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LABORATORY EVAPORATION OF REDOX PR SOLUTION

INTRODUCTION

Since Redox start-up, several samples of Redox PR solution have been evaporated in the laboratory as one step in a study of the Redox - 234 coupling process. Because feed for Task I in 234-5 will be produced by evaporative concentration of Redox and Purex product solutions, and because laboratory work has shown the desirability of filtering Redox solutions after such evaporation (as described within this memorandum), prior to use in Task I, it is felt desirable to summarize the observations which have been made in the course of this work, as a guide in the design of filters for the Redox and/or Purex PR cages.

SUMMARY

Laboratory work with a number of samples of Redox PR solution has shown the following:

1. The samples, as removed from the PR cans in the 231 Building, occasionally contain small amounts of silica and/or alumina.

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2. Even when the samples initially contain no apparent solids, batch evaporation may result in the formation of small amounts of solid matter - the particle size and filtration characteristics being dependent upon the evaporation conditions. Since these particles have been found to carry 40 to 70 per cent of the Zr, Nb activity in the solution, their removal prior to the purification step in Task I may be essential.
3. The aluminum content of current Redox material is sufficiently high (up to 150,000 parts aluminum per million parts plutonium) that aluminum nitrate may be expected to crystallize upon cooling a solution which has been evaporated to a plutonium concentration greater than 150 to 200 g/l.

EXPERIMENTAL

Redox PR samples for laboratory evaluation were removed from PR cans in the 231 Building, using a vacuum transfer procedure which may or may not have picked up solids from the bottom. Evaporations were all done batch-wise, in general using glass equipment. Solid volumes are approximate, no accurate measurement having been made. Analyses were performed in either the 234-5 or 222-S Analytical Laboratory.

DISCUSSION

1. Solids in Redox PR Solutions

Table I, which lists the Redox PR samples which have been examined for solid matter, shows that the chemical composition and amount of the solid material obtained with each sample, has varied greatly since the start-up of Redox. Those solids which have been analyzed have contained either aluminum or silicon as the chief metallic impurity. If present as alumina or silica, these solids probably carry a share of the Zr, Nb fission product activity to the bottom of the can. Where this condition exists, the Beckman readings on the PR cans should show a greater than normal difference between the side and bottom radiation measurements. Most of the data in Table I support this concept, although the method of obtaining samples from the PR can does not ensure removing a representative sample of any material deposited on the bottom of the can. Also, the past practice of using the same can for transferring virgin and recycle material, with the attendant consequence that solids observed in Redox PR solution may have been left in the can from the previous recycle transfer, makes uncertain any characterization of a given run as containing solids prior to its addition to the can.

2. Formation of "Insoluble" Residues

Two problems have arisen in the evaporation of Redox PR solution. One of these, the separation of aluminum nitrate crystals from cool, concentrated solutions, will be discussed later. The other, the appearance of small amounts of solid material during the evaporation (probably by coagulation of colloiddally dispersed alumina or silica), is summarized in Table II. The latter shows

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evaporation procedures, volume reduction factors, plutonium and nitric acid concentrations, filtration behavior, and spectrochemical analyses of the solids formed.

The method and extent of evaporation determine the properties of the solid (SiO_2 and/or Al_2O_3) which is formed. Batch evaporation, to give plutonium concentrations of from 175 to 300 grams per liter, resulted in formation of varying quantities of solids, which were readily removed by filtration through a medium (15 μ) Pyrex filter. Slow evaporation of one run (S-174) to a plutonium concentration of 65 grams per liter produced a finely divided solid which passed through a coarse (40 μ) Pyrex filter and rapidly plugged a medium filter. The use of a filter-aid pre-coat in the latter case permitted satisfactory filtration. Rapid evaporation of a second run (S-176) produced only enough filterable solid to discolor the filter.

Because the results of an evaporation are so dependent upon the conditions used, and because no attempt has been made to duplicate the probable plant procedure, it is difficult to predict the effect of continuous, plant evaporation. However, if it is necessary to concentrate Redox PR solution to 125 to 150 g/l plutonium and 12-13 M HNO_3 in order to remove the excess nitric acid, it is probable that filterable solids will be formed in the evaporation.

Small quantities of alumina and silica, as such, should cause no 234-5 process difficulties, even if they were mixed with the oxalate precipitate, since they would be removed in subsequent process steps. The need to remove these solids prior to precipitation in Task I stems from the observations summarized in Table II, which show that the solids have carried 40 to 70 per cent of the Zr, Nb fission product activity in the solution. These activities are not separated from the plutonium in subsequent process steps.

3. Crystallization of Aluminum Nitrate

Laboratory experience with the deposition of aluminum nitrate (ANN) crystals from concentrated Redox PR solution has been as follows:

- a. Solutions S-52-01-L-105 and -110, evaporated to plutonium concentrations of 165 and 211 g/l, respectively, contained no crystals up to 24 hours after cooling to room temperature. They deposited crystals when they were filtered, giving an equilibrium solubility of 1.1 to 1.4 g/l ANN. Apparently an aluminum content of 5,000 to 10,000 parts per million parts plutonium is the maximum which will be stable under all concentration conditions.

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- b. Large crops of ANN crystals were formed when solutions containing 250 g/l plutonium were cooled to room temperature. Such solutions, diluted to 60 g/l plutonium before cooling, were stable. It is evident, then, that Redox FR solution at present contains so much aluminum as to present a serious obstacle to the precipitation of 1200 gram batches in Task I (1).

REFERENCE

- (1) HW-27563, K. M. Harmon, by J. F. Facer, Jr., The Precipitation of Plutonium(IV) Oxalate in Task I.

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TABLE I
SOLIDS IN REDOX PRODUCT SOLUTIONS

Plant Run Number	Solution	g Pu/l.	g P ⁺ /l.	PR Can Beckman Readings, mr/hr.		Filterable Solids(1)
				Side	Bottom	
S-12-03-L-68	Redox PR	10.7		200		Observed
S-12-03-L-44, 46	AT ⁽²⁾ Sc #868	421				~3 gm. silicicous solids removed from sample can; 5-3000 m Rep/hr; 7-500 m Rep/hr.
S-12-03-L-22	Redox PR	17.4	12.7			60 cc solid (mostly SiO ₂) per Kg plutonium
S-12-05-L-6	Redox PR	15.1				600 cc solid per Kg plutonium Al:Cr:Si:Fe = 500:10:1:1
S-53-01-L-22	Redox PR	13.1	6.3			None
S-53-01-L-94	Redox PR	13.3	4.0	50	70	None
S-53-01-L-98	Redox PR	13.5	3.5	41	50	None
S-53-01-L-105	Redox PR	13.1	5.9	30	50	None
S-53-01-L-110	Redox PR	12.6	4.5	30	42	None
S-53-03-L-44	Redox PR	12.7	3.8	65	120	Grey residue observed after dissolution of Pu(IV) oxalate ppt'd from sol'n at 10 gm pu/l.
S-53-03-L-174	Redox PR	13.0	3.5	90	260	None observed.
S-53-03-L-176	Redox PR	13.2	3.6	108	160	Enough solids to discolor sintered glass filter disk.

- (1) All analyses made spectrochemically in 234-5 Analytical Laboratory.
(2) AT solution prepared from peroxide precipitated from runs S-44 and S-46.

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SOLIDS FORMED DURING EVAPORATION OF REDOX PRODUCT SOLUTIONS

Original Solution			Evaporation		Evaporated Solution			Filterable Solids (2)	
Plant Run Number	Pu Conc. g/l.	H+ Conc. g/l.	Filterable Solids (cc/Kg Pu)	Volume Reduction Factor	Evaporation Procedure (1)	Pu Conc. g/l.	H+ Conc. g/l.	Filter Used	Filterable Solids Formed (cc/Kg Pu) Analysis (3)
	5.8		--	25	Glass partial reflux	220		Pyrex M (15)	2.5 mostly Si
S-12-03-L-22	17.4	12.7	60	9	"	162		"	60 "
S-12-03-L-22	17.4	12.7	60	15	"	260		"	80 "
S-12-05-L-6	15.1		600	20	"	312		"	600
S-53-01-L-22	13.1	6.3	--	13 - 20	"	175-280		"	? mostly Al, slight Si
S-53-01-L-94, 105, 110	12.8 - 13.5	3.7 - 5.5	--	12 - 23	"	165-306	11.5 - 12.7	Small amount	
S-53-02-L-24	12.2		None	25	"	300		"	" (4)
S-53-03-L-44	12.7		None	22	Stainless steel pot-glass condenser	280(5)		"F" Micro-metallic (20.4)	? mostly Al & Si Colored by Fe
S-53-03-L-174	12.9	3.5	None	5	Glass Flask, partial reflux-7 hours	65.5	11.8	Pyrex-C(40.4) 0 Pyrex-M(15.4) 75(6)	
S-53-03-L-176	12.6	3.6	slight	6	Open beaker 35 min.	74.3	11.2	Pyrex M Filter (15.4) Discolored	

- (1) All evaporations made in batch-type equipment, by boiling at atmospheric pressure.
- (2) Include only HNO₃ - insolubles, no ANN.
- (3) Analyses made in spectro-chemical lab., 234-5
- (4) Diluted to 60 g/l Pu, filtered. D.F. for Zr-Nb = 2.8 over evaporation and filtration steps.
- (5) Concentrate was diluted to 60 g. Pu/l prior to filtration.
- (6) Filter rapidly clogged by this material; use of filter-aid pre-coat permitted satisfactory filtration.

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TABLE III

EFFECT OF EVAPORATION AND FILTRATION UPON FISSION PRODUCT SEPARATION

Plant Run Number	Sample Analyzed (1)		Pu		DF	Zr-Nb	
	No.	Obtained From	c/min/mg Pu	c/min/mg Pu		c/min/mg Pu	DF (2)
S-53-02-L-24	1	PR Solution	1.5×10^4	2.3×10^4	--	1.2×10^4	--
S-53-02-L-24	2	Evap'n filtration of No. 1 (3)	1.7×10^4	2.6×10^4	1	0.51×10^4	2.8
S-53-02-L-24	3	Pu (IV) Oxalate ppt'n from No. 1	1.8×10^4	0.31×10^4	9.4	0.27×10^4	5.9
S-53-02-L-24	4	Pu (IV) Oxalate ppt'n from No. 2 at 60 g/l Pu	1.6 - 1.9	$0.17-0.21 \times 10^4$	10-15	$0.13-0.19 \times 10^4$	6.7 - 10.5
S-53-03-L-44	5	PR Solution	1.4×10^4	0.61×10^4	--	Not detected	
S-53-03-L-174	6	PR solution evap'd	3.1×10^4	12×10^4	--	8.2×10^4	--
S-53-03-L-174	7	Filtration (3) of No. 6	3.4×10^4	15×10^4	1	5.1×10^4	1.8
S-53-03-L-176	8	PR solution evap'd	4.3×10^4	15×10^4	--	25×10^4	--
S-53-03-L-176	9	Filtration (4) of	4.1×10^4	14×10^4	1	26×10^4	1

- (1) Analyses made with gamma spectrometer in 222-S Laboratory. Expressed in gamma counts per mg. Pu. Samples 1-5: 3 ml sol'n containing 30 mg. Pu counted; samples 6-9: sample mounted on plate.
- (2) D.F.'s represent comparison of sample 2, 3 and 4 with No. 1, of sample No. 7 with No. 6, and of sample No. 9 with No. 8.
- (3) Solids, formed during evaporation, removed by filtration.
- (4) No solids retained by filter.

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TABLE IV

ALUMINUM NITRATE SOLUBILITY

IN CONCENTRATED PLUTONIUM NITRATE - NITRIC ACID SOLUTIONS

Plant Run Number	Original Solution				Evaporated Solution				
	Pu Conc. g/l.	H+ Conc. g/l.	ANN Conc. Al, ppm g/l.		Pu Conc. g/l.	H+ Conc. g/l.	ANN Conc. (1) Al, ppm g/l.		Vol. ANN Crystals (2) cc/Kg/ Pu
S-53-01-L-22	13.1	6.3	74,000	1	175		74,000	13	None
S-53-01-L-22	13.1	6.3	74,000	1	280		---	--	70
S-53-01-L-94	13.3	3.7	75,000	1	306	11.5	30,000	9	Not measured
S-53-01-L-98	13.5	4.1	37,000	0.5					
S-53-01-L-105	13.1	5.5	150,000	2	165	12.7	6,400	1.1	Not measured (3)
S-53-01-L-110	12.8	4.3	75,000	1	211	12.5	6,400	1.4	Not measured (3)
S-53-03-L-44	12.7		10,000	0.13	280 - 60 (4)		16,000	4.8-1	None (4)

(1) ANN concentration of evaporated solution after cooling to room temperature and filtering; all measured by spectrochemical analysis.

(2) Volume of crystals filtered from solution after cooling to room temperature.

(3) Crystallization of ANN did not start until filtration of solution (at room temperature) was started. Sol'n super-saturated.

(4) The concentrate was diluted to 60 g Pu/l prior to filtration.

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