields for the generation of nitrous acid in varying concentrations of irradiated nitric acid. No evidence for the catalytic oxidation of Np(V) to Np(VI) was found. In future experiments we will investigate the effect of nitrous acid scavengers, added nitrite salts, and the valence state changes in these irradiated solutions.

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