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REDUCTION OF PLUTONIUM(VI) TO PLUTONIUM(III) AND (IV) BY SODIUM NITRITE

by

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Research and Engineering
Chemical Processing Department

October 28, 1963

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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REDUCTION OF PLUTONIUM(VI) TO PLUTONIUM(III) AND (IV) BY SODIUM NITRITE

INTRODUCTION

The application of anion exchange for final plutonium purification[1] in the Redox facility requires the adjustment of plutonium(VI) to plutonium(IV). Two methods of reduction were investigated: The first method was reduction by ferrous sulfamate; the second method was the use of nitrite for reduction.

The use of ferrous sulfamate was adopted due to the rapid rate of reduction and simplicity of the process. It was recommended that 2.5 moles of ferrous sulfamate per mole of plutonium be added to the process solution. The resulting Pu(IV) - Pu(III) mixture is continuously fed to a boiling concentrator which is 7M in HNO_3. Any excess ferrous is oxidized, sulfamate ion is oxidized to sulfate, plutonium(III) is oxidized to plutonium(IV), and thus the resulting feed solution contains the required plutonium(IV) nitrate complex in 7M HNO_3. The main objection to this method is the increase in iron content in backcycle streams.

Efficient reduction by nitrite is limited to solutions below 1.4M HNO_3 with elevated temperatures (above 50 C). Rates of reduction are such that time is also a determining factor. The information gained during the investigation of reduction by nitrite is presented in this paper in hope that it may be of value in future investigations and processes.

SUMMARY AND CONCLUSIONS

The reduction of Pu(VI) by nitrite is dependent on nitrite concentration, temperature, acidity, ferric ion concentration, and time. It is interesting to note that greater than 90% reduction to plutonium(III) by sodium nitrite may be accomplished by controlling the above conditions. Three oxidation states were apparent in most of the solutions and were quantitatively determined by use of a recording spectrophotometer.

EXPERIMENTAL

Analysis

Oxidation state analyses were performed spectrophotometrically[2], using a Beckman Model DK-2 ratio-recording spectrophotometer with 1 cm rectangular silica cells.

(1) J. L. Ryan and E. J. Wheelwright, The Recovery, Purification, and Concentration of Plutonium by Anion Exchange in Nitric Acid, HW-55893. January 2, 1959. (Confidential)

(2) C. A. Colvin and D. A. Dodd, Quantitative Determination of Plutonium Oxidation States In Variable Nitric Acid Solutions - Spectrophotometric, HW-79195, October 14, 1963.

Effect of $NaNO_2$ Concentration

Solution:

Pu(VI)	0.0111M
HNO_3	0.55M
Fe(III)	5×10^{-5}M
$NaNO_2$	Variable
Temperature	60 C

$NaNO_2$ conc.	Time (Min.)	% Pu(VI)	% Pu(IV)	% Pu(III)
0.012M	10	63	21	16
	20	47	30	23
	30	37	37	26
	40	25	46	29
	50	20	50	30
	60	17	52	31
	70	14	55	31
0.024M	10	53	21	26
	20	30	33	37
	30	15	40	45
	40	5	47	48
	50	2	49	49
	60	1	50	49
	70	1	51	48

$NaNO_2$ conc.	Time(Min.)	% Pu(VI)	% Pu(IV)	% Pu(III)
0.049M	10	39	23	38
	20	14	34	52
	30	3	37	60
	40	1	39	60
	50	<1	40	60
	60	<1	41	59
	70	<1	41	59
0.098M	10	18	22	60
	20	2	27	71
	30	<1	28	72
	40	<1	28	72
	50	0	29	71
	60	0	30	70

Effect of HNO_3 Concentration

Solution:

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

HNO_3 Conc.	Time (min.)	% Pu(VI)	% Pu(IV)	% Pu(III)
0.55M	10	16	30	54
	20	2	35	63
	30	1	36	63
	40	1	37	62
	50	1	38	61
	60	1	40	59
1.00M	10	23	58	19
	20	4	75	21
	30	2	78	20
	40	1	79	20
	50	1	80	19
	60	2	81	17
	70	2	82	16
1.25M	10	28	60	12
	20	5	85	10
	30	2	91	7
	40	1	93	6
	50	1	94	5
	60	1	94	5
1.40M	10	31	65	4
	20	7	89	4
	30	3	94	3
	40	2	96	2
	50	2	97	1
	60	1	98	1
	70	1	98	1

Effect of Ferric Ion Concentrations

The rate of reaction is dependent upon the ferric ion concentration.

Solution:

Pu(VI)	0.0111M
HNO_3	0.55M
Fe(III)	Variable
$NaNO_2$	0.049M
Temperature	70 C

Fe(III)	Time (min.)	% Pu(VI)	% Pu(IV)	% Pu(III)
5×10^{-5}M	10	16	30	54
	20	2	35	63
	30	1	36	63
	40	1	37	62
	50	1	38	61
	60	1	40	59
0.01M	10	2	33	65
	20	<1	35	65
	30	<1	36	64
	40	<1	37	63
	50	1	38	61
	60	2	39	59

Effect of Temperature

Reaction was not readily detectable at 25 C.

Solution:

Pu(VI)	0.0111M
HNO_3	0.55M
Fe(III)	5×10^{-5}M
$NaNO_2$	0.049M
Temperature	Variable

Temperature	Time (min.)	% Pu(VI)	% Pu(IV)	% Pu(III)
48 C	10	28	3	69
	20	17	5	78
	30	12	6	82
	40	9	7	84
	50	6	8	86
	60	3	8	89
	70	1	8	91
70 C	10	16	30	54
	20	2	35	63
	30	1	36	63
	40	1	37	62
	50	1	38	61
	60	1	40	59

Gaseous NO_2

Use of gaseous NO_2 in 0.5M HNO_3 solutions at temperatures above 50 C yielded results comparable to those obtained with $NaNO_2$. Attempts to reduce Pu(VI) to Pu(IV) in 7M HNO_3 with gaseous NO_2 indicated that the reaction rate was too low to be of practical use. Also the nitrogen oxides dissolved in the 7M HNO_3 solution after NO_2 sparging would require considerable air sparging for removal before a suitable feed to the anion exchange unit was available.