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EMULSIFICATION AND PRECIPITATION IN THE RECUPLEX COLUMNS

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EMULSIFICATION AND PRECIPITATION IN THE RECUPLEX COLUMNS

By

A. Brunstad

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EMULSIFICATION AND PRECIPITATION IN THE RECUPLEX COLUMNS

I. INTRODUCTION

Extensive emulsification was encountered on February 4, 1958, in the operation of the Recuplex extraction column. Precipitation in the stripping column, with resulting flooding, was also encountered and has been noted subsequently. Finished Products Technology Operation personnel submitted feed and waste samples believed to be representative of the conditions causing the difficulties. The laboratory investigations of these samples are described herein.

II. SUMMARY AND CONCLUSIONS

Laboratory work with the Recuplex process samples indicated the extraction column emulsification to be related to the presence of tributyl phosphate disintegration products and hydrocarbon oil in a feed tank. Dispersed silica contributed to the emulsification. Silica dispersion is related to high fluoride concentration and an insufficient aluminum to fluoride ratio.

Precipitation of a plutonium(IV) compound in the stripping column occurs at acidities in the region of 0.2 M - 0.3 M H^+, in the presence of sulfate ion. The identity of the precipitate has not been definitely established.

III. DISCUSSION

Feed Sample (CAFA)

This sample resembled crankcase sediment. It sank through 2 M HNO_3 without dissolving. When shaken with 2 M HNO_3 and 15 percent TBP, both phases increased in volume. An opaque gelatinous material separated at the interface. A radioassay showed this "feed" material to contain 168 g plutonium per liter and spectrographic analysis indicated high concentrations of phosphorus, silica, and aluminum.

It appears that TBP containing organic solution had been in prolonged contact with feed solutions, resulting in breakdown of the TBP and formation of emulsifying agents by hydrolysis and radiolysis. Radiolysis products of TBP polymerize to form effective emulsifiers. These are not removed by carbonate washing. Radiolysis also produces DBP in quantities slightly greater than polymer. Aged organic TBP solutions containing plutonium are, therefore, sources of emulsifiers. It is especially important that plutonium residence time in the organic phase be kept at a minimum.

"A" Column Interface Crud (Four Liters)

Most of the separated organic and aqueous phases were separated from the "crud" and returned to process. The remaining interface material

(about 250 ml) was composed mainly of a grey emulsion resembling that obtained from the CAFA sample. A 100 ml portion of the interface material was shaken successively with three equal volumes of water. A white material dispersed in the aqueous phase and subsequently settled out from the separated aqueous layer. The dense emulsion remaining from the three water washings separated into a grey semi-solid and an organic liquid. The grey material was separated and washed with water and carbon tetrachloride. Much of the material stuck to the sides of the separatory funnel and gelatinous translucent beads which resembled hydrous silica. Samples of the gelatinous material and of the precipitate from the aqueous phase were submitted for spectrographic analysis.

Both samples contained silica as a major constituent, and contained minor amounts of aluminum phosphorus, calcium, and magnesium.

CAW (H-11)

This sample was used to prepare a series of feed solutions with varying plutonium concentration and with added fluoride as indicated below.

EXTRACTION, SCRUB, STRIP STUDIES WITH FEED SOLUTION PREPARED FROM CAW SAMPLE

Solution Number	Pu g/l	M F^- Added	M Al^{+++} Added	Extractant 15% DBBP	Scrub	Strip
1 a	1	-	-		None	0.05 M HAS
b	1	0.48	-		None	0.05 M HNO_3
2 a	5	-	-		90 g/l	0.05 M HAS
b	5	0.48	-		1 M H^+	0.05 M HNO_3
3 a	10	-	0.50		90 g/l	0.05 M HAS
b	10	0.48	0.50		1 M H^+	0.05 M HNO_3
4 a	20	-	-		90 g/l	0.05 M HAS
b	20	0.48	-		1 M H^+	0.05 M HNO_3

A greyish-brown precipitate settled in the "a" series of feed solutions; the amount was proportional to the amount of plutonium added. A gelatinous material formed in the high fluoride "b" series which aggregated mostly near the top of the solution. When ANN was added to solution "3b," the gelatinous material dispersed but an opaque substance deposited on the sides of the bottle. This resembled the material obtained from the interface crud.

Disengaging times were poor with all feed solutions. Two of the "a" series were left for 1-1/2 hours without complete disengagement. The "b" series disengaged slightly better, but none were disengaged at 10

minutes.

Only a slight amount of light-grey precipitate was evident in the solutions after extraction. The more extensive precipitates which formed when plutonium was added to the original CAW solution would seem, therefore, to have resulted from a flocculation process. It appears that the plutonium adsorption caused the deposition, and that the adsorbed plutonium was readily extracted. The precipitate appeared to be silica.

Extraction coefficients were not determined, but extraction appeared to be as efficient as expected with the extractant employed.

Disengaging times were good in the scrub and stripping operations. A brown precipitate formed in the third and fourth stripping (product) solutions.

"C" Column Precipitate

The brown precipitate which plugged the "C" column plates in Recuplex operations appeared identical to the precipitates which formed in the experimental product stripping solutions. The column precipitation occurred only at the 2/3 to 3/4 column height, which corresponds to the experimental second and third batch stages in which precipitation occurred. Subsequent stripping tests with and without sulfate ion and with and without fluoride ion indicated that precipitation occurs only in the presence of sulfate ion and that fluoride is not a factor. Determinations of acidity in the supernatant solutions showed all concentrations to be in the range 0.2 M - 0.3 M H^+.

The first stripping stages are highest in acidity, and only plutonium(IV) is present. Plutonium(III), plutonium(IV), and plutonium(VI) were found in the product solutions of acidities in the range where precipitation occurred. Plutonium(III) is the main species in the dilute plutonium - low acid last stages. No precipitation occurred in plutonium(III) solutions. Precipitation did take place, however, when solutions of about 0.3 M H^+ reoxidized on standing. It may also be noted that precipitation occurred at a plutonium concentration where sulfate concentration becomes insufficient for the first plutonium(IV) complex; thus permitting disproportion. The precipitate dissolved in 4 M HNO_3 to produce a typical plutonium(IV) solution.

Examination of the dried precipitate by x-ray diffraction did not reveal a definite crystal pattern and the identity of the precipitate could not be established. Analysis of the precipitate indicated sulfate to be carried by the precipitate, but that the precipitate is not plutonium(IV) sulfate.

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