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CHEMICAL TECHNOLOGY

PROGRESS REPORT FOR QUARTER ENDING MAY 31, 1949

F.L.STEAHLY, ASSOCIATE DIRECTOR

Edited By

W.K.EISTER

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CHEMICAL TECHNOLOGY
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ABSTRACT

The chemical process development and design progress on the following problems is reported: Redox, Metal Recovery (UAP and Tributyl Phosphate Solvent Extraction), ORNL Radiochemical Waste Disposal, RaLa Process, "25" Process, "23" Process, and Dry Fluoride.

INTRODUCTION

The Laboratory, Semi-Works, Pilot Plant, and Design phases of chemical development by the Technical Division of Oak Ridge National Laboratory are included in this report.

The ORNL development of the Redox Process for recovery and decontamination of plutonium and uranium from the Hanford reactors is nearing completion. The Semi-Works program is now complete. In the Pilot Plant, the last full Hanford activity level runs are in progress. Laboratory studies on plutonium and ruthenium chemistry are continuing.

The Uranyl Ammonium Phosphate Precipitation Process for the recovery of the uranium from the Hanford metal waste, which was originated in the K-25 laboratory, is being developed on a semi-works scale at ORNL. The inactive breakin runs are nearing completion and active Hanford total waste runs will be started soon, with an anticipated completion date of August 1, 1949.

An alternate process, tributyl phosphate solvent extraction, for the Hanford uranium recovery problem is being developed in the laboratory. The batch laboratory studies are essentially complete, and preliminary counter-current batch and column runs are in progress. The Semi-Works is constructing equipment for the removal of sludge from the ORNL metal waste storage tanks, and a program for the semi-works development of this process is being considered. The laboratory is also considering the waste disposal problems associated with this process.

The evaporator for concentrating the ORNL radiochemical waste is nearing completion, and preliminary tests with water have been made. The semi-works investigation for further reducing the activity in evaporator condensate by ion exchange has been successfully completed. Sodium nitrate crystallization from the concentrated evaporator liquor to concentrate further the radio activity has been demonstrated in the laboratory, and equipment for semi-works test is being

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considered. A thorough survey of the radioactive waste disposal system at ORNL has been made by the Design Section. As a result of this survey, alterations to the present system were recommended and general specifications for future installations were formulated.

Oak Ridge National Laboratory was requested to consider an increase in RaLa production. The present production facilities are not adequate for the present production rate; therefore, it was necessary to review the present process and to recommend the changes necessary to allow the increased production. The Laboratory and Semi-Works are investigating chemical process revisions to aid in decreasing the time cycle and increasing the chemical yield.

Progress in the development of the "25" Process included a laboratory study of the dissolution of aluminum-uranium alloy slugs in preparation for converting the pilot plant solvent extraction equipment for the runs using Hanford-irradiated uranium 235. Shielding calculations for the proposed plant were made by Design. Filtration of the metal solution for crud removal is being studied in the Semi-Works.

Construction of the equipment for the semi-works development of the "23" Solvent Extraction Process was started. Work is continuing in the laboratory to develop a solvent extraction process for the recovery of thorium from the "23" waste.

The equipment development problems included evaluating a radioactivity monitor for the Radiochemical Waste Evaporator and testing commercially available paints for applications where radioactive contamination is probable.

New facilities, which are now being planned, include an area for offices and shop adjacent to the 706-HB Semi-Works, and the Semi-Works and laboratories to be included in the new research building.

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SUMMARY

REDOX

(1) Adequate uranium decontamination of greater than 3×10^5 was obtained with ORNL No. 1 acid deficient process in two cycles in the Pilot Plant at 30% Hanford activity level. The uranium product from the second cycle contains 10% of the beta and 200% of the gamma activity found in natural uranium. Under similar conditions, the ANL acid process gave approximately 7×10^2 decontamination.

(2) The pretreatment of the dissolver solution with acetone and sodium nitrite significantly increased the ruthenium decontamination by the ANL acid process.

(3) The cause for the increased plutonium loss from 0.01 to 0.5% in pilot plant runs when going to full Hanford activity level was not determined. Laboratory studies showed that the metal dissolving procedure and lapse of time between dissolving and oxidation had no significant effect on the plutonium loss.

METAL RECOVERY—UAP PROCESS

(1) Inactive uranyl ammonium phosphate precipitations by the Semi-Works with synthetic Hanford supernatant on a 190 liter scale demonstrated adequate control of the waste dissolving step preceding the first precipitation. The first and second cycle precipitates were readily filtered. High uranium losses were experienced, but these were due to operational difficulties which are being corrected.

(2) The substitution of diammonium phosphate for ammonium nitrate as the precipitating agent was demonstrated in the laboratory on a 500 milliliter scale with Hanford composite waste to decrease significantly the uranium losses with comparable decontamination. This process revision was rejected because K-25 tests indicated poor filterability of the precipitate.

METAL RECOVERY—TRIBUTYL PHOSPHATE EXTRACTION PROCESS

(1) A solvent extraction process for the recovery of uranium from the ORNL and Hanford metal waste was demonstrated in one cycle counter-current batch runs in the laboratory with actual full-activity wastes to give a beta decontamination of 10^4 with uranium losses of 0.1%. The beta activity of the product uranium from the Hanford waste was 3% of the beta activity of natural uranium. The gamma activity of this product was background.

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ORNL RADIOCHEMICAL LIQUID WASTE DISPOSAL

The condensate from the Radiochemical Waste Evaporator can be further decontaminated by a factor greater than 20 by ion exchange.

RaLa PROCESS

The Alkali-Citrate Ion Exchange Process developed in the laboratory to replace the present Cell B barium purification steps has shown a 99% barium yield with 10^3 reduction of strontium and 10^4 reduction of lead, in laboratory tracer runs.

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REDOX

LABORATORY

PLUTONIUM EQUILIBRIA

The investigation of plutonium equilibrium was done under conditions simulating those proposed for the ORNL flowsheet with the aid of a Beckmann model D.V. quartz spectrophotometer making it possible to obtain direct analysis for plutonium in its various valence states without requiring chemical processing (Table 1). In some tests aluminum nitrate solutions were used in place of uranium nitrate since this substitution allowed the measurement of light absorption to be extended to the lower regions of the spectrum. The presence of dichromate in other experiments made it impossible to obtain measurements of light absorption in the region below 800 millimicrons; therefore, in these cases, it was only possible to measure the amount of Plutonium VI.

These experiments were designed to study the behavior of plutonium in feed solutions. It has been demonstrated in other work that several or all of the four valence states can exist in equilibrium with each other in the same solution by the following reactions:

$$3\ Pu^{+4} + 2\ H_2O \rightleftharpoons 2\ Pu^{+3} + PuO_2^{++} + 4\ H^+$$

$$Pu^{+4} + PuO_2^{+} \rightleftharpoons PuO_2^{++} + Pu^{+3}$$

Acid dependence of the equilibrium is produced by the first reaction.

Plutonium Equilibria in Feed Previous to Oxidation. The first problem was to determine the equilibria prevailing in solutions corresponding to possible acidities attained in slug dissolution. It was found that heating 1.3 *M* $Al(NO_3)_3$ solutions, 0.2 *N* in HNO_3 and 0.0007 *M* in plutonium for 2 and 6 hours, and then allowing the solution to stand for 43 hours at 25° C, resulted in different equilibrium quantities of Plutonium IV and VI (Table 2). In the first case, 65% of the total plutonium was in the Plutonium VI state and in the second case, 90% was present as Plutonium VI. Plutonium III, V, and the polymer were not detected.

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TABLE 1

Extinction coefficients of the various valence states of plutonium

Cell length: 10.011 cm

VALENCE STATE	PLUTONIUM CONCENTRATION M	WAVE LENGTH (millimicrons)	MOLAR EXTINCTION COEFFICIENT
III	0.000462	570 and 602.5	40.9 and 39.4
IV	0.00056	477	73.05
V	0.000355	570	15.1
VI	0.000468	837 and 960	170.1* and 20.1

* calibration curve required

TABLE 2

Plutonium equilibrium in aluminum nitrate solutions

Solution: 1.3 *M* $Al(NO_3)_3$, 0.2 *M* HNO_3, 0.0007 *M* Pu

Procedure: Heated at 85° C for time note and then allowed to stand at 25° C for 43 hours.

HOT DIGESTION TIME hrs.	FINAL PLUTONIUM EQUILIBRIUM	
	% IV	% VI
2	44.6	65.2
6	10.4	89.6

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In neutral and acid deficient aluminum nitrate solutions, if Plutonium IV is introduced, it will undergo hydrolysis and polymerization. Therefore, to study the equilibria attained in these solutions, it was necessary to reduce the acidity by hydrolyzing urea in 2.0 *M* acid solutions of Plutonium IV in $Al(NO_3)_3$. It was found that solutions as low in acid as 0.02 *M* acid deficient could be attained without polymer formation (Table 3).

Oxidation of Plutonium by Dichromate. Oxidation of Plutonium IV to Plutonium VI can be carried out quantitatively in acid or acid deficient 1.3 *M* $Al(NO_3)_3$ solutions by 0.1 *M* $Na_2Cr_2O_7$ if heated for 6 hours at 85° C.

It was shown that only 28% of the Plutonium IV in a 1.3 *M* $Al(NO_3)_3$ solution, 0.2 *M* HNO_3, was converted to Plutonium VI on standing at room temperature for 24 hours. When this solution was made 0.1 *M* $Na_2Cr_2O_7$ and heated for 6 hours at 85° C, the plutonium was quantitatively oxidized to Plutonium VI.

A 1.3 *M* $Al(NO_3)_3$ solution, 0.2 *M* in HNO_3, 0.1 *M* in $Na_2Cr_2O_7$ containing Plutonium IV and allowed to stand 24 hours at room temperature, resulted in the oxidation of 92% of the plutonium. When this solution was made acid deficient (*p*H 1.6) and heated for 6 hours at 85° C, the plutonium was quantitatively oxidized (Table 4).

Plutonium Polymer. Plutonium is only slowly depolymerized (less than 65%) in acid deficient 1.3 *M* $Al(NO_3)_3$ solutions even on heating at 85° C for 30 hours, in the absence of an oxidizing agent (Table 5). This was demonstrated with polymer prepared in two different ways. In one test it was formed by merely adjusting the acidity of the $Al(NO_3)_3$ solution containing Plutonium IV to 0.2 *N* acid deficient. In the other test, the polymer was prepared by adding sodium hydroxide to a solution of Plutonium IV in nitric acid until a slight precipitate formed. The precipitate was redissolved in a small amount of nitric acid, diluted with aluminum nitrate solution and the acidity adjusted to 0.2 *N* acid deficient.

Plutonium polymer was also slowly depolymerized in 2 *M* UNH solutions which are 0.2 *N* acid deficient, even after heating for 9 hours (74%) (Table 6).

INVESTIGATION OF PILOT PLANT PLUTONIUM LOSSES

In the first full Hanford level pilot plant runs of the Redox first cycle (48 and 49), abnormally high extraction column plutonium losses of 1.5 and 2 percent, respectively, were observed. Batch tests by the laboratory employing the same pilot plant feed solutions indicated the same losses. Laboratory work was initiated along three general lines: study of the dissolving step, study of pi-

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TABLE 3

Plutonium oxidation during solution neutralization with urea

Solution: 1.3 *M* $Al(NO_3)_3$, 2.0 *M* HNO_3, 0.007 *M* Pu

Procedure: Refluxed at boiling for times note with addition of more urea and continued reflux.

RUN NO.	UREA ADDED grams	REFLUX TIME hours	RESIDUAL HNO_3 M	FINAL PLUTONIUM STATE		
				% IV	% V	% VI
1	5.2	27	0.11	--	5.9	97.2
	1	24	0.02	--	0	100
2	1	24	1.0	45.6	--	57.8
	1	24	0.06	0	--	100

TABLE 4

Plutonium IV oxidation by sodium dichromate

Solution: 1.3 *M* $Al(NO_3)_3$, 0.2 *M* HNO_3, 0.000625 *M* Pu

Procedure: Test No. 1 - stood for 24 hrs. at 25° C
Test No. 2 - Digested 6 hrs at 85° C followed by 18 hrs. at 25° C

TEST NO.	SAMPLE NO	0.1 *M* $Na_2Cr_2O_7$	FINAL PLUTONIUM EQUILIBRIUM	
			% IV	% VI
1	A	no	64.5	28.2
	B	yes	- *	92.3
2	A**	yes	- *	97
	B***	yes	- *	98

* Presence of $Na_2Cr_2O_7$ prevented spectrophotometric determination of IV.

** $Na_2Cr_2O_7$ added to Sample A previous to Test No. 2.

*** This solution was adjusted to *p*H 1.6 before heating.

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TABLE 5

Depolymerization of plutonium in acid deficient aluminum nitrate solution

Solution: 1.3 *M* $Al(NO_3)_3$ - 0.2 *M* HNO_3, 2.1 *pH*, 0.0007 *M* Pu

Procedure: Test No. 1 - Polymer formed by adding NaOH to aluminum nitrate solution containing Pu^{IV} to make 0.2 molar acid deficient.

Test No. 2 - Polymer formed by precipitating Pu^{IV} by addition of NaOH to HNO_3 solution, redissolving with HNO_3 and adding to $Al(NO_3)_3$ solution.

Digested 20 hrs. at 25° C followed by 30 hrs. at 85° C

TEST NO.	DIGESTION		PLUTONIUM EQUILIBRIUM	
	Time (hrs.)	Temp. (°C)	% VI	% Polymer*
1	0	25	4.4	95.6
	20	25	5.5	94.5
	22.5	85	20.0	80.0
	26	85	43.6	56.4
	50	85	68.0	32.0
2	20	25	6.4	93.6
	26	85	39.4	60.6
	50	85	66.2	33.8

* This was calculated by difference. Checks for other ionic species of plutonium were negative.

TABLE 6

Depolymerization of plutonium in acid deficient UNH solution

Solution: 2 *M* UNH, 0.1 *M* $K_2Cr_2O_7$ - 0.2 *M* HNO_3, *pH* 0.9, plutonium polymer

Procedure: Digested 2 hours at 25° C and 16 hours at 85° C

DIGESTION		PLUTONIUM EQUILIBRIUM	
Time (hrs.)	Temp. (°C)	% VI	% Polymer*
2	25	15.4	84.6
3	85	69.3	30.7
6	85	82.6	17.4
9	85	88.4	11.6
16	85	92.0	8.0

* This was calculated by difference.

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lot plant feed solutions for runs 48 and 49, and study of pilot plant waste raffinates from runs 48 and 49.

It was noticed that in the analysis of the pilot plant lAW solutions by LaF_3 and TTA methods, that the values obtained did not agree. The plutonium losses calculated on the basis of LaF_3 were consistently higher than those calculated on the basis of results of TTA analysis. This discrepancy suggested the presence of other alpha emitting elements which were being carried by LaF_3. Studies by the Analytical Research group in the Chemistry Division have shown that approximately 0.5 percent of the alpha activity in the feed solutions was due to americium and curium in about equal quantities. There then remained a real plutonium loss of approximately 1 to 1.5 percent.

Metal Dissolution. Uranium metal was dissolved in nitric acid spiked with Plutonium IV to determine the probability of plutonium polymer formation due to (1) stopping the dissolving with varying amounts of acid present, and (2) allowing the solutions to stand for varying periods of time prior to oxidation and solvent extraction under the conditions of the ORNL (basic) Redox flowsheet. The results indicate that neither the acidity of the final dissolver solution nor the length of time between dissolving and oxidation are responsible for the plutonium losses obtained in the Pilot Plant.

In nearly all cases the plutonium losses were demonstrated by these tests to be less than 0.1%. In one test, after the final heating at 85° C, the feed solution that was dissolved to an acid deficiency of 0.35 molar, gave a plutonium loss of 0.23% (Table 7).

Feed Solution Study. Batch experiments with the feed from run 48 using the ORNL process first cycle conditions and utilizing strong oxidizing agents under acid deficient conditions, indicated that the losses could not be decreased appreciably. Use of persulfate and periodate with twenty-four hour oxidation periods actually produced increased losses (5-7%) indicating, perhaps, their complexing action on plutonium. Use of the ANL flowsheet conditions was found to produce losses of the same magnitude as observed with ORNL runs.

Batch experiments were performed to determine plutonium losses on old samples of feed solutions used in runs 37, 39, and 46 to determine the extent to which inextractable plutonium formation had progressed. This material had been standing for several weeks at 0.2 *N* HNO_3 deficiency in the presence of 0.1 *M* $Na_2Cr_2O_7$. Plutonium losses were observed to have increased in these feeds by factors of 20, 13, and 2, respectively. Re-oxidation at 0.3 *N* HNO_3 with 0.1 *M* $Na_2Cr_2O_7$ at 85° C was found to reduce these latter losses by factors of 1.5 to 2.0.

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TABLE 7

Effect of acidity at end of dissolving and lapse of time between dissolving and oxidation on the plutonium loss

Oxidation procedure: 6 hours at 85° C

Metal solution: 2 *M* UNH
5 x 10^6 plutonium cts/ml/min

ACID NORMALITY OF DISSOLVER SOLUTION**	PERCENT PLUTONIUM LOSS AFTER EXTRACTION TIME BETWEEN DISSOLVING AND OXIDATION			
	18 hours	41 hours	107 hours	*138 hours
2.15	0.004	0.01	--	--
1.14	0.001	0.05	0.01	0.01
-0.03	0.02	0.01	0.01	0.01
-0.17	0.26	--	0.06	0.05
-0.26	0.02	0.04	0.03	0.02
-0.35	0.01	0.02	0.02	0.23

* These dissolver solutions were heated at 60°C for 7 hours just prior to oxidation.

** Negative acid values represent solutions deficient in nitric acid.

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Raffinate Study. It was found that the plutonium in the raffinate from runs 48 and 49 was inextractable, but by making the solution acid before extraction, or heating on the acid deficient side increased the extractibility of the plutonium. Heating the raffinate on the acid side with sodium dichromate was found to make the plutonium most extractable. Ceric ion was not more effective than dichromate in the raffinates from runs 48 and 49.

Conclusions and Future Work. The reasons for the Pilot Plant's high plutonium losses are not understood, as yet, but as a result of the work so far, it is felt that they are not due to Plutonium IV polymer formation. However, to minimize opportunities for its formation, changes in the slug dissolving procedure have been recommended. The dissolving would be stopped at about 0.2 *N* HNO_3 instead of carrying it to an acid deficient condition, $Na_2Cr_2O_7$ being added, and oxidation carried out in an acid medium. After oxidation, the feed solution would be brought to 0.2 *N* acid deficient condition by the addition of NaOH.

It appears more probable that reduction of Plutonium VI to Plutonium V or IV some place in the process is causing the plutonium losses. Work in progress and future plans include the following investigations: (1) possible formation of reducing, decomposition products due to high level of activity, (2) possible reduction in feed due to materials in the displacement fluid, methyl cyclo hexane, (3) examination of feed solution during each step in its preparation in an effort to locate the point during this process at which reduction occurs, (4) further work on raffinate from each pilot plant run, and (5) the use of slightly acid 1AX feed.

ACETONE PRETREATMENT OF METAL SOLUTION

A pretreatment of Redox feed, utilizing sodium nitrite and acetone with digestion at elevated temperatures, has been found to effectively increase ruthenium decontamination especially with ANL conditions where ruthenium D.F.'s have been low enough to limit overall decontamination in the process.

The pretreatment consists of the following: the dissolver solution is adjusted to 2 *M* UNH, 0.3 *N* HNO_3, 0.05 *M* $NaNO_2$, 0.1 *M* acetone and then digested at 85-90° C for four hours. After cooling, the solution is then adjusted to conditions as required in the process. This treatment, by virtue of the formation of inert ruthenium compounds, has been found to effect a more favorable distribution of the element on scrubbing.

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Although complete understanding of reactions involved has not been deduced, use of this pretreatment has progressed beyond the laboratory stage. Reasonable improvements in overall decontamination have been demonstrated in counter-current, semi-work, and pilot plant equipment. The pilot plant run No. 47 with ANL first cycle conditions utilized this pretreatment and decontamination was improved by a factor of ten over normal ANL runs. Followed by an ORNL second cycle, this run produced an overall β D.F. of about 5×10^5, sufficient for process specifications. Counter-current data obtained prior to making this run, indicated the following β D.F.'s at various stages after establishing equilibrium: feed-plate = 2.4, 2nd scrub = 48, 4th scrub = 200, 6th scrub = 730, 8th scrub (final) = 1450, and strip = 2900; overall ruthenium D.F. was about 200.

It has been observed in the semi-works and pilot plant runs that uranium and plutonium losses are not affected by this pretreatment. Further studies will be made in an effort to define more specifically the action of the nitrite and acetone on ruthenium.

SEMI — WORKS — FIRST CYCLE DEVELOPMENT

The semi-works development program for the first cycle of the Redox solvent extraction process for recovery and decontamination of plutonium and uranium demonstrated that the uranium could be satisfactorily decontaminated in two cycles using the ORNL No. 1 Acid Deficient Flowsheet. The ANL Acid Flowsheet was substantially improved by incorporating the acetone-sodium nitrate feed pretreatment ("Gresky effect"). Considering the quantity of aluminum nitrate required, the ANL flowsheet process with "Gresky effect" would be preferred if satisfactory decontamination could be achieved in the same number of cycles. A third process, the ORNL No. 2, gave the highest decontamination, however, not high enough to permit using only one cycle and the quantity of aluminum nitrate required was twice that used in the ORNL No. 1 process (Table 8).

The uranium and plutonium losses for the three processes were comparable and all within required limits, varying from 0.01 to 0.5 percent. Higher losses were occasionally experienced; however, these were due to operational difficulties.

These investigations by the semi-works were made in a two column system consisting of an extraction-scrub column (IA) and a strip column (IC). The column, IB, for the separation of plutonium from uranium was not included, and the data reported reflects only the decontamination, and plutonium and uranium losses in

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TABLE 8

Summary of redox first cycle semi-works runs

Equipment: 1½ in. D. s/s columns packed with ¼ in. x 3/8 in. split rings extraction 13.5 ft. scrub 4 ft. and strip 11 ft.

RUN CONDITIONS

FLOWSHEET	ACTIVE FEED				SCRUB			STRIP	HEXONE	FLOW RATIO	FOOT-NOTES
	U M	Al^{+3} M	H^+ M	$Cr_2O_7^{=}$ M	Al^{+3} M	H^+ M	$Cr_2O_7^{=}$ M	H^+ M	H^+ M	F:S:E:S	
ANL	2.0	--	0.3	0.05	1.3	0.0	0.01	0.1	0.5	1:1:4:2	1
ORNL No. 1	2.0	--	0.2	0.05	2.0	0.2	0.01	0.1	0.0	1:1:4:2	2
ORNL No. 2	0.9	1.2	0.2	0.05	1.3	0.2	0.01	0.1	0.0	2:1:3:3	3

	EXTRACTION LOSSES		DECONTAMINATION FACTORS						FOOT-NOTES
	% U	% Pu	β	γ	Ruβ	Cbβ	Zrβ	Cbβ	4
ANL									
R-2	0.25		120	60	8	370	100	3000	5
R-35	0.07	0.012	40	90	270	160	60	70	6
R-37	0.60	0.01	470	160	650	50	440	280	7
ORNL No. 1									
R-24	0.04	0.13	1810	970	157				9
R-25	0.04	0.10	1880	1090	101				9
R-22	0.34	0.08	2340	760	130				10
R-23	0.25	1.10	1860	895					10
R-34	0.29	0.50	6150	1940	1120	25000	5180	23000	8
R-36	0.46	0.09	4340	1880	440	2300	630	8000	6

(table continued on next page)

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TABLE 8 (continued)

	EXTRACTION LOSSES		DECONTAMINATION FACTORS						FOOT-NOTES
	% U	% Pu	β	γ	Ruβ	Cbβ	Zrβ	Cbβ	
ORNL No. 2									
R-33	0.1	0.04	10350	5900	710			57000	
R-26			2000	2400	500		200	6000	9
R-27	0.12	0.04	14000	6500	890	27000	12000	503000	9
R-29	2.10	0.19	18000	8400	1200		22000	964000	9
R-32	0.53	0.08	8900	6900	590	21000	5200	10^8	9
20A	0.10	0.01	3600	1900	240				5, 10
20B	0.50	0.30	4000	1500	200				5, 10
21	0.01	0.01	7400	2900	4700				10
28	0.12	0.02	16900	5000	890	4900	10300	785000	11
30	0.06	0.05	7600	4200	570	7300	11700	240000	11
31	0.61	0.06	5400	3400	360	7200	7700	850000	11

FOOTNOTES

1. F.S.E.S = Feed Scrub Extractant Strip
2. The ANL flowsheet specifies 0.1 *M* $Na_2Cr_2O_7$ in the feed only; semi-works runs were made per the conditions indicated. Flow ratio was based on 1 = 33.6 gal/hr/sq ft.
3. Flow ratio was based on 1 = 22 gal/hr/sq ft.
4. Gross γ counting was made in the ionization chamber.
5. Only one slug dissolved per feed in these runs; all others had two slugs dissolved.
6. Feed digestion with 0.1 *M* $NaNO_2$ and 1% by volume of acetone.
7. Feed digestion with 1% by volume of acetone.
8. Feed digestion with 0.5% by volume of acetone.
9. 0.1 *M* $Na_2Cr_2O_7$ in feed, 0.01 *M* $Na_2Cr_2O_7$ in scrub.
10. 0.1 *M* $Na_2Cr_2O_7$ in feed; none in scrub.
11. 0.1 *M* $Na_2Cr_2O_7$ in feed; 0.01 *M* $Na_2Cr_2O_7$ in scrub.
    1.0 *M* U in feed.
    1.1 *M* Al in feed.
    1.5 *M* Al in scrub.

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column IA. The activity level of these runs was 5% Hanford level, obtained by dissolving two ORNL slugs per run. The ORNL slugs had been irradiated approximately 1200 days and cooled 30 to 60 days. Approximately 70 liters of feed was used for each 40 hour run. Samples of the metal feed and the product effluent and waste raffinate streams were taken periodically throughout the run.

PILOT PLANT

EVALUATION OF THE ANL JUNE, 1948, FLOWSHEET

The uranium decontamination data for two cycles show that if the ANL acid conditions are used in the first cycle, an adequate gamma decontamination (3×10^5) is unobtainable irrespective of the second cycle flowsheet used. In all cases this lack of decontamination was caused by ruthenium (Table 9). The total uranium losses for both cycles at equilibrium has been found to be of the order of 0.01% irrespective of the flowsheet used.

The decontamination obtained for the plutonium in the first cycle under ANL flowsheet conditions has been found to be 2500 for beta and 1500 for gamma, with ruthenium again being the limiting constituent.

The total plutonium losses, for the first cycle only, has averaged approximately 0.05%, far below process specifications with the major portion of this loss being in the uranium stream leaving the Column IB in which uranium is separated from plutonium.

The use of high purity hexone containing less than 0.03% methyl isobutyl carbinol has been shown to be necessary to permit a first cycle zirconium-columbium decontamination of the order of 10^4, but hexone impurities had no effect on ruthenium decontamination. Ruthenium decontamination in the first cycle has been found to be independent of dissolving procedures including metal heel, concentration of acid, and equipment operation or time intervals anywhere in the feed preparation step. Cerium decontamination was found to be a function of the sodium dichromate concentration when the concentration of this oxidizing agent was below 0.01 *M*. The mechanical operability of this flowsheet in the columns has been found to be highly satisfactory.

The second cycle ANL flowsheet was discontinued mainly because of the low decontamination of ruthenium. The decontamination from other fission products appeared to be adequate if high purity hexone was used but could not definitely

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TABLE 9

ORNL pilot plant redox data

Performance of the June, 1948, ANL flowsheet

FIRST CYCLE DECONTAMINATION

	DECONTAMINATION FACTOR	
	Plutonium	Uranium
Gross Beta	2500	200
Gross Gamma	1500	100
Ruthenium	150	10
Zirconium	2000	1×10^4
Columbium	5000	1×10^4
Cerium	1×10^6	2×10^6

OVERALL URANIUM DECONTAMINATION FOR TWO CYCLES

FIRST CYCLE FLOWSHEET	SECOND CYCLE FLOWSHEET	TWO CYCLE URANIUM GAMMA DECONTAMINATION *
ANL	ANL	7×10^2
ANL	ORNL No. 1	5×10^4
ANL	ORNL No. 2	1×10^5

URANIUM AND PLUTONIUM LOSSES

Total plutonium loss for First Cycle - .05%
Total uranium loss for Two Cycles - .01%

* HEW Specification - 3×10^5

[redacted]

[redacted]

be ascertained because of the high activity background caused by ruthenium. Adequate decontamination of uranium from plutonium was obtained if reducing conditions were used in the second cycle extraction column. This was done by making the aqueous scrub to this column 0.05 molar in ferrous sulfamate. The total uranium losses in the second cycle was found to be less than 0.01%.

Recent laboratory, semi-works, and pilot plant tests have shown that the ruthenium decontamination can be greatly improved by acetone-sodium nitrite pretreatment of the dissolver solution.

A total of 21 first cycle runs were made under the conditions of the ANL flowsheet. Three of these runs contained no fission product or plutonium activity; eleven were made at 10% Hanford production level, and eight were made at 30% Hanford level. The uranium from these first cycle runs was processed through another extraction and stripping cycle to determine overall uranium decontamination for two cycles. The plutonium separated in the first cycle was stored for ultimate recovery or sent to ANL for further processing.

SUMMARY OF PROCESS DATA

Adequate uranium decontamination of 3×10^6 in only two cycles is possible under ORNL flowsheet conditions with an overall uranium recovery of 99.9%. This has been due to the enhanced ruthenium decontamination.

The main change in this flowsheet as compared to the ANL flowsheet is that the extraction is carried out under acid deficient conditions in the ORNL flowsheet as compared to acidic conditions in the ANL flowsheet. The data show that the losses of both plutonium and uranium have increased slightly but are still meeting process specifications. The pilot plant Redox runs at 30% Hanford activity level have been completed.

The plutonium decontamination was shown to be improved by a factor of two or three by use of the ORNL flowsheet. Plutonium recovery is adequate when using the ORNL flowsheet, but the yields to date have not been as high or as consistent as when the ANL flowsheet is used. The explanation for this lies in the fact that Pu^{+4} is extractable under ANL flowsheet conditions but not under ORNL flowsheet conditions. There has been no evidence of polymer formation except in runs 33 and 84 (Table 10). The high losses on these runs are attributed to polymer formation caused by the addition of caustic before oxidation of the dissolver solution. A discussion of feed preparation is given in the next section.

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[redacted]

TABLE 10

*ORNL pilot plant redox data**—Summary of decontamination and losses*

	PLUTONIUM (1 cycle)				SECOND CYCLE FLOWSHEET	URANIUM (2 cycles)		
RUN	βD.F. x 10^3	γD.F. x 10^3	U D.F. x 10^6	Total % Losses		βD.F. x 10^5	γD.F. x 10^5	Total % Losses
ANL FLOWSHEET								
27	2.0	1.0	1.	0.1	ANL	0.02	0.007	0.02
28	2.7	1.3	1.	0.1	ORNL No. 1	0.4	0.2	--
29	---	---	--	---	ORNL No. 2	0.9	0.4	0.01
30	3.3	1.5	0.1	0.1	ORNL No. 2	1.8	1.0	0.01
31	---	---	---	---	ANL	0.5	0.1	0.01
42*	4.6	2.9	1.	0.1	ANL*	0.7	0.3	0.01
47*	21.	6.5	0.04	0.1	ORNL No. 1	4.	1.5	0.01
ORNL FLOWSHEET								
32	23.	5.	1.	0.1	ORNL No. 1	7.2	3.0	0.03
33	12.	4.	0.2	9.0	ORNL No. 2	8.8	5.5	0.01
37	45.	9.	1.0	0.2	ORNL No. 1	10.	5.0	0.2
38	---	---	---	---	ORNL No. 1*	15.	7.5	0.2
39	18.	5.	10.	0.1	ORNL No. 1*	21.	6.	0.05
40	---	---	---	---	ANL*	7.	1.5	0.05
41*	17.	5.	0.3	0.1	ORNL No 1*	9.	1.9	--
43	---	---	---	---	ORNL No. 1*	6.	3.1	--
44	12.	4.6	1.	0.1	ORNL No. 1	4.	2.3	0.01
45	---	---	---	---	ORNL No. 2	5.	3.0	0.01
46	30.	8.4	1.	0.6	ORNL No. 1	6.	3.7	0.01
ORNL MODIFIED FLOWSHEET								
34	62.	12.	0.4	7.	ANL	5.	0.7	0.03
35	---	---	---	---	ORNL No. 1	15.	7.0	0.01
36	54.	6.	2.0	0.2	ORNL No. 2	13.	6.0	0.01

* Feed treated with acetone or acetone and sodium nitrite.

** Data on runs 4 through 26 are reported in ORNL 323, Part II.

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FIRST CYCLE FEED PREPARATION

Source of Irradiated Uranium. The seventeen first cycle runs made in the past period were all at an activity level approximately 30% of ordinary Hanford production. The feed was prepared by dissolving 70% by weight ORNL irradiated uranium slugs and 30% Hanford production slugs.

Coating Removal. The jackets of the slugs were removed by the usual NaOH-$NaNO_3$ method.

Metal Solutions. Variations in the operation of the dissolver have shown that the reaction can be controlled by ordinary industrial instrumentation to yield UNH solution of any desired acidity. The data in Table 11 show that by varying the concentration of the acid and the final specific gravity of the dissolver solution UNH solution can be prepared in the range of from .5 *N* acid to .3 *N* acid deficient with an approximate error of .2 normality units. It is felt that this range of error can be reduced with more operational experience and closer process control, since the ultimate specific gravity of the solution is affected only by the amount and concentration of acid, the amount of metal put into solution, and the vapors lost from the vessel. Recent data not included in this report indicate that for the ORNL flowsheet the operational desirability of producing an acid deficient dissolver solution is outweighed by plutonium chemistry considerations indicating the desirability of terminating the dissolving at about 0.2 *N* acid.

Oxidation. Pilot plant data indicate the necessity for complete oxidation of the feed before acid adjustment with sodium hydroxide. The high plutonium losses of runs 33 and 34 given in Table 10 and 12 were caused by inextractable polymer formation in the feed due to the addition of concentrated sodium hydroxide before the oxidation step. Subsequent runs show that if oxidation is carried out immediately after dissolution by making the feed solution 0.1 *M* in sodium dichromate and heating to 85° C for six hours the plutonium is sufficiently oxidized as indicated by the low losses. This oxidation can be carried out at either acid or acid deficient systems although there are some indications that losses are higher if oxidation is carried out under acid deficient conditions.

Acid Adjustment. Acid neutralization is done by the direct addition of concentrated sodium hydroxide. This step has caused no difficulty except that mentioned in the previous paragraph.

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TABLE 11

ORNL pilot plant redox dissolver data

All uranium 70% by weight ORNL irradiated, 30% HEW irradiated

RUN NO.	HNO_3 CONCENTRATION PERCENT	FINAL Sp. Gr. of DISSOLVER SOLUTION	RESIDUAL ACID *N*	ACTIVITY cts/mgU		
				$\beta \times 10^6$	$\gamma \times 10^4$	$\alpha \times 10^3$
32	60	1.85	.32	4.2	1.3	8.6
33	60	1.85	.45	4.3	1.1	9.4
34-35	60	1.85	.91	3.5	1.0	9.0
36	55	1.85	-.10	3.2	.9	6.0
37	55	1.86	-.35	3.7	1.0	8.2
39	55	1.85	-.02	4.3	1.1	9.8
41	55	1.85	-.22	3.5	.9	10.
42	55	1.85	-.24	3.7	1.0	11.
44	55	1.85	-.1	3.8	1.0	12.
46	55	1.85	-.23	4.8	1.2	10.
47	55	1.85	.07	4.3	1.1	9.4

[redacted]

TABLE 12

ORNL pilot plant redox data

First cycle run objectives and losses

RUN	OBJECT	U LOSSES %		Pu LOSSES %	
		IAW	ICW	IAW	IBW
32	Determine performance of ORNL Redox First Cycle Flowsheet	.004	.0006	.01	.07
33	Determine performance of ORNL Redox First Cycle Flowsheet	.002	.0003	9.	.09
34	Determine performance of ORNL Modified Redox First Cycle Flowsheet	.003	.004	7.	.1
36	Determine performance of ORNL Modified Redox First Cycle Flowsheet	.001	.002	.01	.2
37	ORNL Flowsheet with oxidation being done before acid adjustment	.2	.005	.1	.06
39	ORNL Flowsheet reproducibility run	.001	.002	.08	.06
41	ORNL Flowsheet with acetone treatment during feed preparation	.004	.006	.08	.05
42	ANL Flowsheet plus acetone treatment	.002	.001	.04	.02
44	ORNL Flowsheet reproducibility run	.002	.001	.07	.07
46	ORNL Flowsheet reproducibility run	.009	.001	.56	.09
47	ANL Flowsheet plus acetone treatment	.009	.001	.10	.02

No first cycle runs 35, 38, 40, 43, 45 were made to enable the same sequence of numbers to be used in both first and second cycles.

[redacted]

Acetone Treatment of the Feed. A method for complexing of the ruthenium into the aqueous phase by treating the feed solution with acetone has been tested. This acetone treatment consists of the addition of 0.5% by volume of acetone and occasionally making the feed 0.5 *N* in sodium nitrite while the feed (2 *M* UNH) is .3 *N* in acid. The solution is heated to 80° C for thirty minutes and at 90° C for three hours, after which it is oxidized with dichromate and adjusted to the desired acid concentration.

Feed Filtration. Solution clarification by vacuum filtration of the feed solution through sintered stainless steel has been without incident. The sintered stainless steel element is believed to have a number of small cracks which probably let some solid particles through but this has not affected operation of the columns in any manner.

FIRST CYCLE COLUMN OPERATION—ORNL FLOWSHEETS

The data obtained in first cycle operation with the acid deficient flowsheet has shown a marked increase in decontamination and with no impairment of mechanical operability. The data obtained in the first cycle runs are given in Tables 12-13. The specific conditions of the first cycle flowsheets tested are given in Figs. 1-2. The improvement in decontamination given by the ORNL Modified flowsheet over the ORNL flowsheet was found to be sufficient to warrant the use of the additional $Al(NO_3)_3$ necessary in the ORNL modified flowsheet.

The mechanical operability of the columns has been without incident and no column fouling of any sort has been evidenced although a total of 3000 hours of operation have been completed. The uranium losses with the acid deficient flowsheet show more than adequate recovery of uranium. These losses have consistently been less than .01% except in run 37 when the scrub solution was 1.8 *M* $Al(NO_3)_3$ instead of the 2 *M* as called for by the flowsheet. The data indicate that the plutonium losses are caused by reduced but unpolymerized plutonium, with the exception of runs 33 and 34, where caustic was added to the feed before oxidation. A method is now being developed to insure complete oxidation of the plutonium in the extraction column.

The fission product decontamination except in the case of ruthenium has not been improved to a very marked extent over the ANL flowsheet. The ruthenium decontamination which improved by a factor of 100 over the acid conditions has been the main reason for overall improvement in decontamination. No significant change in the behavior of zirconium or columbium have been observed during these

[redacted]

TABLE 13

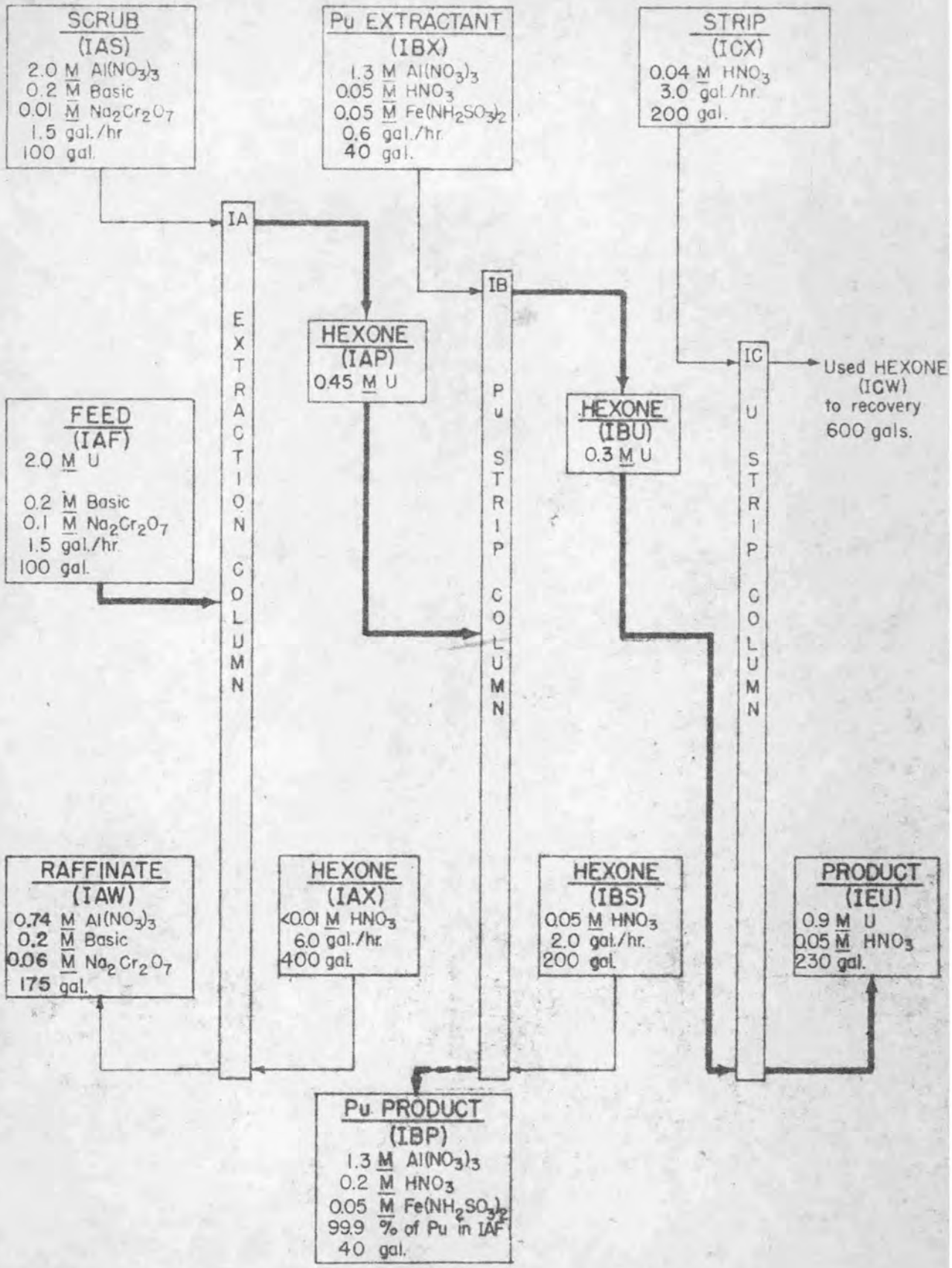
ORNL pilot plant redox data—First cycle decontamination factors

RUN	FLOWSHEET	PLUTONIUM DECONTAMINATION × 10^3					URANIUM DECONTAMINATION × 10^3			
		Beta	Gamma	Ce	Ru	Zr	Beta	Gamma	Ru	Zr
32	ORNL	23.	5.	820	1.7	6.0	31.	16.	1.6	11.
33	ORNL	12.	4.	300	1.3	1.8	8.	2.5	.5	1.
34	ORNL Modified	62.	12.	2600	1.0	8.1	23.	7.1	2.1	6.
36	ORNL Modified	54.	6.	3500	1.1	8.8	22.	5.	2.0	20.
37	ORNL	45.	9.	4300	5.6	7.8	35.	8.	2.1	7.
39	ORNL	18.	5.	44	1.4	4.8	5.	3.	.4	9.4
41	ORNL Plus Acetone Treatment	17.	5.	40	1.2	6.2	7.	4.6	.5	32.
42	ANL Plus Acetone Treatment	4.6	2.9	1700	.2	4.7	.2	.1	.008	23.
44	ORNL	12.	4.6	750	1.1	3.2	6.	4.2	.6	63.
46	ORNL	30.	8.4	440	2.3	7.1	13.	6.1	.7	17.
47	ANL Plus Acetone Treatment	21.	6.5	7100	.9	9.1	1.7	1.0	.07	37.

[redacted]

DWG. 7292

FIGURE



REDOX FIRST CYCLE

ORNL CHEMICAL FLOWSHEET

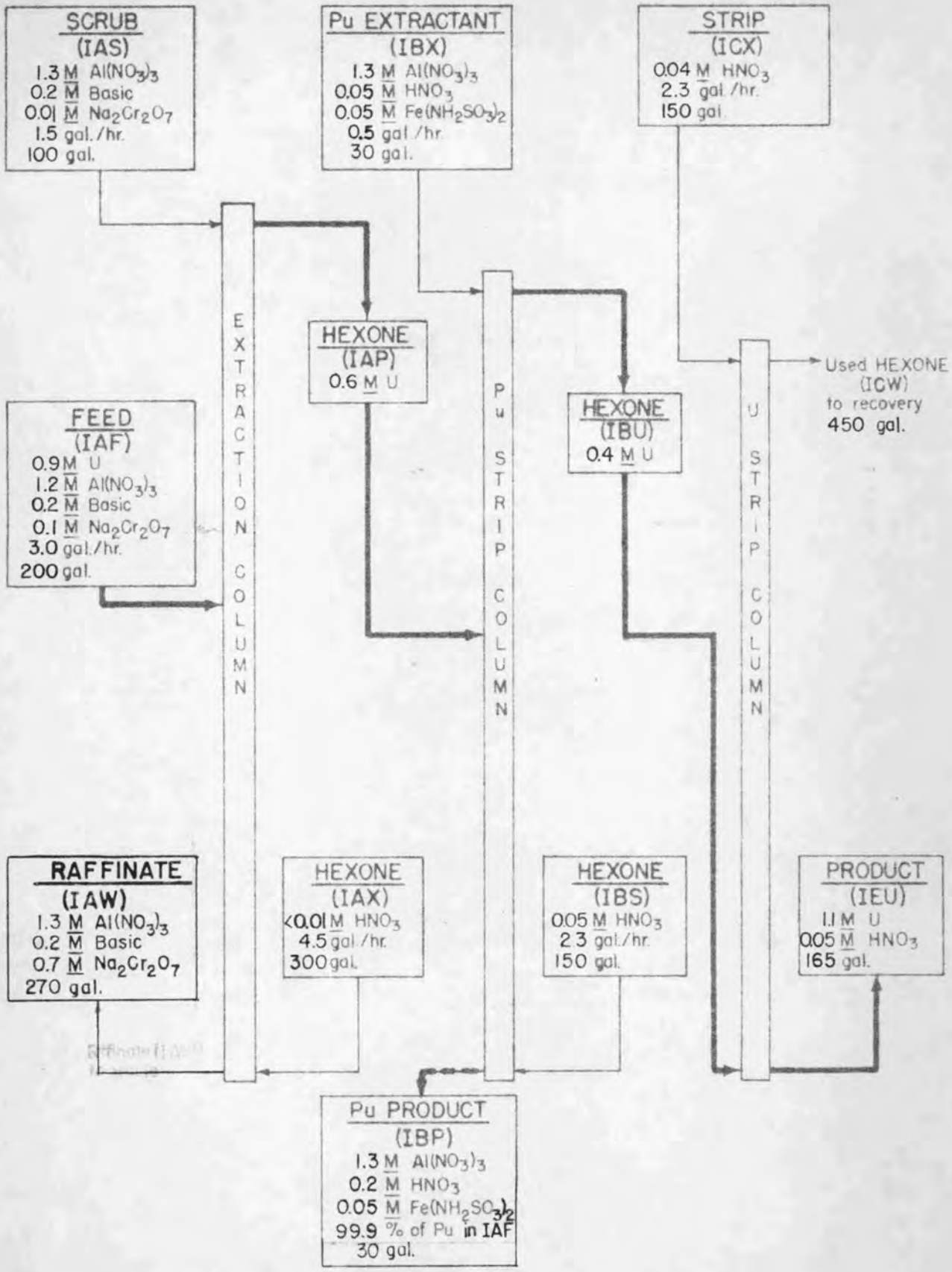
5-15-49

[redacted]

[redacted]

DWG. 7293

FIGURE 2



REDOX FIRST CYCLE

ORNL MODIFIED CHEMICAL FLOWSHEET

5-15-49

[redacted]

[redacted]

basic runs and the dependence of the decontamination on low methyl isobutyl carbinol content of the hexone was found to hold for the basic flowsheet. The cerium decontamination appeared to increase by a factor of ten. The acetone treatment as explained in the preceding section has enhanced ruthenium decontamination but not sufficiently to warrant its inclusion into the flowsheet at this time. Runs under these conditions show promise and indicate that further laboratory development is definitely desirable.

The precipitation observed to occur in the plutonium (1BP) stream from the first cycle partitioning column was found to be eliminated by making the partitioning column scrub 0.05 *N* in HNO_3 and had no effect on plutonium decontamination.

SECOND CYCLE FEED PREPARATION

The feed preparation for the second (uranium recovery and decontamination) cycle is unchanged since the last report, except that sodium hydroxide is used for neutralization. The main objectives of the second cycle investigations has been to compare the various flowsheets. Since the decontamination data obtained in the second cycle is affected by the history of the feed, most of the second cycle runs have been made in groups using a common feed for the entire group. The source of each feed is given in Table 15. The ORNL No. 1 and No. 2 second cycle chemical flowsheets are given in Figs. 3-4.

SECOND CYCLE COLUMN OPERATION

The decontamination and recovery data show that the uranium decontamination and loss specifications can be met in two cycles if the ORNL flowsheets are used in both the first and second cycle. The use of the acidic ANL flowsheet in either of the cycles guarantee adequate uranium recovery but results in insufficient decontamination. The comparison of both ORNL flowsheets show that although the No. 2 flowsheet is slightly better for decontamination the benefits incurred do not warrant the increased consumption of $Al(NO_3)_3$.

The objectives and data of the second cycle runs are summarized in Tables 14-15. The data for two cycles show that the uranium losses are below .01% and that the decontamination obtained in the second cycle is very markedly affected by the decontamination obtained in the first cycle, the second cycle being much higher if a poor decontamination is obtained in the first cycle. Using basic conditions in both cycles, the overall uranium gamma decontamination factor of 3×10^5 are obtained.

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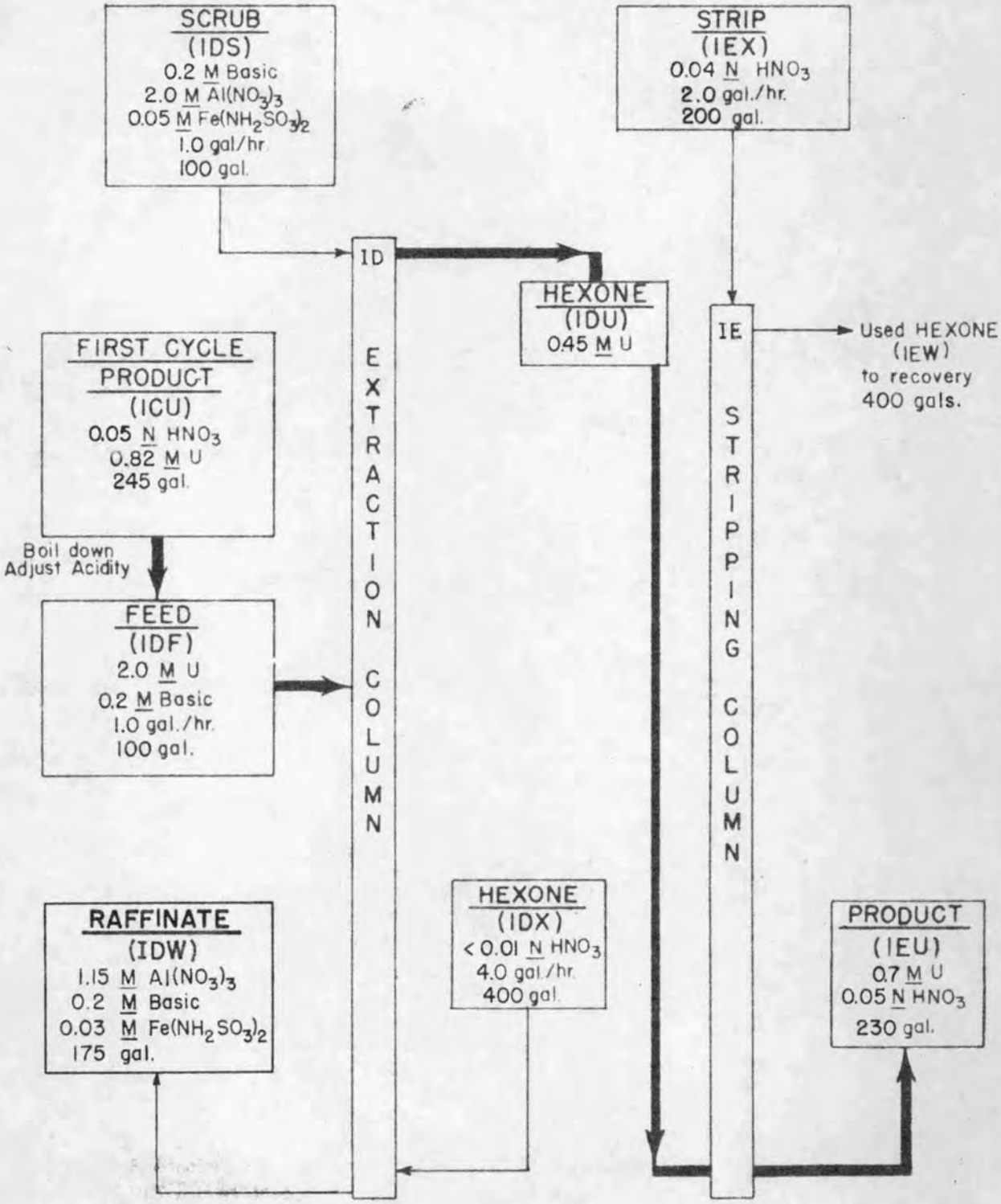
[redacted]

DWG. 7294

FIGURE 3



REDOX SECOND CYCLE

ORNL #1 CHEMICAL FLOWSHEET

5-15-49

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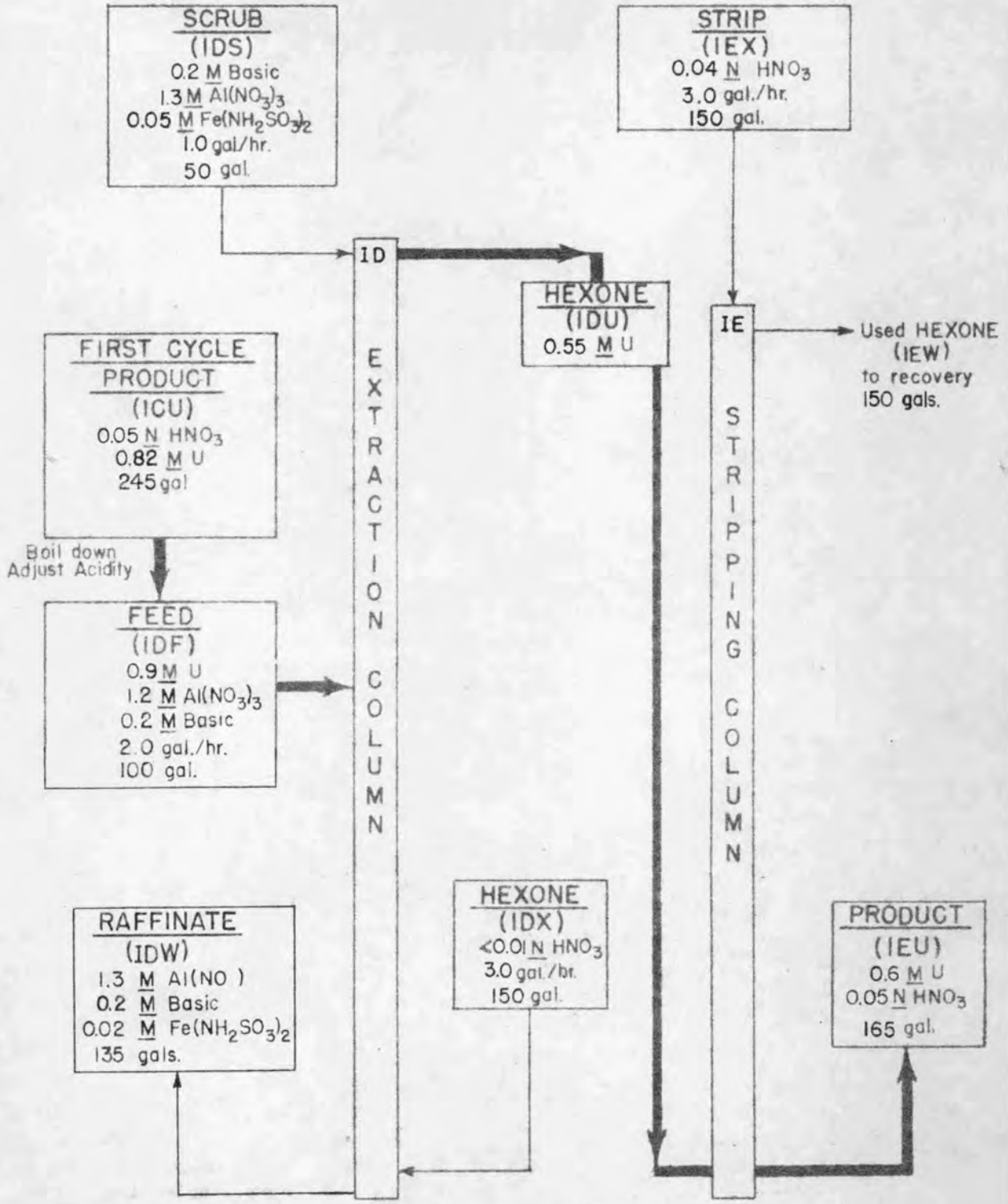
DWG. 7295

FIGURE 4



REDOX SECOND CYCLE

ORNL #2 CHEMICAL FLOWSHEET

5-15-49

[redacted]

[redacted]

TABLE 14

ORNL pilot plant redox data—
Second uranium cycle run objectives and uranium losses

RUN	OBJECT	U LOSSES—PERCENT	
		Ext.	Strip
27	Compare the three second cycle flowsheets using the	.02	.0006
28	product from an ANL first cycle run	---	.001
29		.002	.003
30	Test ORNL No. 1 flowsheet with varying flowrates	.004	.007
31	Compare the three second cycle flowsheets using the	.002	.007
32	product from an ORNL No. 1 first cycle run	.002	.009
33		.006	.001
34	Compare the three second cycle flowsheets using the	.02	.003
35	feed from an ORNL modified first cycle run	.002	.001
36		.0007	.003
37	Compare ORNL No. 1 flowsheet with (38) and without	.002	.001
38	(37) acetone treatment	.0005	.03
39	Duplicate of 38	.05	.01
40	Comparison of acetone treated ANL and ORNL No. 1	.05	.004
41	prepared from acetone treated ORNL first cycle product	---	---
42	Comparison of acetone treated ANL and ORNL No. 1	.006	.005
43	prepared from acetone treated ANL first cycle product	---	---
44	Comparison of ORNL No. 1 and ORNL No. 2 flowsheets	.002	.001
45		.003	.001
46	ORNL No. 1 reproducibility run	.002	.003
47	ORNL No. 1 reproducibility run	.004	.002

[redacted]

[redacted]

TABLE 15

ORNL pilot plant redox data—
Second cycle uranium decontamination data

RUN	FLOWSHEET		SOURCE FEED RUN NUMBER	DECONTAMINATION		
	First Cycle	Second Cycle		Beta	Gamma	Ru
27	ANL	ANL	Mixture	10	14	10
28	ANL	ORNL No. 1	of 27	240	230	200
29		ORNL No. 2	and 28	640	630	600
30	ANL	ORNL No. 1	30	200	500	500
31		ANL	Mixture	2.5	100	1700
32	ORNL	ORNL No. 1	of 32	70	100	500
33	ORNL	ORNL No. 1	and 33	120	100	400
34	ORNL Modified	ANL	Mixture	7	100	650
35		ORNL No. 1	of 34	30	100	260
36	ORNL Modified	ORNL No. 2	and 36	35	100	220
37	ORNL	ORNL No. 1	37	155	75	30
38		ORNL No. 1*	37	230	110	55
39	ORNL	ORNL No. 1*	39	310	370	270
40		ANL*	41	50	110	100
41	ORNL	ORNL No. 1*	41	60	145	210
42	ANL*	ANL*	42	240	390	370
43		ORNL No. 1*	42	2700	3600	3900
44	ORNL	ORNL No. 1	44	140	180	140
45		ORNL No. 2	44	170	200	160
46	ORNL	ORNL No. 1	46	60	60	40
47	ANL*	ORNL No. 1	47	135	180	180

* Feed treated with acetone or acetone and $NO_2^=$

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The use of hexone that contained large amounts of impurities such as methyl isobutyl carbinol and mesityl oxide had no deliterious effect on decontamination. The cerium, columbium and some of the zirconium activities in the second cycle product are extremely low, being very close to background, and the plutonium alpha counting has been discontinued since it was in the range of alpha background for uranium with the analytical procedures used.

In one of the runs (30) the mass thruput of all streams was varied from 50%, 100%, and 175% flowsheet conditions. No effect on decontamination, loss, or operability was found in the data obtained.

In some of the runs U^{237} gamma activity was found to account for 50-80% of the gamma activities in the 1EU stream. This activity was caused by the processing of slugs that had been aged only 50-70 days. The decontamination data presented here has been corrected for this activity.

ANALYTICAL DEVELOPMENT

The obtaining of decontamination factors which meet process specifications result in product streams with activities that are so low that it is necessary to replace the use of ordinary gamma counting techniques by the high pressure ionization chamber. A further evaluation of this tool to determine its accuracy has shown it to be extremely reliable. By the use of this instrument, the lower limit of convenient and accurate gamma activity was reduced by a factor of about 100.

The growth of the natural decay daughters of uranium interfers with the activity measured in the analysis. For this reason a correction must be made on the analytical results obtained and is dependent on the time between sampling and analysis. The correction factor has been re-evaluated and has been found to be 1.5×10^{-4} mv/mg U/day and 2 beta cts/min/mg U/day.

The interference of U^{237} gamma decontamination has been definitely proven to have been caused by the processing of irradiated uranium which had been cooled only 50-70 days. This material was determined by doing exhaustive uranium decontaminations on some of the products from the second cycle columns. The half life and energy of the beta gave close agreement with the literature values although there was some interference with the Ru^{103} beta. The gamma interference for this constituent was determined and the necessary corrections made to the decontamination data.

The interference of an inextractable alpha activity, which caused high losses in the first cycle extraction column raffinates when the LaF_3 method was used,

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has been definitely found to be americium and curium. This material has been found to be present to about 0.6% of the alphas in the feed. Its identity was proven by LaF_3 precipitation under oxidation and reducing conditions, TTA extraction, and pulse analyses. The data and procedures used were sufficient to prove that the alpha activity in the first cycle column waste streams is not polymerized plutonium. Investigations into the history of the Hanford slugs have shown they were of long low level neutron flux irradiations which are condusive to americium-curium production.

PROGRAM

The previously explained ORNL Technical Division Pilot Plant development of the Redox process essentially completes all process investigations. There is to be a series of six 100% Hanford activity level runs to be completed by June 1. The flowsheet to be used for these runs will be the ORNL flowsheet in the first cycle and the ORNL No. 1 flowsheet in the second cycle with no process changes contemplated. At the conclusion of the 100% verification runs, the Pilot Plant will be converted back to 25 recovery process investigations and verification runs. The plutonium separated during the Redox investigations has been stored and will be recovered after the 25 demonstration runs and returned to production channels.

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URANIUM RECOVERY FROM METAL WASTE

URANYL AMMONIUM PHOSPHATE PRECIPITATION PROCESS

LABORATORY DEVELOPMENT

An alternate procedure for the precipitation of uranyl ammonium phosphate was developed and demonstrated on a 500 milliliter scale using diammonium phosphate instead of ammonium nitrate as the precipitating agent. A gross fission product decontamination factor of 10^3 with a uranium loss of one percent was obtained in two precipitation cycles with Hanford supernatant and simulated total waste eliminating the recycle step and the use of ammonium nitrate. In all uranyl ammonium phosphate precipitations with the ammonium phosphates, the product activity consisted of about 21% Ru, 7% Cs, and 71% Ce. The laboratory phase of this study has been completed.

In an effort to reduce the 1% uranium loss in the first precipitation cycle, studies were made to show the effect of long digestion (2 hours) at elevated temperature (90° C) of the UAP product and mother liquor. Results of these tests indicated that the uranium loss may be reduced to about 0.5%; however, fission product decontamination dropped by a factor of about 2 (gamma D.F. of 1300 to 800). This drop in decontamination was probably due to the formation of an insoluble cerium ammonium phosphate which was carried by the uranyl ammonium phosphate (about 70% of the fission activity in the uranyl ammonium phosphate product after two precipitation cycles was cerium).

Experiments have shown that the addition of ammonium nitrate (3%) to the 0.01 *M* HNO_3 wash solutions did not aid the removal of fission product from the UAP product.

Since all previous uranyl ammonium phosphate precipitation work at ORNL was done on Hanford or synthetic supernatant, it was deemed advisable to investigate the behavior of feeds which approximated Hanford total waste. To simulate these solutions, Hanford supernatant was butted with additional uranium and non-uranium salts. The results were comparable to those obtained when using the supernatant feed (Table 16).

To determine the optimum quantity of dibasic ammonium phosphate compatible with good uranium yield and fission product decontamination, several 25 ml scale

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TABLE 16

Precipitation of uranyl ammonium phosphate with diammonium phosphate

Feed: Simulated Hanford total waste made by adding inactive reagents to Hanford supernatant

U - 55 g/l	$SO_4^{=}$ - 23 g/l
$CO_3^{=}$ - 52.8 g/l	$PO_4^{\equiv}$ - 23.5 g/l
NO_3 - 46.5 g/l	NO_2^{-} - 2.3 g/l
1.4×10^7 β cts/min/ml	
2.7×10^4 γ cts/min/ml	

Run Procedure:

First Cycle

1. Simulated Hanford total waste
2. $(NH_4)_2HPO_4$ solution added slowly to make 55 g/l of $(NH_4)_2HPO_4$.
3. Mixture cooled to 25° C at rate of 1° C/min.
4. Agitation continued 2 hours at 25° C.
5. UAP product washed twice with 375 ml portions of 0.01 *N* HNO_3 and 3% HN_4NO_3.

Second Cycle

6. Dissolve UAP product in 285 ml 1.5 *M* HNO_3.
7. Repeat steps 2 through 5.

OPERATION	URANIUM LOSS		DECONTAMINATION FACTORS	
	mg/ml	Percent	Beta	Gamma
First Precipitation Cycle				
Product precipitation	0.13	0.31	14.1	12.1
First wash	0.006	0.008		
Second wash	0.003	0.004		
Overall loss and decontamination first cycle		0.32	64	60.5
Second Precipitation Cycle	0.23	0.57		
First wash	0.004	0.005		
Second wash	0.002	0.003		
Overall loss and decontamination second cycle		0.58	27.8	27.8
Overall loss and decontamination factor first and second cycles		0.9	1785	1680

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runs were made. Results of these experiments indicate that 55 grams of $(NH_4)_2HPO_4$ per liter of total alkaline waste is necessary. To further test this procedure, three 500 ml laboratory scale runs were made. Average results of these runs indicate a uranium loss through two cycles, including washing, of 0.75% with beta and gamma decontamination factors of 1.7×10^3 and 1.6×10^3.

Use of the reducing agents ferrous ammonium sulfate and hydrazine hydrate and the oxidizing agent, periodic acid in concentrations of 0.05 *M* was investigated as an aid in improving the decontamination of uranyl ammonium phosphate precipitations from Hanford supernatant solutions with dibasic ammonium phosphate. Their use was also investigated in wash solutions for removal of the fission product containing mother liquor from the UAP product. No significant improvement was shown.

On precipitating UAP with NH_4NO_3 (K-25 procedure) from Hanford supernatant, the uranium loss in the first cycle is about 4% and about 10% in the second cycle. This high loss necessitates a recycle process for the recovery of uranium from these filtrates. The recycle procedure consists of adjusting the acidity with NH_4OH or NaOH to *p*H 2.0, centrifuging, washing the precipitate, and transferring as a slurry of the precipitate to a subsequent first cycle feed.

It was determined that the uranium loss in the UAP recycle step was decreased from 0.05 to 0.005 milligrams per milliliter when the *p*H was increased from 2 to 5. The decontamination factor was reduced by a factor of ten, but this was not important as the product went back to the first cycle crystallization (Table 17).

No further laboratory development on this problem is proposed at ORNL.

SEMI-WORKS DEVELOPMENT

The Uranyl Ammonium Phosphate Precipitation Process for the recovery and decontamination of uranium from the Hanford metal waste indicated satisfactory operability during the preliminary semi-works runs using synthetic Hanford supernatant containing no fission product activity. The major accomplishment during this phase of development was the demonstration that the basic metal waste could be satisfactorily neutralized and dissolved on the 190 liter scale without previous determination in the laboratory of the nitric acid requirement.

The uranium losses during these runs were high; however, these were due to mechanical difficulties that are being corrected (Table 18). The crystal size seemed to be satisfactory and jetting the precipitate to the filter op-

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TABLE 17

Effect of pH in the UAP recycle process

pH	URANIUM LOSS mg/ml	DECONTAMINATION FACTOR β	DECONTAMINATION FACTOR γ
3	0.05	80	285
3	0.006	7	65
5	0.005	4	27

TABLE 18

Uranyl ammonium phosphate precipitation process---Semi-works development

Uranium losses from synthetic Hanford supernate runs

Run basis - 190 liters (50 gallons) of supernate

All results are based on the weight of uranium in the starting feed - approximately 5.5 kg of uranium

RUN	FIRST CYCLE		SECOND CYCLE		RECYCLE PERCENT LOSS	OVERALL PERCENT LOSS
	Percent to Recycle	Percent Loss in Washes	Percent to Recycle	Percent Loss in Washes		
2	8.23	0.71	5.88	1.11	4.8	6.6
3	6.33	0.47	3.83	0.28	---	---
4	8.98	0.24	4.55	0.56	3.7	4.5

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erated without difficulty. The filtration time for the first cycle was higher than expected by a factor of two to four, but this is now known to be due to restrictions in the discharge line. The losses to recycle, which consisted of the filtrate and first wash, were normal. The unrecoverable uranium losses in the second through the fifth washes were high as expected due to the slurring cake to obtain thorough washing. In general the first cycle filter cake has been readily dissolved using agitation. The highest uranium losses occurred in the recycle step, and were again due to mechanical difficulties which were corrected subsequently.

SEMI-WORKS CONSTRUCTION—DESIGN

The first tank was set in place by the J. A. Jones Construction Company on February 11, 1949; piping was started on February 17, and the construction was completed April 1, 1949.

ORNL instrument men placed the instruments in service, after which TDSI personnel calibrated all tanks.

SEMI-WORKS EQUIPMENT ALTERATIONS—DESIGN

Exhausters. Vacuum tanks WA-6 and WA-7 were originally installed with Schutte and Koerting, Fig. 217, ½ in. steam jet syphons as exhausters using air as the motivating fluid. Contrary to results of previous tests, these jets only produced approximately 10 in. of mercury vacuum which was not sufficient to consistently pull the liquid through the filter media and up to WA-6 or WA-7.

The ½ in. syphons were replaced with one ¾ in. and one 1 in. Fig. 431 Schutte and Koerting exhauster also using air. A vacuum of 17 in. of mercury was then obtained.

WA-9 to WA-11 Decant Line. Recent work at K-25 has shown that when processing total waste it was feasible to decant the supernate from the settled precipitate in the recycle precipitation step in WA-9. Consequently, a decant line and jet, adjustable through the lower fifteen inches of the tank, was installed in WA-9, with the jet discharging to WA-11. The steam inlet line was fabricated from helical, flexible metal hose, and the suction lines slide through a stuffing box packed with shredded Teflon.

Agitators. The first and second cycle precipitators, WA-1 and WC-1, were originally equipped with Patterson gear reduction agitators obtained as complete units from Y-12 surplus. The agitator speeds were 330 rpm. Three bladed pro-

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pellers with a 6 in. radius were used. K-25 personnel felt that these agitators provided too vigorous mixing during the cooling period and recommended that variable speed agitators be installed. Consequently, the K-25 Engineering Development and Research Shops assembled two ¾ in., 110 V, AC-DC, portable drill motors and mounts for use with the original shafts and propellers. A Variac was connected to each motor which allowed the speed to be varied from 0 to 375 rpm. These units were installed on tanks, WA-1 and WC-1. The Jacobs chucks on the motors proved to be so unreliable that the drill motors were replaced with similar units equipped with Morse tapered chucks. Adapters were fabricated to attach the shafts to the drill motors. The units are in service at present.

The agitator shaft on WA-8 developed a violent whip during early runs so that a longer shaft was fabricated and installed. This agitator has caused no further trouble.

Liquid Heel and Solids Holdup. Jet suction lines on WA-1 and WC-1 were originally installed near the walls of the tanks and extended straight down to the dished bottom of the tanks. TDS-I personnel felt that this left too much liquid heel for satisfactory operations. To remedy this condition in both tanks, the suction lines for the jets to the filter and to the hot drain were extended over and down to the center of the tank.

A similar condition existed in WA-8. Since the amount of solids present in this tank was low, the jets to WA-9, recycle precipitator, and the hot drain were connected to the bottom outlet on the tank.

Solids holdup has been troublesome in WA-1 and WC-1. The agitator propeller was high in both tanks, and because of the shaft instability it did not appear feasible to lower the propeller. At the conclusion of a slurry transfer to the filter, the slurry level fell below the agitator and the solids immediately settled out. Filter washes were routed via the precipitator enroute to the filter, but since the propeller was above the wash solution surface, the solids remained almost undisturbed. Air at 15 psi was blown back through the jet-to hot drain suction line. Neither method was successful. Unless drastic changes are made, this difficulty must be accepted and minimized in the first cycle by adding the filter cake dissolving acid through the precipitator.

Filter Gaskets. Considerable difficulty was experienced in securing an adequate seal between the filter element periphery and the filter tank. The filter was designed with a bolt in the center which pulled the filter plate down against a ¼ in. fluorothene circular cross-section gasket held in a groove around the circumference of the filter tank. Different diameters of both solid

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fluorothene and fluorethene tubing have been tried, but all have failed when tested with air pressure under the plate. The amount of solids leaking through has not been enough to stop operations, but in order to hold the recycled material to a minimum a tight seal is essential. Gaskets of 3/8 in. solid butyl rubber may solve this problem if they can be obtained. The use of hot 60% nitric acid has made gasket material selection difficult.

UAP Product Carrier. Two surplus 50 gallon stainless steel tanks from Y-12 were modified to serve as carriers for transferring the UAP product from Bldg. 706-HB to the Y-12 Area. The changes involved removal from a dolly, capping the top nozzles with blind flanges, removing a bottom nozzle and plugging the hole, placing a 1½ in. gate valve on the other bottom nozzle, placing additional bolt holes in the top vessel flange, and adding angle iron stiffeners on the top of the tanks.

Miscellaneous Maintenance. The Eastern Model VW 20A rotary vane pump used in transferring 60% nitric acid developed a bad leak and was sent back to the vendor for repair. The rotary carbon-Teflon seal had been scored, apparently by solid material in the system.

A painting program has been carried out in the building under the direction of TDSI personnel. Pentkote and Prufcoat were applied to the floors in different areas, the exterior walls of the west cell block was coated with Prufcoat, and the cell interiors were coated with Prufcoat followed by Cocoon.

Tools have been fabricated for removing the filter element remotely, and removal safety chains have been installed around the top of the cells.

TRIBUTYL PHOSPHATE EXTRACTION PROCESS

A solvent extraction process has been developed for the recovery of uranium from metal waste. The procedure involves the solution of waste sludge in nitric acid to a free acidity of about three molar, extraction with a 15% tributyl phosphate—85% hexane mixture, and subsequent stripping of uranium from the solvent with water.

Uranium from both ORNL waste sludge (Table 19) and Hanford waste supernate has been recovered in one cycle of batch counter-current solvent extraction with a loss of 0.1%, and a beta decontamination factor of greater than 10^4. The satisfactory mechanical operability of the process has been demonstrated in a one inch laboratory column with comparable uranium losses and decontamination factors.

[redacted]

TABLE 19

ORNL metal waste analysis[a]

TANK NUMBER	PHASE SAMPLED	IONIC						RADIOCHEMICAL[b]					
		U	Na	NO_3	CO_3	PO_4	SO_4	Gross β	Gross γ	Ru β	Ce β	Cs β	Sr β
		mg/ml						cts/ml/min					
								$\times 10^{-5}$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-2}$
W-3	SUPERNATANT	0.02	110	13.7	33.8	2.4	104	1.9	0.58	8.3	0.06	14.3	0.52
W-4	SUPERNATANT	8.9	2.3	14.5	0.4	0.1	8.3	12.7	2.1	4.0	50.0	2.9	1900
W-7	SUPERNATANT	0.02	54.2	15.9	29.3	6.0	132	26.0	0.58	9.6	3.2	17.2	1.7
W-10	SUPERNATANT	0.02	74.1	22.4	33.0	8.7	104	29.8	0.9	8.1	4.7	26.9	4.2
W-8[c]	SUPERNATANT	16.1	39.9	15.4	27.8	7.2	227	8.5	1.4	9.4	50.3	16.9	74.1
		mg/g						cts/g/min					
								$\times 10^{-6}$	$\times 10^{-3}$	$\times 10^{-5}$	$\times 10^{-6}$	$\times 10^{-5}$	$\times 10^{-6}$
W-3	SLUDGE	539	143	22.8	60	12.5	8.6	19.1	14.0	7.4	11.8	3.1	1.2
W-4	SLUDGE	326	190	42.5	51	218	146	4.5	1.3	0.9	1.3	1.2	1.3
W-7	SLUDGE	475	170	34.9	67	90	214	3.2	1.2	7.8	0.7	1.6	0.7
W-10	SLUDGE	485	164	43.5	49	90	105	8.2	2.4	2.0	4.2	2.5	1.5

(a) The samples were taken 11/23/48 by P. B. Orr. Ionic results reported 1/4/49 by P. F. Thomason, and radiochemical results were reported 1/26/49 by C. S. Burros.

(b) Counting done at 10.18% geometry with no adsorber.

(c) This tank is used as a collection tank, and no uranium is precipitated here.

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The high extractive power of tributyl phosphate for uranyl ion indicated the formation of a compound between the uranium and tributyl phosphate. The ratio of uranium and nitric acid in the saturated solvent was found to be ca. 0.5 moles of uranium and ca. 1.0 mole of nitric acid. A complex of the general formula $UO_2(NO_3)_2(Bu_3PO_4)\cdot 2HNO_3$ is indicated and the following reaction could be postulated:

$$UO_2^{++}\ aq + 4NO_3^-\ aq + 2H^+\ aq + 2Bu_3PO_4\ org \rightleftharpoons UO_2(NO_3)_4H_2\cdot 2Bu_3PO_4\ org$$

Although more information, including absorption spectra, is required to establish this postulation, certainly the strong dependence on nitric acid and salt concentration is indicated.

URANIUM EXTRACTION WITH TRIBUTYL PHOSPHATE-HEXANE MIXTURE

The saturation solubility of uranium in Bu_3PO_4 was was 0.5 moles per mole of Bu_3PO_4 (Table 20). At uranium concentrations less than 0.45 molar a linear relationship exists between the amount of uranium extracted and the concentration of Bu_3PO_4 in the hexane (Table 21). Consequently, studies made with a given Bu_3PO_4 concentration may be easily extrapolated to other solvent compositions (Table 22). Since scouting tests indicated that concentrations of 15-20% by volume would yield adequate uranium distribution coefficients in column operations, the effect of different process variables was investigated with the solvent mixture in this range.

EFFECT OF TEMPERATURE AND EQUILIBRATION TIME

Using a 20% Bu_3PO_4—80% hexane mixture, the effect of temperature on uranium extraction was investigated in the range of 10-50° C (Table 23). At 10° C the uranium distribution coefficients (org/aq) was 0.37. This value was decreased by a factor of approximately two upon increasing the temperature to 50° C. This fact may be used to advantage in stripping the uranium from the organic solvent. Higher temperatures were not investigated because of the high volatility of the hexane component.

The equilibrium between uranium and tributyl phosphate is extremely rapid. No variation in distribution coefficients could be observed when equilibration periods were extended from 10 seconds to greater than 20 hours. However, the diffusion rate between solvent and aqueous phases will probably change slightly as the physical makeup of the solvent is altered by variations in diluent or Bu_3PO_4 concentrations.

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TABLE 20

Uranium solubility in tributyl phosphate-hexane mixtures

Aqueous Phase: Saturate (558 mg/ml) $UO_2(NO_3)_2$, 0.16 *N* HNO_3 (*p*H 0.3)

Organic Phase: One equal vol. pass. tributyl-phosphate hexane mixture

Equil. Time: 22 hours at 20° ± 0.2°

CONCENTRATION OF TRIBUTYL PHOSPHATE		MOLES Bu_3PO_4
Percent	M	Mole U
1	0.036	2.1
5	0.180	2.08
10	0.360	2.11
15	0.540	2.49
20	0.720	2.05
30	1.080	2.22
50	1.80	2.2
100	3.60	2.48

TABLE 21

Effect of uranium concentration on uranium extraction with tributyl phosphate-hexane

Aqueous Phase: Varying Concentration of $UO_2(NO_3)_2$ at reagent acidity

Organic Phase: One equal vol. pass. 20% tributyl phosphate—80% hexane

Equilibration Time: 18 hour batch extraction

Temperature: 20° C ± 0.2

INITIAL URANIUM CONCENTRATION		HNO_3		URANIUM DISTRIBUTION COEFFICIENT
Mg/ml	M	Org.	Aq.	Org/Aq
10.6	0.045	0.02	0.05	0.11
21.0	0.088	0.03	0.02	0.23
42.4	0.181	0.01	0.04	0.43
85.0	0.356	0.01	0.05	0.65
127.0	0.50	0.01	0.08	0.64
212.0	0.93	0.01	0.05	0.56
424.0	1.87	0.01	0.10	0.26
542.0	2.28	0.01	0.10	0.20

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TABLE 22

Effect of tributyl phosphate concentration on uranium extraction at low uranium concentration

Aqueous Phase: 0.12 *M* $UO_2(NO_3)_2$, 0.01 *M* HNO_3

Organic Phase: One eq. vol. pass. of tributyl phosphate-hexane mixtures

Equilibratiom Time: 22 hours at 20° C

Bu_3PO_4 CONCENTRATION		U DIST. COEFF.	MOLES Bu_3PO_4
Percent	M	Org/Aq	Mole U
1	0.036	0.0014	0.00444
5	0.180	0.098	0.0238
10	0.360	0.119	0.0311
20	0.720	0.29	0.0379
30	1.080	0.41	0.0321

TABLE 23

Effect of temperature on uranium extraction with tributyl phosphate

Aqueous Phase: 0.1 *M* U, reagent acidity

Organic Phase: One equal vol. pass. 20% tributyl phosphate-hexane

Equilibration Time: 5 min batch extraction

RUN NO.	TEMP. °C	U CONCENTRATION (mg/ml)		U DIST. COEFF.
		Org	Aq	Org/Aq
1	10	7.10	19.15	0.37
2	20	6.40	22.0	0.29
3	30	4.90	20.48	0.235
4	50	3.62	23.00	0.157

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EFFECT OF SALT CONCENTRATION ON THE EXTRACTION OF URANIUM

At low concentrations of uranium the concentration of salt in the aqueous phase ($NaNO_3$) is one of the most significant variables in affecting uranium extraction. Upon varying the amount of sodium nitrate from 0.0 to 5.0 *N* uranium distribution coefficients (org/aq) increased from 0.24 to greater than 200 (using a 20% Bu_3PO_4—80% hexane mixture and all other variables being held constant), (Table 24).

Although phosphates and sulfates are present in metal wastes in appreciable quantities, (ca. 0.2 *M*) analyses of uranium product solutions recovered by this process have shown no traces of these ions. Results of uranium/nitrate ratios indicate that two moles of nitrate extract with each mole of uranium, excluding the nitrate from nitric acid transfer.

EFFECT OF NITRIC ACID CONCENTRATION ON URANIUM AND FISSION PRODUCT EXTRACTION

In the absence of uranium the saturation solubility of nitric acid in tributyl phosphate-hexane mixtures was ca. 1.0 mole of nitric acid per mole of Bu_3PO_4.

At low uranium concentration (0.1 *M*) changing the nitric concentration of the aqueous phase from 0.02 to 5.46 *M* increased the distribution coefficients (org/aq) from 0.25 to 12.8. Higher nitric acid concentrations gave no additional increase in extraction coefficients (Tables 25-26).

The concentrations of nitric acid concentration permissible in the process have an upper and lower limit. The lower limit is approximately 1.0 *M* since this is about the lowest acidity at which solution of the waste sludge can be maintained. The upper limit corresponds to about 5.0 *M* since concentrations appreciably above this figure would begin to salt out the components of the aqueous feed.

EFFECT OF SULFATE AND PHOSPHATE ON URANIUM EXTRACTION

As expected considerable decreases in uranium distribution coefficients were observed in the presence of phosphates and sulfates. This effect is apparently overcome, however, by increasing the nitric acid concentration of the feed up to 5.0 *N*. The highest concentration of sulfates and phosphates to be encountered in waste solutions will be of the order of 0.2 *M*. With the aqueous feed 3-5 molar in nitric acid, and this concentration of Na_3PO_4 and Na_2SO_4 present, no evidence

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TABLE 24

Effect of sodium nitrate on uranium extraction with tributyl phosphate-hexane

Aqueous Phase: 0.09 M $UO_2(NO_3)_3$, $NaNO_3$ reagent acidity

Organic Phase: One equal volume pass. 20% tributyl phosphate 80% hexane

Equilibration Time: 18 hours at 20° C

RUN NO.	$NaNO_3$ CONC. M/1	URANIUM CONCENTRATION (mg/ml)		U DIST. COEFF. (Org/Aq)
		Org	Aq	
1	0.0	4.05	16.75	0.24
2	0.1	6.45	14.30	0.45
3	0.25	10.05	11.10	0.91
4	0.50	12.88	7.69	1.67
5	1.0	17.25	4.12	4.19
6	2.0	20.0	1.18	16.9
7	3.0	20.9	0.45	46.8
8	5.0	20.5	0.062	200.0

TABLE 25

Effect of nitric acid concentration on uranium extraction

Feed: 28 mg/ml U, varying acidities, indicated amounts of Na_2SO_4 and Na_3PO_4

Organic: 15% tributyl phosphate in hexane, equal volume extractions

Equilibration Time: 2 hours at 20° C ± 0.2° C

HNO_3 IN FEED M	CONTROL*	URANIUM DISTRIBUTION COEFF. (O/A)		0.1 M PO_4^{-3} and 0.2 M SO_4^{-2}
		0.2 M SO_4^{-2}	0.1 M PO_4^{-3}	
0.0	0.22	0.039	----**	----**
0.1	0.39	0.097	----**	----**
0.5	1.11	0.49	----**	----**
1.0	2.40	1.37	1.12	0.66
2.1	5.77	3.49	2.46	2.01
3.1	8.83	6.50	3.96	3.48
5.2	12.8	9.17	6.26	4.97
8.0	7.90	5.91	4.63	4.25

* No $SO_4^{=}$ or $PO_4^{\equiv}$ present

** Solution was not obtained at these acidities.

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TABLE 26

Effect of nitric acid concentration on uranium and fission product extraction from metal waste solution

Aqueous Phase: Solution of ORNL Waste Sludge in HNO_3 140 mg/ml U 4×10^6 beta c/m/ml

Solvent: Mixture of hexane and Bu_3PO_4

Five minute batch equilibration of equal volumes of solvent and feed

HNO_3 CONC. IN FEED N	% Bu_3PO_4 IN SOLVENT MIXTURE	DISTRIBUTION COEFFICIENTS				
		EXTRACTION (O/A)			FIRST STRIP	SECOND STRIP
		U	Beta	HNO_3		
1.0	10	0.5	8×10^{-5}	.05	5.3	14
1.8	10	0.6	4×10^{-5}	.02	5.0	17
2.6	10	0.5	3×10^{-5}	.02	4.4	20
3.4	10	0.5	4×10^{-5}	.02	4.8	20
4.2	10	0.5	3×10^{-5}	.02	4.8	20
5.0	10	0.5	4×10^{-5}	.02	---	22
5.8	10	0.5	4×10^{-5}	0.02	4.2	19
1.0	20	1.1	6×10^{-4}		1.7	3.5
1.8	20	1.4	3×10^{-4}		1.5	3.1
2.6	20	1.4	1.5×10^{-4}		1.3	3.1
3.4	20	1.5	1.1×10^{-4}		1.3	3.2
4.2	20	1.7	8×10^{-5}		1.2	2.3
5.0	20	1.6	7×10^{-5}		1.2	2.2
5.8	20	1.6	7×10^{-5}		1.1	2.1

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of unextractable uranium was observed after as many as five batch extractions (Table 25).

The high density of Bu_3PO_4 (0.97) made the use of a diluent necessary. Hexane (density 0.66) was arbitrarily chosen although a number of additional inert compounds of low density would have been satisfactory.

COUNTER-CURRENT BATCH EXPERIMENTS

Uranium from both ORNL waste sludge and Hanford waste supernatant has been recovered in one cycle of batch counter-current solvent extraction with a loss of 0.1% and a beta fission product decontamination factor of greater than 10^4.

From the results of laboratory batch studies, it was concluded that the optimum range of HNO_3 for the aqueous feed was 2 to 3.5 *N* and the optimum concentration of tributyl phosphate in the solvent mixture was 10 to 20%. Five of the six counter-current runs were made using these feeds and solvent conditions with no significant difference noted in either uranium loss or decontamination, (Table 27).

In batch work it had been found that with the solvent near saturation with uranium (0.5 moles of uranium per mole of Bu_3PO_4) the fission products and HNO_3 distribution coefficients (org/aq) are low. In Table 27 the uranium, HNO_3, and fission product concentrations are given for the successive stages in the extraction section. The solvent contained 0.5 *N* HNO_3 and 9×10^3 beta c/m/ml in the last extraction stage. This was reduced to 0.2 *N* HNO_3 and 800 beta c/m/ml at the feed plate. This drop in HNO_3 concentration and beta activity was attributed to the 'salting out' effect as the solvent neared saturation with uranium. The solvent was 70% saturated with uranium in the first stage.

The uranium distribution coefficient varied from stage to stage. At the feed plate the uranium distribution coefficient (org/aq) was about 2 while in the second stage it was 10. The lower distribution coefficient at the feed plate is due to the degree (70%) of saturation of the solvent with uranium. Below the second stage, the distribution coefficient drops sharply to 0.3 in the fifth stage. The uranium remaining after the fifth stage (about 0.1%) was not extracted in additional extraction stages and was constant from run to run regardless of run conditions.

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TABLE 27

Tributyl phosphate extraction of uranium from metal waste—Counter-current batch runs

Feed: Solution of ORNL waste sludge from waste tank W-10

Solvent: Mixture of tributyl phosphate and hexane

Scrub: As indicated in table

Strip: Water

Equilibration Time: 3 minutes in counter-current batch tubes; 5 extn. stages, 4 scrub stages, 5 strip stages

SOLUTION			SCRUB		SOLVENT		STRIP	% U LOSS		DECONTAMINATION FACTOR	
HNO_3 Conc. (M)	U Conc. (Mg/ml)	Vol. Ratio	HNO_3 Conc. (M)	Vol. Ratio	% Bu_3PO_4	Vol. Ratio	Vol. Ratio	IAW	IBW	Beta	Gamma
3.2	188	4	0.0	1	40	5	---	0.27	---	3.4×10^3	---
3.4	100	3	3.0	2	15	10	10	0.10	0.07	1.6×10^4	1000
3.2*	120	3	3.0	2	15	10	10	0.06	0.03	3.0×10^4	6000
3.5	140	3	3.0	2	15	10	10	0.24	---	1.6×10^4	----
3.1	136	3	3.0	2	15	10	10	0.15	0.15	1.4×10^4	-----
2.5	105	3	1.5	2	15	10	10	0.10	0.05	1.4×10^4	----

* Run was made with a feed prepared from Hanford supernatant (200 ml). The uranium was precipitated at *p*H 7 by neutralizing the supernatant with HNO_3, filtering and redissolving in HNO_3.

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Run 1 in the counter-current batch equipment was made with 70% hexane-40% Bu_3PO_4. The beta decontamination factor for this run was 3×10^3, a factor of 5 lower than the runs using 85% hexane—15% Bu_3PO_4. The 40% Bu_3PO_4 mixture also gave emulsions when contacted with the aqueous phase. Just on the basis of the physical properties of the solvent, about 20% seems to be the maximum amount of Bu_3PO_4 that can be used in the solvent mixture.

LABORATORY COLUMN RUNS

Two column runs made in a one inch laboratory column demonstrated the satisfactory mechanical operability of the system in a counter-current column, and confirmed the decontamination factors (10^4) obtained in batch runs. The column consisted of 8 ft of extraction section packed with ¼ in. × 3/8 in. split rings, 3½ ft of scrub section packed with 3/16 in. Fenske rings. The strip column was 6 ft in length packed with 3/16 in. Fenske rings. Several feed rates were tried during the runs. With Fenske packing, the flooding rate was only 200 gal/hr/ft^2, but below this flow rate, no mechanical difficulties were encountered.

The feed for Run 1 was a cold UNH solution, 3.0 *M* in nitric acid. The scrub solution consisted of 3.0 *M* HNO_3 and the strip solution was demineralized water. The feed for Run 2 was prepared by dissolving 20 liters of W-10 sludge in 70% HNO_3 to an acid normality of 3, and filtering through a sintered glass filter plate. The final uranium concentration was about 0.6 *M* (132 mg/ml). The scrub and strip solutions were 3.0 *N* HNO_3 and demineralized H_2O, respectively. The uranium losses were 0.5-1% for both runs which occurred primarily in stripping (Table 28).

In future runs it is planned to use ¼ in. × 3/8 in. split rings for both extraction and stripping columns and to lengthen the extraction section to 10 ft, the scrub section to 4 ft, and the strip column to 10 ft. The column runs will be coordinated with the counter-current batch runs to establish optimum process conditions.

WASTE INVESTIGATION

Nitric Acid Recovery. Synthetic waste from the tributyl phosphate uranium recovery process was evaporated in order to concentrate the waste and to decontaminate and recover nitric acid. Without any special method of separating entrainment, a decontamination factor of 10^3 was obtained using either old X-metal

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TABLE 28

Tributyl phosphate extraction of uranium from metal waste—Continuous counter-current column runs

Column: One inch glass pipe, extraction section—8 ft packed with ¼ in. x 3/8 in. split rings scrub section—4 ft packed with 3/16 in. Fenske rings. Strip column—6 ft. packed with 3/16 in. Fenske rings.

Feed: Run 1—UNH solution—Run 2—Solution of ORNL waste sludge from W-10

Solvent: 85% hexane—15% tributyl phosphate

Scrub: As indicated in table

Strip: Demineralized water

RUN NO.	FEED SOLUTION (IAF)			SCRUB (1AS)		SOLVENT FLOWRATE	PERCENT URANIUM LOSS DECONTAMINATION			
	HNO_3 Conc. N	U Conc. mg/ml	Flow-rate cc/min	HNO_3 Conc. N	Flow-rate cc/min	cc/min	IAW	IBW	Beta	Gamma
1	3.0	132	20	3.0	5	50	0.2	1.0	---	---
2	3.0	100	20	3.0	10	60	0.3	0.5	2.4×10^4	10^3

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solution or ruthenium tracer as a source of activity indicating that no significant amount of volatile fission products are present in the condensate. Using a 20 in. Vigreaux column with reflux produced by air cooling of the column, about 2 *M* HNO_3 was delivered from the top decontaminated greater than 10^4, and 9 *M* HNO_3 from the bottom decontaminated 10^3. An evaporation rate of about 15 ml/min could not be exceeded in the 3 liter evaporator because of foaming. A volume reduction of about 20 was obtained but with some salt formation. It is planned to study nitric acid recovery in conjunction with the other waste crystallization projects.

Sodium Nitrate Separation and Decontamination. Sodium nitrate from the evaporated raffinates of the tributyl phosphate-hexane uranium recovery process has been crystallized and decontaminated using nitric acid and volume reduction by evaporation. Sodium nitrate yields of over 90% per crystallization have been obtained with beta decontamination to 36 β/m/mg of sodium nitrate and gamma decontamination to background. This represents beta and gamma decontamination factors of 1000. A volume reduction factor of about 8 is obtained in the crystallization step.

A process developed at ORNL for the recovery and decontamination of uranium from waste solutions consists of the dissolution of the precipitated sodium diuranate with nitric acid, extraction with tributyl phosphate-hexane, and water stripping of the uranium from the solvent. The raffinates from this process contains large amounts of sodium nitrate in addition to small amounts of sodium sulfate, sodium phosphate and essentially all of the fission product activity. In order to reduce the volume of these raffinates for storage and subsequent disposal it is necessary to remove a large amount of the salt present with a high degree of fission product decontamination.

I. R. Higgins of ORNL has found that sodium nitrate could be removed from non-uranium waste solution by crystallization using nitric acid and volume reduction of the solutions by evaporation obtaining a high sodium nitrate yield and excellent fission product decontamination. Since the raffinates from the uranium recovery process are approximately 3 *M* in nitric acid, the above procedure for sodium nitrate crystallization is applicable.

Preliminary laboratory investigation of the crystallization at 25° C from uranium depleted ORNL waste metal raffinates has shown a sodium nitrate yield of 93% with beta and gamma decontamination factors of 77 and 95 through one crystallization and two 1/5 volume washes 70% HNO_3. A second crystallization cycle gave a sodium nitrate yield of 91% with beta and gamma decontamination

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factors of 16 and 25. The gamma activity of the sodium nitrate through two cycles was reduced to background while the beta activity was 36 β c/m/mg. A volume reduction factor of about 8 was obtained in the crystallization feed. Tentative proposals contemplate either the reuse of the nitric acid used in the washes in a subsequent crystallization, or recovery of the nitric acid by distillation for reuse.

Preliminary ionic analysis of the filtrates, washes and products indicate that essentially all of the phosphate and sulfate ions are removed from the sodium nitrate.

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ORNL RADIOCHEMICAL LIQUID WASTE DISPOSAL

EVAPORATOR CONDENSATE DECONTAMINATION BY ION EXCHANGE

Simulated condensate from the radiochemical waste evaporator has been run through ion exchange beds (1½ in. diameter by 2 ft high) with about 95% adsorption of total activity on the cation ion exchange resin, Dowex 50, and a total of 95 to 99% adsorption on the Dowex 50 cation and Dowex A-2 anion resin using W-6 waste diluted 10^3 with demineralized water with added X-metal solution as a source of activity. This decontamination was maintained over 5000 bed volumes of feed without breakthru and also after repeated resin reactivations. Elemental iodine, I_2^{131}, adsorbed on anion resin Amberlite IRA 400, or Dowex A-2, in the hydroxyl form with a decontamination factor of 10^3. No breakthru point has been observed after feeding as much as 5000 bed volumes. When a breakthru point occurs, the resin can be readily reactivated with 10 to 15 column volumes of 6 *N* HNO_2 for the Dowex 50 or 5% NaOH for the Dowex A-2.

For 5000 gallons per day of condensate at 600 gal/hr/sq ft, columns of a minimum diameter of 8 inches and 4 to 8 ft high are recommended for the tank farm evaporator. No further work will be done on this problem unless the operation of the ORNL Radiochemical Waste Evaporator demonstrates the need for further decontamination of the condensate.

DECONTAMINATION OF SODIUM NITRATE BY CRYSTALLIZATION

A total decontamination factor of 1.8×10^5 has been attained by three crystallizations of sodium nitrate from nitric acid with about 10^3 total disintegrations per gram of final sodium nitrate product. Decontamination factors of 10 to 300 were obtained per stage of crystallization. The inconsistent decontamination per cycle is believed to be due to erratic variations in the mechanical separation of crystals and liquor on incomplete washing. No fission products are quantitatively carried by the crystals. The remaining problem is to demonstrate this process on a semi-works scale. It is planned to set up either filter

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equipment or a continuous centrifuge for separating crystals and liquor. The centrifuge is favored because of simplicity of operation, more complete liquid-solid separation and probably more efficient washing.

LIQUID WASTE SURVEY

The results of the liquid waste survey completed during the last quarter were published in a report entitled 'Liquid Waste Disposal at Oak Ridge National Laboratory,' ORNL 328, dated March 28, 1949.

EVAPORATOR FOR ACTIVE LIQUID WASTE

Construction of the evaporator was started in the pase period and is now essentially complete. Items remaining to be finished are the sampler, two hot piping tie-ins, installation of the condensate monitor, and placing the last roof slabs and feed manifold pit shielding slabs after completion of testing.

Tests of the condensate monitor in the Semi-Works showed excessive plating of fission products on the Geiger-Mueller tube. The monitor was redesigned and the tube is now suspended above a free flowing liquid surface. Current tests indicate this will be satisfactory.

A preliminary test of the evaporator with water and clean equipment showed that evaporation rates in excess of 700 gallons per hour were possible. The operating evaporation rate will be considerably less since it will be limited by scaling and decontamination.

Calibration and leak checking now in progress will be followed by a water run and a dilute nitric acid run before the first hot run.

RECOMMENDATIONS FOR RADIOCHEMICAL AND METAL WASTE SYSTEM

A study was made to determine the necessary additions and alterations to the existing liquid waste system in order to establish waste monitoring systems for metal waste and radiochemical waste. The recommendations resulting from this study have been recorded in a report issued to the Austin Company as a guide for their future design work.

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Recommendations include proposals for the liquid waste facilities for the new Research Building, the new Semi-Works, and the new Physics of Solids Laboratory as well as proposals for changes and additions to existing liquid waste facilities.

Figure 5 schematically presents the recommendations of the Chemical Design Group for improving the ORNL liquid waste situation. The following sections summarize these recommendations.

PHILOSOPHY OF LIQUID WASTE DISPOSAL

The responsibility for separate collection of radiochemical and metal wastes will occur at the source by providing each source with a corrosion resistant collection tank for each type of hot waste. Proper operation of the waste system will allow the tank farm and evaporator operators control over the flow of waste to the various waste handling facilities and will minimize the activity in the cold process waste stream by-passing the evaporator.

SPECIFICATION FOR WASTE SYSTEM EQUIPMENT

Recommended specifications for collection tanks, hot sinks and hot drains in source buildings, transfer devices and lines, and instrumentation for hot waste systems have been established.

CHANGES TO EXISTING FACILITIES

The following changes are anticipated for existing equipment:

(1) Transfer the pile fan and filter cell drains from the W-1 and W-2 system to the cold process system.

(2) Install one hot sink for each hot laboratory in Bldg. 205, and connect the drain to the W-1 and W-2 system.

(3) Remove the Bldg. 205 roof drains from the W-1 and W-2 system.

(4) Transfer cooling water discharge in Cell 5, Bldg. 205 and in Cell 3, Bank 2, Bldg. 706-C from hot drains to the cold process waste system.

(5) Install a 3 in. stainless steel radiochemical waste line from Bldg. 706-D to tank W-5 and the evaporator. The line is to be laid in the same trench with the New Isotope Area radio-chemical waste line; the old connection between the Bldg. 706-D and the Bldg. 706-C radiochemical waste lines is to be blanked.

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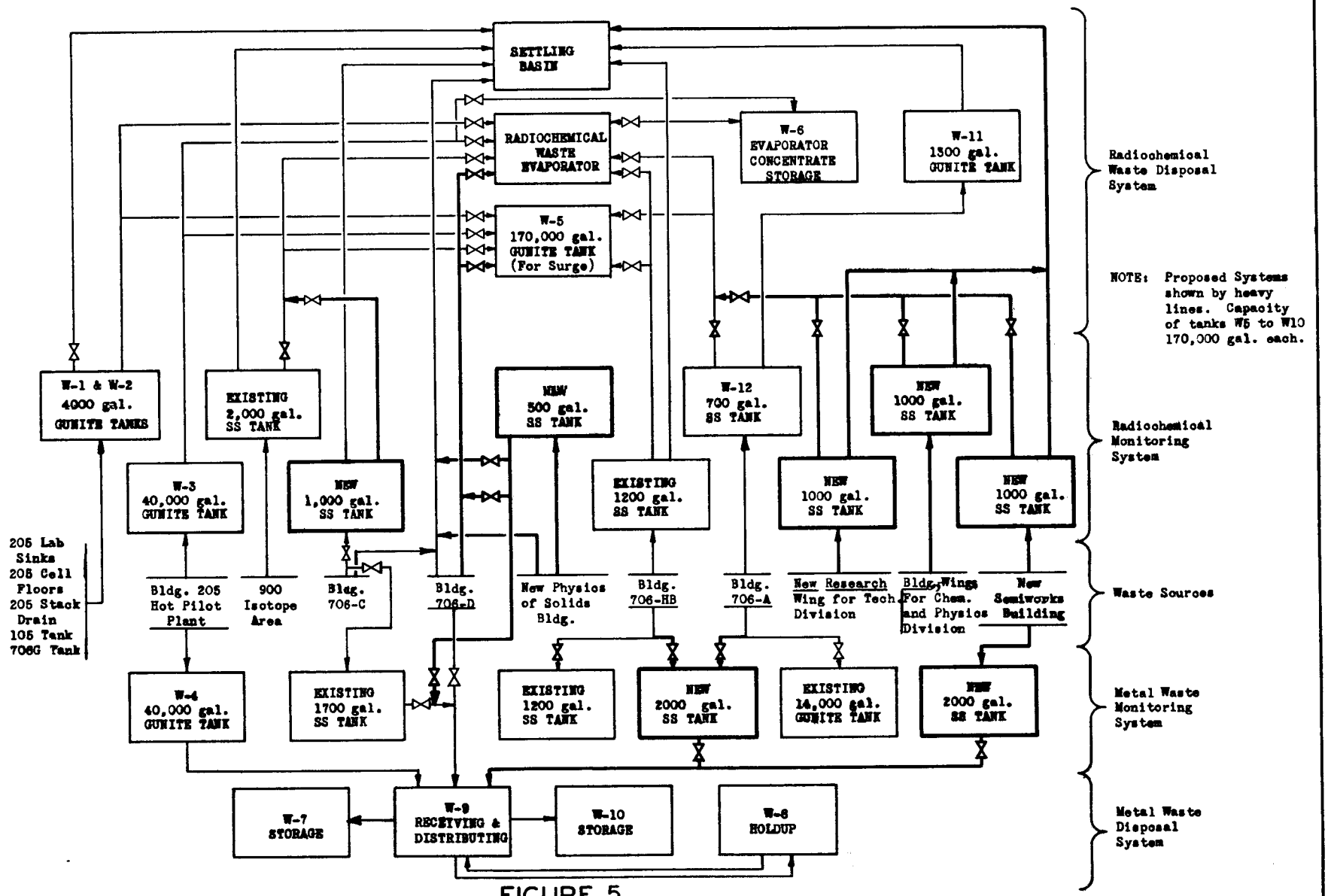

FIGURE 5

SCHEMATIC ARRANGEMENT OF ORNL LIQUID WASTE SYSTEMS

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(6) Provide Bldg. 706-C with a 1000 gallon stainless steel collection tank to be located at N-22029 and E-31072 in the South Tank Farm. The existing 3 in. stainless steel line from Bldg. 706-C to tank W-12 is to be connected to the tank. The tank is to discharge to tank W-5 and the evaporator through a connection to the radiochemical waste line from the New Isotope Area.

(7) Leave tank W-12 as the Bldg. 706-A radiochemical waste collection tank.

(8) Provide Bldg. 706-A and Bldg. 706-HB with a 2000 gallon stainless steel collection tank for uranium to be located near the existing 14,000 gallon concrete tank between Bldgs. 706-A and 706-HB. The metal waste drains from both buildings are to feed this tank, and a 2 in. stainless steel discharge line to the tank farm is to be installed.

ADDITIONS FOR NEW FACILITIES

Present plans call for the following new equipment installations:

(1) Provide one 1000 gallon stainless steel collection tank for radiochemical waste to serve the two Chemistry Division Wings and the Physics Wing of the new Research Building. The first tank is to be buried south of the West Chemistry Division wing. It is to receive waste from the three wings through a 2 in. stainless steel header south of the building and to discharge to the tank farm through a new 3 in. stainless steel line.

(2) Provide the new Semi-Works with one 1000 gallon stainless steel collection tank for radiochemical waste and one 2000 gallon stainless steel tank for metal waste. The radiochemical tank should also serve the Technical Division Wing of the new research building. The radiochemical tank should discharge to the proposed 3 in. stainless steel line from the Chemistry and Physics Divisions tank to the Tank Farm. The metal waste tank should discharge to the proposed 2 in. stainless steel line from the 706-A and 706-HB metal tank to the Tank Farm.

(3) Provide a 500 gallon stainless steel collection tank for the new Physics of Solids Laboratory. This tank is to serve for both radiochemical and metal waste because of the expected small quantities of both types of waste from this source. The tank should discharge through a 2 in. stainless steel line to an existing valve box at the west end of Building 706-C, where connections to the Building 706-D metal and radiochemical lines to the tank farm are available. The cold laboratory sinks, cold floor drains, and storage pit overflow should drain through a 4 in. vitrified-pipe line to a connection to the process waste system between Buildings 706-C and 717-BB.

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ALTERATION TO BUILDING 706—HB WASTE TANK—DESIGN

The discharge jets for the Building 706-HB radiochemical waste tank were tested to determine the reason for their unsatisfactory performance. One suction line was replaced because it was too small and had too many sharp bends. The piping was rearranged to allow the decant jet to discharge to the Settling Basin and the total draw-off jet to discharge to the tank farm. If the jet still does not transfer the waste to the evaporator feed tank after these changes have been made, it will be submerged in the tank to test the performance under this condition.

PROGRAM—DESIGN

During the next quarter detailed specifications will be developed and recommended for such liquid waste system auxiliary equipment as agitators, steam jets, level and specific gravity instruments, hot sinks, and samplers. A typical jet installation and materials of construction for specific lines and tanks will also be recommended. Surveys of hot sink requirements and of the process waste system are planned.

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RaLa PROCESS DEVELOPMENT

PURIFICATION OF BARIUM^{140} BY ION EXCHANGE —LABORATORY

An ion exchange process has been developed and a tentative flowsheet is presented for the purification and recovery of Barium^{140} subsequent to the metathesis step in the present RaLa process. The ion exchange process would replace the electrolysis and ether hydrochloride steps now used. The advantages of an ion exchange process are (1) ease of operation, (2) higher yield and purity of product. A major disadvantage may be gas formation due to ionization of H_2O by the high level of activity on the resin. Development work is underway to investigate the feasibility of up flow in resin columns to minimize operational troubles caused by gas formation. Optimum geometry of such a resin column will also be studied.

The procedure for the Alkali-Citrate Process for Barium^{140} purification in the RaLa process by ion exchange is as follows:

Step 1. After metathesis make the Ba-Pb nitrate solution 0.5 *M* in $CO_3^{=}$ free NaOH. Filter or centrifuge to remove $Fe(OH)_3$, $Ni(OH)_2$, the bulk of Cr *vs* $Cr(OH)_3$, and any dissolver crud.

Step 2. Pass the filtrate through a Dowex 50 resin column (approx. 1 liter of resin) previously activated with 0.6 *M* NaOH where the Ba and Sr would be adsorbed while the plumbite and any chromite anions pass through.

Step 3. After washing the resin with 0.5 *M* NaOH followed by H_2O, the Sr and any trace of Pb remaining is selectively eluted with 0.1 *M* sodium citrate, *p*H 9.0.

Step 4. Elute the Ba in 6 *N* HCl or HNO_3 (see flowsheet Fig. 6).

Trial runs on 1/100 the scale of the RaLa process for the separation of lead and strontium from barium by the above alkali process using Dowex 50 resin show yields of the order of 99% for barium which contain approximately 0.1% of the strontium and less than 0.01% of the lead originally present (Table 29).

The use of IR-105 resin was investigated for this process and found unsatisfactory for two reasons: (1) The resin swells about 30 percent in alkaline solution, and (2) lead is adsorbed from the alkaline solution.

An alternate ion exchange process, the Citrate-Acetate Process was developed which would start after the electrolysis step. This procedure would be less desirable from both an efficiency and ease of operation standpoints than

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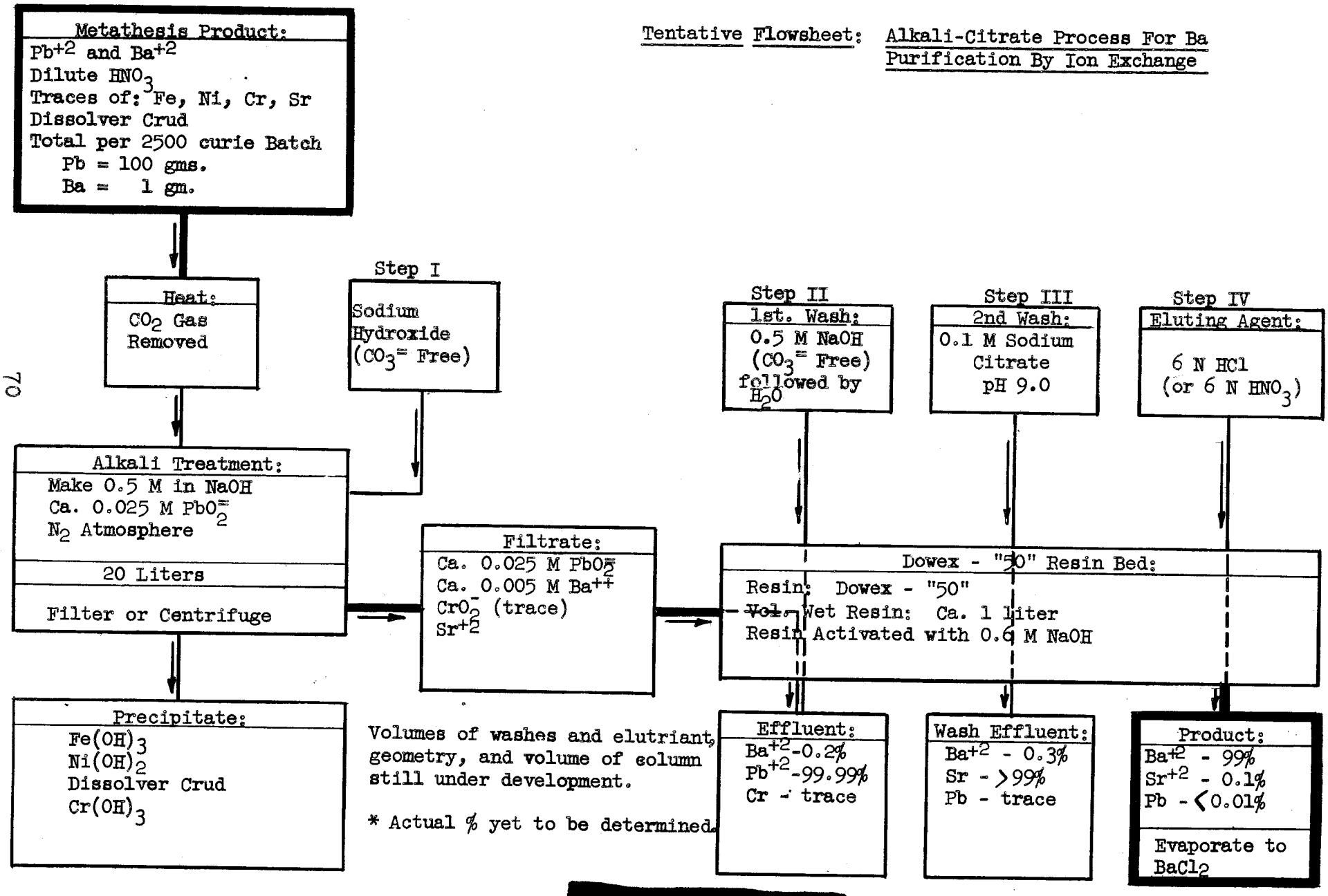
Drawing No. 7191

Figure 6

Tentative Flowsheet: Alkali-Citrate Process For Ba Purification By Ion Exchange



Volumes of washes and elutriant, geometry, and volume of column still under development.

* Actual % yet to be determined.

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TABLE 29

Separation of barium from lead and strontium by ion exchange

CONDITIONS:

Column: Dowex 50 resin (140-200 mesh), volume = 10 ml, column diameter = 1.5 cm

Activation: Resin initially put in Na form with 0.5 M NaOH ($CO_3^=$ free)

Flow Rate: 0.5 ml/cm^2/min

Feed: 5 mg/ml Pb as $PbO_2^=$ + 0.05 mg/ml Ba + tracer
0.05 M NaOH ($CO_3^=$ free)
1 mg Sr + tracer added for Runs Ba-9 and Ba-11
volume = 202 ml, 3000 ml for Run Ba-7

Washes: I: 30 ml 0.5 M NaOH ($CO_3^=$ free) followed by 30 ml H_2O
II: As shown (for removal of Sr and traces of Pb)
Ba elutriant: 300 ml 6 N HCl (large excess)

RUN NO.	% Ba vs Effluent & First Wash	SECOND WASH				PRODUCT Ba			Ba Material Balance
		Composition	% Sr	% Pb	% Ba	% Sr	% Pb	% Ba	
Ba-3	0.07	150 ml 1.0 M Na Acetate pH 6.0	---	< 0.16	< 0.01	---	< 0.04	97	97.08
			second wash and product combined						
Ba-4	--	150 ml 0.5 M Na Citrate pH 7.8	---	---	---	---	< 0.08	ca.300*	ca.300*
Ba-6	0.33	"	---	< 0.1	104.5	---	< 0.07	0.1	104.83
Ba-11	0.08	15 ml 0.5 M Na Citrate pH 7.8	86.5	---	0.97	6.7	---	107.8	108.85
Ba-7	0.3	"	---	8×10^{-4}	1.4	---	< 0.003	94.2	95.7
Ba-5	0.15	150 ml 0.1 M Na Citrate pH 9.0	---	< 0.15	0.14	---	< 0.10	100-0.29 =>99.5	---
Ba-9	0.01	"	103	< 0.2	0.34	0.11	< 0.04	94.3	94.65

* No Ba tracer used—Gravimetric Analysis for 'cold' Ba resulted in poor material balance

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the Alkali-Citrate Process which eliminates the electrolysis procedure. The relative distribution coefficients for Ba, Pb, Sr, Ni, Cr, and Fe between Dowex 50 resin and ammonium acetate, *p*H 6.0; oxalic acid and ammonium oxalate at *p*H's 0.78, 3.0, 7.8; and citric acid and ammonium citrate at *p*H's 1.7, 3.0, 7.8 have been determined. A number of scouting runs have been made in order to actually test the relative effectiveness of these eluting agents for removing these cations from Dowex 50 and IR-105 resins. Any appreciable quantities of Pb cause difficulties as a result of its low solubility in citrate solutions between *p*H's of 1.8 and 9.0. Oxalate elution was found to be unsatisfactory due to the low solubility of Ba, Pb, Sr, and Ni oxalates. As a result of these studies, the following procedure for the Citrate-Acetate Process for the purification of Barium^{140} in the RaLa process was proposed:

At present the solution is evaporated to dryness after the electrolysis step.

Step 1. Dissolve precipitate in 0.5 *M* ammonium acetate and pass through resin where all cations are adsorbed.

Step 2. Remove most of the lead by selective elution with ammonium acetate.

Step 3. Remove Fe, Cr, Ni, Sr, and the balance of the Pb by selective elution with ammonium citrate, *p*H 3.

Step 4. Elute barium in 6 *N* HCl.

A trial run using this procedure was not successful in that too much citric acid was used resulting in the elution of the barium with the other ions. The exact elution curves will be determined for this system to remedy this condition.

EXTRACTION AND METATHESIS STEPS INVESTIGATION — SEMI-WORKS

Equipment has been installed by the Semi-Works to investigate the extraction and metathesis steps of the Barium^{140} separations process on one-half plant scale. The major object of this work is to demonstrate the extraction and metathesis steps using either filtration or centrifugation for the separation of the precipitates. Decontation is now used in the plant and high erratic losses are experienced. A secondary object of this study will be to increase the uranyl nitrate concentration of the extraction solution thus increasing the capacity of the present equipment.

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RECOMMENDATIONS FOR REVISING RaLa PRODUCTION FACILITIES—DESIGN

Further effort has been directed toward determining where modifications of procedures, equipment, and building could be made to improve RaLa production, minimize losses and process time, and reduce air contamination to a minimum. Because of the uncertainties in the long range overall RaLa program, four alternate construction programs and one experimental program were recommended for the ORNL area.

A complete discussion of the recommendations for RaLa process alterations is given in a report to L. B. Emlet, entitled 'RaLa Process Study—Preliminary Report No. 1' by Culler, Goeller, and Unger issued April 6, 1947.

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"25" PROCESS

PILOT PLANT PLANNING

A program is being formulated for the resumption of the Pilot Plant investigation of the 25 recovery process upon termination of the Redox investigation about June 1, 1949. The conditions of the final 25 process separations plant will be more nearly approximated if the Hanford irradiated 25 slugs are processed as soon after July 1 as possible, and for this reason, the recovery of plutonium from the Redox process investigation will be postponed until later in the year.

Dissolving procedures for U-Al alloys are being studied, and the results of the Redox investigation are being reviewed for data which might be applicable to the 25 process. It is planned that a series of eight runs will be made using natural uranium irradiated at Hanford. These runs will be made to investigate the effect equipment changes necessary for the Redox process and to investigate minor modifications of the 25 flowsheet. The final phase of the 25 process investigation will consist of six process verification runs made using a $U^{235}Al$ alloy irradiated in the Hanford pile.

DESIGN PROGRESS

No active design effort was expended on the development of the 1200 Area design. However, a review of existing data on the 1200 (and 1300) Area was prepared for presentation to the MTR Review Meeting held at Oak Ridge National Laboratory on April 25-26, 1949. Effort was expended primarily in obtaining construction cost data and on operating manpower and cost data. Some work was done on 12-1300 area site plan and on the 25 process canyon arrangement. Rough shielding calculations indicated the need for six, four, and two feet of concrete for the first, second and third cycle feed solution activities, respectively.

CRUD REMOVAL

The 25 metal solution was filtered through Celite 545 Filter Aid 700 × 60 mesh stainless steel cloth at an average rate of 20 gallons per hour per square foot of filter area at 10 inches of mercury vacuum and yielded a water clear

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solution. Approximately 0.5% of the uranium was held up on the filter cake which was reduced to 0.03% by washing with nitric acid.

Silicon-Aluminum alloy 'crud' remains in the 25 solvent extraction metal solution feed, when the MTR fuel assemblies are dissolved by the proposed nitric acid, mercuric nitrate catalyst method. Removal of 'crud' is necessary for satisfactory extraction column operation and filtration is being investigated as the procedure for 'crud' removal. Requirements for 'crud' removal are:

1. Substantially complete removal of particles which might cause emulsions or plugging of liquid-liquid extraction column.

2. Not more than 0.01% uranium loss.

3. Procedure as simple and as economical of process time as possible.

FILTRATION RATE

The amorphous 'crud' in the solution of ORNL reactor slugs has been removed satisfactorily by filtration through a Micrometallic sintered stainless steel filter disc (approx. 10 micron pore size) in pilot plant runs; however, exceedingly low filtration rates are obtained, and drastic chemical treatment (hot caustic fluoride) is required to clean the filter element for re-use. This type of sintered filter element was found unsatisfactory for silicon-aluminum alloy 'crud' removal in preliminary trials, because the crud quickly blocked the entire filter surface and the filtration rate dropped to zero. Approximately 10 gallons of assembly solution could be passed per square foot of filter area until plugging was complete. The hot caustic fluoride treatment was again necessary to restore the filter; water washing was inadequate.

Celite 545 (the most coarse commerical grade of Johns-Manville filter aid) was selected for testing because it was retained well on the 700 × 60 filter screen (Dutch twill) and because it in turn retained the 'crud' wuite well. A thin precoat was applied to prevent initial wash-through of crud, and considerably more filter aid was mixed into the solution to be filtered. The filtrate from pre-coating was slightly cloudy, but was not important (Table 31).

The filtration rate was increased by increasing amounts of filter aid over the whole range studied, 0.2-1.5% by weight of solution. The rate at 1.5% was 4 times the rate at 0.2%. Since satisfactory rates are obtained at 0.5% filter aid or less, the amount of filter aid will probably be restricted to the lower range to minimize uranium losses.

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TABLE 30

Crud removal from solution of MTR assemblies

Solution: $Al(NO_3)_3$ 1.8 M, sp. gr. 1.35
Uranium content 2.5 grams/liter
pH approx. 0, except Runs 9 and 10 pH approx. 1
Silicon-Aluminum Crud Content 9.3 gm/liter/
(approx. 1.65) crud/liter expected in actual
assembly solutions)
Temperature 160-170° F. except Run 1-115° F.

Filter:
Metallic cloth, 700 x 60, 1.49 sq in. area.
Precoat 2.5 mg/sq cm. Johns-Manville Celite 545

RUN NO.	% FILTER AID BY WEIGHT OF SOLUTION	VACUUM IN. HG.			FILTRATION RATE Gal/hr/sq ft.		
		Start	Middle	End	Start	Middle	End
1	.22	1	10	20	92	29	25
2	.29	5	10	20	79	23	31
3	37	2	20	20	39	31	17
4	44	1	10	10	62	74	27
5	44	10	10	20	252	53	20
6	73	1	10	20	142	44	35
7	.73	10	10	10	409	74	25
8	1.10	10	10	10	294	82	26
9	1.32	10	10	10	357	88	34
10	1.46	10	10	10	161	112	45

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Increasing the temperature from 23° to 68° C increased the filtration rate by 136%. Filtration at a vacuum of 20 inches of mercury is restricted to lower than 68° C, the boiling point at this pressure.

No appreciable difference in filtration rate was noted between runs at *p*H 0 and *p*H 1.

URANIUM LOSS

Nitric acid washing has been found quite effective in reducing the uranium content of filter aid to virtually zero. Most of the adsorbed uranium was washed from the filter cake, without slurrying, using a volume of 3 *M* HNO_3 at 54° C equal to 10% of the filtrate volume. The uranium remaining on the filter cake, usually less than 0.05% of the original uranium, was further reduced by slurrying the cake with 2 or 3 washes of 70% HNO_2 at 54° C totaling 5% of the filtrate volume. The fate of the residual uranium was traced by analyzing the successive HNO_3 washes and completely dissolved samples of the crud filter aid cake for uranium content. These analyses showed (1) that the 70% HNO_3 washing (5% of the filter volume) is almost adequate, and (2) that the residual uranium can easily be reduced to 0.015-0.030% of the total filtered uranium with the foregoing washing procedure. These results merely established order of magnitude, and improvements in the completeness of washing are expected to place the uranium loss definitely below 0.01%. In addition, the reported ultimate uranium content of the filter cake samples (36 and 75 micrograms per gram) was near the lower limit of the analytical method (fluorometric), and hence not very accurate.

The solution used in the filtration tests contain 6 times more crud (9.3 gm per liter) than expected in actual assembly solutions. The amount of filter aid required, and hence the uranium loss data are therefore probably considerably increased.

A series of "filtrations" of previously filtered assembly solution over various quantities of filter aid permitted a correlation between the amounts of filter aid and the amounts of uranium recovered in subsequent washing. Large amounts of 70% HNO_3 (15% of filtrate volume) were used to insure essentially complete removal of adsorbed uranium. From Table 32 it was concluded that 0.5% filter aid or less would be preferred in order to limit the amount of uranium which would have to be recovered by means of washing. In actual operations, it is expected that the nitric acid washings would be used to dissolve subsequent assembly batches, thereby eliminating any special processing of wash solutions.

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TABLE 31

Amount of uranium retained by filter aid

% FILTER AID BY WT. OF FILTRATE	% U REMOVED BY 3 M HNO_3	% U REMOVED BY CONC. HNO_3
0.04	0.31	0.024
0.19	0.68	0.035
0.38	0.81	0.029
0.76	1.57	0.15
1.52	3.28	0.58

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"23" PROCESS

THORIUM RECOVERY FROM WASTE—LABORATORY

The recovery and decontamination of thorium from 23 raffinates is being investigated using tri(n)butyl phosphate-hexane as the extractant.

Two butyl phosphate-hexane mixtures have been investigated (25%-75% and 50%-50%) for thorium extraction from 1.3 *M* $Th(NO_3)_4$, 0.3 *M* $Al(NO_3)_3$, and 0.17 *M* NaF feeds (equal volume passes) to determine thorium distribution coefficients and fission product decontamination factors. Results of the experiments indicate a thorium distribution coefficient of 0.3 for the 25% butyl phosphate-75% hexane mixture and 0.7 for the 50-50 mixture. Fission product decontamination factors in both cases have been about 10^3 for beta and gamma. The addition of nitric acid to the feed did not improve the thorium distribution coefficient but did decrease the fission product decontamination factor from 10 to 10^2.

It is planned to investigate higher butyl phosphate concentrations to improve the thorium distribution coefficient.

SEMI-WORKS DESIGN

All design drawings were completed and approved for construction by May 6, 1949. A bill of materials has been made by the Engineering Department and cost of work done so far by the ORNL maintenance forces for procurement of material and for engineering has been 143,435. The J. A. Jones Company has been authorized to complete the installation and construction was started on May 16, 1949.

Fabrication of all tanks and panel boards is now complete. Reports from Argonne National Laboratory indicate that the performance of the Chicago Bellows pump is not as satisfactory as had been expected; however, it will still be used in the 1300 Product Semi-Works. This installation will be used as a test facility for direct pumping of hot solution; other pumps will be investigated as replacements for the bellows type pump. If hot pumping proves unsatisfactory, head tanks for hot column feed can be readily installed. Replacement bellows for the Chicago pumps have been received.

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EQUIPMENT DEVELOPMENT

RADIOACTIVITY MONITOR FOR EVAPORATOR CONDENSATE — SEMI-WORKS

It was proposed to use a Geiger-Mueller tube to monitor the condensate for radioactivity from the Radiochemical Waste Evaporator. The tube was initially immersed in the simulated condensate and then finally suspended over the surface of the liquid. Suspending the G-M tube over the surface of the liquid was the more successful method; however, in both cases the background quickly built up to the point that the tube would not be sufficiently sensitive to detect variations due to activity in the condensate.

A bare Geiger Mueller tube was immersed in synthetic condensate containing 107 β counts/min/ml while it was recirculated at 300 gal/hr for 2-1/3 hours. A Brown instrument recording the activity level indicated 11,000 counts initially and was off scale (20,000 counts) at the end of the run. The reading of 20,000 counts persisted when the condensate was drained from around the G-M tube. It was thought these readings resulted from activity plating out on the G-M tube, and the condensate chamber. This assumption was confirmed by: (1) an analysis of the condensate at the end of the run which indicated a decrease in counts by a factor of 2, and (2) 0.1 *N* to 0.5 *N* HNO_3 recirculated through the chamber reduced the counts of 20,000 to approximately 4,000 counts. The 'plating out' effect seemed to occur uniformly throughout the equipment and was not restricted solely to the G-M tube and condensate chamber.

It was concluded that it is not feasible to monitor evaporator condensate with an immersed G-M tube.

A lead shielded G-M tube was suspended about one inch above the surface of the condensate which contained 66 β cts/min/ml and was circulated at 300 gal/hr. With no condensate in the chamber, the Brown recorder read 800 counts. When condensate chamber was filled, the reading rose to 1850 then gradually decreased to 1400 at the end of a six hour run. With the chamber empty at the end of the run, the reading actually *increased to 2900*, owing perhaps to the shielding effect of the condensate. Analysis of condensate taken at the end of the run showed 50% reduction in β counts as in the previous test.

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PROTECTIVE COATINGS — SEMI-WORKS

The use of protective coatings as a means of controlling contamination in radiochemical laboratories and attendant facilities has been investigated. For these applications a coating should withstand the chemical attack of hexone and 3 *M* solutions of HNO_3, HCL, H_2SO_4, and NaOH. Sixty-eight protective coatings were tested against the foregoing reagents and none withstood all the reagents during a testing period of seven days. All coatings with the exception of Devan Resin, Duralon-35, Monsanto J-653, and Spraylat were attacked by hexone in 1-5 minutes.

Test results are presented in Table 33 wherein the coatings are arranged in four groups in their probable order of usefulness.

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TABLE 32

Chemical resistance of various protective coatings

CONDITIONS: 1. 3/8 dia. wood dowels coated and dried according to manufacturers specifications
2. Immersion in hexone and 3 M HNO_3, HCL, N_2SO_4, and NaOH
3. Test period—7 days
4. Reagent temperature—approx. 20° C

GROUP I	GROUP II	GROUP III	GROUP IV
Coatings that resisted the aqueous reagents but failed against hexone in 1-5 minutes.	Coatings that resisted hexone for 24 hours or more but failed against one or more aqueous reagents.	Coatings that failed against hexone and one or more aqueous reagents.	Coatings that failed all tests within 48 hours.
Acanal white *Amercoat* No. 31, No. 44, No. 55 *Bisonite* M-100(strip), M-101, M-109 *Brevon (strip)* 536-2-253 *Coopeel(strip)* No. 97 *Corrosite Plastic* gray, No. 8228 *G. E. Cocoon(strip)* *Glidden* RL-8222, RL-8319-E vinyl *Gordon Lacey* J211E, A248B, J220F, A89A *Glidden* RL-8222, RL-8319-E vinyl *Gordon Lacey* J211E, A248B, J220F, A89A *Pen-Kote** *Proxcoat* 19-70-3, 19-17-4 *Prufcoat* *Pyroflex* white, black, gray *Ucilon* 400-9	Monsanto J-653 withstood hexone HCL, H_2SO_4 for 7 days, but failed against HNO_3 and NaOH in 160 and 96 hours. Duralon-35 withstood hexone, NaOH, and H_2SO_4 for 7 days- failed against HNO_3 in 18 hours. Devan Resin, K-5925 resisted all aqueous reagents for 7 days- failed against hexone in 24 hours Spraylat withstood hexone for 24 hours- failed against HCL, NaOH, HNO_3, and H_2SO_4 in 48, 24 and 144 hours respectively.	*Bisonite* 751 *Co-Loidal-Ac* L1C26-T1, L1B9-T1 *(N) Coprene* 40106 *Corrosite* 541 *Geon* 31X *Garland* (N)Supernate varnish *Glidden* Y505, (S)150-B900, (S)Alkyd-B-6104, (N)90-B-11, (N)Plinamel-815, (N)RGL18511, RGL-19678 *Gordon Lacey* (S)J241B *Liquid Strip* 553-45A *Lithglow* LC-600 gray, LC-600 clear *Patterson Sargent* No. 1 and (N) No. 2 permanite FAH **Polytherm* 583 white, 60-9 clear *Rigortex* 2202 *(N)Shiller* No. 3 white *(S)Suydam* WC-1516-E *Ucilon* 451 (N) failed against NaOH, (S) failed against NaOH and HNO_3 all others against 3 of the 4 reagents **Unichrome* B-124, B-124-1 **Zapon-H* 4092BA6298 *(N)Batrett* No. 20BK	*Acanal* (could not be gray applied) *Bituplastic* 28 *Cotoid* gray *Corrosite* plastic coating aluminum *Plasticol* 77R-88 *Rubalt* 615 *Ucilon* 1601
*NaOH test doubtful		*Coatings to baked and rechecked	

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Group I: Coatings (26) That Exhibited Superior Resistance Against the Aqueous Reagents but Failed Against Hexone. These coatings offer the greatest protection against common laboratory reagents but little is known about their resistance to abrasion. Prufcoat, Pen-Kote and strippable G. E. Cocoon of this group have been used in service applications. In a nine months test on a concrete floor, Prufcoat and Pen-Kote demonstrated excellent resistance to abrasion. Pen-Kote, however, is extremely difficult to apply and has a rougher surface than Prufcoat. Its use was discontinued.

Strippable G. E. Cocoon has been thoroughly tested both in service applications and in the laboratory. It is recommended for walls and ceilings and general laboratory equipment but not as a permanent covering for floors. Although it is attacked by all the aqueous reagents and hexone, a cocoon membrane 0.048 mils thick will prevent penetration of 'bleed through' of activity and will remove 99.9% on being stripped. Cocoon can be stripped from glass, metals, composition boards, concrete, Prufcoat (aluminum type preferred), Pen-Kote, and Duralon-35. It cannot be stripped from the Amercoats, Lucite, unpainted wood, or oil base paints. In such cases, a parting agent such as Kemtone must be used. In a test on a concrete floor subject to heavy foot traffic, cocoon resisted scuffing and abrasion for 45 *working* days but deteriorated in approximately 75 *working* days. Satisfactory use has been obtained on cell walls and ceilings, hoods, laboratory benches, tools, valve handles and cement shielding blocks.

It is estimated that a typical concrete cell 6 ft × 6 ft × 30 ft can be coated at least 50 times with cocoon for the initial material cost of 20 gauge stainless steel to cover the same area.

Group II: Coatings (4) That Exhibited Superior Resistance to Hexone but Failed Against One or More Aqueous Reagents. This group is useful where a ketone or similar solvent is involved and resistance to specific reagents is not as important.

Group III: Coatings (31) That Failed Against the Ketone and One or More Aqueous Reagents. These coatings are of doubtful value for general use.

Group IV: Coatings That Failed in All Tests. The Semi-Works program on Protective Coatings is now completed. A final evaluation of all coatings, however, awaits decontamination data from the Biology Division. These data will soon be available and a joint Technical-Biology report will be issued.

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DRY FLUORIDE DEVELOPMENT

Information is now being accumulated on which to base development of dry fluoride separation processes for decontamination and recovery of uranium and fission products. Such processes would have the advantage of small volumes of radioactive waste and simple separation procedures.

Valuable information supporting the feasibility of this study has been obtained in conferences at K-25. Other information was obtained from ORNL personnel who were familiar with the fluoride work at Y-12, SAM early development at the University of Chicago and Clinton Laboratories.

The future development program is not clearly defined, but two major problems are now apparent. First is the fluorination of the metal, and second is the rectification of the volatile fluorides to obtain the required decontamination.

The equipment for the preliminary metal fluorination study has been fabricated.

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NEW FACILITIES—ARCHITECTURAL PLANNING

Criteria were established in February to enable the Austin Co. to proceed with a study for the new Semi-Works and Radio-Isotope building. This study was intended to investigate possible reduction of initial costs which might be affected by integration of plan elements needed for the two functions involved. It was later determined that any possible savings would be more than offset by undesirable possibilities of cross contamination of the respective areas, and a probable delay caused one group by uncrystallized planning needs of the other. The Semi-Works and the Radio-Isotope facilities are now being considered separately, but with the thought in mind that the two units may be juxtaposed in one structural system if possible.

Discussions are being carried on with regard to the Semi-Works cell block, in order to determine imperative design criteria, around which related functions may be grouped to best advantage. At the same time, thoughts of future expansion of the Semi-Works are being considered, in order to provide for later needs. This data will soon be ready for the Austin Company.

Design criteria for the 205 building were received by Austin, and their translation into working drawings is nearing completion.

A request for an office and shop structure to provide 706-HB with much needed space has been developed and passed on to the chairman of the building committee to obtain approval. This building would be 40 ft × 60 ft, and be composed of stock structural units in order to effect maximum flexibility at minimum cost.

Work has continued on the determination of design criteria for the new Research Building; several alternate schemes are being studied to get comparative cost data.

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The following chart lists the persons whose work is represented by the material in this report.

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O. Sisman, Group Leader - Radiation & Stability of Materials

C. D. Bopp

W. K. Kirkland, Technician

R. L. Towns, Technician

A. S. Kitzes - Coolant Problem

W. S. Farmer - Solvent Extraction

*Dual Capacity