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REDUCTION OF PLUTONIUM(VI) WITH HYDROGEN PEROXIDE

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REDUCTION OF PLUTONIUM(VI) WITH HYDROGEN PEROXIDE

INTRODUCTION

Hydrogen peroxide has been used to reduce plutonium(VI) in nitric acid solution to the (IV) valence state. However, reduction of plutonium(VI) solutions containing iron has often been incomplete when hydrogen peroxide was used as the reducing agent. Since reduction of plutonium(VI) has been applied in plant solutions containing iron, a study of the plutonium(VI) reduction with hydrogen peroxide was undertaken. Variables tested included plutonium, nitric acid, and iron concentrations.

SUMMARY AND CONCLUSIONS

Pure solutions of plutonium(VI) nitrate in nitric acid are rapidly reduced with hydrogen peroxide to plutonium(IV), which is subsequently reduced to plutonium(III). Re-oxidation of plutonium(III) to (IV) occurs rapidly with high, and more slowly with low plutonium concentrations. The reduction rate of plutonium(VI) also increases with increasing plutonium concentration.

Iron greatly reduces the rate of reduction, and may prevent the complete reduction of plutonium(VI) by hydrogen peroxide. The presence of iron in concentrations greater than 1.0 g/l may prevent the complete reduction of plutonium(VI).

The hydrogen peroxide-plutonium ratio has little effect on the reduction of plutonium(VI) if sufficient peroxide is present to completely react with the plutonium.

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Hydrogen ion concentration has a small effect on reduction of plutonium(VI). The reduction proceeds most rapidly in 3.5 M HNO_3 .

Light has no detectable effect on the reduction rate.

Estimates of plutonium(VI) remaining after 10 minutes of reaction time may be made using the empirical equations:

$$(1) Y = -9 P + 6.1 F + 109$$

$$(2) Y = -0.7 P + 4 F + b, \text{ and}$$

$$(3) P = 0.253 F - 0.12 b + 13.1 \quad \text{where}$$

Y = per cent plutonium(VI) remaining after 10 minutes,

P = plutonium concentration in grams per liter,

F = iron concentration in grams per liter,

b is taken from Figure 4, and is determined by the hydrogen ion concentration.

The first equation is used for plutonium values below those given by the third equation, for a particular iron and hydrogen ion concentration, while the second equation is used for higher plutonium values.

EXPERIMENTAL

A solution of plutonium nitrate containing 100 per cent plutonium(VI) was obtained by boiling a 1.0 M HNO_3 solution of plutonium(IV) (50 g/l) for six hours under reflux. The solutions for the runs were made by adding a weighed amount of iron (as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), a measured volume of nitric acid, a measured volume of plutonium(VI) solution, and diluting to 10 ml. with distilled water. Sufficient hydrogen peroxide (16.6 M) was then added to make the solution 0.25 M H_2O_2 , except in runs 3, 5, and 12, which were made only 0.125 M H_2O_2 . All reactions were started at room temperature (21-25 C). Samples were taken at 1/2, 10, and 40 minutes, and 24 hours. Samples of some runs were also taken at 120, 200, and 300 minutes. The samples were immediately diluted with cold (0 C) 2 M HNO_3 to stop the reaction and lower the plutonium concentration to a suitable level (3 g/l) for the absorption spectra scan. Runs 10 and 29 were run without dilution. A Beckman DK-2 recording spectrophotometer was used for the absorption measurements. The extinction coefficients for calculation of the valence states were those published in a previous report(1).

RESULTS AND DISCUSSION

The results obtained from the reduction of plutonium(VI) and (IV) with hydrogen peroxide are shown in Table I. Figure 3 shows typical DK-2 plots obtained during a run.

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Reduction of pure solutions of plutonium(VI) to plutonium(IV) with hydrogen peroxide proceeds quite rapidly, the rate increasing with increasing plutonium concentration. For example, in run 14, containing 15.8 g/l plutonium, reduction was complete in ten minutes. The plutonium(IV) is further reduced by the peroxide to plutonium(III). Re-oxidation of plutonium(III) to (IV) occurs within a few minutes (too rapidly to obtain accurate measurements) with high plutonium concentrations (100 g/l), but may require several days with low plutonium concentrations (run 23 contained 90 per cent plutonium(III) after 24 hours). The re-oxidation is probably done by nitric acid, after the peroxide has been catalytically destroyed by plutonium.

The presence of iron lowers the rate of reduction of plutonium(VI) with hydrogen peroxide, and may prevent the complete reduction of plutonium(VI).

In low plutonium concentration runs with low iron to plutonium ratios (0.15 - 0.20) as in runs 7, 7R, 8, and 8R, complete reduction of plutonium(VI) occurs in 24 hours. When the iron to plutonium ratio is increased to greater than one, as in runs 4, 6, 10, 20, 20R, 21, and 22, 40-70 per cent plutonium(VI) remains after 24 hours. In runs 10, 17, 20, 20R, and 22, no reduction occurred in 10 minutes and only 0-5 per cent in 40 minutes.

With higher plutonium concentration runs, and low iron to plutonium ratios (0.03 - 0.3), as in runs 2, 5, 11, and 12, complete reduction occurs in 24 hours. Complete reduction occurred in 10 minutes with runs 2 and 11, and 40 minutes with run 5. With an increased iron to plutonium ratio (0.35 - 1.0), as in runs 1, 1R, 3, 13, 15, 15d, 25, 26, and 27, 11 to 33 per cent plutonium(VI) remained after 24 hours. Only slight reduction occurred after 40 minutes.

No temperature rise was noted when hydrogen peroxide was added to pure plutonium solutions, but maximum rises of two and five degrees, due to catalytic decomposition of the peroxide, were observed in approximately 10 minutes, when 5 and 25 g/l iron were present, respectively, in the 10 ml. sample.

The hydrogen peroxide-plutonium ratio has little effect if sufficient peroxide is present to react with the plutonium. In runs 18 and 19, 0.6 mole of hydrogen peroxide per mole of plutonium was present, consequently the stoichiometric amount or only 60 per cent of the plutonium was reduced. When iron is present, catalytic decomposition of the peroxide may reduce the peroxide concentration appreciably, leaving insufficient peroxide to completely reduce the plutonium(VI), although an excess was originally added. However, the presence of excess peroxide at the end of 40 minutes is indicated by the observation of traces of plutonium(IV)-peroxy complex in runs 1, 1R, 3, 6, 15, 15d, 20, 20R, 26, and 27 (which were not reduced after 40 minutes). Hence, the failure to reduce is not due to the lack of peroxide in these latter runs.

Hydrogen ion has a small effect in the reduction of plutonium(VI) with peroxide. The greatest reduction rate was obtained in 3.5 M HNO_3 solutions with the exception of runs 7 and 7R (6 M HNO_3). The effect is shown in Figure 4 which shows b values (per cent of plutonium(VI) remaining due to hydrogen ion effect) versus hydrogen ion concentration. Precipitation of

plutonium peroxide occurred in low acid, high plutonium concentration runs 3, 5, and 12 (which are 1.5 M HNO_3 and 27.9, and 15.2 g/l plutonium, respectively) when the peroxide to plutonium ratio was increased from the values in Table I to 2.2, 2.2, and 7.8, respectively.

The absence of light had little effect on the reduction of plutonium(VI), as two duplicate runs, one in the light (15), and the other in the dark (15d) showed very little difference in reduction rate.

The data are reliable at the points measured, except runs 7 and 7R, 8 and 8R, which showed a wide deviation between duplicate runs. Run 7 had no plutonium(VI) remaining after 10 minutes, while 7R had 33 per cent. Run 8 had 83 per cent plutonium(VI), while 8R had 96 per cent. Other duplicate runs (15 and 15d), 9 and 16, 20 and 20R) agree very closely. The best correlation of the data is obtained through the use of two intersecting straight lines as shown in Figures 1, 2, and 3. Since the data lie in three groups, the use of the straight line equations can only give approximate values when used in areas between the groups of the data.

Estimates of the amount of plutonium(VI) remaining after 10 minutes, assuming a 100 per cent plutonium(VI) starting solution, with an original hydrogen peroxide concentration of 0.25 M H_2O_2 , are made using the following equations:

- (1) $Y = -9P + 6.1 F + 109$
- (2) $Y = -0.7P + 4F + b$
- (3) $P = 0.253 F - 0.12 b + 13.1$

where Y = per cent plutonium(VI) remaining after 10 minutes,
 P = plutonium concentration in grams per liter,
 F = iron concentration in grams per liter,
 b is found from Figure 4, knowing the acid concentration of the solution.

Equation (1) applies for plutonium concentrations less than those given by equation (3) with the acid and iron concentration used. (For 1-10 g/l iron and 1.5 - 6 M H^+ , equation (3) values range from 13 - 16.3 g/l plutonium.) Equation (2) applies for higher plutonium concentrations. Negative values obtained using these equations indicate complete reduction will occur. The average deviation of the calculated per cent plutonium(VI) from the data, using equation (1), is $\pm$ eleven. Excluding runs 4, 7, 7R, and 8R, which have deviations of 21, 65, 27, and 34, respectively, the average deviation becomes $\pm$ three. The data from runs 7, 7R, 8, and 8R are somewhat questionable, as shown above. The largest deviation of the calculated per cent plutonium(VI) from the data, using equation (2), is four, with an average deviation of less than $\pm$ one. These equations can also be used when no iron is present, however, the calculated per cent plutonium(VI) will be higher than the observed value (for run 23 the calculated value is 57 per cent plutonium(VI), but only 30 per cent was found).

Helpful discussions with J. A. Merrill of the Statistics Unit are acknowledged.

References: (1) Myers, M. N., Absorption Spectra of Plutonium and Impurity Ions in Nitric Acid Solutions. HW-44744, July 31, 1956.

TABLE I

REDUCTION OF PLUTONIUM(VI) WITH HYDROGEN PEROXIDE

Run No.	Pu Conc. (g/l)	Iron Conc. (g/l)	H ⁺ Conc. (g/l)	Moles H ₂ O ₂ Moles Pu	Per Cent Plutonium(IV) and (VI) Present ⁽¹⁾ at							
					10 min.		40 min.		120 min.		24 hours	
					(IV)	(VI)	(IV)	(VI)	(IV)	(VI)	(IV)	(VI)
1	25.9	9.12	6.0	2.3	66	34	66	34			71	29
1R	23.8	9.12	6.0	2.5	67	33	65	35			74	26
2	26.0	0.88	6.0	2.3	100	0	100	0			100	0
3	27.9	9.12	1.5	1.1 ⁽²⁾	75	25	84	16	86	14	89	11
4	5.15	9.12	6.0	11.6	21	79	42	58			46	53
5	27.8	0.88	1.5	1.1 ⁽²⁾	95	4	85	0	100	0	100	0
6	5.01	9.12	1.5	11.9	12	88	59	41	61	39	62	38
7	5.29	0.88	6.0	10.9	69	0 ⁽⁹⁾	100	0			100	0
7R	5.91	0.88	6.0	10.1	67	33	100	0			100	0
8	4.19	0.88	1.5	13.9	17	83	43	57	99	1 ⁽³⁾	100	0
8R	5.72	0.88	1.5	10.4	4	96	37	63			100	0
9	15.3	5.0	3.5	3.9	98	2	99	1			99	1
10	2.84	5.0	4.8	21.3	0	100	0	100			28	72
11	35.5	5.0	3.5	1.7	100	0	100	0			100	0
12	15.2	5.0	1.5	3.9 ⁽²⁾	81	19	99	1			100	0
13	15.4	5.0	6.0	3.9	76	24	76	24			76	24
14	15.8	0.0	3.5	3.8	25	0 ⁽⁹⁾	15	0	7	0 ⁽⁴⁾	100	0
15	16.7	10.0	3.5	3.6	77	23	76	24			78	22
15a ⁽⁵⁾	15.7	10.0	3.5	3.8	77	23	75	25			81	19

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TABLE I (Cont.)

Run No.	Pu. Conc. (g/l)	Iron Conc. (g/l)	H ⁺ Conc. (g/l)	Moles H ₂ O ₂ Moles Pu ⁺	Per Cent Plutonium(IV) and (VI) Present ⁽¹⁾ at							
					10 min.		40 min.		120 min.		24 hours	
					(IV)	(VI)	(IV)	(VI)	(IV)	(VI)	(IV)	(VI)
16	15.7	5.0	3.5	3.8	99	1	99	1			99	1
17	0.3	5.0	3.5	200	0	100	0	100	0	100 ⁽³⁾		
18	95.0	4.0	5.2	0.6	60	40 ⁽⁶⁾						
19 ⁽⁷⁾	100.0	3.0	5.6	0.6	100	0						
20	4.20	5.0	3.5	14.1	0	100	3	97	52	48 ⁽³⁾	48	52
20R	4.28	5.0	3.5	13.9	0	100	2	98	49	51 ⁽³⁾	47	53
21	8.69	10.0	3.5	6.9	11	89	61	39			59	41
22	4.38	5.0	6.0	13.6	0	100	5	95			50	50
23	5.8	0.0	3.5	11.5	70	30	14	0 ⁽⁹⁾	14	0	9	0
24	4.82	3.2	3.5	12.3	15	85	44	56			79	21
25	23.6	25.0	3.5	2.6	71	29	68	32			67	33
26	14.6	15.0	3.5	4.1	64	36	62	38			81	19
27	26.2	10.0	3.5	2.3	85	15	84	16			85	15
28	4.96	0.88	3.5	12.0	23	77	71	0	100	0 ⁽⁴⁾	100	0
29 ⁽⁸⁾	1.1	0.0	2.0	0.5	60	0 ⁽⁹⁾	33	0				

- Notes: (1) Starting solution 100 per cent plutonium(VI) with the exception of runs 19 and 29.
 (2) Precipitation occurred when double this concentration of H₂O₂ was used.
 (3) Analysis was obtained at 200 minutes.
 (4) Analysis was obtained at 300 minutes.
 (5) This run was kept in the dark during intervals between sampling and exposure to light minimized during sampling.
 (6) Reaction stopped after 2 minutes.
 (7) Reaction reached completion in 3 minutes. The original solution was 40 and 60 per cent plutonium(IV) and (VI), respectively.
 (8) Original solution was 100 per cent plutonium(IV).
 (9) Difference is plutonium(III).

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FIGURE 1
PLUTONIUM (VI) REDUCTION WITH HYDROGEN PEROXIDE,
WITH 9.1-10 g/l IRON PRESENT

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FIGURE 2
PLUTONIUM (VI) REDUCTION WITH HYDROGEN PEROXIDE,
WITH 5 g/l IRON PRESENT

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FIGURE 3
PLUTONIUM (VI) REDUCTION WITH HYDROGEN PEROXIDE
WITH 0-0.88 g/l IRON PRESENT

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FIGURE 4

EFFECT OF HYDROGEN ION ON PLUTONIUM(VI) REDUCTION
WITH HYDROGEN PEROXIDE; b VALUES

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FIGURE 5

REDUCTION OF PLUTONIUM (VI) WITH HYDROGEN PEROXIDE - DK-2 SCAN

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