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REDOX THIRD Pu CYCLE
LABORATORY STUDY OF EFFECTS OF
DECREASED ACTIVITY

AUTHOR

J. L. Bradford and M. [redacted]

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REDOX THIRD Pu CYCLE
LABORATORY STUDY OF EFFECTS OF DECREASED ACIDITY

by

J. L. Bradford and M. H. Curtis

Process Chemistry
Chemical Development Unit
Separations Technology Sub-Section

January 4, 1954

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INTRODUCTION

The design and proposed construction of the new PR facility for Redox is based on the need for 1) increased capacity for plutonium processing (4.25 kg./day, equivalent to the 8.3 tons of U/day for Redox phase II rate), and 2) reduced acid-to-Pu ratios in the final product to permit satisfactory processing in Task I of the 234-5 operation.[3]

A number of alternate Pu cycle flowsheets have been scouted and proposed in the past several years.[2,4] One such flowsheet decreases the acid-to-Pu ratio in the 3BP product by eliminating acid from the 2AX and 3AX, thus requiring either an increased solvent flow, or an increased ANN salting strength. This does not, however, provide additional Pu processing capacity. A second alternative flowsheet involves the reflux of 97.5% of the 2BP stream back to the 2A Column. The reflux flowsheet meets both of the needs outlined above, but on the basis of nuclear safety considerations is not yet considered ready for adoption in the Redox Plant.

This report deals with the laboratory testing of a third alternative for reducing the acid concentration in the final product by decreasing the acidity of both scrub and feed streams to the third cycle.

OBJECTIVES

The objectives of this laboratory work were to study the third plutonium cycle flowsheet variables from the standpoints of:

1. Nitric acid-to-plutonium ratios in 3BP,
2. Plutonium losses, and
3. Fission product decontamination.

SUMMARY AND CONCLUSIONS

Four continuous counter-current solvent extraction runs were made in a "Mini" miniature mixer-settler 3A-3B cascade using Redox Plant 2BP solution for the 3A feed preparation. These runs demonstrated:

1. A reduction of nitric acid-to-plutonium mole ratios in the 3BP from a maximum of 67 (obtained with the current flowsheet) to a minimum of 2.

2. Plutonium losses were not increased with decreased feed and scrub solution acidities in the range investigated, although too great a reduction of 3A Column acidity would be predicted to give high Pu losses in the 3AW.

3. Gross decontamination factors for both beta and gamma were increased by more than a factor of 2 with lower 3A acidities.

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EXPERIMENTAL

The four runs were made in a 3A-3B cascade of 1/2-inch miniature mixer-settlers whose influent streams were fed and controlled by Milton-Roy Mini-pumps. At least 10 complete volume displacements were made per run to assure reaching equilibrium, and all runs were made at a rate of 2.7 displacements per hour. All feed solutions were prepared from the same Redox Plant 2BP solution by dilution with a 68% ANN solution and nitric acid as required. This same ANN solution (acid-deficient as supplied by the General Chemical Co. to the Redox Plant) was also used to prepare the scrub solutions, again adjusted with nitric acid where necessary. The extractant (3AX) was prepared in the laboratory by blending C.P. 70% nitric acid with Redox plant-distilled hexone. Run details and results are presented in Table I. Runs 1 and 2 were made using current flow ratios. The ratios for Runs 3 and 4 were adjusted on the basis of the ANN requirements to give the desired acidities to the scrub and blended feed solutions.

DISCUSSION

All current Redox second and third plutonium cycle flowsheets are based on Pu(IV) chemistry, and thus, though in practice about 95% of the plutonium in the Pu cycle is Pu(VI), the control of acidity in the extraction sections of the 2A and 3A Columns is a most important consideration in the prevention of high losses of Pu(IV) to aqueous waste.

The distribution ratio of Pu(IV) in uranium-free aqueous solutions is closely approximated by the following equation:[1]

$$\log E_a^o = -1.2057 + 3.0425 \log [NO_3^-] - 0.3661 \text{ pH}.$$

Thus, in the bottom of the extraction section, the Pu(IV) distribution ratio is directly affected by both salt strength and acidity. Since both the 3AX acid concentration (0.49 M) and the aqueous salt strength in this region (1.3 M ANN) were the same for all four runs, and since the 3AW nitric acid molarity varied only from 0.24 to 0.37, little change in plutonium extraction behavior would have been expected. However, a 10-fold drop in waste losses was observed between Runs 1 and 3 having identical 3AW acidities.

Previous discussions of low-acid plutonium cycle flowsheets have stressed the need for close control of the extraction section acidity,[2,6] for it was believed that if solution make-up were not held to very close tolerances for acidity (very difficult to measure and adjust for) high Pu waste losses would result. Runs 2 and 4 were made by diluting the acid-deficient ANN (as received) for scrubs, and in Run 4 this same ANN was used for feed make-up with no additional acid adjustment. The results show no serious detrimental effects, perhaps chiefly because of the acid contribution of the extractant. Although the acid-deficiency of the ANN, as received, varies ± 10%, the 3AX acidity, a much more vital consideration, varies as

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much as ±15% under present plant practices and therefore is probably the controlling factor on arriving at a safe, low-acid flowsheet for plant operation. None of these four runs was of low enough acidity to define this critical acid limit, and based on the results presented in Table I, it might thus be concluded that a wider latitude of acidity is permissible than was originally believed to be possible. The increased acid-deficiency in the scrub section is reflected as increased fission product decontamination.

One factor not yet investigated is the possible effect of the low-acid conditions on physical operating behavior of the plant columns. Disengaging time studies in the laboratory have shown that the scrub section exhibits increased disengaging times with increased acid-deficiency. If proposed plant tests of a low-acid 3A flowsheet(5) show column operating instability, acidification of the feed should be investigated first as a means of obtaining operating stability without sacrificing all of the lower nitric-to-plutonium features of such a flowsheet.

Since a 30-fold reduction in nitric acid concentration in the plutonium product is not required immediately, an intermediate flowsheet might be adopted which would give a reduced nitric-to-plutonium ratio but would still remain in the conservative region insofar as the possible deleterious effects of 3AX acidity variations are concerned. If plant techniques for blending nitric acid into solvent can be improved for more dependable control within closer limits, then lower nitric-to-plutonium ratios may be readily achieved.

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TABLE I

REDOX THIRD Pu CYCLE
EFFECT OF REDUCED ACID CONCENTRATION

Method: Miniature mixer-settlers used for 3A-3B extraction cycle.
3A: 12 extraction and 6 scrub stages
3B: 12 strip stages
Length of runs: Not less than 10 complete 3A bank volume displacements

Feeds: All 3AF solutions prepared from a single sample of Redox plant 2BP, by adjusting with 68% ANN solution and HNO_3. Dichromate was added to stabilize Pu valence over duration of series of runs.

Flowsheet and Stream Compositions:

Run No.	Flow Ratios (IAF = 100) 3AF	3AS	3AX	3BX	Composition(1) 3AF Total Pu,(2) Cts./Min./Gal.	Gamma, Microcuries/Gal.	HNO_3, M	ANN, M	$Cr_2O_7^{=}$, M	3AS HNO_3, M	ANN, M	3BX HNO_3, M
1	14.9	14.9	23	9	4.9×10^{11}	318	0.29	1.30	0.01	0.0	1.3	0.04
2	14.9	14.9	23	9	5.1×10^{11}	240	0.07	1.30	0.02	-0.15	1.3	0.04
3	18.0	18.0	27.6	9	3.9×10^{11}	230	0.17	1.50	0.01	-0.09	1.1	0.02
4	18.0	18.0	27.6	9	3.8×10^{11}	220	-0.06	1.52	0.02	-0.15	1.1	0.02

Results:

Run No.	M HNO_3/M Pu	Plutonium Distribution, Percent of 3AF 3AW	3BW	3BP	Decontamination Factors, Arithmetic D.F. Beta	Gamma	Nitric Acid Molarity 3AW	3AP(3)	3BW	3BP	Remarks
1	67.3	0.113	0.005	82	1.57	3.08	0.37	0.20	0.025	0.660	Current Flowsheet
2	21.3	0.096	0.001	64	1.76	3.76	0.24	0.12	0.011	0.158	
3	8.6	0.013	0.0007	129	2.28	4.95	0.37	0.07	0.029	0.120	Proposed Flowsheet
4	1.9	0.085	0.0005	70	3.29	6.72	0.25	0.03	0.008	0.014	

(1) 3AX in all runs = 0.49 M HNO_3.
(2) Pu(IV) in Run 2 = 8.4×10^8 (0.17%); in Run 4 = 1.54×10^9 (0.40%).
(3) Calculated by difference across 3A system.

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