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REDUCTION OF PLUTONIUM(VI) TO PLUTONIUM(V), (IV), AND (III) BY NITRITE IN A NITRATE SYSTEM			
C. A. Colvin			
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REDUCTION OF PLUTONIUM(VI) TO PLUTONIUM(V), (IV),
AND (III) BY NITRITE IN A NITRATE SYSTEM

by

C. A. Colvin

Separations Chemistry Laboratory
Research and Engineering Department
Chemical Processing Division

ATLANTIC RICHFIELD HANFORD COMPANY

Richland, Washington

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REDUCTION OF PLUTONIUM(VI) TO PLUTONIUM(V), (IV),
AND (III) BY NITRITE IN A NITRATE SYSTEM

Introduction

Nitrite ion plays an important role in the aqueous processing of the actinide elements. For plutonium valence adjustment to the Pu(IV) state, it is particularly useful since it is capable of oxidizing Pu(III) to Pu(IV) as well as reducing Pu(VI) to Pu(IV). Many analytical methods as well as aqueous processes rely upon plutonium being in the quadrivalent state.

At times, the presence of nitrite is detrimental to aqueous processing, such as when it is desired to maintain plutonium in the trivalent state in a nitric acid system. Oxidation of Pu(III) by nitrate according to the reaction $3\text{Pu}^{+3} + 4\text{H}^+ + \text{NO}_3^- \longrightarrow 3\text{Pu}^{+4} + \text{NO} + 2\text{H}_2\text{O}$ is slow. However the reaction is autocatalytic, since the NO formed reacts to produce HNO_2 which greatly increases the rate of oxidation. Holding reductants such as sulfamic acid or hydrazine may be added to destroy the HNO_2 as soon as it is formed and thus retard the rate of oxidation.

It is therefore surprising to many people that nitrite addition to a Pu(VI) nitric acid solution may result in reducing plutonium to the trivalent state. In fact, solutions containing greater than 80% of the plutonium as Pu(III) have been thus achieved. Intermediate solutions consisting of considerable Pu(V) suggest the probable mechanism for attaining such solutions.

This paper presents rate of reaction data concerning the reduction of Pu(VI) by nitrite to the other valence states under varying conditions.

Summary

Reaction rate studies involving the reduction of Pu(VI) by nitrite in low nitric acid have resulted in four valence states simultaneously apparent in many of the solutions. Quantitative determinations of each valence state vs. time have been made by use of a recording spectrophotometer.

Plutonium(VI) may be reduced to greater than 80% plutonium(III) by nitrite in a nitrate system. Intermediate solutions have indicated a plutonium(V) content of as much as 76%. Valence state distribution is dependent on acidity, temperature, nitrite concentration, ferric ion concentration, and time. Gross amounts of metal ions such as uranyl ion sharply accelerate the reaction rate and thus result in rapid reduction to Pu(IV) which is the ultimate end product for all of the systems studied.

Efficient reduction by nitrite is limited to solutions below 1.5 M HNO₃ and temperatures above 45° C.

Experimental

Reagents and Solutions

- (a) Plutonium(VI) was obtained by refluxing plutonium nitrate in 1.0 M HNO₃.
- (b) Nitrite was added to the solution (at the experimental temperature) as sodium nitrite crystals.

Analysis

Valence state analyses were performed spectrophotometrically⁽¹⁾ utilizing a Beckman DK-2A ratio-recording spectrophotometer with 1 cm rectangular silica cells. Samples were immediately cooled in an ice bath and scanned in the spectrophotometer at 25° C.

Results and Discussion

Extreme Low Acid Reduction

Reduction at extremely low acid allows one to view the stepwise reduction through Pu(V). Data in Table I also illustrates the chemistry involved between the ions representing the four oxidation states of plutonium.

It is possible for finite concentrations of all four oxidation states of plutonium to exist in equilibrium with one another in the same solution. Such behavior, unique for plutonium among all the elements of the periodic table, is due to the interplay of two phenomena: (1) the tendency of Pu(IV) and Pu(V) ions to disproportionate, and, (2) the slow rate of reactions involving formation or rupture of plutonium-oxygen bonds (such as exist in PuO_2^+ and PuO_2^{+2}), as compared to the much faster reactions involving only electron transfer⁽²⁾.

The overall reaction for the disproportionation of Pu(V) may be written as follows: $3\text{PuO}_2^+ + 4\text{H}^+ \rightleftharpoons \text{Pu}^{+3} + 2\text{PuO}_2^{+2} + 2\text{H}_2\text{O}$. The absence of Pu^{+4} is due to the rapid reaction $\text{Pu}^{+4} + \text{PuO}_2^+ \longrightarrow \text{PuO}_2^{++} + \text{Pu}^{+3}$ which is part of the overall reaction⁽³⁾. It can be seen that unlike the disproportionation reaction of Pu(V) to form Pu(IV) and Pu(VI) which requires the rupture of plutonium-oxygen bonds, the reaction of (IV) and (V) to give (III) and (VI) involves only electron transfer. As no bonds need be made or broken, the reduction of plutonium(IV) by (V) is rapid, and consequently Pu(IV) does not accumulate during the disproportionation of plutonium(V), until the plutonium(V) is nearly exhausted⁽⁴⁾.

As illustrated in Table I, Pu(IV) was not detectable during the first 30 minutes. There was no significant Pu(IV) accumulation until the Pu(V) had decreased to a low level.

Table I also illustrates the accelerating effect of temperature increase.

Note that the HNO_3 concentration was changed to 0.25 M for the 60° C run to avoid possible polymeric plutonium formation.

TABLE I

Pu(VI) 0.0112 M
 HNO_3 0.20 M
 Fe(III) 5×10^{-4} M
 NaNO_2 0.098 M
 Temperature Variable

<u>Temperature</u>	<u>Time (Min.)</u>	<u>% Pu(VI)</u>	<u>% Pu(V)</u>	<u>% Pu(IV)</u>	<u>% Pu(III)</u>
43° C	10	20	67		13
	20	20	64		16
	30	20	59		21
	40	18	57	0.4	24
	50	18	51	1	30
	60	17	45	2	36
	70	18	36	4	42
	80	17	29	6	48
51° C	10	13	76		11
	20	15	71		14
	30	15	66		18
	50	15	53	1	31
	70	11	39	3	48
	90	10	20	6	64
	110	5	5	16	74
60° C (0.25 <u>M</u> HNO_3)	10	24	63		13
	20	19	57		24
	30	17	44	2	38
	40	12	31	5	52
	50	8	16	8	67
	60	5	9	11	75
	70	3	3	14	79
	80	2	1	16	81

Effect Of HNO_3 Concentration

Efficient reduction by nitrite is limited to solutions below 1.5 M HNO_3 .

At 1.5 M HNO_3 and above, considerable Pu(VI) remained after reaction times exceeding one hour.

The rate of Pu(VI) reduction is slightly decreased as the HNO_3 concentration is increased from 0.55 M to 1.4 M. The amount of Pu(III) produced is sharply decreased as the HNO_3 is increased until practically all of the plutonium is in the quadrivalent state at 1.4 M HNO_3 within one hour.

TABLE IIBeginning Solution

Pu(VI) 0.0111 M
 HNO_3 Variable
 Fe(III) 5×10^{-5} M
 NaNO_2 0.049 M
 Temperature 70°C

<u>HNO_3 Conc.</u>	<u>Time (Min.)</u>	<u>% Pu(VI)</u>	<u>% Pu(V)</u>	<u>% Pu(IV)</u>	<u>% Pu(III)</u>
0.55 <u>M</u>	10	22	15	23	40
	20	6	3	32	59
	30	5		34	61
	40	3		35	62
	50	2		37	61
	60	2		39	58
1.00 <u>M</u>	10	23		58	19
	20	4		75	21
	30	2		78	20
	40	1		79	20
	50	1		80	19
	60	2		81	17
1.25 <u>M</u>	10	28		60	12
	20	5		85	10
	30	2		91	7
	40	1		93	6
	50	1		94	5
	60	1		94	5

TABLE II (Cont.)

<u>HNO₃ Conc.</u>	<u>Time (Min.)</u>	<u>% Pu(VI)</u>	<u>% Pu(V)</u>	<u>% Pu(IV)</u>	<u>% Pu(III)</u>
1.40 <u>M</u>	10	31		65	4
	20	7		89	4
	30	3		94	3
	40	2		96	2
	50	2		97	1
	60	1		98	1

Effect of Uranyl Nitrate Concentration

The presence of gross amounts of uranyl nitrate accelerates the rate of reduction as well as considerably decreasing the amount of Pu(III) formed. Pu(V) was not detectable in any solution containing greater than 0.1 M uranium.

TABLE III

Pu(VI) 0.0112 M
 HNO₃ 0.55 M
 Fe(III) 5×10^{-4} M
 NaNO₂ 0.049 M
 UO₂(NO₃)₂ Variable
 Temperature 60° C

<u>UO₂(NO₃)₂ Conc.</u>	<u>Time (Min.)</u>	<u>% Pu(VI)</u>	<u>% Pu(V)</u>	<u>% Pu(IV)</u>	<u>% Pu(III)</u>
0	10	59	21	9	12
	20	29	11	31	28
	30	8	2	51	39
	40	3		55	42
	50	2		51	47
	60	2		49	49
0.1 <u>M</u>	10	<1		57	43
	20			55	45
	30			55	45
	40			56	44
	50			61	39
0.5 <u>M</u>	10			82	18
	20			82	18
	30			80	20
	40			86	14

TABLE III (Cont.)

<u>UO₂(NO₃)₂ Conc.</u>	<u>Time (Min.)</u>	<u>% Pu(VI)</u>	<u>% Pu(V)</u>	<u>% Pu(IV)</u>	<u>% Pu(III)</u>
1.92 M	10	<1		>99	
	20			100	
	30			100	

Effect of Nitric Acid Concentration at Low Acid and High Uranium

Table IV is presented to indicate that some plutonium(III) is formed in the presence of high uranium at very low HNO₃ concentrations.

TABLE IV

Pu(VI) 0.0112 M
HNO₃ Variable
Fe(III) 5×10^{-4} M
NaNO₂ 0.049 M
UO₂(NO₃)₂ 1.92 M
Temperature 60° C

<u>HNO₃ Conc.</u>	<u>Time (Min.)</u>	<u>% Pu(VI)</u>	<u>% Pu(V)</u>	<u>% Pu(IV)</u>	<u>% Pu(III)</u>
0.064 M	10			88	12
	20			89	11
	30			88	12
0.55 M	10	<1		>99	
	20			100	
	30			100	

Effect of Sodium Nitrite and Ferric Iron Concentrations(5)

Increasing the nitrite concentration, accelerates the reduction rate as well as markedly increasing the amount of plutonium(III).

The rate of reaction is increased by an increase in ferric ion concentration.

Acknowledgement

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