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**SELECTIVE REDUCTION OF PLUTONIUM(VI)
TO PLUTONIUM(IV) IN A PLUTONIUM(IV-VI)
NITRIC ACID SOLUTION**

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INTRODUCTION

Plutonium separation by solvent extraction or ion exchange is generally dependent upon a specific valence state. For example, plutonium must be present in the four-valence state for extraction by thenoyltrifluoroacetone or n-tributylphosphate, ⁽¹⁾ or for absorption on an anion exchange resin. ⁽²⁾

When a plutonium(IV) nitrate solution of 2 M nitric acid or less is concentrated by heating, a plutonium(IV-VI) system is formed. The concentration of each valence state is a function of time, temperature and initial nitric acid concentration.

This report describes the development of a technique for adjusting the valence of the plutonium in this plutonium(IV-VI) system to the four-valence state necessary for efficient solvent extraction or anion exchange.

BACKGROUND

In most mineral acids, plutonium(IV) will disproportionate as follows: ^(3, 4)

In addition, plutonium will form complexes with a number of anions. ⁽⁵⁾ Nitric acid solutions of 1 M and below exhibit this disproportionation and a very undesirable formation of polymer. ⁽⁶⁾ Between 1 and 5 M nitric acid, a plutonium nitrate complex with the formula $\text{Pu}(\text{NO}_3)^{+3}$ is postulated. ⁽⁷⁾ The brown color of the plutonium solution can be attributed to this complex. At 7.7 M nitric acid and above, the brilliant green color is attributed to formation of the $\text{Pu}(\text{NO}_3)_6^{-2}$ complex. ⁽⁷⁾

If a plutonium(IV) solution 2 M or less in nitric acid is heated, some of the plutonium(IV) is oxidized to plutonium(VI). ⁽⁸⁾ The oxidation is rapid at low nitric acid concentrations and is inhibited at higher concentrations. At 7 M virtually no oxidation occurs. The rate of oxidation increases as the temperature increases. The longer the temperature is maintained, the greater the oxidation. Thus, when a low-acid plutonium(IV) nitrate solution

is concentrated by heating, a plutonium(IV-VI) system results, with the concentration of each valence state a function of time, temperature and initial nitric acid molarity.

According to Seaborg and Katz,⁽⁴⁾ the ferrous ion will reduce plutonium(VI) and (IV) to valence state three by the following reactions:

The purpose of this investigation could thus be accomplished by reducing both valence states to three with the ferrous ion, and subsequently oxidizing to the four-valence state with nitrite. This reaction was the basis of this investigation. Ferrous sulfamate was selected as the source of the reducing ion because of its demonstrated stability in nitric acid solutions.

SUMMARY

The valence of the plutonium in a plutonium(IV-VI) nitric acid solution is adjusted to four by reduction with ferrous sulfamate. It was not necessary to reduce the valence to three and then oxidize to four with nitrate. Dilution, time elapsed, and nitrite formed due to radiation degradation of nitric acid do not affect the reaction. Nitric acid concentration must be between 2 and 6 M to avoid plutonium disproportionation on the one hand or sulfamate precipitation on the other. Temperature during the reaction has no importance between 23 C and 50 C. Ferrous sulfamate concentration is kept below 1 M to prevent crystal formation after the reaction. Plutonium concentration may be as high as 250 g/l.

APPARATUS AND REAGENTS

A Beckman DK-2 recording spectrophotometer, calibrated for plutonium(III), (IV) and (VI),⁽⁹⁾ was used for all measurements.

A 4 M nitric acid solution containing 250 g of plutonium per liter was prepared and found to contain 200.2 g/l of plutonium(IV) and 49.8 g/l of plutonium(VI). Dilutions were made using 4 M nitric acid.

Ferrous sulfamate was obtained from General Chemical Company in 50 per cent solution.

EXPERIMENTAL WORK AND RESULTS

The possibility of changing the plutonium valence distribution by dilution or by nitrite formed by radiation degradation of nitric acid was studied. The valence change obtained in a plutonium(IV-VI) system by reaction with ferrous sulfamate was investigated. The variables considered were: the effects on the reaction of plutonium concentration, nitric acid concentration, and temperature, and the stability of the valence adjustment with respect to time. Two other sources of ferrous ion were investigated. All reactions were performed at 23 ± 2 C unless otherwise indicated.

Effect of Dilution

The stock solution was diluted with 4 M nitric acid and analyzed for valence states. The results are in Table I.

TABLE I
EFFECT OF DILUTION
ON PLUTONIUM VALENCE STATE DISTRIBUTION

<u>Total Pu (g/l)</u>	<u>Pu(IV) (g/l)*</u>	<u>Pu(VI) (g/l)*</u>
250	200.3	49.8
25	200.0	50.8
12.5	200.2	49.5

* The plutonium ion concentrations were normalized to the stock solution concentrations for ease of comparison.

Each dilution was analyzed at eight-hour intervals over a period of 25 hours. No change in valence state distribution was observed.

Effect of Nitrite Formed by Radiation Degradation

Sodium nitrite was added to a one-to-ten dilution of the stock solution and the resulting solution analyzed for valence states. The results are shown in Table II.

TABLE II
EFFECT OF NO₂⁻ CONCENTRATION ON PLUTONIUM VALENCE
STATE DISTRIBUTION IN A 4 M HNO₃ SOLUTION

<u>Nitrite Concentration (M)</u>	<u>Pu(IV) (g/l)</u>	<u>Pu(VI) (g/l)</u>
0	200.1	49.7
1.5×10^{-3}	200.3	49.6
1.5×10^{-2}	199.9	49.7
0.15	200.1	49.6

No change in valence state distribution in these solutions was observed after a 16-hour standing period.

Reaction with Ferrous Sulfamate

The reaction of 0.8 M ferrous sulfamate with the stock solution was studied in two different ways. First the ferrous sulfamate was added in 0.016 millequivalent units to a dilution containing 25.0 mg of plutonium from the stock solution. The results of plutonium-ion concentration measurements taken during this titration are listed in Table III.

TABLE III
SEQUENTIAL PLUTONIUM VALENCE CHANGES
DUE TO ADDITION OF FERROUS ION IN A 4 M HNO₃ SOLUTION

<u>Millequivalents of Fe(II)</u>	<u>Pu(IV) (mg)</u>	<u>Pu(VI) (mg)</u>	<u>Pu(III) (mg)</u>
0.000	20.0	5.0	---
0.016	21.8	3.1	---
0.032	23.9	1.2	---
0.048	23.6	---	1.5
0.064	20.2	---	4.8
0.080	16.4	---	8.4

The reaction was further verified by precalculated stoichiometric additions of ferrous sulfamate to stock solutions containing various concentrations of plutonium(VI). The results are in Table IV.

TABLE IV
ADJUSTING A PLUTONIUM(IV-VI) SYSTEM
TO PLUTONIUM(IV) WITH FERROUS SULFAMATE IN A 4 M HNO₃ SOLUTION

<u>Initial Pu Concentrations</u>		<u>Millequivalents of</u> <u>Fe(II) Added</u>	<u>Final Pu Concentrations</u>	
<u>Pu(IV) (mg)</u>	<u>Pu(VI) (mg)</u>		<u>Pu(IV) (mg)</u>	<u>Pu(VI) (mg)</u>
20.0	5.0	0.042	24.95	----
21.8	3.1	0.026	25.05	----
23.9	1.2	0.010	24.90	----

Standard Deviation, $\sigma = 0.72\%$.

Effect of Plutonium Concentration

The possibility of side reactions occurring in more concentrated plutonium solutions was investigated by adjusting the valence of increasingly-concentrated aliquots of the stock solution to the four state. The results are listed in Table V.

TABLE V
EFFECT OF PLUTONIUM CONCENTRATION
ON VALENCE ADJUSTMENT IN A 4 M HNO₃ SOLUTION

<u>Initial Pu Concentrations</u>		<u>Millequivalents of</u> <u>Fe(II) Added</u>	<u>Final Pu Concentrations</u>	
<u>Pu(IV) (mg)</u>	<u>Pu(VI) (mg)</u>		<u>Pu(IV) (mg)</u>	<u>Pu(VI) (mg)</u>
2.0	0.50	0.0042	2.495	----
20.0	5.0	0.042	24.89	----
200.0	50.0	0.420	249.6	----

Effect of Nitric Acid Concentration

The effect of nitric acid concentration on the reaction is shown in Table VI.

TABLE VI
VALENCE STATES OBSERVED AS A FUNCTION
OF NITRIC ACID CONCENTRATION AT THE TIME OF ADJUSTMENT

<u>M HNO₃</u>	<u>Plutonium Concentration (g/l)</u>		
	<u>Pu(IV)</u>	<u>Pu(VI)</u>	<u>Pu(III)</u>
1.0	22.5	1.8	0.5
2.0, 3.0, 4.0, 5.0	24.95	----	----

A voluminous precipitate of sulfamate was obtained with nitric acid concentrations above 6 M.

Effect of Temperature

Temperatures during all the previous experiments were maintained at 23 ± 2 C. In considering the temperature, the maximum was set at 50 C due to the greater possibility of oxidation by nitric acid noted by Kraus.⁽⁸⁾ Stoichiometric valence adjustment was successfully performed at 50 C. The solution was maintained at 50 C for six hours after adjustment but no valence change was observed.

Stability With Respect to Time

The stability of the valence adjustment with respect to time is shown in Table VII.

TABLE VII
VALENCE STATE STABILITY WITH RESPECT TO TIME
AFTER ADJUSTMENT IN A 4 M HNO₃ SOLUTION

<u>Time Since Valence Adjustment</u> <u>(Days)</u>	<u>Plutonium Concentration (g/l)</u>	
	<u>Pu(IV)</u>	<u>Pu(VI)</u>
0	24.90	----
1/4	24.91	----
1/2	24.89	----
1	24.90	----
3	24.91	----
5	24.90	----

Ferrous Ion Chemistry

When ferrous sulfamate more concentrated than 1 M was added to 250 g/l plutonium at 23 C, a few transparent, colorless crystals formed after a four-hour standing period. These crystals did not appear when the solution was maintained at 50 C. Crystal formation had no effect on the valence adjustment.

In nitric acid solutions of ferrous sulfamate, a nitric acid concentration of over 6 M causes formation of a voluminous precipitate of sulfamate.

Ferrous ammonium sulfate and ferrous sulfate were tried in place of ferrous sulfamate. Both compounds were unsatisfactory because of their instability in nitric acid.

DISCUSSION

These investigations show that plutonium(VI) could be reliably reduced to plutonium(IV) with ferrous sulfamate. The original concept of reduction to plutonium(III) with ferrous sulfamate followed by oxidation to plutonium(IV) with nitrite was abandoned.

If a mistake is made during the adjustment step and a plutonium(IV-III) system is formed, the readjustment can be accomplished by adding the stoichiometric quantity of plutonium(VI) to oxidize the plutonium(III) to plutonium(IV). While this reaction was only performed once, added evidence was observed each time an adjustment was made. At the instant of contact between the stock solution and ferrous sulfamate, a bright blue band formed at the interface, visually indicating the presence of plutonium(III). After 30 seconds of mixing, there was no plutonium(III) present, as indicated in Table III.

An attempt was made to determine the time dependence of the reaction; however, the reaction was always complete within the minimum analytical time lag of three minutes after the reactants were mixed.

During the entire series of experiments, plutonium polymer was observed only in the case of valence adjustment in a one normal nitric acid solution. Detection was by the method of Brunstad.⁽⁶⁾

Of the variables considered, time, nitrite concentration and dilution were found to have no effect. Nitric acid concentration had a two-fold limit. The first was the minimum concentration of 2 M to prevent formation of plutonium(III); the second was the maximum of 6 M to prevent sulfamate precipitation. Temperature could be varied between 23 C and 50 C with no undesirable consequences. The maximum of 50 C is recommended to avoid secondary oxidation by nitric acid. Plutonium at any concentration up to 250 g/l could be stoichiometrically adjusted by this method. The reaction rate can be considered instantaneous.

RECOMMENDED PROCEDURE

The plutonium valence state concentrations of the solution to be adjusted are determined spectrophotometrically. The ferrous ion addition is calculated according to the equation:

The calculated quantity of ferrous ion is prepared in 1/2 M nitric acid of such a volume to provide the final desired conditions in acidity and plutonium concentration. The plutonium nitrate solution is added to the prepared reducing solution. After a five-minute agitation period, the valence adjustment is checked on the spectrophotometer. From this point on, any desired acid adjustment may be made. The brown colored solution turns emerald green after butting to 7 M nitric acid or above as noted by Kraus.⁽⁸⁾

The critical conditions of the technique are: preparation of the ferrous sulfamate must fall within prescribed conditions; the nitric acid concentration of the adjusted solution must be between 2 and 6 M; the temperature of the reducing solution should be no greater than 50 C.

If the calculated millequivalents of ferrous sulfamate are in error, a second adjustment may be made by adding more ferrous ion to reduce any remaining plutonium(VI), or by adding more plutonium(IV-VI) to oxidize any plutonium(III) that is present. Nitrite may be used for this oxidation, but an excessive quantity is needed because it reacts with the sulfamate before it oxidizes the plutonium(III). A significant amount of nitrogen dioxide is evolved during the reaction.

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