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The redox chemistry of neptunium in γ-irradiated aqueous nitric acid in the presence of an organic phase

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Abstract

The radiolytic changes in oxidation state for solutions of initially Np(V) and/or Np(VI) were investigated by gamma-irradiation in conjunction with UV/Vis spectroscopy of the aqueous phase. Samples were irradiated in varying concentrations of nitric acid, and with or without the presence of 30% TBP in dodecane. At short irradiation times Np(V) was oxidized to Np(VI), even in the presence of the organic phase. Upon the radiolytic production of sufficient amounts of nitrous acid, reduction of Np(VI) to Np(V) occurred in both phases. This was accompanied by stripping of the previously extracted Np(VI). Nitric acid concentrations of 6 M mitigated this reduction.

Keywords

Neptunium, redox chemistry, radiation chemistry, solvent extraction

Introduction

Liquid-liquid extraction from aqueous solutions of nitric acid using tri-*n*-butylphosphate (TBP) is the most important process for the separation of neptunium from dissolved nuclear fuel. The reliable solvent extraction of neptunium depends upon the maintenance of a valence state amenable to complexation by TBP. Of the three common oxidation states, Np(V) is almost inextractable while Np(IV) and Np(VI) are well extracted, using the PUREX (Plutonium Uranium Redox Extraction) process, for which the solvent is 30 % TBP in a normal paraffinic hydrocarbon diluent [1]. However, regardless of the initial neptunium oxidation state, redox reactions occur under process conditions that result in a mixture of the extractable and inextractable neptunium species, especially at the nitric acid concentration of ~ 3 M typically used in PUREX processing. Nitric acid is a Np(V) oxidizing agent, while nitrous acid acts as a reducing agent for Np(VI), according to an equilibrium first reported by Siddall and Dukes [2]:

$$NpO_2^+ + 3/2H^+ + 1/2NO_3^- \leftrightharpoons NpO_2^{2+} + 1/2HNO_2 + 1/2H_2O \quad (1)$$

Some concepts for the future closed fuel cycle envision recovery of neptunium and its incoporation into mixed oxide fuels. However, if the neptunium valence is not controlled, losses to the aqueous phase will occur during attempted neptunium extraction.

A number of authors have reported equilibrium constants for this reaction, with the values falling in the range log K = -2.77– -3.57 [3]. Yet it is reported that the reaction is autocatalytic, meaning that a small amount of HNO_2 is required to initiate the oxidation. Gregson et al., for example, reported that no oxidation of Np(V) occurred even in 5 M HNO_3, when residual HNO_2 was removed by de-gassing, but that oxidation occurred when 1 mM sodium nitrite was added [4]. Similarly, Siddall and Dukes reported that the addition of small amounts of sodium nitrite was necessary to initiate neptunium oxidation in up to 4 M HNO_3 [2]. The mechanism of oxidation of Np(V) by a known Np(VI) reducing agent has never been explained, although Tochiyama et al, [5] suggested that the actual oxidizing agent was $^{\bullet}NO_2$ radical, produced by HNO_2 decay. However, in our

own unpublished experiments we have been unable to oxidize 2.8 mM Np(V) by bubbling 4 M HNO_3 solutions with 5 ppm $^{\bullet}NO_2$ gas.

Assuming constant temperature, according to Eq. 1 the extent of Np(V) oxidation should increase with increasing nitric acid concentration and when nitrous acid concentrations are elevated above the autocatalytic oxidation requirements neptunium should be reduced [2, 3, 4]. Taylor et al, [6] demonstrated Np(VI) was favored in 5 M HNO_3 at 50 ^{o}C, containing initially 1 mM HNO_2, but that this depended on the ratio of [HNO_2]/[Np(V)]. They successfully ran a multi-stage centrifugal contactor test using a simulated fuel dissolution feed solution at that temperature and acid concentration that resulted in 99% neptunium recovery.

Since nitrous acid is a radiolysis product of nitric acid, the irradiation of acidic nuclear fuel dissolution by dissolved fission products complicates this system. For example, radiolytically-produced nitrous acid reduced Np(VI) to Np(V) in 4 M HNO_3 solution, but only after the amount of produced nitrous acid was sufficient to counter-act the action of oxidizing free radicals produced from water and nitric acid radiolysis [7]. Thus, equilibrium between these oxidation states might be expected depending on the acid concentration and the total absorbed radiation dose. The radiation-induced redox chemistry of neptunium was successfully predicted using a kinetic model that included the radiolysis reactions of water and the published rate constants for the reactions of free radicals with neptunium species [7]. Only Np(V) and Np(VI) were predicted or measured in that work.

The introduction of organic compounds further complicates the irradiated system. Precek et al., reported that the addition of 50 or 100 mM of the nitrous acid scavenger methylurea resulted in the reduction of neptunium to Np(IV) in irradiated 4 M HNO_3 [8]. Valdimirova et al., reported that when Np(VI) in 30 % TBP/dodecane was irradiated,

reduction to Np(V), and then to Np(IV) occurred [9]. Reduced neptunium was complexed by dibutylphosphoric acid (HDBP), a radiolysis product of TBP, and a Np(IV)/HDBP precipitate occurred at absorbed doses above 700 kGy. In continued work, these authors reported that even trace amounts of TBP or trioctylphosphine oxide in 3 M HNO_3 facilitated the radiolytic generation of Np(V) and Np(IV) from Np(VI) [10]. Recently, Carrot et al, [11] showed that, even in the absence of radiation, neptunium was reduced in an acidified Grouped ActiNide Extraction (GANEX) solvent consisting of 0.2 M N,N,N',N'- tetraoctyl diglycolamide (TODGA)/0.5 M N,N'-(dimethyl-N,N'-dioctyl)hexylethoxymalonamide (DMDOHEMA) in odorless kerosene. Reduction of Np(VI) to Np(V) occurred, following which Np(IV) was produced by Np(V) disproportionation. Similarly, Sinkov et al, [12] reported that an N,N'-dimethylbicyclic diamide complexed and reduced Np(V).

To better understand the behavior of neptunium redox chemistry under PUREX conditions, here we have irradiated nitric acid solutions of neptunium in the presence of an equal volume of 30% TBP/dodecane. The neptunium speciation changes were observed by UV/Vis spectroscopy of the aqueous phase of the irradiated solutions.

Experimental

Neptunium samples were prepared by metathesis in the appropriate nitric acid concentration of aliquots of a 237 mM ^{237}Np solution in an unknown nitric acid concentration. This was a stock solution on-hand at the Idaho National Laboratory. The final neptunium concentration was 2.4 mM, in 1.0, 2.0, 4.0, or 6.0 M HNO_3, and 2.0 mM neptunium in 0.5 M HNO_3. The repetitive heating of neptunium in nitric acid resulted in the preparation of solutions containing predominantly Np(VI). The 4.0 M HNO_3 solution was aged, resulting in a mixture of Np(V) and Np(VI). Speciation for both unirradiated and irradiated samples was determined by UV/Vis absorbance using a Cary 6000 UV/Vis atomic absorption spectrophotometer (Varian Inc., Palo Alto, CA, USA). The absorbance of Np(V) was measured using its sharp peak at 981 nm, while the Np(VI) was determined

at the maximum absorbance of the broad peak centered at 1225 nm. The aqueous spectrum of the nitrous acid was measured at the multiplet between 300-400 nm. A second series of samples using the 0.5, 2.0, and 6.0 M aqueous solutions above was prepared by adding an equal volume of 30% TBP/dodecane to the aqueous phase. The TBP solution was pre-equilibrated with five sequential contacts with the appropriate nitric acid concentration. The UV/Vis spectra of only the aqueous phase were also collected for these samples.

Irradiation of aqueous and mixed-phase solutions was performed in screw-capped 1-cm cuvettes (Helma USA, Plainville, NY, USA) containing a minimum of headspace to minimize the loss of nitrous acid. The headspace volume was 0.2 mL out of a total cuvette volume of 3 mL. Due to the short irradiation times and small volumes employed, there was no pressure build-up in the irradiated samples. There was also no temperature change above ambient room temperature due to irradiation. The irradiator was a Nordion Gammacell 220E (Nordion Corp., Ottawa, Canada) containing a 20,000 Ci ^{60}Co source. The dose rate at the time of these irradiations was 6.0–6.3 kGy h^{-1}, as determined by decay-corrected Fricke dosimetry at the time of the experiments. The cuvettes were irradiated for an amount of time sufficient to deliver a desired absorbed dose, then removed from the irradiator, the phases were mixed, and then the sample was inserted into the cell-holder of the Cary 6000 to record the spectrum. Rapid phase separation allowed for absorbance measurements to be made in the aqueous phase. The sample was then returned to the irradiator to receive any subsequent absorbed dose increment.

Results and discussion

Irradiation of the aqueous phase

When a mixture of Np(V) and Np(VI) was irradiated in 4 M HNO_3, oxidation of Np(V) to Np(VI) occurred in the early stages of irradiation, followed by reduction to Np(V) at higher absorbed doses. The change in neptunium speciation is shown in Fig. 1, and the results are similar to those we previously reported, with the initial oxidation thought to be

143 the result of free radical reactions and the subsequent reduction due to produced nitrous
144 acid [7, 13]. Neptunium (IV) was not observed. In the current experiment, the reduction
145 of Np(VI) became measurable when the concentration of HNO_2 exceeded ~0.4 mM, for
146 ~ 2.5 mM neptunium.

147

148 For samples containing initially nearly quantitative Np(VI) in 0.5 M, 1.0 M, 2.0 M, and
149 6.0 M HNO_3, Np(V) was ultimately produced in solutions of all irradiated nitric acid
150 concentrations. As has been previously reported, the radiolytic yield of nitrous acid
151 increases with the concentration of the irradiated nitric acid [7, 14]. However, this does
152 not necessarily result in higher yields of Np(VI) reduction with higher nitric acid
153 concentration, since nitric acid is also the oxidizing agent. The result of these competing
154 reactions is a non-trivial relationship between Np(V) yield and nitric acid concentration.
155 As can be seen in Fig. 2, the yield of Np(V) in 2 M HNO_3 was slightly higher than for 1
156 M HNO_3, presumably due to the higher HNO_2 yield, but at the higher concentration of
157 6.0 M HNO_3, the yield of Np(V) was substantially reduced. Prior to the onset of the
158 reduction of Np(VI), oxidation also occurred at low absorbed doses for these samples.
159 The low dose increment of the data of Fig. 2 is reproduced on an appropriate scale in Fig.
160 3 for clarity. Figure 3 shows that conditions were oxidizing at low absorbed doses, with
161 the switch to reducing chemistry occurring at higher absorbed doses for higher acid

concentrations.

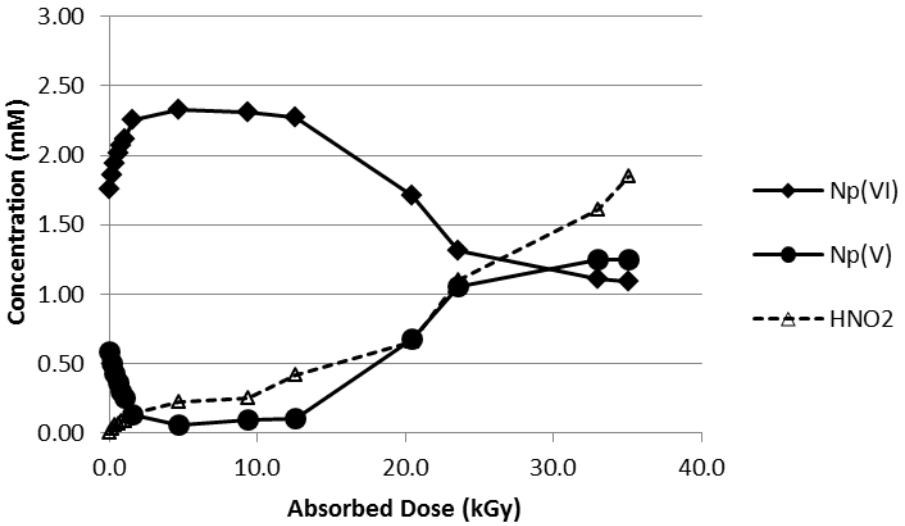

Fig. 1 The change in neptunium speciation with absorbed dose for a mixed Np(V), Np(VI) solution in 4 M HNO_3

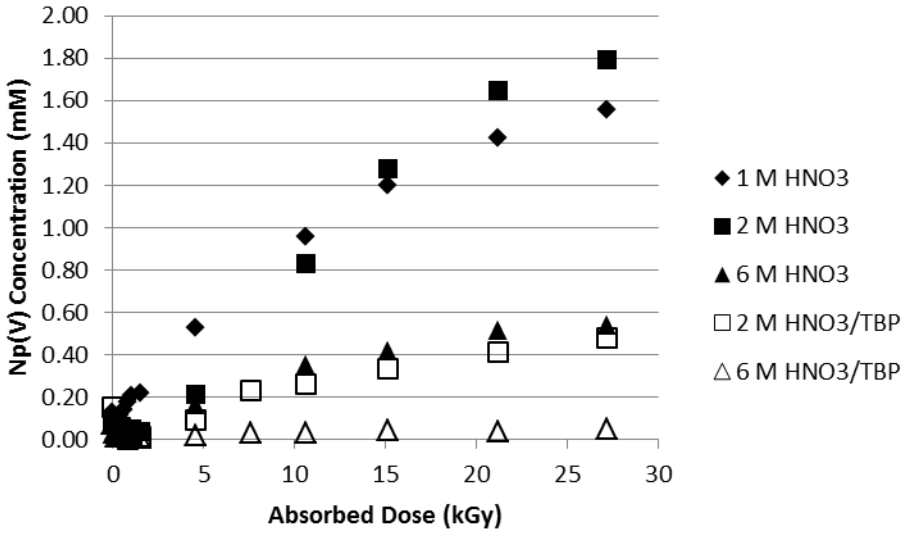

Fig. 2 The increase in Np(V) in irradiated solutions of predominantly Np(VI) at different nitric acid concentrations for pure aqueous phases, and for aqueous phases irradiated in contact with 30% TBP/dodecane

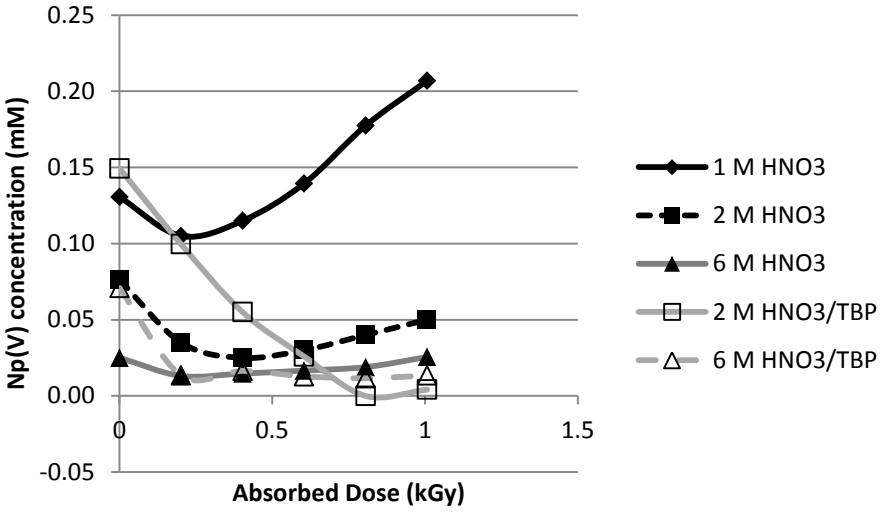

Fig. 3 The decrease and then increase in Np(V) in irradiated solutions of predominantly Np(VI) at different nitric acid concentrations for pure aqueous phases, and for aqueous phases irradiated in contact with 30% TBP/dodecane; data of Fig. 2 scaled to show trends at low absorbed doses

Thus it may be concluded that for aqueous phase irradiation, the overall result is the reduction of neptunium to inextractable Np(V), with a yield that depends on the concentration of nitric acid and produced nitrous acid. Neptunium (IV) was not produced under any condition of pure aqueous phase irradiation. These conclusions are in agreement with our previous work [7].

Biphasic irradiations

To observe the effects of the organic phase on neptunium speciation in irradiated solution, irradiation experiments were performed for solutions containing equal volumes of the same acidic aqueous phases and 30% TBP/dodecane. Neptunium speciation in only the aqueous phase was observed using UV/Vis spectroscopy for these biphasic solutions, and it is reasonable to assume that the neptunium freely crosses the phase boundary depending on its oxidation state. Fig. 2 shows the increase in Np(V) in the aqueous phase

for irradiated mixed phases at 2 and 6 M HNO_3, while Fig. 4 shows changes in both oxidation states, as well as the appearance of HNO_2 and the extraction of neptunium into the organic phase for the 2 M HNO_3 mixed phase sample.

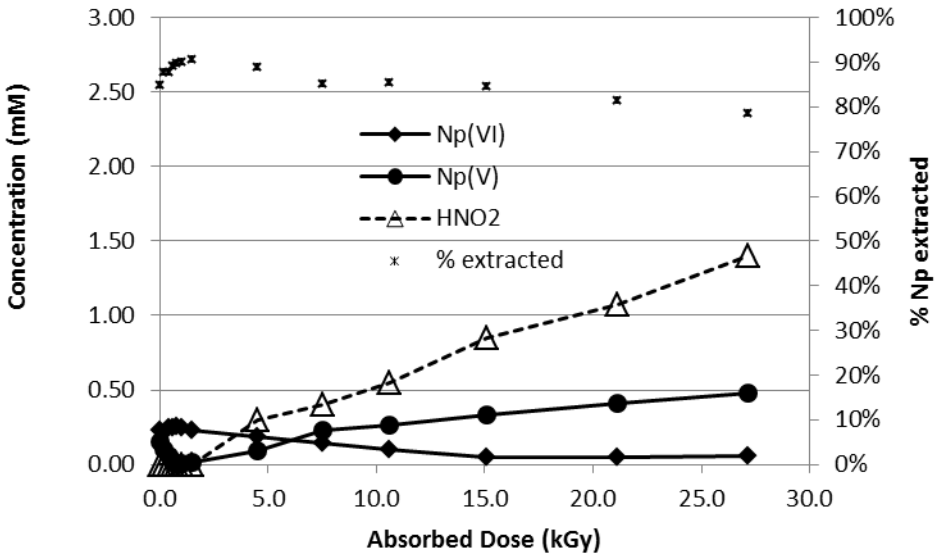

Fig. 4 The change in neptunium speciation in the aqueous phase for 2 M HNO_3, irradiated in the presence of an equal volume of 30 % TBP/dodecane. The total neptunium concentration was 2.4 mM.

Similarly to the irradiated pure aqueous phases, the small amount of Np(V) in the 2 M HNO_3 aqueous phase of the mixed phase experiment showed initial oxidation to Np(VI), which was accompanied by an increase in the amount of neptunium extracted into the organic phase. The percent extracted shown in Fig. 4 was calculated by mass balance after summing the aqueous Np(V) and Np(VI) concentrations and comparing to the initial total neptunium concentration of 2.4 mM. Thus, even in the presence of the organic phase, oxidizing radicals reacted with neptunium in the aqueous phase. As the irradiation continued and nitrous acid accumulated, neptunium was then reduced to Np(V). Any Np(V) produced in the organic phase would be stripped and detected in the aqueous phase, accounting for the slightly increasing aqueous phase total neptunium concentration

and decreasing distribution ratios shown. Neptunium reduction apparently occurred in both phases. At the highest absorbed dose of 27 kGy, the extraction of 78 % of the total neptunium concentration corresponds to a D_{Np} of 3.6. If it is assumed that only Np(VI) extracts, the $D_{Np(VI)}$ is 33 (96 % extracted), slightly higher than typically reported values of 7-10 (88-91 % extracted) for Np(VI). However, it must be kept in mind that these previous measurements were probably made in the presence of a small amount of Np(V). For example see ref [15]. This suggests that equilibrium had been reached between the phases.

The reduction yield for Np(VI) was lower in the presence of the organic phase, as shown in Fig. 2 for both the 2 M HNO_3, and 6 M HNO_3 mixed phases. For example, for 2 M HNO_3 the Np(V) concentration was 1.8 mM in the pure aqueous phase, while in the aqueous solution in contact with TBP, the Np(V) concentration was only 0.48 mM, at the maximum absorbed dose of 27 kGy. This may be due to relative stabilization of the hexavalent oxidation state by TBP complexation. In the case of the 6 M HNO_3 mixed phase irradiations, there was very little reduction of neptunium, presumably due to the more oxidizing aqueous phase, also shown in Fig. 2. Further, in both 2 M and 6 M HNO_3, the initial concentration of Np(V) was slightly higher in the unirradiated mixed phase solutions than in just nitric acid, implying some reduction of Np(VI) by the organic phase itself. Fast reduction of Am(VI) by 30% TBP/dodecane has also been reported [15].

The production of nitrous acid measured in the aqueous phases was approximately the same in the mixed phase case as in the pure aqueous systems for the higher acid concentrations. At the maximum absorbed dose of 27 kGy the nitrous acid concentrations were 1.4 vs. 1.1 mM for 2 M HNO_3, and 2.8 vs. 2.7 mM for 6 M HNO_3, for neat aqueous vs. mixed phase solutions, respectively. However, the increase in HNO_2 concentration in the aqueous phase of mixed-phase 0.5 M HNO_3 samples was more dramatic. In the mixed phase system a final concentration of 0.33 mM HNO_2 was achieved at 35 kGy, with only 0.1 mM produced at the same absorbed dose in pure 0.5 M HNO_3. The reason for this higher than expected yield is unknown. The effects on neptunium speciation in a

mixed phase system at this acidity are shown in Fig. 5. After a short lag time during which HNO_2 was produced, the Np(VI) began to reduce to Np(V), and the amount of neptunium measured in the aqueous phase increased, until at 35 kGy it was present quantitatively as the pentavalent oxidation state. This indicates that all neptunium was reduced, including that in the organic phase. In this case, the reduction of neptunium was greater in the mixed phase system than in pure 0.5 M HNO_3, perhaps merely due to the low concentration of oxidizing HNO_3 being unable to mitigate reduction by the combination of produced nitrous acid and the inherent reducing tendency of the organic phase. Although the mixed-phase 0.5 M HNO_3 system was the most reducing system investigated, Np(IV) production was not detected.

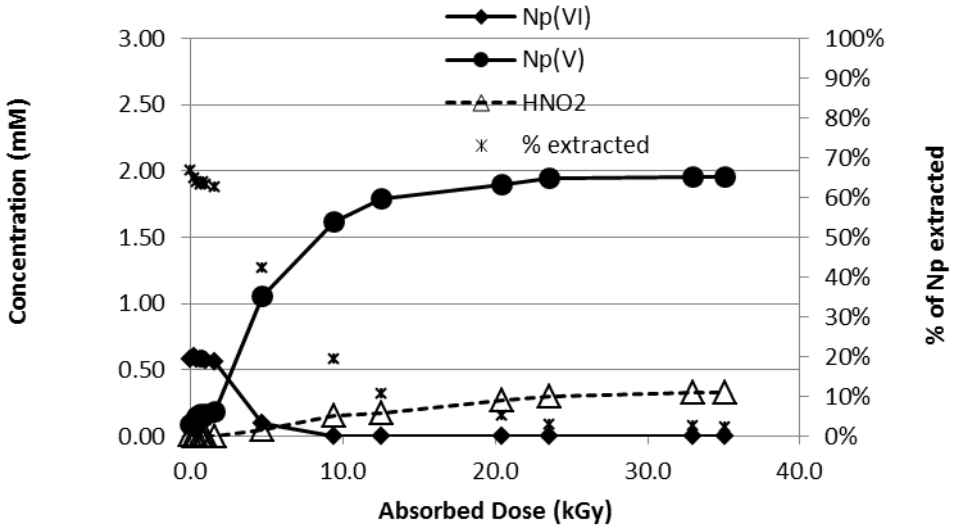

Fig. 5 The change in neptunium speciation for 0.5 M HNO_3 irradiated in the presence of 30% TBP/dodecane

Conclusions

The redox chemistry of neptunium in irradiated nitric acid tends to produce a mixture of Np(V) and Np(VI), for which the equilibrium depends on the concentrations of HNO_3

and HNO_2. Although the radiolytic yield of HNO_2 is higher at higher HNO_3 concentrations, the oxidizing action of the HNO_3 results in lower yields of reduction of Np(VI). The presence of the 30% TBP/dodecane phase produced a more reducing system than for pure HNO_3 alone. At the low HNO_3 concentration of 0.5 M, neptunium was reduced to Np(V), apparently in both phases and this was accompanied by its stripping to the aqueous phase at fairly low absorbed doses, although at this low acid concentration some amount of reduction is expected even in the absence of radiation. Even for higher concentrations of up to 6 M HNO_3 the presence of the organic phase reduced a small amount of Np(VI) even in the absence of irradiation. At higher HNO_3 concentrations, the production of HNO_2 as measured in the aqueous phase was similar for the pure aqueous phase, and the mixed phase systems.This implies that the partition ratio of HNO_2 is similar to its biphasic radiolytic production yields.

However, the organic phase did not prevent the transient oxidation of Np(V) to Np(VI) by free radical species in the early stages of the irradiation. This indicates that the organic phase does not completely scavenge oxidizing free radicals. Upon reaching high enough concentrations of HNO_2, reduction of Np(VI) to Np(V) occurred in the mixed phase systems as has been previously reported for aqueous systems. The overall result was that, just as in aqueous solution, an equilibrium was sought between Np(V) and Np(VI) that varied depending on the aqueous nitric acid concentration for mixed phase systems. Neptunium (IV) was not detected in any experiment. Interestingly, despite its reducing tendencies the presence of the organic phase actually seemed to protect Np(VI) in irradiated solution at higher nitric acid concentrations, possibly because it was less readily reduced by HNO_2 when complexed by TBP.

Acknowledgements

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