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Literature Review: Reduction of Np(V) to Np(IV)- Alternatives to Ferrous Sulfamate

Advanced Fuel Cycle Initiative

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SUMMARY

The baseline approach to control of Np oxidation in UREX and PUREX separation processes is the reduction of Np(V) and Np(VI) to Np(IV) using ferrous sulfamate. Use of this reagent results in increased sulfur and iron concentrations in the liquid waste streams from the process. Presence of these two elements, especially sulfur, increases the complexity of the development of wasteforms for immobilizing these effluents.

Investigations are underway to identify reductants that eliminate sulfur and iron from the Np reduction process. While there are a variety of chemical reductants that will reduce Np to Np(IV) in nitric acid media, the reaction rates for most are so slow that the reductants are not be feasible for use in an operating plant process.

In an attempt to identify additional alternatives to ferrous sulfamate, a literature search and review was performed. Based on the results of the literature review, it is concluded that photochemical and catalytic processes should also be investigated to test the utility of these two approaches. The catalytic process could be investigated for use in conjunction with chemical oxidants to speed the reaction rates for reductants that react slowly, but would otherwise be appropriate replacements for ferrous sulfamate. The photochemical approach, which has received little attention during the past few decades, also shows promise, especially the photocatalytic approach that includes a catalyst, such as Pt supported on SiC, which can be used in tandem with an oxidant, for Np reduction.

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ACRONYMS

AHA – acetohydroxamic acid

FHA – formohydroxamic acid

FN- ferrous nitrate

FS – ferrous sulfamate

HAN – hydroxylamine nitrate

nDD – normal-dodecane

TBP - tributylphosphate

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SEPARATIONS CAMPAIGN

LITERATURE REVIEW: REDUCTION OF Np(V) TO Np (IV)- ALTERNATIVES TO FERROUS SULFAMATE

1. INTRODUCTION

Np exists in the IV, V or VI valence state in the nitric acid solutions that are typical of nuclear processing. Np(III) would generally not be present in an oxidizing acid and Np(VII) would not be present except in alkaline or solid state systems. Separations are normally performed by exploiting the chemical differences between NpO_2^+ and either Np(IV) or NpO_2^{2+} . NpO_2^+ is the common valence state of Np ions in nitric acid solution unless either oxidizing or reducing species are present to adjust the valence state. Nitrous acid, which is normally present in nitric acid solutions, interacts with Np to oxidize it to either NpO_2^+ or NpO_2^{2+} depending on the conditions. Nitrous acid also will under certain conditions reduce NpO_2^{2+} to NpO_2^+ . Additionally NpO_2^{2+} under higher nitric acid concentrations (i.e. 5 to 9 M nitric acid) will disproportionate to Np(IV) and NpO_2^{2+} resulting in the possibility of Np being present in two to three valence states in the same solution. The existence of multiple valence states complicates complete recovery and separation of Np in chemical processes and has historically led to processes that either used ferrous sulfamate (FS) to control the valence state to Np(IV) or used an oxidant (such as ceric ion or permanganate) to control the valence state to NpO_2^{2+} . Either method was used with success but resulted in significant amounts of soluble cations that contributed to waste volumes. Sulfamate or to a lesser extent hydrazine was used as a nitrous acid scavenger to control the nitrous acid concentration to a level where it does not significantly interfere with the stability of the Np valence state. Sulfamate causes downstream problems however as it degrades to ammonium ion and sulfate. Production of ammonium is a problem if the waste is converted to an alkaline state as volatile and flammable ammonia gas is then released. Large amounts of sulfate in the waste can cause problems in the formulation of glass waste forms. Avoiding the use of chemicals for valence adjustment/nitrous acid scavenger that contribute significantly to the salt content of the waste is clearly highly desirable to the extent that the necessary separations can still be performed.

For the current work scope, efforts were made to perform literature reviews on the options for reduction of NpO_2^+ to Np(IV). This included the open published literature as well as the Savannah River Site internal literature where significant efforts were expended at process development to support the recovery of ^{237}Np from site fuels and recycle of Np from the ^{238}Pu production efforts starting in the late 1950's. Three areas of potential solutions were identified items: chemical reductants, photochemical reduction, and heterogeneous catalysis.

2. Chemical Reductants - Reduction to Np(IV)

Historically, ferrous sulfamate (FS) has been used in both ion exchange and solvent extraction applications to reduce either Pu or Np to Pu(III) or Np(IV). During waste minimization efforts at SRS in the 1980's, FS usage in the F-Canyon 1st cycle process was reduced by partially substituting hydroxylamine nitrate (HAN, NH_2OH) for a portion of the FS, referred to as the FS/HAN split scrub.

Other alternatives that were considered at that time were the generation of U(IV) (stabilized with hydrazine) and the substitution of ferrous nitrate (FN) (also stabilized with hydrazine) for ferrous sulfamate. Review of the literature reveals several distinct methods utilized for reduction of Np: 1) use of a metal ion (such as Fe(II)); and 2) use of organic or simple inorganic chemicals (ascorbic acid, HAN, $\text{NH}_2\text{OH}\cdot\text{HNO}_3$, N_2H_4 , and H_2O_2).

Table 1 lists most of the classical approaches to the reduction of NpO_2^{2+} to Np(IV) as reported in available references^{1,2,3,4,5,6}. Some of the information on the reductions is not reported in nitric acid but that should not be taken to mean that the reduction cannot be performed in nitric acid. The same references show a number of reasonable choices for the reduction of NpO_2^{2+} to NpO_2^{+} but unfortunately the reduction of NpO_2^{+} to Np(IV) is harder due to the Np-O bonds that must be broken; subsequently, the options are fewer. At higher nitric acid concentrations, disproportionation of NpO_2^{+} to produce Np(IV) and NpO_2^{2+} becomes increasingly important. Disproportionation can also be a significant reduction mechanism in nitrate-based solutions with greater than ~4M nitric acid concentrations. In addition, disproportionation combined with a reducing agent reagent (to convert NpO_2^{2+} to NpO_2^{+}) can result in nearly quantitative reduction to of higher oxidation states of Np to Np(IV).

Table 1. Reagents for the Reduction of NpO_2^{+} to Np(IV).

Reagent	Matrix	Temperature/ °C	Rate
H_2O_2	0.5M HNO_3	25	Very slow
	6-8M HNO_3	20	Moderately Fast
NH_2OH	1M H^+	Ambient	Very slow
NH_2NH_2	1M HNO_3	90	Very slow
	1.5M HNO_3	50	1-2 hr when catalyzed by Fe or Cu
	4M HNO_3	Ambient	Slow, catalyzed by Fe
	4M HNO_3	50	1-3 hr catalyzed by Fe
AHA		Ambient	Very slow
FHA		Ambient	Very slow
Acetaloxime		50	Extremely slow
Ascorbic Acid		41	> 9 min
Fe(II)		25	Very rapid
I^-	HCl	25	40 min
SO_2	H_2SO_4	Ambient	Very slow, catalyzed by F^-
Sn(II)	HCl	Ambient	Very slow
V(III)	HClO_4	Ambient	Slow
Cr(II)	HClO_4	25	Very rapid
U(IV)	HClO_4 , HCl	25	Moderately fast
Pu(IV)	HClO_4	25	Very slow
Pb(0)	HClO_4	25	Slow

Within the classical methods of NpO_2^{2+} reduction, only a few reagents had appreciable reduction rates under any conditions (Fe(II), U(IV), Cr(II), Ascorbic acid, H_2O_2 , NH_2NH_2). Several of the examples that were performed under higher nitric acid concentrations appear to reflect reduction by disproportionation where the added reagent is only reducing the NpO_2^{2+} intermediate. In a low to moderate acid environment, Fe(II) is the only reagent that performs well at reducing Np to Np(IV), but it appears to be reasonable to use it as a hydrazine stabilized nitrate reagent rather than as a sulfamate. In a feed treatment step, a moderate reaction rate may be something that can be tolerated, but for valence adjustment during

solvent extraction stripping, fast kinetics are going to be needed. FN should be the comparison point for alternatives. It eliminates the sulfate in the waste but retains the Fe. Depending on the acidity, another reductant (such as HAN) could be used to reduce the Fe(III) back to Fe(II) effectively recycling the Fe as a catalyst.

Significant work has been performed over the last 20 years looking at catalysts to improve the kinetics of the slow reactions with hydrazine or similar reducing compounds. Other work has attempted to generate reducing species in-situ capable of accomplishing the Np reduction. Examples of such work include the use of reductants to reduce soluble Fe(III) to Fe(II) and then let the Fe(II) reduce the NpO_2^+ , the use of solid supported catalysts (Pt or Pd) to lower the activation energy of the reducing species (hydrazine, HAN, formic acid or derivatives) or photocatalysis to assist the reduction of Np with hydrazine or derivatives.

3. Catalytic Reduction

The conversion of Np(V) to Np(IV) in solution by organic reagents is a possible alternative to use of ferrous sulfamate. A promising set of catalysts include platinum (Pt), palladium (Pd), and transition metals such as molybdenum (Mo). Many studies focused on the use of a heterogeneous catalyst, where the catalyst is placed on a solid support such as SiO_2 . Silica-gel is preferred as a result of its high chemical stability in acids. A number of investigators have utilized this approach for the conversion of higher oxidation states of Np (V and VI) to Np(IV).

3.1 Reduction of Np(VI) to Np(IV)

Ananiev et al⁷ reported that in the presence of 0.5M HNO_3 , 0.2M formic acid, 0.05 to 0.5 M urea and ~1.0 % Pt/ SiO_2 catalyst, Np(VI) reduces to Np(IV) over approximately 175 minutes. The temperature was held at 60 °C. The catalyst was prepared according to Ananiev et al⁸. Variables such as rate of argon bubbling, and solid-to-liquid mass/volume ratio, and concentration of reactants were investigated.

The reduction of Np(VI) to Np(IV) was also observed by Anan'ev⁹ to proceed with 0.1M HCOOH in 1M HClO_4 in the presence of a 1% Pt/ SiO_2 in approximately 35 minutes ($T = 60\text{ }^\circ\text{C}$). Perchloric acid was chosen for these experiments to preclude the influence of HNO_2 on reduction kinetics. Therefore eliminating the need for nitrite scavenger agents that may be reducing or decompose in the presence of heterogeneous catalysts. The rate of reduction was dependent on the intensity of stirring of the reaction mixture and the bubbling rate. The reaction stops at ~95% conversion.

3.2 Reduction of Np(V) to Np(IV)

The reduction of Np(V) by formic acid in the presence of a 1 % Pt black on an Al_2O_3 support was studied by Logvis' and Krot.¹⁰ The catalyst was prepared by impregnating the 3-5nm Al_2O_3 particles with a Pt solution. The product was dried at 70 °C and subsequently calcined for 3 hr at 600 °C. The catalyst was activated by gently boiling it in 1M HCOOH for 1-2 hr. The activity of the catalyst significantly decreases in air. Therefore, portions were stored under 1M HNO_3 . The starting Np(V) and HCOOH concentrations were each 0.5 M. 100 mg of catalyst was added and stirred by the addition of argon at 60 °C. Within 3 hr, nearly all of the Np had been reduced to Np(IV). After a few days, the Np(IV) began to re-oxidize to Np(V) by air.

A study by Nakamura¹¹ was performed investigating the reduction rates of Np(V) to Np(IV) by Pt black. A Np(V) solution was added to a nitric acid solution containing hydroxyl ammonium nitrate (HAN). Pt

black was then added and stirred. A 3 mM (Np(V) solution, with initial concentrations of $[H^+] = 3\text{ M}$, $[NH_3OH] = 6.25 \times 10^{-1}\text{ M}$, and $[Pt] = 5\text{ g/L}$, was reduced in approximately 25 minutes at room temperature.

Np(V) reduction in hydrazine with Pt/SiO₂ at 30-40 °C was studied by Tananaev et al.¹² Reaction conditions of $[Pt] = 2\%$, $[Np(V)] = 5 \cdot 10^{-5}\text{ M}$, $[HNO_3] = 2\text{ M}$, $N_2H_5 = 0.2\text{ M}$, $t = 40\text{ °C}$ reduced Np(V) in approximately 30 minutes; stirring did not affect the reduction rate. In 4M HNO₃, all the Np was completely converted to Np(IV); however, reduction was not complete in solutions below 2M HNO₃, leaving 2-4% Np(V) in solution. Increasing Pt from 1% to 2% increased the reaction rate. The authors concluded this catalytic reduction is best carried out above 70 °C, where hydrazine decomposes in the presence of the catalyst.

The reduction of Np(V) to Np(IV) by hydrazine, catalyzed by molybdenum, was studied by Koltunov¹³ in a solution of HClO₄ and NaClO₄. For these experiments, concentration and the order of reactant mixing were studied: $[N_2H_4] = 0.02\text{-}0.4\text{ M}$, $[Mo(VI)] = 10^{-3}\text{-}10^{-4}\text{ M}$, $[H^+] = 0.4\text{ to }1.9\text{ M}$, $Np(V) = 3.2 \cdot 10^{-3}\text{ M}$, temperature = 60 - 88 °C. Where Np was added last, there was an induction period of 5-10 minutes. Within several minutes Mo(VI) was reduced to Mo(V), even before addition of Np(V). When hydrazine or molybdenum was added last, Mo(IV) initially formed, rapidly reducing some of the Np(V) to Np(IV) for up to 2 minutes without an induction period. After induction or acceleration was observed, reaction rates were similar. Approximately 1.7 moles of hydrazine were consumed per mole of Np(V). Reduction of Np occurred in as little as 4 minutes.

Boltoeva et al¹⁴ investigated the reduction of Np(V) with formic acid in perchloric acid solutions catalyzed by Pd/SiO₂. Perchloric acid was chosen to preclude the effect of complexation of Np ions. At 30 °C, a 1.25 mM solution of Np(V) is completely reduced in 1 M HClO₄ and 0.2 M HCOOH within 20 minutes. Reduction of Np(IV) is followed by partial reduction to Np(III).

4. Photochemical Oxidation State Adjustment

It is also possible to adjust the oxidation state of metal ion in aqueous solutions utilizing photochemical processes. While this aspect of Np aqueous chemistry has not received as much attention as solely “chemical” processes, it is a viable alternative to the chemical approach because it allows the modification of the Np oxidation state with out the addition of chemical species that will ultimately require dispositioning as waste. Even though the primary objective of this literature review is to find a replacement for the ferrous sulfamate (a reductant that is utilized for reducing Np to the tetravalent state), this discussion will include the photochemical processes that have been investigated for both oxidation and reduction of aqueous Np species, including the oxidation (Np(IV) to Np(V) and Np(V) to Np(VI)) and the reduction (Np(VI) to Np(V) and Np(V) to Np(IV)) processes. These investigations were all performed in acidic media; however, the type of acid varied

4.1 Reduction of Np(VI) to Np(V)

The earliest investigation of this photochemical reduction in perchloric acid media, with 253.7 nm light (light source was 4 W Hg lamp with a filter), was reported by Zielen et al.¹⁵ In this investigation, the $[Np(VI)]$ was essentially constant (varied from 0.0423 M to 0.0450 M) and $[H^+]$ varied from 0.22 to

1.00 M. Dilutions of the initial stock solution were performed with perchloric acid-sodium perchlorate solutions in an attempt to keep the ionic strength constant. Based on the results, the apparent quantum yield^a 0.032 ± 0.011 was computed, and the computed rate constant for the conversion reaction was $k = 5.8 \cdot 10^{-9}/\text{sec}$. During this investigation, it was recognized that autoredution, due to the radiolytic conversion of Np(VI) to Np(V), also contributed to the conversion. This autoredution process was also investigated and the rate constant for the autoredution process was determined to be $k = 3.1 \cdot 10^{-9}/\text{sec}$.

The Np(VI) to Np(V) reduction in nitric acid media has also been investigated.¹⁶ During this investigation the Np(VI) to Np(V) photochemical reduction (254 and 300 nm radiation from unspecified sources) was studied as a means of adjusting the valence of Np. During this investigation it was recognized that the reaction enhancement was due to the generation of nitrite, which reduced Np(VI) to Np(V). Quantum yields, as a function of acid concentration, were computed for each wavelength. At 254 nm, the yields ranged from 0.04 to 0.02 as the acid concentration varied from 0.1 M HNO_3 to 4 M HNO_3 ; at 300 nm, the yields ranged from 0.001 at 0.1 M HNO_3 to 0.002 in 1 M HNO_3 .

During the late 1900's, the utility of the photochemical process was tested for separation of U and Np, utilizing miniature mixer-settlers (8 stages) in simulated fuel processing solutions.¹⁷ The solvent (70% nDD, 30%TBP) was fed at a 20 mL/h to the first stage; the organic feed, containing 97.9 g/L U and 107 mg/L Np in 30% TBP/70% nDD was fed to the second stage at 100 mL/h; and the Np scrub (3 M HNO_3 with 0.01 M CH_3OH) was fed to the eighth stage. The photochemistry was performed on the aqueous phase from the settler of stages 2, 4, and 6 by diverting that phase to the photochemical cell (200 W Hg lamp emitting unfiltered radiation) then returning it to the mixer (of the same stage) after irradiation. The result of the separation experiment was that 90% of the Np was recovered in the Np product stream and 95% of the U was present in the organic stream.

Photochemical reduction, utilizing a photocatalyst (10% Pt on TiO_2 , with the Pt present as a coating on the TiO_2 (1 kW Xe lamp, unfiltered radiation) has also been investigated.¹⁸ In this investigation, it was concluded that the Np(VI) to Np(V) reduction was a consequence of the presence of HNO_2 , and that any rate enhancement was due to the photolytic generation of HNO_2 from HNO_3 and that the photocatalyst did not provide further rate enhancement.

4.2 Reduction of Np(V) to Np(IV)

The photoreduction of Np(V) to Np(IV) has been investigated with¹⁹ and without¹⁶ a photocatalyst. In catalyst-free experiments, radiation of either 300 or 254 nm (filtered radiation of unknown origin) was utilized along with ethanol ($\text{C}_2\text{H}_5\text{OH}$) which was added as a redox agent. Quantum yields were not very large, ranging from 0.006 up to 0.011 (at 254 nm) as the perchloric acid concentration was increased from 0.1 to 4.0 M and 0.004 (at 300 nm) for a perchloric acid concentration of 1.0 M. The authors believed the reduction in perchloric acid was complicated by competing oxidation reactions caused by the presence of HClO_4 .¹⁶

^a The definition of quantum yield (QY) utilized throughout this manuscript is
 $\text{QY} = (\# \text{ of ions reduced or oxidized})/(\# \text{ of photons absorbed})$.

The most efficient Np(V) to Np(IV) conversion was accomplished slurring the 1 mM Np/1 M hydrazine (N_2H_4) solution and a Pt catalyst on SiC substrate present at 5 g/L (10wt% on SiC), which resulted in the complete conversion of 1 mM Np(V) in about 20 minutes while irradiating the solution (unfiltered 0.7 kW/cm³ Xe lamp). Lowering the hydrazine content to 0.1 M extended the time for complete conversion to 30 minutes. A 5 g/L 10wt% Pt on anatase TiO_2 photocatalyst utilized with a 1 mM Np/20% ethanol solution was less effective, resulting in only 70% conversion after 2 hours.¹⁹

4.3 Oxidation of Np(V) to Np(VI)

The photo-oxidation of Np(V) can be accomplished with or without the presence of a photocatalyst. The catalyst-free process in nitric acid media has been studied and is well understood.^{20,21} Investigations of the oxidation of 1 mM Np(V) solutions showed that to facilitate the conversion of Np(V) to Np(VI), it is necessary to scavenge the nitrite ion from the solution by the addition of urea since the irradiation of the solution creates HNO_2 , which reduces Np(VI) to Np(V). The oxidation reaction appears to be roughly first-order in $[\text{H}^+]$.²¹ The reaction does not appear to be very fast, as it took about 300 minutes for a 1.8 mM Np(V) solution containing 0.1 M urea in 3 M HNO_3 to be completely converted to Np(VI) when utilizing an SVD-120A Hg lamp.

In another investigation,¹⁸ a solution containing nearly equimolar concentrations of Np(V), 0.8 mM, and Np(VI), 1 mM, in 3 M HNO_3 was irradiated (1 kW/cm³ Xe lamp, unfiltered radiation) and the concentrations of the two Np species were spectrophotometrically monitored as a function of irradiation time. After about 90 minutes the Np(V) had been completely converted to Np(VI). The catalyst-free oxidation of Np(V) to Np(VI) has also been studied in perchloric acid media.¹⁶ Quantum yields for the oxidation at 254 nm varied with acid concentration, from 0.004 in 0.1 M HClO_4 to >0.010 in 4.0 M HClO_4 .

Photo-oxidation of Np(V) to Np(VI) with a catalyst has also been investigated.¹⁸ In this investigation, a solution containing nearly equimolar concentrations of Np(V), 0.8 mM, and Np(VI), 1 mM, in 3 M HNO_3 was irradiated (1 kW Xe lamp, unfiltered radiation) and the concentrations of the two Np species were spectrochemically monitored as a function of irradiation time. After about 90 minutes the Np(V) had been completely converted to Np(VI). The experiment was repeated with a photocatalyst present at 2 g/L (10wt% Pt on TiO_2), and the rate of reaction appears indistinguishable from the un-catalyzed experiment. It is likely that these two sets of results were affected by the presence of HNO_2 , which reduces Np(VI) to Np(V). When additional experiments were performed on solutions to which urea, a nitrite scavenger, had been added at 0.1 M, the photocatalyzed oxidation proceeded at a reaction rate $\sim 4 \cdot 10^{-4}$ moles/L/hour as compared to the un-catalyzed rate of $\sim 3 \cdot 10^{-4}$ moles/L/hour.

4.4 Oxidation of Np(IV) to Np(V)

Photooxidation of Np(IV) to Np(V) has been investigated utilizing 254 nm radiation (of unknown origin) in perchloric acid solutions.¹⁶ Quantum yields for the reaction ranged from 0.02 in 0.1 M HClO_4 to >0.010 in 4.0 M HClO_4 . The utility of this process seems questionable if it is to be utilized to produce Np(V) since the appearance of Np(VI), from the Np(V) oxidation, occurred after only 70 minutes of irradiation when less than 40% of the Np(IV) had been consumed.

5. CONCLUSIONS AND SUGGESTIONS FOR FUTURE STUDIES

There are a variety of alternatives to the use of ferrous sulfamate for the reduction of Np to Np(IV) in spent fuel processing solutions. There are presently experimental efforts (at ANL) aimed at identifying alternative chemical reductants that could be substituted for ferrous sulfamate. Based on this literature reviewed, it is concluded that future investigations ought to include the testing of catalytic and photochemical processes as well. In addition, it is concluded that in future studies FN should be utilized as the “benchmark” for comparison of Np reductants.

Alternative chemical approaches that involve the utilization of reducing agents that decompose to produce volatile species would result in the reduction of solids waste streams (as compared to a baseline process that results in the addition of ferrous sulfamate that results in both Fe and S in processing effluents); however, the reaction rate for the Np(V) (present as NpO_2^+) to Np(IV) reduction for most reductants is too slow to be utilized in a chemical processing facility, due at least in part to the number of bonds and the strength of the bonds being broken. Utilizing a noble metal catalyst, such as Pt or Pd, or a noble metal supported on SiO_2 , Al_2O_3 or a transition metal oxide, in tandem with a chemical reductant could increase the reaction rate sufficiently to allow the use of some of the chemical reductants that reduce Np(V) slowly in the absence of a catalyst.

The utilization of photochemical processes to modify the oxidation states of actinides in spent fuel processing solutions attracted considerable attention about 30 years ago; however, it appears that there has been little work done in this area in the past decade or more. An advantage to this approach is that it appears to be compatible with the nitric acid media; however, it does require the addition of chemical reagents to the fuel processing solutions, and it is likely that these reagents will result in increased volumes of waste effluents. One photolytic application that would appear to be promising is the photocatalytic approach in which photolysis is utilized along with a catalyst, for the reduction of Np(V) to Np(IV). Based on the previous work in this area, it would appear that a Pt catalyst on SiC substrate would be a promising starting point for further investigation. It would appear that other structurally similar semiconductor materials that have similar electronic properties might also be appropriate for this catalytic application.

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