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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

SOME EXPERIMENTS ON THE PRECIPITATION OF PLUTONIUM COMPOUNDS FROM TRIBUTYL PHOSPHATE SOLUTIONS

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LOS ALAMOS SCIENTIFIC LABORATORY
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SOME EXPERIMENTS ON THE PRECIPITATION OF PLUTONIUM COMPOUNDS FROM TRIBUTYL PHOSPHATE SOLUTIONS

Work done by:	Report written by:
L. J. Mullins	W. J. Maraman L. J. Mullins

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ABSTRACT

A survey of the feasibility of precipitating plutonium(IV) compounds from 35 per cent tributyl phosphate in Gulf BT solution has been made. In general, the precipitations were made using an anhydrous salt, a saturated aqueous solution and a dilute aqueous solution. The anhydrous precipitants which showed promise for further study were Na_2O_2 and NaF. Promising aqueous solutions were H_2O_2, NaF, HF and K_2SO_4. The oxalate, hydroxide, iodate, phosphate, sulfite and sulfide systems either gave precipitates of poor physical characteristics or resulted in high plutonium solubilities in the organic phase.

The precipitation of plutonium(III) in the same solvent was not studied because of the relatively rapid oxidation of plutonium(III) to plutonium(IV) in TBP solution containing HNO_3.

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Introduction

Direct precipitation of plutonium from the pregnant solvent in the tributyl phosphate processing operation would have advantages over conventional aqueous stripping methods. Laborious concentration steps (evaporation, ion exchange or solvent extraction) and purification steps from dilute aqueous solutions would be eliminated. Selective precipitants would offer a variety of plutonium compounds.

Miscellaneous experiments since 1951 have shown that plutonium could be precipitated from TBP by aqueous solutions of HF,[1] NH_4F,[1] NH_4OH,[2] Na_2CO_3,[1] or H_2O_2[1] as well as by the addition of solid Na_2O_2,[3] NH_4F,[3] or $H_2C_2O_4 \cdot 2H_2O$[3] and by sparging with gaseous HF,[4] SO_2,[3] or NH_3[3].

The experiments described in this report were designed to explore the feasibility of precipitating plutonium from 35 per cent TBP in Gulf BT using peroxide, fluoride, sulfide, sulfite, sulfate, oxalate, hydroxide, iodate and phosphate ions from anhydrous, dilute and concentrated aqueous sources.

It was originally planned to study plutonium in both the tri- and tetravalent form; however, the plutonium(III) study was not undertaken because of its relative instability in TBP solutions containing nitric acid.

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Method of Precipitation of Plutonium(IV) Compounds from TBP Solution

Plutonium(IV) compounds were precipitated in 40 ml centrifuge cones using 25 ml of 35 per cent tributyl phosphate in Gulf BT containing about 2.5 grams Pu/liter as a feed solution. The feed was prepared by equilibrating equal volumes of 35 per cent TBP-GBT and 0.01 M $Pu(NO_3)_4$ - 6 M HNO_3 solutions. The resulting organic phase was scrubbed four times with an equal volume of 2.2 M $Al(NO_3)_3$. About ten times the stoichiometric amount for precipitation was added in the form of an anhydrous salt or gas, a saturated aqueous solution or a dilute aqueous solution. The mixture was stirred for 15 minutes. Those precipitates which visually possessed good physical characteristics were centrifuged, washed and sampled for microscopic examination and x-ray diffraction analysis. The supernate was sampled for plutonium radio-analysis.

Instability of Plutonium(III) in TBP-GBT-HNO_3 Solutions

Although $Pu(NO_3)_3$ can be extracted, the precipitation of plutonium(III) from TBP solutions was not studied because of the relative instability of plutonium(III) in TBP solutions containing HNO_3. Plutonium(III) is oxidized to plutonium(IV) in such solutions. There is an induction period which depends upon the HNO_3 concentration, and the oxidation rate curve is an

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S-shaped curve typical of autocatalytic reactions, the slope of which varies with the HNO_3 concentration.

The TBP solution was prepared by equilibrating equal volumes of 35 per cent TBP in Gulf BT with $Ca(NO_3)_2$-$Pu(NO_3)_3$-NH_2OH solutions of varying HNO_3. Plutonium oxidation was followed spectrophotometrically. The acidity of the organic phase after plutonium oxidation was determined by titration with standard NaOH in a saturated $K_2C_2O_4$ solution. Oxidation was complete in 40 minutes for 0.076 M HNO_3, 140 minutes for 0.010 M HNO_3 and 72 hours for 0.002 M HNO_3 with TBP solutions 0.0016 M in plutonium.

Precipitation of Plutonium(IV) by Solid and Anhydrous Precipitants

Plutonium(IV) was precipitated from TBP-GBT solutions using anhydrous solid or gaseous precipitants containing $O_2^=$, F^-, $S^=$, $SO_3^=$, $SO_4^=$, $C_2O_4^=$, OH^-, IO_3^- and $PO_4^{\equiv}$. Results of these precipitations are given in Table I.

The most promising precipitant was NaF, which produced the readily filterable, definite compound $PuF_4 \cdot H_2O$. The plutonium solubility in the organic supernate was 5 mg/liter and the data were reproducible. Gaseous HF gave similar results except that there was considerable evolution of heat.

Na_2O_2 gave a precipitate having better settling characteristics than NaF or HF. The plutonium-peroxide-oxide compound formed was easily soluble in HNO_3. The erratic organic solubility can probably be corrected by controlling the HNO_3 concentration in the organic supernate and by an improved organic-solid phase separation technique.

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H_2S gave excellent removal of the plutonium from the solvent down to 0.2 mg/liter; however, free sulfur and considerable heat were liberated and the precipitate was not identified.

K_2SO_4, HIO_3 and K_3PO_4 precipitated no plutonium from the solution. $(NH_4)_2SO_3 \cdot H_2O$, $Na_2C_2O_4$ and NaOH removed some plutonium from the solution, but the precipitates formed had poor physical characteristics and the compounds formed were not identified.

Precipitation of Plutonium(IV) by Aqueous Precipitants

Plutonium(IV) was precipitated from TBP-GBT solutions using saturated and dilute aqueous precipitants containing $O_2^{=}$, F^-, $S^{=}$, $SO_4^{=}$, $C_2O_4^{=}$, OH^-, IO_3^- and $PO_4^{\equiv}$. Results of these precipitations are given in Table I.

As with the solid precipitants fluoride ion gave the best results. Supernate loss was low, 4 mg/liter, and the data were reproducible. The $NaPuF_5$ precipitated by dilute NaF solutions had good settling characteristics. $PuF_4 \cdot H_2O$ was formed by both dilute and concentrated HF solutions, but its settling characteristics were not as desirable as those of the compound produced by the anhydrous method.

Dilute K_2SO_4 solutions yielded a definite compound, $K_4Pu(SO_4)_4 \cdot 2H_2O$, which had good settling characteristics. The supernate loss could be controlled by acidity adjustments.

Dilute H_2O_2 solutions gave only fair results and 30 per cent H_2O_2 precipitated no plutonium.

Dilute solutions of $Na_2C_2O_4$, NaOH, HIO_3 and H_3PO_4 produced precipitates

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which had poor settling characteristics, but gave good solvent clean up. Concentrated HIO_3 and H_3PO_4 were not successful precipitants.

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2. R. S. Winchester, LAB CMR-11-875, November, 1951.
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Table I

PRECIPITATION OF PLUTONIUM(IV) FROM TBP SOLUTION

Description	Amount[1]	Pu in TBP Supernate, g/liter[2]	Settling Characteristics[3]	Precipitate Micro Examination	Precipitate X-ray Examination	Remarks
Solid and Anhydrous Precipitants						
Na_2O_2	10S	0.02-0.2	Good	PuO_2 + peroxide	No pattern	$O_2^=/Pu = 1.55$
NaF	10S	0.005	Fair	$PuF_4 \cdot H_2O$	Uncertain	
HF(g)	Saturated	0.003	Poor	$PuF_4 \cdot H_2O$	$PuF_4 \cdot H_2O$	Heat evolution
H_2S(g)	Saturated	0.0002	Fair	Unidentified	Unidentified	Same, S^0
$(NH_4)_2SO_3 \cdot H_2O$	10S	0.5	Fair	Unidentified	Unidentified	
K_2SO_4	10S	2.5	-	None	None	No precipitate
$Na_2C_2O_4$	10S	0.5	Poor	None	None	
NaOH	10S	0.05	Fair	None	None	
HIO_3	10S	2.5	-	None	None	No precipitate
K_3PO_4	10S	2.2	-	None	None	No precipitate
Aqueous Precipitants						
30% H_2O_2	3 ml	1.31	-	None	None	No precipitate
10% H_2O_2, 0.1 M H_2SO_4, 2 M HNO_3	15 ml	0.01	Fair	None	None	
1 M NaF	2 ml	0.004	Good	$NaPuF_5$	Uncertain	
0.8 M HF, 1 M NaF, 0.5 M HNO_3	15 ml	0.004	Good	None	None	
27 M HF	0.1 ml	0.002	Poor	$PuF_4 \cdot H_2O$	$PuF_4 \cdot H_2O$	
2 M HF, 1 M HNO_3	5 ml	0.02	Fair	$PuF_4 \cdot H_2O$	$PuF_4 \cdot H_2O$	
0.7 M K_2SO_4	2 ml	0.1	Good	$K_4Pu(SO_4)_4 \cdot 2H_2O$	Unidentified	
0.57 M K_2SO_4, 0.1 M H_2SO_4, 10% C_2H_5OH	10 ml	0.002	Good	$K_4Pu(SO_4)_4 \cdot 2H_2O$	Unidentified	
0.2 M $Na_2C_2O_4$, 1 M HNO_3	10 ml	0.002	Poor	None	None	
1.7 M NaOH	15 ml	0.0002	Poor	None	None	
20 M HIO_3	0.5 ml	1.1	-	None	None	No precipitate
1 M HIO_3, 1 M HNO_3	10 ml	0.0001	Poor	None	None	
14.9 M H_3PO_4	0.2 ml	0.07	Poor	None	None	
3 M H_3PO_4, 0.1 M HNO_3	10 ml	0.004	Poor	None	None	

1. 10S is 10 times the stoichiometric amount of the anion required for complete precipitation of the Pu compound.
2. Beginning TBP feed solution contained 2.5 grams Pu/liter.
3. Qualitative observation based on settling rate, phase wetting and physical appearance of precipitate.

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