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Subject Category: TECHNOLOGY-PLUTONIUM

UNITED STATES ATOMIC ENERGY COMMISSION

PURIFICATION AND CONCENTRATION OF
SOLVENT EXTRACTED PLUTONIUM BY
OXALATE PRECIPITATION

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January 1956

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TECHNOLOGY — PLUTONIUM

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LOS ALAMOS SCIENTIFIC LABORATORY
of the
UNIVERSITY OF CALIFORNIA

Report written:
January 1956

Price \$ 0.25

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

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OF SOLVENT EXTRACTED PLUTONIUM
BY OXALATE PRECIPITATION

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CLASSIFICATION CANCELLED

DATE APR 1 1957

For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

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INTRODUCTION

The plutonium nitrate product from the tributyl phosphate extraction plant contained too many impurities (Table 1) and was too dilute in plutonium to be a satisfactory routine feed for the metal production facility. This product was obtained by a twenty-fold evaporation concentration of the strip product stream of a TBP extraction process.

The present coupling system (Fig. 1) consists of an oxalate strike on the strip product stream, conversion of the precipitated plutonium-III oxalate to a low temperature oxide and dissolution of the oxide in a nitric-hydrofluoric acid mixture. Some 41 kg of plutonium have been purified and concentrated by this procedure to date. This nitrate is of sufficient purity (Table 2) and plutonium concentration (200 to 225 g/l) to be a satisfactory routine feed for the metal production line.

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PLUTONIUM PURIFICATION OPERATION

The plutonium in the strip product stream from the TBP mixer-settler unit is 5-15 g/l of which at least 95 per cent is trivalent since 0.1N $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ is employed as the stripping reagent. Solid oxalic acid is added to 12 liters of this solution in a 3.5 gallon polyethylene container at a weight ratio of 1.25 gram per gram of plutonium. The mixture is stirred for 30 minutes. (If the blue color of plutonium-III persists after precipitation, an additional amount of oxalic acid at a ratio of 0.3 to 1 is added.) The plutonium-III oxalate precipitate, which is readily filterable, settles rapidly, and after 30 minutes the supernate is decanted through an in-line Micro Metallic grade G stainless steel filter. The precipitate is washed twice with 500 ml of water. The slurry is washed into a 600 ml medium fritted glass funnel. The average plutonium concentration in the combined filtrates and washes is 20 mg/l. This solution and the distillate, below, are recycled through the TBP plant.

The precipitate is vacuum dried and transferred to an 800 ml stainless steel beaker. The oxalate is heated for about two hours on a hot plate until it is converted to oxide, which can be determined by a color change. The oxide is weighed on a triple-beam balance for batch control. About 360 grams of plutonium as oxide are transferred into a 5 liter round bottom

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pyrex flask which is heated by a Variac-controlled Glascol aluminum jacketed mantle. The dissolving acid, 1.5 liters of 16N HNO₃ - 0.05N HF, is added. The mixture is refluxed for 2 hours using a vertical water cooled condenser. The condenser is turned to a horizontal position and the mixture distilled for about 3 hours until 1 liter of distillate is collected. The plutonium solution is allowed to cool and filtered through a medium fritted glass filter. The concentrate is diluted with 1 liter of water and stirred.

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CONCLUSIONS FROM LABORATORY TESTS

Some of the more important variables affecting the efficiency of the plutonium-III oxalate precipitation for this operation were studied briefly in the laboratory. These included plutonium and oxalate concentration, acidity and digestion time. Synthetic product solutions containing 10 and 1.05 grams Pu/l in 0.1N $\text{NH}_2\text{OH}\cdot\text{HCl}$ were used. The results are summarized below:

1. Precipitations made at 0.1N acidity with varying oxalate concentrations indicated a minimum supernate loss of 0.036 gram Pu/l at 150 per cent of the stoichiometric oxalate requirement for 1.05 grams Pu/l feed; losses ranged from 0.34 to 0.05 g/l from 70 to 200 per cent. With 10 grams Pu/l feed, the minimum occurred at 120 per cent with 0.096 g/l loss; the range was 0.34 to 0.11 g/l from 94 to 146 per cent. These precipitations were carried out with 4 hours stirring and overnight standing before separation.
2. Precipitations were made using 100 per cent of the stoichiometric oxalate requirement for 1.05 grams Pu/l feed and acidities less than 0.1N. The acidity was

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adjusted by caustic to a final value of between pH 1 and 7 during stirring. Supernate loss ranged from 0.07 to 0.0001 g/l. Rapid oxidation of plutonium-III to plutonium-IV at pH greater than 3 caused hydroxide precipitation without an apparent decrease in the filterability characteristic.

3. Stirring and digestion time studies were made on precipitations at 0.1N acidity. The supernate loss increased from 0.067 to 0.089 g/l for 15 minutes to 16 hours for the 1.05 gram Pu/l feed using 100 per cent of the stoichiometric oxalate requirement. At 150 per cent the loss ranged from 0.008 to 0.02 g/l.

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TABLE 1

Nitrate Product Purity - Evaporation Procedure

Element	Concentration,* ppm of Pu	
	Lot No.	
	<u>37</u>	<u>43</u>
Li	< 2	3
Be	< 2	< 2
Na	4,000	Est. 10,000
Mg	2,000	4,000
Ca	500	2,000
Al	500	600
La	200	200
K	< 500	< 500
Si	10	5
Pb	500	500
Cu	30	30
Ni	5	5
Cr	10	15
B	Est. 100	Est. 500
Mn	15	20
Sn	12	12
Bi	< 5	< 5
Fe	120	1,200
V	< 20	< 20
Cd	< 5	< 5
Co	< 5	< 5
Ba	< 20	< 20
Mo	< 20	< 20
Ag	5	10
Zn	400	600
Pu	245 g/l	331 g/l

*Spectrochemical analysis for all except Fe and Pu

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TABLE 2

Nitrate Product Purity - Oxalate Procedure

Element	Concentration, * ppm of Pu				
	Lot No.				
	100	102	166	168	169
Li	1	< 0.2	< 0.4	< 0.4	< 0.4
Be	0.2	< 0.2	< 0.4	< 0.4	< 0.4
Na	400	500	300	300	< 20
Mg	600	300	70	50	40
Ca	0.1 to 1%	0.1 to 1%	0.1 to 1%	0.1 to 1%	0.1 to 1%
Al	20	10	40	70	< 5
La	1000	50	< 20	< 20	< 20
K					
Si	< 1	< 1	< 5	5	< 1
Pb	600	175	200	200	200
Cu	5	80	3	3	25
Ni	6	40	15	10	3
Cr	10	< 5	5	5	5
B	35	300	50	75	100
Mn	15	15	5	10	15
Sn	10	10	10	3	3
Bi	500	400	75	20	
Fe	600	600	< 70	< 35	200
V	< 10	< 20	< 20	< 20	< 30
Cd	50		10	10	
Co	< 20		< 10	< 10	
Ba			300	200	
Mo	< 10	< 20	15	< 10	
Ag	50	10	3	3	3
Zn	< 100	10	200	200	100
Pu	269 g/l	260 g/l	214 g/l	216 g/l	226 g/l

* Spectrochemical analysis for all except Fe and Pu

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PLUTONIUM PURIFICATION FLOWSHEET

Figure 1

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