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Abstract

The reliable separation of neptunium from dissolved nuclear fuel assumes the ability to maintain a preferred oxidation state. However, regardless of its initial redox speciation, a series of reactions occurs in nitric acid to create a mixture of oxidation states including Np(V), Np(VI) and sometimes Np(IV). To further complicate the situation, irradiated solutions such as fuel dissolution contain both transient and long-lived radiolysis products which may be strongly oxidizing or reducing. Thus, irradiation may be expected to impact the equilibrium distributions of the various neptunium valences.We have irradiated nitric acid solutions of neptunium with ^{60}Co gamma-rays, and measured radiolytically-induced changes in neptunium valences, as well as the nitrous acid concentration, by UV/Vis spectroscopy. It was found that in 4M HNO_3 at low absorbed doses, the oxidizing radicals oxidized Np(V) to Np(VI). However, as the irradiation proceeded the concentration of nitrous acid became sufficient to reduce Np(VI) to Np(V), and then continued irradiation favored this reduction until an equilibrium was achieved in balance with the oxidation of Np(V) by nitric acid itself. The starting abundances of the two neptunium valences did not affect the final equilibrium concentrations of Np(V) and Np(VI), and no Np(IV) was detected.

Keywords: neptunium; redox speciation; free radicals; radiolysis; nitrous acid

1. Introduction

In aqueous solutions of nitric acid, neptunium may exist as Np(V), Np(IV) and/or Np(VI). The cationic charge of Np(V) ($z = 2.2$ [1]) in its monovalent dioxocation is the lowest among actinides and causes the lowest separation yields in both liquid/liquid and solid/liquid separations, while higher cationic charges of both Np(VI)

and Np(IV) provide satisfactory yields. The success of a selected separation method relies on the ability to maintain neptunium in an appropriate oxidation state.

Regardless of the initial valence state of Np, a series of redox reactions leading to the generation of mixed valence solution occurs. The valence state of neptunium in aqueous nitric acid was reported to be a function of the concentration of nitrous acid, and according to Eq. 1 nitrous acid should reduce Np(VI), favoring production of Np(V) [2]:

$$2NpO_2^+ + 3H^+ + NO_3^- \leftrightarrows 2NpO_2^{2+} + HNO_2 + H_2O \qquad (1)$$

Excess nitrite has been used to set the valence at Np(V) [3, 4]. On the other hand, HNO_2 appears to behave as a catalyst, promoting the rate of oxidation of higher relative abundances of Np(V) by nitric acid. With mixed success, this effect has been utilized industrially during separation of neptunium by the PUREX process [5]. An explanation of this behavior has been proposed by Tochiyama et al [6], who suggested that the catalytic effect of nitrous acid is facilitated by the $^\bullet NO_2$ radical from N_2O_4, which is formed by interaction of nitric and nitrous acids:

$$^\bullet NO_2 + {}^\bullet NO_2 + H_2O \leftrightarrows N_2O_4 + H_2O \leftrightarrows HNO_2 + H^+ + NO_3^- \qquad (2)$$
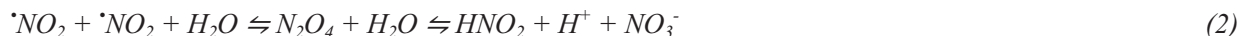
The $^\bullet NO_2$ radical then acts as the actual oxidizing agent:

$$NpO_2^+ + {}^\bullet NO_2 \rightarrow NpO_2^{2+} + NO_2^- \qquad (3)$$

and the oxidation of Np(VI) in the presence of low concentrations of HNO_2 may actually be due to reaction of Np(V) with the nitrogen dioxide radical ($^\bullet NO_2$), rather than with HNO_2 itself [7].

Neptunium speciation thus clearly depends on the concentration of HNO_2 in a nitric acid solution. Nitrous acid is produced during processing of spent nuclear fuel by multiple sources, primarily from dissolution of the spent oxide fuel and from radiolysis of both aqueous and organic solutions of nitric acid [8]. HNO_2 is a weak acid with a low dissociation constant ($pK_a = 3.3$ at 25°C, [9]), which leads to almost complete protonation of nitrite anions in solutions with higher concentrations of nitric acid, which are relevant to reprocessing of spent nuclear fuel. Once in molecular form, nitrous acid is also easily extracted by tributylphosphate into the organic phase [10], where it also influences the chemistry of extracted neptunium [11].

This study was conducted to analyze the effect of gamma radiation on neptunium redox speciation in aqueous nitric acid solutions, primarily to identify the importance of the radiolytic production of nitrous acid.

2. Experimental

Acidic solutions of ^{237}Np were prepared from on-hand stocks available at the Idaho National Laboratory (INL) and Oregon State University (OSU). Concentrations of nitric acid were confirmed by titration with NaOH, standardized by potassium biphtalate. Concentration of ^{237}Np was confirmed spectroscopically and by gamma-spectrometry on a high-purity germanium detector. Prepared solutions were irradiated in sealable 1-cm pathlength cuvettes and 0.4cm width (supplied by Hellma USA for INL and by Starna Cells, Inc. for OSU) that have fused quartz optical windows that do not darken upon γ-irradiation.

For determination of the radiolytic yield of nitrous acid in aqueous solutions of nitric acid 0.7 mL snap-cap polypropylene centrifuge vials (VWR) were utilized. To minimize the effects of air and the volatility of NO_2, sample vials were filled to the top so that when sealed, the gaseous headspace was of < 5%of the vial volume.

The pre-irradiation oxidation state of Np was adjusted electrochemically using a BASi Epsilon E2 potentiostat and a PWR-3 current booster. The electrolysis was performed in a custom-built H-cell with the oxidizing and reducing compartments separated by a glass frit. The working electrode was a coiled platinum wire inserted into a constantly stirred Np solution, while the auxiliary compartment contained a wire platinum electrode and Ag/AgCl reference electrode. Hexavalent Np was prepared by application of +1250 mV potential to the working electrode while Np(V) was prepared at +700 mV [12].

Irradiation was performed using ^{60}Co-sources (Nordion Gammacell 220) available at both the Idaho National Laboratory (dose rate 7.0 kGy/h) and Oregon State University (dose rate 0.38 kGy/h). The dose rates for both irradiators were determined using standard Fricke dosimetry and the absorbed doses to the samples were calculated based on the duration of the irradiation.

The post-irradiation concentrations of HNO_2, Np(V) and Np(VI) were determined by absorption spectroscopy: Cary 6000 UV/Vis absorption spectrophotometer (wavelength range 350 - 1350nm) at INL, OceanOptics QE6500 (200-1000nm) and OLIS RSM 1000 (900-1350nm) spectrophotometers at OSU.

The absorbance of Np(V) was measured using its sharp absorbance peak at 981 nm, while the Np(VI) concentration was determined at the maximum absorbance of the broad peak centered at 1225 nm. The molar extinction coefficients were determined independently for each instrument.

The aqueous spectra of the nitrite anion and nitrous acid are well known [13]: the broad absorption band of the NO_2^- anion between 300-400 nm transforms into a distinct peak multiplet for molecular HNO_2.

3. Results and Discussion

3.1. Nitrous acid yield

Radiolytic production of HNO_2 in aqueous nitric acid solutions has been studied extensively in the past (see Table 1); however, most authors (e.g., [14, 15]) were only interested in the primary radiolytic yields of HNO_2, which are substantially larger than the real net yields due to rapid interactions of HNO_2 with other products of nitric acid radiolysis, e.g. hydrogen peroxide (H_2O_2) [16].

Table 1. Comparison of results of studies of net radiolytic yields of HNO_2 from nitric acid solutions

Study	Radiolytic yield of HNO_2	Conditions
1959 - Burger & Money [21]	G = 0.056 μmol/J	3M HNO_3, dose rate = 9 kGy/h
1973 - Bhattacharya & Saini [15]	G = 0.026 μmol/J	1M HNO_3, $\dot{D}$ = 2.9 kGy/hr
2010 - Precek et al. [17]	G = c(HNO_3, M) × (0.013±0.001) μmol/J	(1-8) M HNO_3, dose rate = 0.45 kGy/hr closed vials with > 25% headspace
2012 - Precek et al. [present study]	G = c(HNO_3, M) × (0.019±0.001) μmol/J	(0.5-6) M HNO_3, dose rate = 7.0 kGy/hr closed vials with < 5% headspace

Aqueous solutions containing different concentrations of nitric acid (0.5 – 6 M HNO_3) were irradiated at a dose rate of 7.0 kGy/h up to dose of 70 kGy. Post-irradiation analysis confirmed that production of HNO_2 increases with radiation dose (Fig. 1) and with the initial concentration of HNO_3. Within the dose range studied, concentrations of produced HNO_2 were not observed to reach a plateau. Evidently, a significant amount (millimoles) of HNO_2 can be produced and affect the chemistry of Np in separation systems. The dependence of the yield of HNO_2 on the concentration of nitric acid was linear and can be summarized by relationship:

$G(HNO_2) = c(HNO_3, mol/L) \times (0.019\pm0.001)$ μmol/J   (4)

Furthermore, we have observed that the yields of nitrous acid significantly depend on headspace volume of the irradiated samples. The ~3/4 filled vials earlier [17] versus the full vials (present data) explain the lower yields and the plateaus in the yield curves obtained for the same systems previously. No measurable difference for decomposition of HNO_2 was observed between air and nitrogen atmosphere in the headspace. Thus, yields of nitrous acid are significantly dependent on the headspace volume of the irradiated samples. Estimation of nitrous acid produced in acidic solutions should consider its decomposition in the headspace above the solution over a longer period of time [18–20].
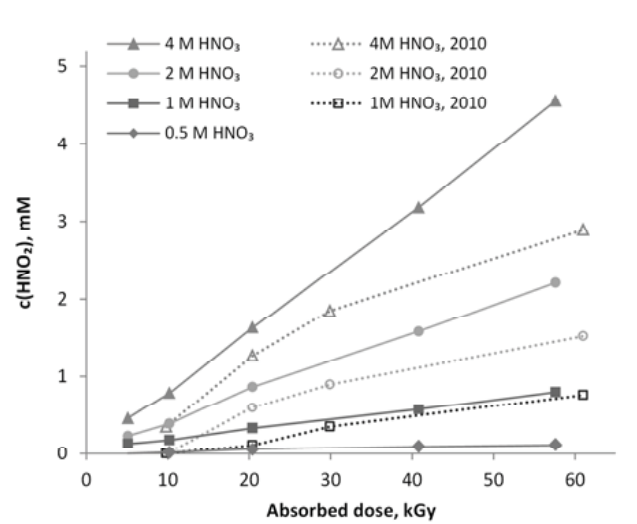
Fig. 1. Nitrous acid production by γ-radiolysis of aqueous solutions of nitric acid of different concentration: comparison of the presented and our previously (2010) reported data [17].

3.2. Neptunium radiolysis

3.2.1. Effects of gamma radiation on neptunium(VI) in 4M HNO$_3$

A solution of pentavalent neptunium in 4M HNO$_3$ was first electrolytically oxidized to predominantly Np(VI), with a resulting molar fraction of Np(VI) up to 94% and 6% of Np(V) in 4M HNO$_3$. Aliquots of this solution were then irradiated with a dose rate of 7.0 kGy/h; also an aliquot was saved as a reference. The results for the irradiation of such a solution with a total Np concentration 6 mM are shown in Fig. 2. No tetravalent Np was detected in any post-irradiation spectrum, and a successful mass balance was always achieved as the sum of Np(V) and Np(VI). No changes in the distribution of neptunium species with time were observed in the non-irradiated reference solution.

Initially, at the lower radiation doses, these samples showed oxidation of the small amount of Np(V) to Np(VI). This effect is most likely explained by the effect of oxidizing •NO$_3$ and •NO$_2$ radicals produced from nitric acid radiolysis, combined with the oxidizing effects of •OH radical from water radiolysis. However, by ~ 1 kGy, the oxidation of Np(V) ended, and the reduction of Np(VI) to Np(V) by the radiolytically produced HNO$_2$ began to occur and continued to the end of the experiment, to a total dose of 18.5 kGy.

The linear portion of the obtained data for doses between 2.7 and 11.6 kGy (Figure 2) allows for the calculation of a radiolytic yield for Np(V) of $G_{Np(V)} = 0.144$ μmol/J. This value appears to be almost a double of the net radiolytic yield of HNO$_2$ of 0.075 μmol/J in 4M HNO$_3$ obtained from the dependence displayed in Figure 1. As expected from the redox equilibrium (Eq. 1): $G_{Np(V)} \approx 2 \times G_{HNO2}$.

It can also be seen in Fig. 2 that the concentration of radiolytically-produced HNO$_2$ grows continuously with increasing absorbed dose in the irradiated solutions; however, the initial rate slows after ~ 1 kGy when the concentration of HNO$_2$ reached 0.16M. This break in the HNO$_2$-growth slope may be explained by the consumption of HNO$_2$ by Np(VI). Therefore, the effective yield of HNO$_2$ is lower in the presence of Np than in irradiated 4M HNO$_3$ in absence of neptunium (Fig. 1).
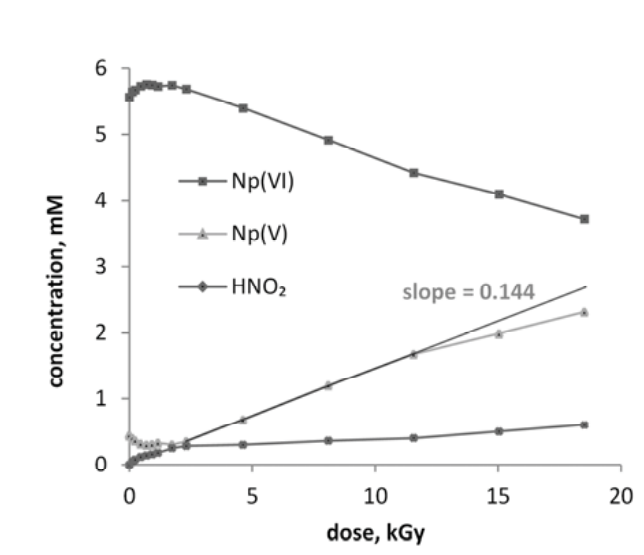
Fig. 2. The concentrations of Np(V), Np(VI) and HNO$_2$ versus absorbed dose for 6 mM initially ~ 93% Np(VI) in 4 M HNO$_3$, dose rate 7.0 kGy/h

3.2.2. Influence of nitric acid concentration

Four different samples of 2.5 mM neptunium were prepared in sealable quartz semi-micro cuvettes (Starna Cells) with a 1cm pathlength. Three of these samples contained a Np(VI):Np(V) ratio of 93:7 and were prepared in three concentrations of nitric acid (0.5, 1.0 and 4.0 M HNO$_3$). They were observed to have long-term stability, and the 4M HNO$_3$ sample was labeled as #1. Another 4M HNO$_3$ sample (#2) was prepared by reducing the initially 93% Np(VI) with a substoichiometric amount of hydrogen peroxide to Np(V):Np(VI) ratio close to 1:1 [22]. The redox reaction was complete within 2 hours.
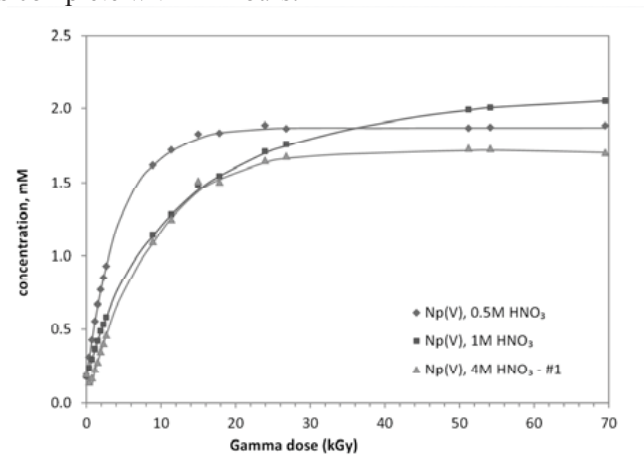

Fig. 3a: Irradiation at the 0.38 kGy/h dose rate: Concentration profile of Np(V) versus absorbed dose in concentrations of HNO$_3$. Np(VI) concentration (not plotted) should be assumed to be complementary to Np(V), balancing the 2.5 mM of total Np

Irradiation of sealed vials was performed with a low dose rate of 0.38 kGy/h. The irradiation was practically continuous with 0.5 hour interruptions for measurement. The concentration of HNO$_2$ in the irradiated samples was determined by the deconvolution of the known nitrous acid spectrum from the absorption shoulder of

neptunium-VI in the UV region 350-400nm. The error in the value of HNO_2 concentration was estimated as 0.05mM. The results of the experiment are summarized in Figures 3a, b:

The effect of radiation on neptunium oxidation state for all 3 different nitric acid concentrations (Fig. 3a) caused reduction of Np(VI) to Np(V), ultimately approaching a predominantly pentavalent state. However, in the 4M HNO_3 samples (Fig 3b), the initial Np(V) oxidation to Np(VI) was observed until 1 kGy of absorbed dose, similar to the effects observed for the higher dose rate in Figure 2. This initial oxidation of Np(V) and the production of HNO_2 was not observed at the lower nitric acid concentrations.
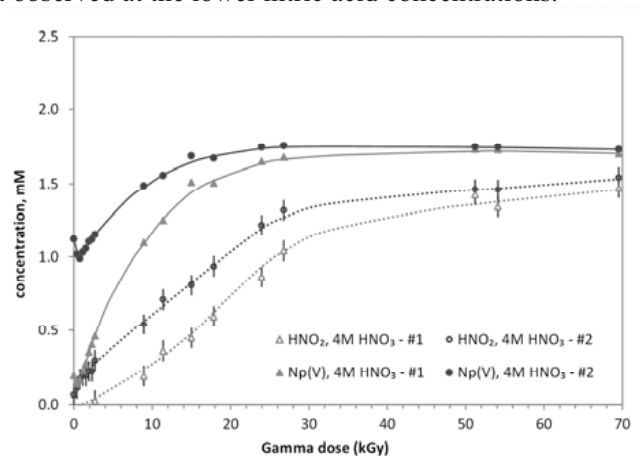

Fig. 3b: Irradiation at the 0.38 kGy/h dose rate. Concentration profile of Np(V) and HNO_2 versus absorbed dose in two Np samples in 4M HNO_3. The samples #1 and #2 differ in their initial fraction of Np(V) in total Np: #1=7%, #2 =45%.

For the initial range of absorbed doses between 0.4 and 2.5 kGy, the observed radiolytic yield of Np(V) in 0.5, 1.0 and 4.0 M nitric acid with initial concentration of 93% Np(VI) was of 0.27, 0.151 and 0.146 µmol/J, respectively. The value of the Np(V) yield 0.146 µmol/J in 4 M HNO_3 is in agreement with the radiolytic yield determined in the previous experiment with 18-fold higher dose rate (Fig.2), 0.144 µmol/J.

The decrease in Np(V) yield with increasing HNO_3 concentration suggests that the reducing effect due to the radiolysis of aqueous nitric acid cannot be primarily attributed to the reaction with radiolytically produced HNO_2, at least not in lower concentrations of HNO_3. Reducing radiolytic species, such as H_2O_2, and H_2 are other possible candidates, since their yield increases with decreasing HNO_3 concentration [23].

Only the samples with 4M HNO_3 exhibited any concentrations of HNO_2 above 0.05 mM. Absolute differences in the HNO2 concentration measured for the two 4M HNO_3 samples (dotted lines in Figure 3b) can be explained by the effect of spontaneous oxidation of Np(V) by nitric acid (Eq. 1), producing an excess of HNO_2 in the sample #2 (sample with the 45:55 initial ratio Np(V):Np(VI)).

During the course of the irradiation, both the 4M HNO_3 samples trended toward a common steady state redox speciation with an approximate ratio of Np(V):Np(VI) = 70:30, which was reached near 30 kGy of absorbed dose. At this point the increase in the HNO_2 concentration also slowed down, approaching a steady state concentration. Initially, the concentration of HNO_2 in both 4M HNO_3 samples rose with a slope of ~0.04 mM HNO_2/kGy, which is approximately 50% lower than the yield that was observed in the absence of neptunium in 4M HNO_3 in Fig. 1.,This observation can be expected since, according to Eq. 1., HNO_2 is consumed by its reaction with Np(VI).

After 20 kGy dose, the fast increase in the Np(V) concentration slowed down, achieving a steady state concentration at about 30kGy. At that point also the linear increase of the HNO_2 concentration slowed to approach a steady state concentration. This may indicate the loss of HNO_2 to the gas phase, since only 0.6 mL of the 2.6 mL cuvette volume was occupied by the liquid phase.

It is interesting to note that the equilibrium yield of Np(V) in irradiated 1 M HNO_3 (Fig. 3a) is higher than in both 0.5 and 4M HNO_3. We suggest that the increase of steady-state concentration of Np(V) between 0.5 and 1M HNO_3 can be explained by the decreasing concentration of •OH radicals, primarily responsible for reoxidation of Np(V) back to Np(VI), by their reaction with molecular nitric acid. The rate constants for the reaction of •OH with molecular HNO_3 ($k = 1.4 \times 10^8$ $M^{-1}s^{-1}$)[24] and with Np(V) ($k = 4.3 \times 10^8$ $M^{-1}s^{-1}$)[25] are of comparable magnitude. Due to incomplete protonation of HNO_3 [26], the concentration of molecular HNO_3 in 0.5M and 1M nitric acid is approximately 4-fold higher, 7.4 and 27mM, respectively. Thus, the steady-state concentration of the •OH radical can be expected to decrease (by ~ 60%) as a result of increased scavenging of the hydroxyl radical by molecular HNO_3, and consequently, the absolute rate of oxidation of 2mM Np(V) by the •OH radical gets approximately 2.5-times slower. The •NO_3 radical also acts as an oxidizer of Np(V); however, the rate constant of this reaction ($k = 1 \times 10^5$ $M^{-1}s^{-1}$)[7] is lower by three orders of magnitude compared to the rate of Np(V) oxidation by the •OH radical.

Further increase in nitric acid concentration from 1 to 4 M leads to considerably greater yields of oxidizing •NO_3 and •NO_2 radicals (Eq.2) which decrease the Np(V) steady-state concentration.

4. Conclusion

During irradiation of neptunium solutions in nitric acid, nitrous acid represents an important radiolytically produced species. In 4 M HNO_3, the rise of HNO_2 concentration is followed by reduction of Np(VI) to mostly the pentavalent state; however, in the 1 and 0.5 M HNO_3 solutions of neptunium the reduction of Np(VI) has not been accompanied by a quantitative rise in HNO_2 concentrations. Eventually, a steady-state ratio was established between Np(V) and Np(VI) in the irradiated aqueous nitric acid solution, which occurred regardless of the initial relative concentrations of these oxidations states.

The initial production of radical species during irradiation of 4M HNO_3 by different dose rates favored Np(V) oxidation; however, as the irradiation proceeds, the HNO_2 concentration increases and the Np(VI) reduction to Np(V) becomes predominant. A lower degree of the Np(VI) reduction to Np(V) was favored in 4 M nitric acid, as opposed to 1 and 0.5 M HNO_3 solutions, which is related to the different yields of the radical species versus molecular radiolysis products in these matrices.

Comparison of two irradiation experiments of Np in 4M HNO_3 showed that the radiolytic yield of Np(V) was affected neither by the dose rate nor the total concentration of Np in these experiments.

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