HYDRAZINE REDUCTION OF Np(V) AND Pu(IV)

DP--1601

DE82 010816

D. G. KARRAKER

Approved by

H. D. Harmon, Research Manager
Actinide Technology Division

DISCLAIMER
This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Publication Date: November 1981

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Np(V) and Pu(IV) in 8M HNO₃ were reduced by hydrazine at 50°C in 1/2 to 2 hours. In 4M and 1.5M HNO₃, Np(V) reduction by hydrazine was more rapid and complete with a Cu(II) or an Fe(III) ion catalyst.

CONTENTS

Introduction 5

Experimental 5

 Neptunium 5

 Plutonium 6

Results 7

 Neptunium Reduction 7

 Plutonium Reduction 10

Discussion 11

HYDRAZINE REDUCTION OF Np(V) AND Pu(IV)

INTRODUCTION

The recovery and decontamination of neptunium by anion exchange and solvent extraction processes depend principally upon processing neptunium as the (IV) ion. Currently, Np(V), the natural Np valence in most process solutions, is reduced by ferrous sulfamate (FeSA) or FeSA-hydrazine nitrate solution. FeSA is a principal contributor to solids in the waste streams $[\text{Fe}(\text{OH})_3, \text{Na}_2\text{SO}_4]$, and increased corrosion of waste evaporators has been attributed to the sulfate produced by sulfamate decomposition. Thus, there is an economic incentive to reduce or to eliminate FeSA in plant processes.

Similarly, recovery and decontamination of plutonium depend upon control of its valence — Pu(IV) extracts into TBP, and is absorbed on anion exchange resin. In particular, the separation of ^{238}Pu from ^{237}Np in the anion exchange process depends upon the absorption of Np(IV) on the anion resin and the poor absorption of Pu(III). Control of the actinide valences is crucial to the success of this process. Presently, hydrazine nitrate and FeSA are used in control of Np and Pu valences.

FeSA-hydrazine nitrate solutions are normally used at ambient temperatures (ca 28 to 33°C). At these temperatures, hydrazine acts only as a holding reductant, protecting FeSA and other reduced species [Np(IV), Pu(III)] from nitrous acid-catalyzed oxidation. Hydrazine is a strong reducing agent, but high temperatures and metal-ion catalysts are often necessary to achieve acceptable reaction rates. This work explores the use of hydrazine to reduce Np(V) and Np(VI) to Np(IV) and Pu(IV) to Pu(III).

EXPERIMENTAL

Neptunium

Solutions of the approximate concentration of plant neptunium solutions were prepared by mixing stock solutions of 0.83M $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, 0.22M (52.4 g/L) Np(V) in 2M HNO_3 , 10M HNO_3 , 1M $\text{Cu}(\text{NO}_3)_2$ and 2M $\text{Fe}(\text{NO}_3)_3$. The test solutions were heated to 50°C for periods ranging from 1/2 to 3 hours; then, the Np valence.

and amount of each valence were determined by the absorption spectrum from 6000 to 13000 Å with a Cary 14 spectrophotometer. Blank solutions containing all reagents except Np were used as reference.

Determination of the valence from absorption spectra used the absorption maxima and molar absorptivities shown in Table 1.

TABLE 1

Np Valence Determination Spectra*

<u>Np Valence</u>	<u>λ max, Å</u>	<u>ϵ m (M-cm)⁻¹</u>
VI	12,300	40
V	9,800	230
	10,950	14
IV	7,000	50
	9,800	30

* 4M HNO₃ solution.

The molar absorptivities vary somewhat with nitric acid concentration and with the resolution of the spectrophotometer. The values chosen for Np(V) were determined in this work; other values come from recent ORNL work.¹ An older SRL study² showed little variation for the 7000 Å peak of Np(IV) between 1 and 6M HNO₃, but the absolute values of that study were low because of the model spectrophotometer used. Because of the variation of molar absorptivities with nitric acid concentration and the interference between Np(V) and Np(IV) peaks at 9800 Å, small values for Np(V) species have considerable relative uncertainty.

Plutonium

Solutions for study were prepared by mixing a stock solution of Pu(IV) (49.83 g Pu/L, 0.208M) with stock solutions of 10M HNO₃, 0.83M N₂H₄•HNO₃, 1M Cu(NO₃)₂, 2M Fe(NO₃)₃ and 0.5M Na₂MoO₄. The test solutions were treated as described for Np studies, and the Pu valence resulting from the treatment determined spectrophotometrically from the absorbance of Pu(IV) at 4800 Å and Pu(III) at 6000 Å. The molar absorptivities of Pu(IV) and Pu(III) determined in 8M HNO₃ are shown in Table 2.

TABLE 2

Pu Valence Determination Spectra

Pu Valence	λ max, Å	ϵ_m (M-cm) ⁻¹	
		8M HNO ₃	0.2M HClO ₄
IV	4820	47	56
	6015	22	4
III	6015	35	37
	4820	3.5	3

The values determined agree for Pu(III) in 0.2M HClO₄, (Reference 3), and the disagreement for Pu(IV) probably reflects spectral changes caused by strong nitrate complexing of Pu(IV). Corrections for the interference of Pu(IV) with Pu(III) spectra were applied to the data.

RESULTS

Neptunium Reduction

The reaction rate and reaction products of hydrazine oxidation are known^{4,5} to depend upon acid concentration and reaction temperatures. Therefore, experiments were carried out at three different acid strengths, 1.5M HNO₃, 4.16M HNO₃, and 7.92M HNO₃. Experiments in 1.5M HNO₃ are summarized in Table 3.

TABLE 3

Np(V) Reduction in 1.5M HNO₃*

Catalyst	Time, hr	Temp, °C	% Np(V)	% Np(IV)
None	1	70	~100	-
0.008M Cu(II)	1	70	20	80
0.004M Cu(II)	2	50	-	~100
0.008M Fe(III)	2	50	-	~100
0.003M Fe - 0.004M Cu(II)	2	50	-	~100

* Initial solution concentrations: 1.5M HNO₃, 0.10M N₂H₄, and 0.018M Np(V).

These results show that heating and catalytic amounts of either Cu(II) or Fe(III) lead to essentially complete reduction of Np(V) in 1.5M HNO₃.

In 4M HNO₃, the reduction of Np(V) was improved by Fe(III) catalyst, but Cu(II) had no catalytic effect at this acid concentration. The results are shown in Table 4.

TABLE 4

Np(V) Reduction in 4M HNO₃*

Catalyst	Time, hr	Temp, °C	% Np(V)	% Np(IV)
None	2	50	13.5	86
0.003M Fe(III)	1	50	15	85
0.003M Fe(III)	2	50	3.5	96
0.003M Fe(III)	3	50	3.9	96
0.006M Fe(III)	2	50	3.6	96

* Initial solution concentration: 4.16M HNO₃,
0.018M Np(V), 0.10M N₂H₄

The best data indicate 96 to 97% reduction in 2 to 3 hours at 50°C, but uncertainties in the molar absorptivity values are great enough that the reaction may be essentially complete.

Absorption spectra (Figure 1) show that Np(V) disproportionates instantly at room temperature in 8M HNO₃, according to

Assuming the molar absorptivities are the same in 8M HNO₃ as in 4M HNO₃, the solution contained 17% Np(V), 40% Np(IV), and 43% Np(VI). From these data, the approximate equilibrium constant, K, is about 10⁻⁶. The driving force for the disproportionation comes from the fourth power acid dependence on the equilibria, and the nitrate complexing of Np⁴⁺, both of which act to shift the equilibrium to the right. Reduction of Np(V) and Np(VI) in 8M HNO₃ took place in 30 minutes at 50°C, without a metal ion catalyst. Experimental results are summarized in Table 5.

FIGURE 1. Absorption Spectra of Np(V) in 1M HNO₃ and 8M HNO₃.

TABLE 5

Np(V)-Np(VI) Reduction in 8M HNO₃*

<u>N₂H₄ Conc, M</u>	<u>Time, hr</u>	<u>Temp, °C</u>	<u>% Np(IV)</u>	<u>% Np(V)</u>
0.10	1/2	50	~100	-
0.10	1	50	~100	-
0.10	1.5	50	~100	-
0	1/3	25	40	17
0	2	25	40	17
0	2	50	40	17
0.10	2	50	~100	-
0.10**	2	50	~100	-
0.01	2	50	~100	-
0.0033	1/2	50	73	7

* Initial solution concentration: 7.92M HNO₃, 0.018M Np.

** 0.003M Fe(III) added.

Assuming complete oxidation of hydrazine in the last experiment of Table 5, two moles of Np(V) [as a mixture of Np(IV), Np(V), and Np(VI)] were reduced per mole of hydrazine.

Plutonium Reduction

Plutonium reduction was investigated only in 8M HNO₃, the acid concentration for Pu(IV)-Np(IV) absorption for anion exchange processing. All tests were run at 50°C, since the above results showed complete reduction of Np(V) in 30 minutes. The aim of these tests was to develop a procedure that would permit reduction of Pu(IV) to Pu(III) under the same conditions.

The results of the tests are shown in Table 6. Pu(IV) was completely reduced in one hour by 0.12M N₂H₄•HNO₃ with 0.017M Cu(-II) as a catalyst. Fe(III) and Mo(VI) showed no catalytic effect; hydrazine alone reduced Pu(IV) slowly, about 60% in two hours at 50°C.

TABLE 6

Reduction of Pu(IV) by Hydrazine in 8M HNO₃ at 50°C*

Catalyst	Time, hr	% Pu(III)
-	-	0
-	1/2	32
-	1	62
-	2	68
0.0166M Cu(II)	1/2	70
0.0166M Cu(II)	1	100
0.0166M Cu(II)	1-1/2	100
0.0083M Cu(II)	1/2	46
0.0083M Cu(II)	1	77
0.0083M Cu(II)	1-1/2	100
0.0083M Cu(II)	2	100
0.0033M Fe(III)	1/2	58
0.0033M Fe(III)	1	58
0.0033M Fe(III)	2	57
0.004M Na ₂ MoO ₄	2	58

* Initial solution concentration: 7.92 M HNO₃, 0.010M Pu(IV)

DISCUSSION

These data can be applied to a valence adjustment for the anion exchange coabsorption of ²³⁸Pu and ²³⁷Np. In 8M HNO₃, 0.12M N₂H₄•HNO₃ at 50°C will reduce Np(V) completely to Np(IV), and about 30 to 35% of the Pu(IV) will reduce to Pu(III) in 30 minutes. Since the absorption of Pu(IV) by anion exchange resin shifts the Pu(IV)-Pu(III) equilibrium rapidly, it is expected that both Np and Pu would be essentially completely absorbed by the anion resin from this solution.

Reduction by hydrazine with Cu(II) catalyst produces an Np(IV)-Pu(III) solution that can be the feed for an anion exchange separation of ²³⁸Pu from ²³⁷Np. Hydrazine reduces Np(V) to Np(IV) in 30 minutes at 50°C and with the addition of 0.016M Cu(II) as a catalyst, Pu(IV) is reduced to Pu(III) in one hour. Thus, hydrazine nitrate can be used for the reductant for anion exchange partitioning, reducing the use of FeSA to partition-washing only. Ascorbic acid use could be eliminated entirely.

Hydrazine catalyzed by Fe(III) has a potential use in the reduction of Np(V) for solvent extraction processing with 4M HNO₃, again reducing the use of FeSA for feed adjustment. However, the use of FeSA in the scrub solution would still be necessary, since at ambient temperature (~28 to 33°C), reduction by hydrazine is too slow to prevent the loss of Np(V).

The spectrophotometric study of the reduction of Np(V) in 8M HNO₃ at 50°C showed the reduction to be 3 to 4 times more rapid than reduction in 4M HNO₃, and two moles of Np(V) were reduced per mole of N₂H₄ oxidized. In 5M HClO₄ at 90°C⁶, one mole of Np(V) was reduced per mole of N₂H₄. However, in 8M HNO₃, the Np(V) added very rapidly disproportionates to a mixture of 40% Np(IV), 17% Np(V), and 43% Np(VI), and the reduction of Np(V)-Np(VI) can take place by three different routes: (a) the one-electron reduction of Np(VI) to Np(V), followed by a one-electron reduction of Np(V) to Np(IV), as (acid hydrogens omitted)

or (b) reduction of Np(VI) to Np(V), as in reaction (1), followed by disproportionation of Np(V) to Np(VI) and Np(IV) (p.8); or (c) a two-electron reduction of Np(VI) to Np(IV),

with the disproportionation of Np(V) producing more Np(VI) as the reaction continues. Reaction sequences (a) and (b) reduce one mole of the "average" Np(V) per mole of hydrazine; reaction sequence (c) reduces two moles of "average" Np(V) per mole of hydrazine. From the experimental stoichiometry, it is inferred that the major part of the reduction of Np(V) in 8M HNO₃ actually proceeds via reaction sequence (c), the direct two-electron reduction of Np(VI) to Np(IV) by hydrazine. Further evidence is that reaction (2) in 1.5M or 4M HNO₃ is slower, even with a metal catalyst, than the reaction in 8M HNO₃, indicating that the reaction in 8M HNO₃ takes place through a different mechanism.

The reduction of Pu(IV) by hydrazine has been previously studied in 1.9M HNO₃ and 50°C.⁷ The reduction had a half-time of about 40 minutes, which agreed with a 40- to 50-minute half-time for the uncatalyzed reduction in this work. In later work,⁸ it was found that 4 x 10⁻³M Mo(VI) as a catalyst increased the reaction rate by a factor of four. An unavailable Russian treatise⁹ is quoted on catalysis by Fe(III), probably in ~2M HNO₃. This work showed no appreciable catalysis by either Mo(VI) or Fe(III) in 8M HNO₃. Pu(IV) is present in 8M HNO₃ as a nitrate complex ion, so the difference in the behavior of the reaction is not unexpected.

In conclusion, this work has shown several procedures for reduction of Np(V) and Pu(IV) that appear to be applicable to separations processes. Confirmatory anion exchange and solvent extraction experiments on process solutions will be conducted. If successful, plant application of these techniques will be recommended.

REFERENCES

1. H.A. Friedman and L.M. Toth. J. Inorg. Nucl. Chem. 42, 1347 (1980).
2. E. K. Dukes and W. E. Shuler. Spectrophotometric Determination of Mixtures of Neptunium(IV) and Neptunium(V) in Nitric Acid Solutions. USAEC Report DP-543, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (1960).
3. D. Cohen. J. Inorg. Nucl. Chem. 18, 211 (1961).
4. R. E. Kirk and A. W. Browne. J. Am. Chem. Soc. 50, 337 (1928).
5. W. C. Bray and E. J. Cuy. J. Am. Chem. Soc. 46, 858 (1924); 46, 1786 (1924).
6. V. S. Koltunov and M. F. Tikhonov. Radiokhimiya 15, 789 (1973); 17 560 (1975).
7. V. S. Koltunov and G. I. Zhuravieva. Radiokhimiya 16, 84 (1974).
8. V. S. Koltunov and G. I. Zhuravieva. Radiokhimiya 22, 57 (1980).
9. V. S. Koltunov. Reaction Kinetics of the Actinides (in Russian) p. 228, Atomizdat: Moscow, USSR (1974).