

Investigation of HNO₂ Production in Solvent Extraction Organic Phases

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September 2014



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**Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

Investigation of HNO₂ Production in Solvent Extraction Organic Phases

Fuel Cycle Research & Development

***Prepared for
U.S. Department of Energy
Materials Recovery and Waste Form
Development Campaign***

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28th September, 2014
FCRD-SWF-2014-000593***



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SUMMARY

This document is a letter report that was prepared to meet FCR&D level 4 milestone M4FT-14IN0304054, “Investigate HNO₂ production in solvent extraction organic phases.” This work was carried out under the auspices of the Fundamental Radiation Chemistry FCR&D work package. This document reports on an initial tests performed to follow HNO₂ formation in reference flowsheet relevant organic phases.

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ACRONYMS

FCR&D Fuel Cycle Research and Development

INL Idaho National Laboratory

US DOE United States Department of Energy

UV-Vis Ultraviolet-visible

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

1. Introduction

As the US develops advanced separation methods for the processing of used nuclear fuel, the option for co-extraction of uranium, neptunium and plutonium is becoming increasingly attractive for the first cycle process. However, neptunium has a rich redox chemistry and offers two oxidation states that can be extracted in such a process, but a third that is inextractable. The Np(IV) and Np(VI) ions can both be extracted by 30% TBP in an organic diluent for used nuclear fuel processing purposes. Recent research has highlighted that in aqueous solution where Np , HNO_3 , HNO_2 are present redox control of the Np ions becomes difficult.¹⁻³ This becomes further complicated in irradiated solutions of Np . Although these reactions have been explored in the aqueous phase there is as yet very little information on these species in the organic phase. This letter report details the researchers' initial findings of the production of HNO_2 in irradiated TBP in a normal alkane diluent solutions and the related effects on neptunium speciation.

2. Experimental

Solutions of Np(VI) were generated electrochemically in 0.1 M HNO_3 then aqueous phase acidity adjusted to either 0.1, 1, 2, 4, 6 or 8M by the addition of appropriate concentrations of nitric acid. Traditional solvent extraction experiments were then performed to extract Np(VI) into TBP organic phase. The organic phase was then loaded into a 1-cm UV-vis cuvette. Steady-state γ -radiolysis was performed on the cuvettes containing either the organic phase only and organic/ aqueous phase in contact with each other. A Cary 6000i UV-vis spectrophotometer was used to measure absorbance changes the organic phase after irradiation to monitor oxidation state changes.

3. Results

Initial experiments were run at all acidities and varying gamma dose, in the absence of Np , to identify if HNO_2 would be produced from the extracted HNO_3 present in the organic phase. Figure 1 shows the results of this study for 1.0 M HNO_3 . This change in the absorbance spectrum indicates a build-up of HNO_2 as the total dose increased. Further, it appears that there is a second species that forms that is as yet unidentified. Research performed where the initial aqueous phase only had 0.1 M HNO_3 present showed, after extraction, an organic phase spectrum for HNO_2 production similar to that observed in water without the large broad peak attributed to the additional species.

For the irradiation experiments where Np was present, a UV-vis spectra of the organic phase was taken prior to initiating the gamma radiolysis study to identify that there was no substantial change in oxidation state of the neptunium post extraction. Invariably there was a small amount of Np(V) found in the TBP phase, however these were not expected to have influenced the

outcome of the experiment as at low dose (short irradiation times) the Np(V) present was seen to oxidize to Np(VI) . At low acid concentrations the Np oxidation reaction was found to reverse when the samples had received ~ 5.35 kGy absorbed dose.

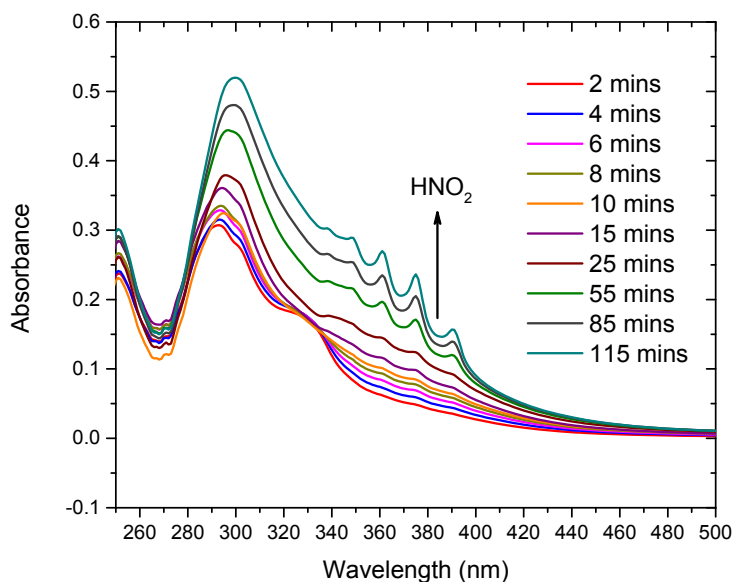


Figure 1. Differences in the absorbance spectra of extracted nitric acid as a function of time in the gamma irradiator. In this example the initial aqueous phase concentration of HNO_3 was 1.0 M HNO_3 .

Above an absorbed dose of 5.35 kGy there is enough Np(V) present in the organic phase that Np(V) cation-cation complexes (CCC's) begin to form. The absorbance peak at 1001 nm is indicative of this (Figure 2).³ However, with both Np(V) and Np(VI) ions present in these organic phase solutions it is not clear if these CCC's are $\text{Np(V)}\text{-Np(V)}$ complexes or $\text{Np(V)}\text{-Np(VI)}$ complexes.

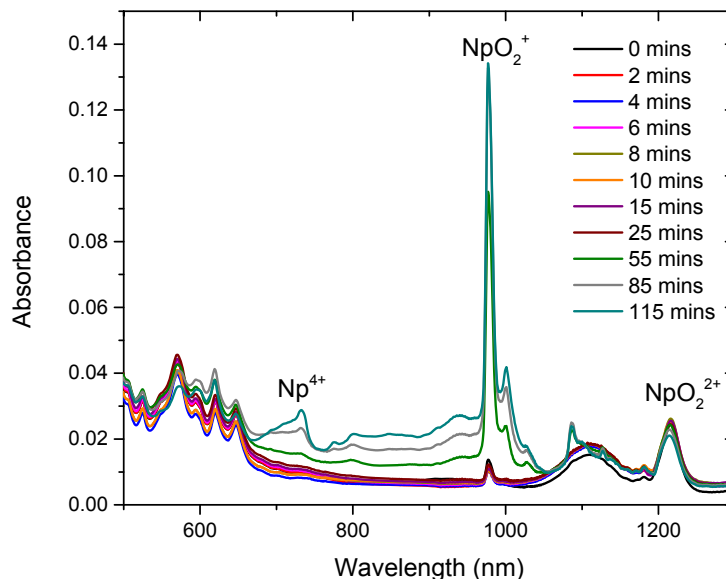


Figure 2. UV-vis spectra of changing organic phase Np speciation with absorbed dose. Extracted Np ~ 6 mM, initial aqueous phase acidity 1.0 M HNO_3 .

Figure 3 is indicative of the behavior observed at higher initial aqueous phase acidities (above 4.0 M) large quantities of Np(V) are only observed briefly, swiftly followed by an increase in Np(IV) in the organic phase. The presence of Np(IV) is taken to be evidence of disproportionation that is known to be significantly faster in TBP/kerosene organic phases. This is the most significant difference in behavior from the aqueous phase where no Np(IV) is observed with increasing dose. Disproportionation may also account for why there is only a small reduction in the Np(VI) concentration throughout the course of the experiment. However, further investigations are required to verify the disproportionation behavior.

All experiments were performed in the presence and absence of an aqueous phase. In the samples where an aqueous phase was present there was not found to be any appreciable Np(V) back extraction. This was an unexpected result as Np(V) is not usually stable in TBP solutions. It is envisaged that in the low volume 1 cm cuvette the surface tension between the organic and aqueous phases was high enough that it prevented adequate mixing between the two phases such that the Np(V) would back extract.

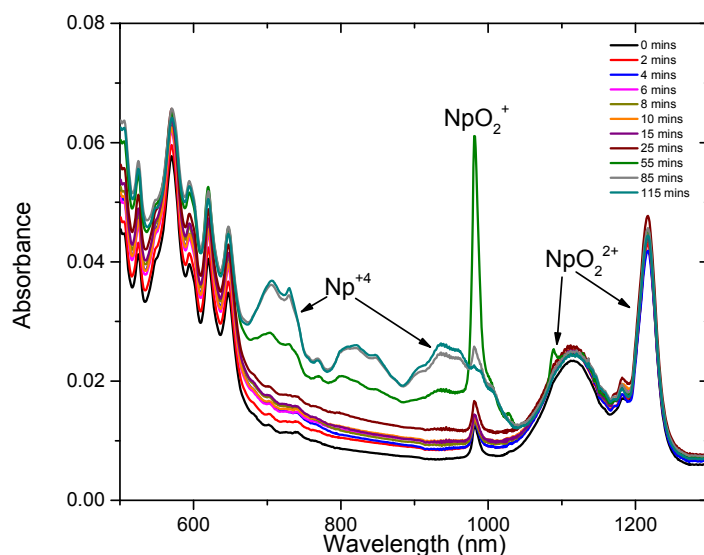


Figure 3. UV-vis spectra of changing organic phase Np speciation with absorbed dose. Initial organic phase $[\text{Np}] \sim 6 \text{ mM}$, initial aqueous phase acidity 4.0 M HNO_3 .

4. Conclusions

Irradiated organic TBP solutions containing extracted Np(VI) were found to behave similarly to those in aqueous solution up to an absorbed dose of 5.35 kGy . Above this dose the chemistry appears to deviate from that of the aqueous phase example with significant production of Np(V) . The large amount of Np(V) produced leads to the formation of Np(V) cation-cation interactions being observed spectroscopically however, it is not clear if these are $\text{Np(V)}\text{-Np(V)}$ complexes or $\text{Np(V)}\text{-Np(VI)}$ complexes. There was found to be no observable differences in the samples that contained both the organic and aqueous phases to the organic only samples (no Np back extraction to the aqueous phase). However, this may be due to poor mixing between the two phases in the UV-vis cuvette. Unlike the prior aqueous phase work, evidence of Np(V) disproportionation is observed through the eventual presence of Np(IV) .²

5. References

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6. Milesotne Participants

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