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Technology - Plutonium

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AEC RESEARCH AND DEVELOPMENT REPORT

NOTES PERTAINING TO RECUPLEX PRODUCT EVAPORATION

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April 28, 1954

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by the
General Electric Company under Contract #W-31-109-Eng-52

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NOTES PERTAINING TO RECUPLEX PRODUCT EVAPORATION

INTRODUCTION

The process difficulties associated with the evaporation of uranyl nitrate - tributyl phosphate - hydrocarbon mixtures are well known.^(1, 2) Since the Recuplex product evaporator will evaporate similar, plutonium-bearing solutions to give plutonium concentrations as high as 400 grams per liter, it was desirable to determine whether or not any possibility of explosion existed, whether or not a plutonium "red oil"⁽³⁾ formed, and the effect of any organic residues upon subsequent processing operations. This report summarizes the laboratory work done to answer these questions.

SUMMARY AND CONCLUSIONS

A red-brown liquid, similar to "red oil," formed during the evaporation of simulated Recuplex product solutions containing plutonium, nitric acid, carbon tetrachloride and tributyl phosphate (TBP). The liquid is soluble in carbon tetrachloride.

Concentration of solutions containing a TBP to plutonyl nitrate weight ratio of 0.15 or greater to a pot temperature of 150 C caused reactions which produced enough heat to bring the pot contents to a red heat with copious evolution of gases.

Evaporation path curves and boiling point data were obtained from batch evaporations with minimum reflux and are presented in Figure 1. Polymeric plutonium (IV) was formed upon concentrating plutonium nitrate solutions of low nitric acid content. The region of polymer formation was defined and is presented in Figure 2.

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Neither the red-brown phase nor gross amounts of TBP-CCl₄ added to plutonium nitrate solutions interfered with either plutonium (IV) oxalate or plutonium peroxide precipitation from these solutions.

TRIBUTYL PHOSPHATE-PLUTONIUM NITRATE REACTION

The reactivity of TBP-plutonium nitrate mixtures apparently depends mainly on the relative amounts present. With a TBP to plutonyl nitrate weight ratio of 0.15 or higher, violent reactions were initiated when evaporations were carried out to pot temperatures over 150 C. No reactivity was noted at lower weight ratios, or lower temperatures. Work at Savannah River⁽¹⁾ indicated a critical ratio of 0.12 for TBP-uranyl nitrate mixtures. No reactions were found at lower ratios for systems at atmospheric pressure. Temperatures for initiation of the TBP-UNH reaction were comparable to those found here.

The heat of the TBP-plutonium nitrate reaction was sufficient to raise the pot contents to red heat in a matter of seconds, with violent but not explosive evolution of gases. The pyrex apparatus remained intact in every case.

A heavy, red-brown liquid formed during evaporation of TBP-plutonium-carbon tetrachloride mixtures. This liquid was similar to that described for TBP-hydrocarbon-uranium systems,⁽³⁾ except that its miscibility in carbon tetrachloride precludes its being termed a "third phase". No attempt was made to analyze this material, it being assumed to consist of TBP and DBP-plutonium complexes.

EFFECTS OF ORGANIC PHASES ON PRECIPITATION AND FILTRATION

Testing both oxalate and peroxide precipitations, the only effect from the presence of Recuplex organic phases appeared to be the formation of organic cruds from precipitate fines. The cruds remained with the filter cake, holding up organic phosphates. This should present no problem.

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however, since removal should be effected during hydrofluorination of the cake. Both the red-brown liquid formed during evaporation and gross amounts of TBP-CCl₄ were tested. Losses were not affected significantly (Table I), and settling and filtration rates were comparable to those for control runs.

TABLE I
EFFECT OF ORGANIC PHASES ON PLUTONIUM LOSSES
DURING PRECIPITATION

Precipitant	Losses to Supernatant,		Per Cent of Run
	No Organic Present	Red Liquid Present Two Volume Per Cent	TBP-CCl ₄ Present Ten Volume Per Cent
Hydrogen Peroxide	2*	1	2
Oxalic Acid	2*	3	2

* Average of two runs

The plutonium solution used was obtained by dissolving metal buttons in hydrochloric acid and converting to nitric acid solution. It was not contacted with TBP-CCl₄ until preliminary digestions for the above runs were made.

BOILING POINT OF PLUTONIUM NITRATE SOLUTIONS

Boiling point data and evaporation paths were obtained by analyzing a small sample and noting the boiling temperature at several points during the open-vessel evaporation of plutonium nitrate solutions. The results have been plotted on graph paper and smooth curves drawn through the

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data (Figure 1). The boiling points were determined in a closed hood under negative pressure and are several degrees lower than would be expected for standard conditions, but should be of sufficient precision for Recuplex design. Vigorous boiling with ceramic chips was assumed to indicate very little superheating.

REGION OF POLYMER FORMATION

Attempts to evaporate high-plutonium, low-acid solutions, such as are expected from Recuplex, led to vigorous foaming and precipitation of polymeric plutonium(IV). The region in which this behavior may be expected upon heating was delineated and is shown in Figure 2.

RAP:ms

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FIGURE 1

BOILING TEMPERATURES

Plutonium Nitrate - Nitric Acid

FIGURE 2
REGION OF POLYMER FORMATION