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SOLVENT EXTRACTION OF IRRADIATED NEPTUNIUM TARGETS.
I. VALENCE STABILIZATION

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ABSTRACT

Solvent extraction of ^{237}Np and ^{238}Pu from irradiated neptunium is being investigated as a possible replacement for the currently used anion exchange process at the Savannah River Plant. Solvent extraction would reduce separations costs and waste volume and increase the production rate. The major difficulty in solvent extraction processing is maintaining neptunium and plutonium in the extractable IV or VI valence states during initial extraction. This study investigated the stability of these states. Results show that:

- The extractable M(IV) valence states of neptunium and plutonium are mutually unstable in plant dissolver solution (2 g/l ^{237}Np, 0.4 g/l ^{238}Pu, 1.2M Al^{3+}, 4.6M NO_3^-, and 1M H^+)
- The reaction rates producing inextractable species from extractable M(IV) or M(VI) are fast enough that ≥99.9% extractable species in ^{237}Np-^{238}Pu mixtures cannot be maintained for a practicable processing period (24 hours).

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SOLVENT EXTRACTION OF IRRADIATED NEPTUNIUM TARGETS. I. VALENCE STABILIZATION

INTRODUCTION

Studies are in progress at the Savannah River Laboratory to design a tributyl phosphate (TBP) solvent extraction flowsheet for the recovery, decontamination, and partitioning of ^{237}Np and ^{238}Pu. Replacing anion exchange processing by solvent extraction would lower cost by 75%, reduce waste volume by 65%, and increase the overall production rate by 25%. However, stabilization of extractable M(IV) and M(VI) species is difficult because of the high specific activity of ^{238}Pu and the stability of inextractable Np(V) in this solution (Composition: 2 g/l ^{237}Np, 0.4 g/l ^{238}Pu, 1.2M Al^{3+}, 4.6M NO_3^-, and 1M H^+). Two studies were undertaken to find means of adjusting neptunium and plutonium simultaneously to extractable M(IV) or M(VI) valence states:

- Nitrite-scavenging compounds were tested for their effect in inhibiting the action of this radiolysis product on actinide valence.

- The thermodynamic stabilities of the valence states were calculated from available data.

RESULTS AND DISCUSSION

The valences of both neptunium and plutonium must be controlled for extraction with TBP. The extractability of neptunium and plutonium valence states into TBP decreases in the order: $Pu(IV) > Np(VI) > Np(IV) \approx Pu(VI) >> Np(V) \approx Pu(III)$. Because of their low distribution coefficients, Np(V) and Pu(III) are considered inextractable.

Maintaining neptunium and plutonium in extractable valences is necessary to separate both species from fission products. This is difficult for two reasons. First, the intense alpha radiation from ^{238}Pu decomposes water and HNO_3 into products that can oxidize or reduce neptunium and plutonium ions. Second, the most stable neptunium valence in solutions of the expected composition is the inextractable Np(V) state.

Alpha Radiolysis Effects

Alpha radiation decomposes H_2O into free radicals and molecules:[1]

$$H_2O \rightarrow H,\ OH,\ H_2,\ H_2O_2 \qquad (1)$$

The molecular products H_2 and H_2O_2 predominate. The subsequent reactions shown in Reactions 2-5 may alter the relative amounts of these species:

$$H + H \rightarrow H_2 \qquad (2)$$

$$OH + OH \rightarrow H_2O_2 \qquad (3)$$

$$OH + H_2 \rightarrow H + H_2O \qquad (4)$$

$$H + H_2O_2 \rightarrow OH + H_2O \qquad (5)$$

If nitric acid is present, Reactions 6-8 can also occur, as well as the direct radiolytic decomposition of nitrate ion and undissociated nitric acid (Reactions 9 and 10):[2]

$$H + NO_3^- \rightarrow NO_2 + OH^- \qquad (6)$$

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \qquad (7)$$

$$OH + NO_2^- \rightarrow NO_2 + OH^- \qquad (8)$$

$$NO_3^- \xrightarrow{\alpha} NO_2^- + O \qquad (9)$$

$$HNO_3 \xrightarrow{\alpha} NO_2 + OH \qquad (10)$$

Molecular oxygen can result from the combination of oxygen atoms:

$$O + O \rightarrow O_2 \qquad (11)$$

The reactions of ions and radicals formed by radiolysis are complex functions of the concentration of species formed, the concentration of other ions present, and reaction rates. In general for alpha radiation, radical recombination reactions predominate. The final products include nitrite ions, hydrogen peroxide, hydrogen, and oxygen.[3]

The yield of H_2, formed by Reactions 1 and 2, can be decreased by Reaction 4. In addition, when NO_3^- is present, H atoms are rapidly scavenged by Reaction 6. Therefore, H_2 yields decrease as HNO_3

concentration increases. Oxygen yields increase with nitrate concentration, but the presence of either H_2 or O_2 in the solution does not effect valence adjustment or stabilization. Oxygen is already present in solutions exposed to air.

Peroxide can react with either neptunium or plutonium to cause valence changes. However, H_2O_2 reacts with HNO_2 in acidic media and will not accumulate in alpha-irradiated solutions containing >0.5M HNO_3.[4]

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \qquad (12)$$

The initial product in the reaction of HNO_2 with H_2O_2 is pernitrous acid (HO_2NO), which can last for 2 to 3 seconds before rearranging to give HNO_3.[5] Therefore, the pernitrous acid or the radicals[5] and ions[6] that form during rearrangement may react with neptunium or plutonium. Of nitrous acid and hydrogen peroxide, only the compound in excess will accumulate in the solution.

Nitrous acid production increases with nitric acid concentration, and nitrous acid destroys hydrogen peroxide. Therefore, nitrous acid was assumed to be the principal molecular species available for oxidation-reduction reactions. Nitrite reacts with plutonium according to the following reactions:

$$Pu^{3+} + HNO_2 + H^+ \rightarrow Pu^{4+} + NO + H_2O \qquad (13)$$

$$PuO_2^{2+} + HNO_2 + H^+ \rightarrow Pu^{4+} + NO_3^- + H_2O \qquad (14)$$

The reduction of Np(VI) and oxidation of Np(IV) may be written as

$$2NpO_2^{2+} + HNO_2 + H_2O \rightarrow 2NpO_2^+ + 3H^+ + NO_3^- \qquad (15)$$

$$Np^{4+} + HNO_2 + H_2O \rightarrow NpO_2^+ + NO + 3H^+ \qquad (16)$$

Reactions 13 and 16 are autocatalytic because the nitric oxide formed during the oxidation produces nitrous acid:[7]

$$2NO + H_2O + HNO_3 \rightleftarrows 3HONO \qquad (17)$$

To suppress undesired oxidation and reduction reactions with nitrous acid, nitrite scavengers are added. The function of a scavenger is to react with nitrous acid as it is formed so that it does not react with neptunium or plutonium. Nitrous acid combines with amino and imino groups.[8] The course of the reaction depends on the concentrations of the reactants and on the temperature.[9] If rapid reactions occur and the scavengers are completely destroyed, the overall reactions are:[8]

Amino group $R\text{-}NH_2 + HONO \rightarrow R\text{-}NHNO + H_2O \rightarrow R\text{-}OH + N_2 + H_2O$ (18)

Imino group $R{=}NH + HONO \rightarrow R{=}N\text{-}NO + H_2O$ (19)

Sulfamic acid and aminoguanidine salts are examples of compounds with amino and imino groups that react rapidly and completely with HNO_2, yielding either soluble products or gases.[8,10]

Sulfamic acid $NH_2SO_3H + HONO \rightarrow H_2SO_4 + H_2O + N_2$ (20)

Aminoguanidine $NH_2\text{-}C{=}(NH)NHNH_2 + 4HONO \rightarrow 5H_2O + 4N_2 + CO_2$ (21)

Stabilization of Np(VI)-Pu(VI)

Compounds containing both amino and imino groups were tested for nitrite-scavenging ability. Preliminary tests with solutions containing only Pu(VI) showed that this species was actually destabilized by addition of the agents (Table 1). $^{238}PuO_2^{2+}$ in dilute HNO_3 solutions has been reported to be stable for days;[11] apparently, the addition of other compounds makes possible the radiolytic production of reducing ions and molecules. The distribution coefficient* expected for Np(VI) between 7.5 vol % TBP and 4M HNO_3 is 2.4, on the basis of data with 30 vol % TBP.[12] Aminoguanidine and m-nitroacetanilide produced inextractable species with distribution coefficients characteristic of Np(V). Table 2 shows that urea and sulfamic acid stabilize Np(VI) in 4M HNO_3 without ^{238}Pu present.

Batch extraction of Np(VI) and Pu(VI) from simulated dissolver solution adjusted with MnO_2 gave the results in Table 3. No published results are available on the distribution of Np(VI) and Pu(VI) between 7.5 vol % TBP and solutions of these concentrations. Our data show average distribution coefficients for Np(VI) and Pu(VI) of 17 and 5.1, respectively. The low distribution coefficients for both neptunium and plutonium at time zero show that aminoguanidine, succinic acid dihydrazide, 2-furoic acid hydrazide, and methyl hydrazine act as reducing agents. All four of these compounds are derivatives of hydrazine, a well-known reducing agent. Most plutonium distribution coefficients did not change drastically except when Pu(III) was formed. However, it is not possible to conclude that Pu(VI) was stabilized because

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* The distribution coefficient is the organic/aqueous concentration ratio at equilibrium.

TABLE 1

Oxidation States of Plutonium in Solutions[a] Containing NO_2^- Scavenging Agents

Scavenger	*Time, hr*[b]	*Amount, %*		
		Pu(III)[c]	*Pu(VI)*	*Pu(IV)*
None	0	0.2-0.5[d]	$\geq$99.5	$<$0.05
	6	0.2-0.5[d]	$\geq$99.5	$<$0.05
	24	1.0	97.4	1.6
	120	0.9	75.1	24.0
Sulfamic acid	0	0.2-0.5[d]	$\geq$99.5	$<$0.05
	6	1.0	85.6	13.4
	24	3.0	51.9	45.1
	120	40.5	$<$0.05	59.5
Urea	0	0.2-0.5[d]	$\geq$99.5	$<$0.05
	6	2.7	97.3	$<$0.05
	24	2.2	95.7	2.1
	120	50	46.1	3.9

---

a. Solution: 0.4 g/l ^{238}Pu, 1.2M Al^{3+}, 4.6M NO_3^-, 1M H^+, 0.05M scavenger.

b. From valence adjustment and addition of scavenger to introduction of sample to column.

c. Includes other inextractable forms, such as sulfate complexes.

d. Minimum amount of inextractable species detected.

TABLE 2

Effect of NO_2^- Scavenging Agents on Extraction of Np(VI) by 7.5 vol % TBP from 4M HNO_3

Scavenger	*Neptunium Distribution Coefficient*[a]
None	1.30 ±0.16
Sulfamic acid	1.83 ±0.13
m-Nitroacetanilide	0.16 ±0.01
Urea	2.16 ±0.05
Aminoguanidine sulfate	0.05 ±0.01

---

a. Measured 16-18 hours after valence adjustment; average of duplicate analyses.

its reduction to Pu(IV) would produce an even more extractable species. The high plutonium distribution coefficient with sulfanilamide at 0 hours is probably due to such reduction. Sulfanilamide also reduces Np(VI) to Np(V), as indicated by the small distribution coefficient at 0 hours.

Although sulfamic acid and urea were effective in stabilizing Np(VI) in 4M HNO_3, neither was able to stabilize neptunium for 24 hours with ^{238}Pu present.

TABLE 3

Effect of NO_2^- Scavenging Agents on Extraction of Np(VI) and Pu(VI) by 7.5 vol % TBP from Simulated Dissolver Solution[a]

	Distribution Coefficient							
	Neptunium				*Plutonium*			
Scavenger[b]	*0 hr*	*24 hr*	*96 hr*	*120 hr*	*0 hr*	*24 hr*	*96 hr*	*120 hr*
Sulfamic Acid	19	0.95	0.16	0.14	4.6	6.5	8.5	6.1
Urea	17	1.4	0.56	0.64	5.1	5.3	6.0	5.2
Sulfamic acid - urea[c]	16	0.67	0.06	0.15	5.2	6.0	7.8	7.0
Aminoguanidine	0.03	0.32	1.6	0.20	2.8	1.4	1.2	1.5
Dimethyl formamide	14	0.08	0.10	0.14	4.2	3.4	5.9	5.9
Ammonium nitrate	17	0.45	0.11	0.12	5.2	4.4	6.0	6.2
Acetamide	16	0.56	0.10	0.12	4.8	5.6	5.4	5.8
Succinic acid dihydrazide	1.4	0.27	1.4	1.7	3.7	2.4	1.5	1.9
Sulfanilamide	0.13	0.82	1.4	1.8	6.9	4.2	1.5	2.2
2-Furoic acid hydrazide	0.04	1.2	2.5	2.3	3.3	0.34	0.23	1.7
Methylurea	16	0.70	0.09	0.10	4.8	4.8	5.2	6.5
Methylhydrazine	2.6	0.24	1.1	0.64	3.4	1.9	1.2	1.2
Control	17	0.33	0.10	0.14	4.5	5.0	5.0	5.9

---

a. Solution: 2 g/l ^{237}Np, 0.4 g/l ^{238}Pu, 1.2M Al^{3+}, 4.6M NO_3^-, 1M H^+.

b. 0.05M in dissolver solution.

c. 0.025M in each.

Stabilization of Np(IV)-Pu(IV)

Table 4 shows the results of batch extraction tests on Np(IV) and Pu(IV) individually; Np(IV) was obtained by reduction of Np(V) with ferrous sulfamate (FeSA), Pu(IV) by reduction to Pu(III) with FeSA and then oxidation to Pu(IV) with NO_2^-. The resultant initial distribution coefficient for neptunium without NO_2^- scavenger (3.6) agrees with the value obtained (3.5) by extrapolation from systems with 2 to 3.6 vol % TBP and 1.2M Al^{3+} in 0 to 0.5M HNO_3.[13] But the initial distribution coefficient for plutonium without NO_2^- scavenger (18) is lower than that estimated from published data (28).[14] Sulfamic acid, aminoguanidine nitrate, and urea tend to stabilize Np(IV) but destabilize Pu(IV); aminoguanidine nitrate, in particular, appears to reduce Pu(IV) to Pu(III). Russell and Tober[15] have shown that aminoguanidine reduces Fe^{3+} to Fe^{2+} but does not directly reduce Pu(IV) to Pu(III). Therefore, a possible mechanism for Pu(IV) reduction includes reduction of Fe^{3+} (present from FeSA valence adjustment) by aminoguanidine followed by reaction of Fe^{2+} with Pu(IV). Without a NO_2^- scavenger, Np(IV) is oxidized to inextractable Np(V) in HNO_3 solution.

Additional batch extraction tests were made on simulated dissolver solutions containing both neptunium and plutonium adjusted to Np(IV)-Pu(IV) in 0.05M NO_2^- scavengers (similar to tests for Np(VI)-Pu(VI) shown in Table 3). The distribution coefficients ranged from 1.3 to 2.2 for neptunium* and 1.6 to 6.6 for plutonium.** These values show that neither neptunium nor plutonium was completely in the M(IV) state.

TABLE 4

Effect of NO_2^- Scavenging Agents on Extraction of Np(IV) and Pu(IV) by 7.5 vol % TBP from Simulated Dissolver Solution[a]

	Distribution Coefficient							
	Neptunium				*Plutonium*			
Scavenger	*0 hr*	*24 hr*	*96 hr*	*120 hr*	*0 hr*	*24 hr*	*96 hr*	*120 hr*
None	3.6	1.1	0.27	0.26	18	19	18	19
Sulfamic acid	3.3	2.9	2.6	2.9	16	14	13	9.6
Urea	2.8	2.1	2.0	1.6	16	14	13	12
Aminoguanidine nitrate	3.0	2.6	3.0	2.6	8.7	3.1	18	14

[a] Solution: 2 g/l ^{237}Np, 0.4 g/l ^{238}Pu, 1.2M Al^{3+}, 4.6M NO_3^-, 1M H^+, 0.05M scavenger.

The valence adjustment of neptunium and plutonium to Np(IV)-Pu(IV) was studied potentiometrically. Figure 1 shows the potentiometric curve obtained when a simulated dissolver solution is adjusted with FeSA and titrated with NO_2^-. When sulfamate ion has been destroyed by NO_2^-, Fe^{2+} is autocatalytically oxidized to Fe^{3+}, and Pu(III) is oxidized to Pu(IV); additional NO_2^- oxidizes Np(IV) to Np(V). Although analyses varied by 2 to 3%, they show

---

* 3.5 is expected for Np(IV).

** Values between 18 and 28 are expected for Pu(IV).

that Np(IV) and Pu(IV) do not coexist in this system in the presence of free NO_2^- concentrations. However, the solution potential increases by 400 millivolts during Fe(II) and Pu(III) oxidation. This increase suggests the possibility of using another couple to maintain the potential at which Np(IV) and Pu(IV) coexist. No couple was identified for testing in this potential range. Calculations show solutions 0.05M in scavenging agent should be sufficient to react with radiolytically produced nitrite for 17 to 70 days. Because the solutions are stable for <24 hours, reaction with nitrite is not the only factor involved. Other radiolysis products are presumably effective in adjusting valences of neptunium and plutonium.

Hydrogen peroxide is produced in good yield by radiolysis and in the absence of nitrous acid can presumably react with the actinides. Peroxide rapidly reduces Np(VI) to Np(V), but reduces Np(V) to Np(IV) very slowly in 1M HNO_3.[16] Its reaction with plutonium is rapid and complex, reducing Pu(VI) but giving mixtures of Pu(III) and Pu(IV) by means of two competing reactions.[17] No reagent is known that will react to remove peroxide without affecting neptunium and plutonium valences. Peroxide reactions probably suffice to explain the observed behavior of Np-Pu solutions, although other products of radiolysis may also be involved; any process for separating neptunium and plutonium must allow for this effect.

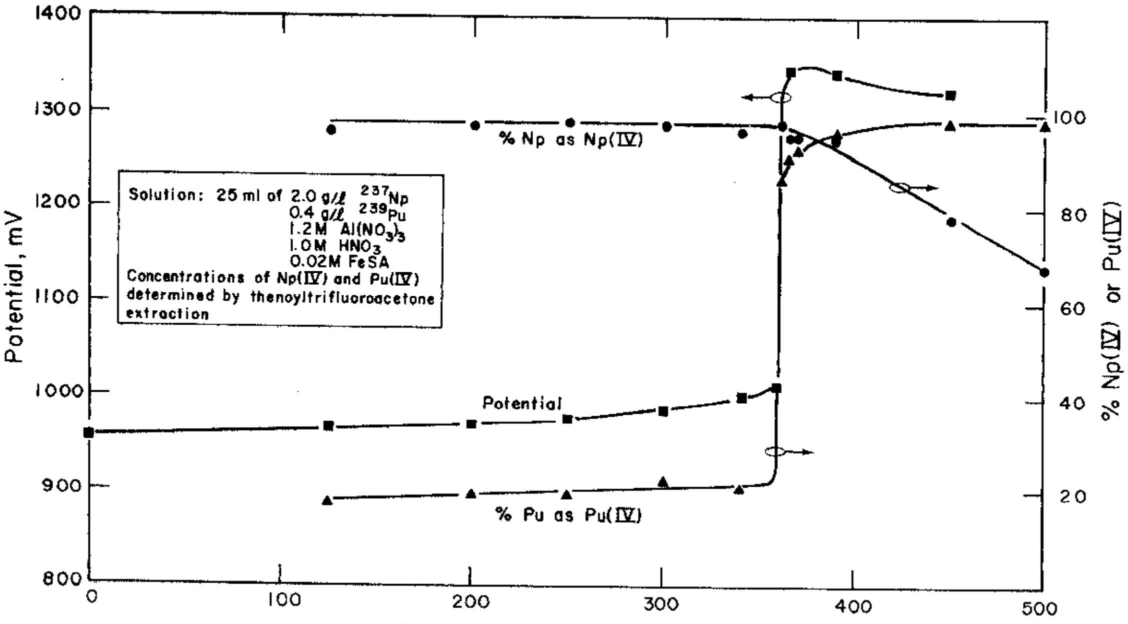

FIGURE 1. Potentiometric Titration of Pu(III) and Np(IV) with Nitrite

Thermodynamic Calculations for the Np-Pu System

Because of the experimental difficulties encountered in preparing stable Np(IV)-Pu(IV) solutions, thermodynamic calculations were made to determine whether Np(IV) and Pu(IV) can coexist at equilibrium in solution at the nitric acid and nitrate concentrations used in our tests. One report indicated that these species can react under some conditions to form Pu(III) and Np(V).[18]

The fractions ($F_{M(IV)}$) of Np(IV) and Pu(IV) present at equilibrium may be expressed as follows:

$$F_{Np(IV)} = \frac{1}{1 + \frac{Np(V)}{Np(IV)} + \frac{Np(VI)}{Np(IV)}} \qquad (22)$$

and

$$F_{Pu(IV)} = \frac{\frac{Pu(IV)}{Pu(III)}}{1 + \frac{Pu(IV)}{Pu(III)} + \frac{Pu(V)}{Pu(III)} + \frac{Pu(VI)}{Pu(III)}} \qquad (23)$$

No oxidation states other than those shown are assumed to be present. The quantity M(N) is assumed to include all ions of element M with valence N, whether complexed or not. Expressions required to calculate the ratios in Equations 22 and 23 are derived in the appendix.

The fractions of Np(IV) and Pu(IV) in 1M HNO_3 - 4.6M total nitrate and 2.5M HNO_3 - 6.1M total nitrate were calculated at potentials from 0.6 to 1.3 volts (Figure 2). These calculations show that 80 to 90% of both Np(IV) and Pu(IV) exist at equilibrium at 0.88 volt and nitrate concentration of 4.6M. Increasing the nitrate concentration to 6.1M by adding acid greatly increases Np(IV) stability because oxidation of Np(IV) is inversely dependent on the fourth power of the hydrogen ion concentration. The neptunium and plutonium curves overlap at ∿0.96 volt, and at equilibrium 99% of each is Np(IV) and Pu(IV). Increasing the nitrate further would ensure greater overlap of Np(IV) and Pu(IV), but the solution would be undesirable for solvent extraction. This acidity would cause extraction of fission products and lower decontamination factors for the product solutions. Also, electrochemical couples from 0.95 to 1.0 volt, which could stabilize the solution potential, were not identified for testing.

Similar calculations for Np(VI) and Pu(VI) show that in this system a potential of 1.21 volts is required to maintain >99% Np(VI) and Pu(VI). Electrochemical couples in this range oxidize fission product ruthenium to volatile RuO_4 and may cause corrosion problems.

The thermodynamic calculations and tests show that the Np(IV)-Pu(IV) and Np(VI)-Pu(VI) systems are unstable for solution concentrations practical for solvent extraction. Products of radiolysis provide a mechanism for oxidation of Np(IV) and reduction of Np(VI) and Pu(VI). Extraction experiments show that the reaction rates of destabilizing reactions are fast enough that the systems cannot be stabilized for a practicable time for plant processing.

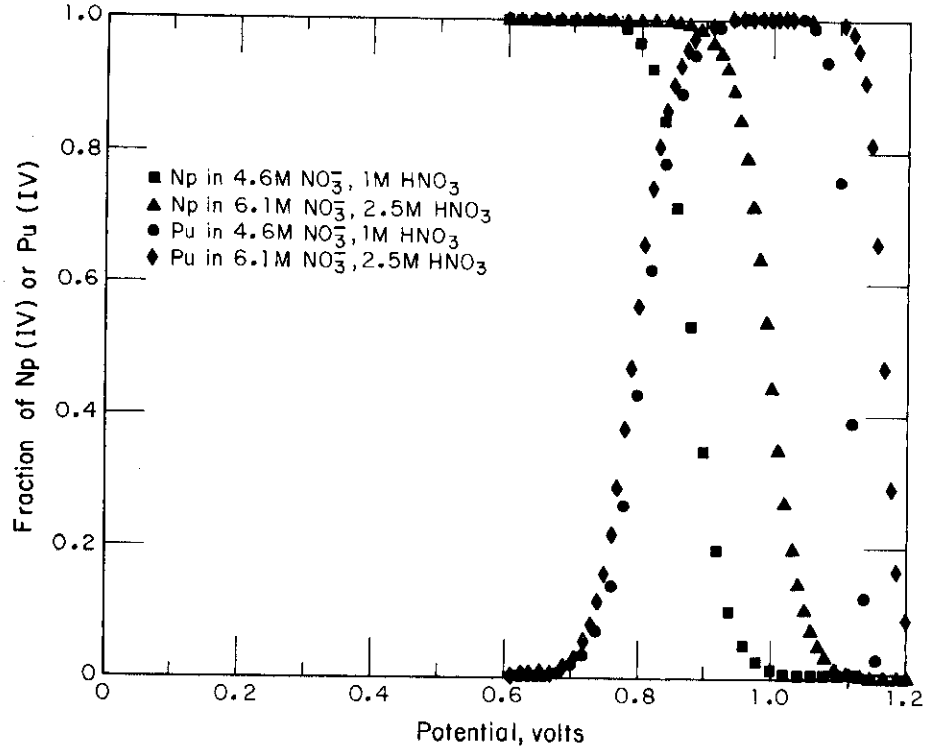

FIGURE 2. Fraction of Np(IV) or Pu(IV) in Nitrate Solutions at Thermodynamic Equilibrium

EXPERIMENTAL DETAILS

Neptunium and plutonium were adjusted to the tetravalent state with ferrous sulfamate followed by sodium nitrite. Oxidation to the hexavalent state was accomplished by reaction with MnO_2.

Column Tests

To identify actinide valences, Pu(III), (IV), and (VI) or Np(IV), (V), and (VI) were separated on a column by reversed-phase partition chromatography. Tri-n-octyl phosphate (TOP) was the stationary phase, and nitric acid was the mobile phase. A 0.28-cm-diameter column was filled to a height of 8 cm with 200-325 mesh porous glass containing 0.5 g TOP/g glass.[19] The column was conditioned with 1.0-1.5M HNO_3. Feed to the column was 1 μl of a 0.4 g/l Pu solution or 10 μl of a 2 g/l Np solution. Plutonium or neptunium was eluted at 23°C with 1.0 and 1.5M HNO_3 pre-equilibrated with TOP; flow was 0.34 ml/(min)(cm^2). Eluate fractions were analyzed by alpha counting. A typical elution of plutonium is shown in Figure 3. A similar curve is obtained with neptunium.

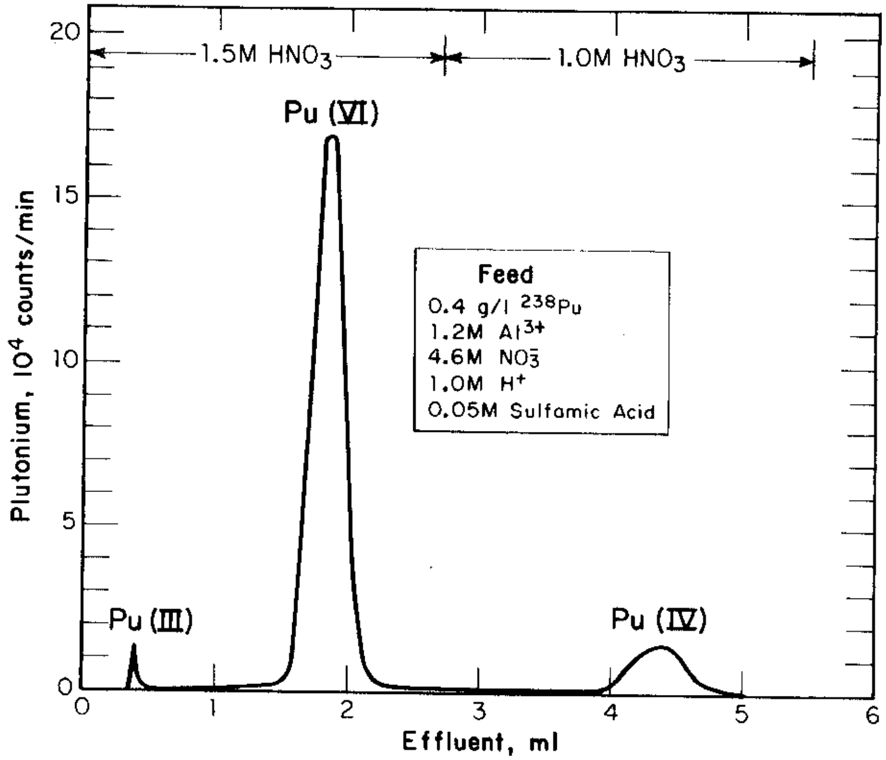

FIGURE 3. Determination of Plutonium Valence States by Reversed-Phase Partition Chromatography

The effectiveness of sulfamic acid or urea in stabilizing Pu(VI) was determined with a solution containing 0.4 g/l ^{238}Pu. Plutonium was oxidized by MnO_2 and filtered into a vial containing NO_2^- scavenging agent. After the desired time period (0 to 120 hours after valence adjustment), 1 μl of solution was pipetted to the top of the bed and eluted as described. The percentages of Pu(III), Pu(VI), and Pu(IV) were determined by graphical analysis of elution data.

Batch Extraction Tests

The TOP column method cannot be used for mixtures of ^{238}Pu-^{237}Np because peak overlap occurs, and the much higher specific activity of ^{238}Pu precludes simple determination of ^{237}Np. Thus, this method was replaced by the following equilibration technique. Solutions of neptunium oxidized with MnO_2 were added to 3 ml portions of 4M HNO_3 containing 0.05M NO_2^- scavenging agent and were stored overnight (16-18 hours). Scavengers tested were sulfamic acid, m-nitroacetanilide, urea, and aminoguanidine sulfate. An equal volume of 7.5 vol % TBP was added, and the phases were equilibrated at 25 ±0.1°C by shaking in a constant temperature bath for 2 hours, separated, and analyzed for neptunium (Table 2). Additional tests were made on simulated feed solution by precipitating MnO_2 in situ to give Np(VI) and Pu(VI), filtering, and pipetting 20-ml aliquots into vials containing candidate NO_2^- scavengers. After standing for the desired time (0 to 120 hours), samples were extracted with 7.5 vol % TBP and analyzed for neptunium and plutonium.

To obtain Np(IV) and Pu(IV), FeSA was added to solutions of neptunium or plutonium to give Np(IV) and Pu(III). Plutonium was then oxidized to Pu(IV) with nitrite. Nitrite scavengers were added to 0.05M. After storage for 0 to 120 hours, aliquots were extracted and analyzed for neptunium or plutonium.

Potentiometric Study of Np(IV)-Pu(IV) System

For potentiometric measurements, a solution of 2 g/l ^{237}Np plus 0.4 g/l ^{239}Pu (stand-in for ^{238}Pu) in 1.2M $Al(NO_3)_3$ and 1.0M HNO_3 was adjusted to 0.02M FeSA and titrated with 2.84M $NaNO_2$. A platinum combination electrode filled with AgCl-saturated KCl solution was used to monitor the titration. Concentrations of Np(IV) and Pu(IV) were determined during titration by extraction of aliquots with thenoyltrifluoroacetone.

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APPENDIX – CALCULATION OF FRACTIONS OF M(N) AT EQUILIBRIUM

The fractions $F_{M(IV)}$ of Np(IV) and Pu(IV) present at equilibrium may be expressed as follows:

$$F_{Np(IV)} = \frac{1}{1 + \frac{Np(V)}{Np(IV)} + \frac{Np(VI)}{Np(IV)}} \tag{A-1}$$

and

$$F_{Pu(IV)} = \frac{\frac{Pu(VI)}{Pu(III)}}{1 + \frac{Pu(IV)}{Pu(III)} + \frac{Pu(V)}{Pu(III)} + \frac{Pu(VI)}{Pu(III)}} \tag{A-2}$$

No oxidation states other than those shown are assumed to be present. The quantity M(N) includes all ions of element M with valence N, whether complexed or not. In nitrate medium, various nitrate complexes are formed so that for trivalent plutonium, for example,

$$Pu(III) = [Pu^{3+}] + [Pu(NO_3)^{2+}] \ldots + [Pu(NO_3)_N^{3-N}] \tag{A-3}$$

If

$$[Pu(NO_3)_N^{3-N}] = \beta_N\ [Pu^{3+}]\ [NO_3^-]^N \tag{A-4}$$

where β_N is the overall stability constant, and Equation A-4 is substituted in Equation A-3, then

$$Pu(III) = [Pu^{3+}]\ (1 + \sum_{i=1}^{N} \beta_i\ [NO_3^-]^i) \tag{A-5}$$

If

$$1 + \sum_{i=1}^{N} \beta_i\ [NO_3^-]^i = g \tag{A-6}$$

Then

$$Pu(III) = [Pu^{3+}]\, g_{Pu(III)} \tag{A-7}$$

Expressions similar to Equation A-7 can be derived for the other valence states. Division of the expression of each valence by Equation A-7 gives

$$\frac{Pu(IV)}{Pu(III)} = \frac{[Pu^{4+}]}{[Pu^{3+}]} \frac{g_{Pu(IV)}}{g_{Pu(III)}} \tag{A-8}$$

$$\frac{Pu(V)}{Pu(III)} = \frac{[PuO_2^+]}{[Pu^{3+}]} \frac{g_{Pu(V)}}{g_{Pu(III)}} \tag{A-9}$$

$$\frac{Pu(VI)}{Pu(III)} = \frac{[PuO_2^{2+}]}{[Pu^{3+}]} \frac{g_{Pu(VI)}}{g_{Pu(III)}} \tag{A-10}$$

The ratios of activities of the free metal ions can be obtained from the Nernst equations for the following reactions:

$$Pu^{3+} \rightarrow Pu^{4+} + e^- \tag{A-11}$$

$$Pu^{3+} + 2H_2O \rightarrow PuO_2^+ + 4H^+ + 2e^- \tag{A-12}$$

$$Pu^{3+} + 2H_2O \rightarrow PuO_2^{2+} + 4H^+ + 3e^- \tag{A-13}$$

Rearrangement of the Nernst equations for Reactions A-11, A-12, and A-13 gives

$$\frac{[Pu^{4+}]}{[Pu^{3+}]} = e^{\frac{F}{RT}(E-E_{34})} \tag{A-14}$$

$$\frac{[PuO_2^+]}{[Pu^{3+}]} = \frac{a_w^2}{[H^+]^4} e^{\frac{2F}{RT}(E-E_{35})} \tag{A-15}$$

$$\frac{[PuO_2^{2+}]}{[Pu^{3+}]} = \frac{a_w^2}{[H^+]^4} e^{\frac{3F}{RT}(E-E_{36})} \tag{A-16}$$

where E_{34} is the potential of the Pu(III)-Pu(IV) couple, etc. (Table A-1), F is the faraday constant (96,500 coulombs), and a_W is the activity of water. Substitution of Equations A-14, A-15, and A-16 in Equations A-8, A-9, and A-10 gives

$$\frac{\text{Pu(IV)}}{\text{Pu(III)}} = \frac{g_{\text{Pu(IV)}}}{g_{\text{Pu(III)}}} e^{\frac{F}{RT}(E-E_{34})} \qquad \text{(A-17)}$$

$$\frac{\text{Pu(V)}}{\text{Pu(III)}} = \frac{a_W^2}{[H^+]^4} \frac{g_{\text{Pu(V)}}}{g_{\text{Pu(III)}}} e^{\frac{2F}{RT}(E-E_{35})} \qquad \text{(A-18)}$$

$$\frac{\text{Pu(VI)}}{\text{Pu(III)}} = \frac{a_W^2}{[H^+]^4} \frac{g_{\text{Pu(VI)}}}{g_{\text{Pu (III)}}} e^{\frac{3F}{RT}(E-E_{36})} \qquad \text{(A-19)}$$

Similar equations were derived for neptunium. Np(III) was not included because it is not stable in nitrate solutions.

$$\frac{\text{Np(V)}}{\text{Np(IV)}} = \frac{a_W^2}{[H^+]^4} \frac{g_{\text{Np(V)}}}{g_{\text{Np(IV)}}} e^{\frac{F}{RT}(E-E_{45})} \qquad \text{(A-20)}$$

$$\frac{\text{Np(VI)}}{\text{Np(IV)}} = \frac{a_W^2}{[H^+]^4} \frac{g_{\text{Np(VI)}}}{g_{\text{Np(IV)}}} e^{\frac{2F}{RT}(E-E_{46})} \qquad \text{(A-21)}$$

The ratios obtained from Equations A-17 through A-21 were used in Equations A-1 and A-2 to calculate the fraction of Pu(IV) and Np(IV) as previously shown in Figure 2.

Stability constants required for Equations A-17 through A-21 (Table A-2) were chosen for the highest available ionic strength (I); I = 8 to 10 in our solutions. Lahr and Knoch have reported Pu^{3+} stability constants at I = 8; however, the values were very high and appeared questionable when compared to Am^{3+} and the rare earths.[22] Therefore, the stability constants for Eu^{3+} at I = 4 (highest available) were substituted for Pu^{3+}.[23] The increase in ionic strength from 4 to 8-10 would not be expected to significantly decrease the stability constants. Use of published neptunium, plutonium, and europium stability constants measured at lower ionic strengths resulted in small shifts in the Pu(IV)-Np(IV) stability regions and did not alter the conclusions derived from the calculations.

The necessary water activities (a_w) and hydrogen and nitrate ion activity coefficients are not available for the nitric acid-aluminum nitrate system. However, values for a_w and H^+ activity coefficients were estimated from equations developed by Davis et al. for the water - nitric acid - uranyl nitrate system.[24] Water activities of 0.83 and 0.75 and H^+ activity coefficients of 2.8 and 4 were obtained with 1.0M and 2.5M HNO_3, respectively, with sufficient uranyl nitrate (1.8M) to give the desired total nitrate concentrations. Nitrate concentration was used in Equations A-17 through A-21 instead of activity because the stability constants[22] were calculated by using concentration.

TABLE A-1

Electrochemical Potentials

Couple	*Potential, volts*[20,21]
Np(IV)-Np(V)	0.739
Np(IV)-Np(VI)	0.938
Pu(III)-Pu(IV)	0.914
Pu(III)-Pu(V)	1.049
Pu(III)-Pu(VI)	1.006

TABLE A-2

Stability Constants[a] of Neptunium and Plutonium Nitrates Complexes[22,23]

Metal Ion	*Temperature, °C*	*Ionic Strength (I)*	β_1	β_2	β_3	β_4
Np^{4+}	20	8	0.03	0.68	0.15	0.13
NpO_2^+	20	8	0.53	-	-	-
NpO_2^{2+}	20	8	0.57	1.57	-	-
Pu^{3+}	25	4	1.48	0.19	-	-
Pu^{4+}	20	8	4.88	2.66	-	0.19
PuO_2^{+}[a]	20	8	0.53	-	-	-
PuO_2^{2+}	20	8	0.27	0.28	-	-

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[a] The stability constants for Np(V) and Pu(V) were made identical because data were lacking for Pu(V), and their stabilities are expected to be similar.

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