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Quarterly Report, January Through March, 1951

Chemical Research Section

TO

R. B. Richards

FROM

O. F. Hill, F. J. Leitz

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CHEMICAL RESEARCH SECTION

by

O. F. Hill and F. J. Leitz
Chemical Research Section
Technical Divisions

April 16, 1951

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QUARTERLY REPORT JANUARY THROUGH MARCH 1951CHEMICAL RESEARCH SECTIONI. 234-5 COUPLING STUDIES (W. H. Reas, Group Leader)A. PLUTONIUM PEROXIDE PRECIPITATION FROM IIBP SOLUTION (K. M. Harmon)

The current Redox flowsheet proposes precipitation of plutonium peroxide from IIBP solution concentrated by evaporation to 10 g Pu/l and ca. 5.5 M HNO_3 . Such a solution might have an Al^{+++} concentration as high as 0.02 M with stainless steel corrosion product concentrations of the order of magnitude of those found in AT solution diluted to 10 g Pu/l.

Methods for the precipitation of plutonium peroxide from this type of solution, either with or without partial neutralization of the nitric acid have been described (HW-20053, pp 4-5). Recent work has been devoted to an investigation of the extent to which aluminum, chromium, iron, and other contaminating elements are separated from plutonium by peroxide precipitation.

Plutonium peroxide was precipitated from two samples of AT solution diluted to simulate evaporated Redox IIBP solution. After addition of aluminum nitrate and nitric acid, the composition of the solution was as follows: 10 g Pu/l; 0.02 M Al^{+++} ; 0.0006 M Fe^{+++} ; 5.5 M HNO_3 . One-half hour after addition of 42% $(\text{NH}_4)_2\text{SO}_4$ and 30% $(\text{NH}_4)_2\text{SO}_3$ to give concentrations of 0.20 M sulfate and 0.05 M sulfite, Sample No. 1 was precipitated by rapid addition of 30% H_2O_2 until an H_2O_2 concentration of 15% was achieved. In Sample No. 2, the HNO_3 concentration was reduced to 2 M with 10 M NaOH prior to addition of the other reagents. The H_2O_2 concentration was 11%.

The results from spectrochemical analyses of the thoroughly washed precipitates are listed in Table I. Aluminum was not detected. The high boron content was probably introduced from the Pyrex precipitation vessels.

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Table I

SPECTROCHEMICAL ANALYSES OF PLUTONIUM COMPOUNDS
PRECIPITATED FROM SIMULATED IIBF SOLUTIONS

Compound Element	Impurity Concentrations ppm of Pu			
	Peroxide No. 1	Peroxide No. 2	(III) fluoride	(IV) fluoride*
Ag	< 1	< 1		2
Al	< 10	< 10	2000	200
As	< 50	< 50		< 50
B	5	20		500
Ba	< 10	< 10	< 20	< 200
Be	< 0.02	< 0.02	< 0.02	< 2
Bi	500	1000		500
Ca	< 200	< 200	1000	< 1000
Cd	10	10	< 20	100
Ce	< 200	< 200	< 2000	< 20
Co	< 10	< 10		
Cr	5	10	20	< 10
Cu	10	10		10
Fe	500	500		100
Hg	< 200	< 200		
In	< 2	< 2	< 100	< 2
K	5	5		100
La			4000	
Li	< 1	< 1	2	< 2
Mg	100	100	400	50
Mn	10	10	< 20	20
Ni	250	250	1000	500
Ni	< 20	20		20
P	> 1000	> 1000		< 100
Pb	100	100	< 100	100
Sb	< 50	< 50		200
Si	20	20		
Sn	500	500		10
Sr			< 4	
V	< 200	< 200		< 200
Zn	100	100	< 100	< 100
Tl	< 100	< 100	< 100	

* Precipitated as Plutonium (III) fluoride at ca. 100°C. and converted, after washing, to PuF₄ at 100°C.

B. PLUTONIUM FLUORIDE PRECIPITATION FROM IIBF SOLUTION (K. M. Harmon)1. PRECIPITATION OF PLUTONIUM(III) FLUORIDE

PuF₃ precipitated at room temperature from a pure plutonium stock solution containing 40 g Pu/l, 2.3 M HNO₃, and 1-3 M HF, has been shown (HW-19739)

to exhibit a high bulk density, a rapid settling rate, and a low solubility.

An investigation of the precipitation of PuF_3 from a simulated Redox IIBP solution, carried out with an AT solution diluted to 40 g Pu/l, 1.25 M HNO_3 , and ca. 0.002 M Fe^{+++} , and containing 0.08 M Al^{+++} , has yielded the following additional information (see Table II):

1. Reduction of Pu(IV) to Pu(III) goes equally well with either the sulfate or hydrochloride salt of hydroxylamine. In 1.25 M HNO_3 , the reaction is very slow at room temperature, but is rapid at 70-100°C.
 2. A precipitate formed at room temperature by making the reduced solution 2 or 3 M in HF, does not settle well, and has a relatively low bulk density. This is presumably caused by the presence of the Al^{+++} . Stand-in experiments with La^{+++} showed the same effect, i.e., LaF_3 formed in the presence of 0.08 M Al^{+++} settled very slowly and to a volume 1 to 3 times as great as that observed when the solution contained no Al^{+++} .
 3. Precipitation at elevated temperatures markedly improves the physical characteristics of the precipitate. PuF_3 formed at 100°C. in 2 M HF settled rapidly, to a volume corresponding to a bulk density of 0.2 - 0.4 g Pu/ml. The bulk densities decreased with lower temperatures, although precipitation with 5 M HF at 80°C gave a precipitate which settled well and had a normal bulk density.
- Two samples, when HF was added at 100°C, were rapidly oxidized; and what appeared to be PuF_4 was precipitated. The HF addition was accompanied by appreciable gas evolution. The conditions necessary to maintain the plutonium as Pu(III) in this system at 100°C. have not yet been worked out.
4. PuF_3 peptizes severely upon washing two or three times with distilled water. Use of a 2 M HF, 1 M HNO_3 wash solution minimizes the peptization.

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The results from the spectrochemical analysis of PuF_3 precipitated at 70°C ., washed, and filtered in a Pyrex sintered glass funnel, are listed in Table I. The separation from Al^{+++} was poor. The source of the Na^+ is unknown

Table II

PRECIPITATION OF PLUTONIUM FLUORIDES FROM SIMULATED IIBP SOLUTION

Solution Composition: 40 g Pu/l; 0.08 M Al^{+++} ; 1.25 M HNO_3 ;
0.002 M F_3^{+++}

Expt. No.	Compound Precipitated	HF Conc (M)	Precipitation Temp ($^\circ\text{C}$)	Bulk Density (g Pu/ml)		Sol'y. g Pu/l	% Loss
				1 hr Settled	Centri- fuged		
3-23-1	PuF_3	2	91	ca. 0.2	0.5	0.01	0.0
3-23-4	PuF_3	5	80	ca. 0.2	0.6	0.01	0.2
3-23-2	PuF_4	2	100	ca. 0.6	1	0.1	2
3-23-3	PuF_4	2	100	ca. 0.5	1	0.7	2

Table III

PRECIPITATION AND WASHING OF PuF_3 -
CONVERSION OF PuF_3 TO PuF_4

(Precipitation and Conversion at 100°
Washing at Room Temperature, 2 M HF)

Procedure	Bulk Density (g Pu/ml)		Solubility (g Pu/l)		% Loss	
	20 Min. Settled	Centrifuged	20 Min. Settled	Centrifuged	20 Min. Settled	Centrifuged
Ppt'n of PuF_3	0.4	0.9	0.14	0.054	0.4	0.2
1st wash of PuF_3			0.14	0.012	0.4	0.03
2nd wash of PuF_3			0.11	0.015	0.3	0.04
Conversion to PuF_4	~1	~1	0.48	0.45	1.3	1.3

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2. PREPARATION OF PLUTONIUM(IV) FLUORIDE FROM IIBP SOLUTION

As mentioned above a compound which resembled PuF_4 was twice obtained upon attempting to precipitate PuF_3 at 100°C . The solid had a remarkably high bulk density and settling rate (see Tables II and III), although its solubility was also higher than that of PuF_3 (0.5 to 0.7 g Pu/l compared with values $\ll 0.1$ g Pu/l).

An attempt to repeat the precipitation of PuF_4 in this manner, with 500 mg Pu, gave only PuF_3 . This material was washed twice with 2 M HF 1 M HNO_3 . This process served to remove any reducing agent (NH_4OH^+). The solid was then mixed with more wash solution, heated to 100°C , and stirred for 20 minutes. After 10 minutes the color of the precipitate had changed from the violet characteristic of PuF_3 to a tannish pink, presumed to be evidence of PuF_4 . Solubilities and bulk densities were measured and are listed in Table III. The complete process was attended by a loss of 1.5 to 2.5%.

Justifying the hope that the change of crystal habit which accompanied the conversion would improve the purity of the final product the spectrochemical analysis recorded in Table I shows a satisfactory clean-up from Al and Fe. The high boron content presumably resulted from filtration of the precipitate upon a Pyrex sintered glass filter.

3. ATTEMPTS TO DRY PLUTONIUM FLUORIDE PRECIPITATES

It is hoped that PuF_3 and/or PuF_4 suitable for reduction to the metal can be prepared without the use of anhydrous HF. Such a process would involve the precipitation of PuF_3 or PuF_4 and a subsequent drying operation.

From a statement in the literature (CN-3551) to the effect that PuF_3 hydrolyzes in water at temperatures as low as 70°C ., it seems advisable either to remove the water at a temperature below 70°C ., or to make the final wash of the precipitate with a wash solution containing HF. Because of the care presumably

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necessary to prevent hydrolysis, it also seems advisable to filter the solid and dry the resulting cake at as low a temperature as will give a satisfactory rate of water removal.

Two 1/2 g samples and two 5 g samples of PuF_3 , precipitated at 70°C ., and one 1/2 g sample of " PuF_4 ", prepared as described in Section I. B-2, have been dried by heating in a stream of dry argon. Although identification of the products is as yet incomplete, the phenomena observed are recorded below:

1. A sample of PuF_3 which had been heated at 100°C . until it reached a constant weight showed no weight change upon treatment at 175°C .
2. A temperature of 200°C . is too high for PuF_3 . One sample showed a change of color, another one an increase in weight at this temperature. At 300°C ., the conversion of PuF_3 to oxide or oxyfluoride in argon containing traces of oxygen was quite rapid.
3. The physical characteristics of the dried solid were found to depend upon the conditions of precipitation and washing. One sample of PuF_3 powdered nicely, but had a gray color. Two other samples, which had peptized while being washed, dried to hard lumps which were purple in color.
4. The PuF_4 came to a weight which was essentially constant at 125 - 200°C . Subsequent conversion to PuO_2 gave a weight change which suggested a parent mixture of 80% PuF_4 with 20% PuOF_2 or PuF_3 . The color of the dried fluoride was a grayish tan, rather than pink. Because of the method of preparation, however, the composition of the wet fluoride is uncertain and the weight changes give no proof of the composition of the dry compound.

C. PLUTONIUM(III) OXALATE PRECIPITATION (P. M. Brown)

A final pair of plutonium(III) oxalate precipitations was made for coupling Redox to Metal Production, adhering as closely as possible to plant conditions which would be encountered as far as solution compositions, volumes,

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washing and settling times are concerned. These experiments were carried out on a 150 mg Pu scale and the data are presented in Table IV.

Table IV
PRECIPITATION OF PLUTONIUM(III) OXALATE IN THE
PRESENCE OF ALUMINUM NITRATE

<u>Concentrations</u>		<u>I</u>	<u>II</u>
Starting solution	HNO ₃	1.5 M	1.5 M
	Pu	50 g/l	50 g/l
	Al	0.1 M	0.1 M
Reduction	HI	1.5 M	1.0 M
Precipitation	H ₂ C ₂ O ₄	0.343 M	0.373 M
	HNO ₃	0.57 M	0.57 M
	Pu	23 g/l	23 g/l

<u>Sample Time</u>	<u>g/l Pu</u>	<u>% Loss</u>	<u>g/l Pu</u>	<u>% Loss</u>
After precipitation				
15 min. settling	0.0221	0.0951	0.0133	0.0577
30 min. settling	0.0172	0.0751	0.0101	0.0440
45 min. settling	0.0215	0.0933	0.0180	0.0784
After first water wash plus				
20 min. settling	0.00712	0.0310	0.0153	0.0665
After second water wash plus				
20 min. settling	0.00353	0.0154	0.0105	0.0451

The lower hydriodic acid concentration is sufficient for complete reduction and allows a slight increase in the oxalic acid concentration. Slightly lower losses were obtained at the higher oxalic acid concentrations.

At the same conditions as in experiment II above, one run was made to determine the amount of carrying of uranium through the oxalate precipitation. With the starting solution 0.1 M UO₂(NO₃)₂, the same procedure was carried out and the precipitate was analyzed for uranium. The analysis showed a decontamination factor of 12 for uranium.

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D. PLUTONIUM(III) SULFATE (P. M. Brown)

During an attempt to reduce a plutonium nitrate solution from Pu(VI) to Pu(III) with ferrous ammonium sulfate prior to an oxalate precipitation, a blue precipitate formed, which was thought to be Pu(III) sulfate. Further experiments in which sulfate ion was added after reduction with hydroxylamine chloride, confirmed this hypothesis. Since the precipitate was ideally granular and rapid settling, a further investigation of the best conditions for its precipitation was begun. Variables studied were reducing agents, HNO_3 concentration, sulfate ion concentration, temperature and also the effect of alcohol on the sulfate solubility. Results of these experiments are found in Table V.

In the first run employing alcohol, ammonium sulfate was added to an aqueous Pu(III) hydroxylamine sulfate solution and the dark blue, granular sulfate allowed to crystallize out and, then, upon addition of alcohol, a fine white precipitate formed in the supernatant, which in a few minutes turned to a pale blue. In the second run, before precipitation had started, alcohol was added to the cold solution and immediately a pale blue, almost flocculent precipitate formed, leaving a clear, colorless supernatant. This precipitate (ca. 32 mg Pu) settled fairly well to a volume of 0.4 ml. in five minutes. The centrifuged precipitate occupied only ca. 0.13 ml. The bulk density of the settled and centrifuged precipitates are 0.08 and 0.25 g/cc, respectively.

The composition of the sulfate precipitate was uncertain; consequently a sample of the solid was submitted for sulfate and plutonium analysis. The precipitate was first washed free of sulfate with alcohol, filtered on a sintered glass disc after each wash, then dissolved in HNO_3 for analysis. For two separate samples, the analysis gave a sulfate to plutonium ratio of ca. 2.1. If the experimental value is correct, the precipitate is a double salt with the ammonium ion, probably $\text{NH}_4\text{Pu}(\text{SO}_4)_2$. An extensive investigation of Pu(III) sulfate double salts has been carried out previously (1) indicating the solid composition to be $\text{NH}_4\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.
(1) H. H. Anderson, MDGC-1128

Table V
PLUTONIUM(III) SULFATE
Solubility and Conditions for Precipitation

Run No.	HNO ₃ M	SO ₄ ²⁻ M	Reducing Agent	Temperature	Pu g/l		Percent Loss
					Total	Supernatant	
47-1	1.5	1.97	0.985 M (NH ₄) ₂ Fe(SO ₄) ₂	25°C.	76.7	21.35	30.0
47-3	0.15	1.3	0.524 M (NH ₄) ₂ Fe(SO ₄) ₂	25°C.	24.9	12.57	50.8
51-1	2.0	3.13	0.9 M	Boiling	54.25	18.5	19.3
51-1	1.75	1.52	0.74 M	"	53.5	9.74	17.2
51-3	1.0	1.2	1.0 M (NH ₄) ₂ FeCl ₂	"	32.0	5.19	19.3
48-1	0.205	0.5	0.7 M (NH ₄) ₂ FeCl ₂ / 1/2 H ₂ SO ₄	"	26.5	4.53	15.9
53-1	2.0	3.2	2.0 M (NH ₄) ₂ FeCl ₂	"	54.25	2.47	3.84
48-3	0.289	2.4	2.0 M	25°C.	32.0	2.4	7.5
55-2	0.033	1.33	0.57 M	25°C., 30% alcohol	18.9	1.73	9.17
55-1	0.833	1.33	0.57 M	Boiling, 30% alcohol	21.4	0.572	3.4

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F. CONCENTRATION OF REDOX END-STREAM FOR COUPLING OPERATIONS (P.J. Richardson)

The IIBP or IIIBP Redox product streams contain about one gram of plutonium per liter and are about one molar with respect to nitric acid. This stream is then concentrated to ca. 10 g Pu/l to facilitate subsequent product purification and metal reduction. If it is desired to couple Redox material directly into 234-5 operations (e.g. Pu(III) oxalate or Pu(IV) peroxide precipitation) further volume reduction of this solution is necessary because of equipment limitations in the 234-5 process line. Further, simply evaporating this solution to a volume compatible with the precipitation tank size is not self-sufficient as this solution contains concentrated nitric acid. Therefore, evaporation to a much smaller volume is necessary to remove most of the nitric acid associated with the plutonium, and once this is accomplished the product may then be diluted with water to reduce the acidity.

Laboratory studies on the evaporation of Redox material have been carried out in two stages. A preliminary run was made using synthetic IIBP solutions containing 0.002 M $Al(NO_3)_3$ and 0.70 M HNO_3 (no Pu). Approximately 800 ml of this solution was evaporated to ca. 30 ml in a large flask and then transferred to a smaller flask where further evaporation was continued until a volume of 1.5 ml was obtained. Some cake formed on the walls but was readily dissolved upon swirling the remaining liquid in the flask.

Additional concentration studies have been made with a IIBP solution obtained from AML. The solution contained 1.14 g Pu/l, $<10^{-5}$ M Fe, $<10^{-6}$ M Cr, ca. 10^{-6} M UO_2^{++} , and 2.08 M HNO_3 . Aluminum nitrate was added to make this solution 0.002 M since plant streams may contain gross amounts of aluminum. Approximately 800 ml. of this solution was evaporated (in two stages) to ca. 1.5 ml. The last stage of the evaporation was carried out with the assistance of an air stream. Some caking occurred and this is believed to be due to improper

heating (heating mantle operating at too high a temperature) and the absence of any reflux in the flask (due to the air stream). On cooling this concentrated product solution to room temperature the liquid solidified. The solid appeared to be dark brown and gelatinous. The solid was re-dissolved in excess concentrated HNO_3 and re-evaporated to about 3 ml whereupon a very fine, light yellow precipitate appeared which did not dissolve on addition of hot concentrated nitric acid. The supernatant was decanted from the precipitate, transferred to a graduated centrifuge cone and then evaporated to a volume of 2.8 ml. After standing at room temperature for several hours the concentrate solidified. This solution was eventually evaporated to about 1.5 ml with an infrared lamp and, while hot, 2 M HNO_3 was added resulting in a solution which had a volume of 3.5 ml. This solution remained in the liquid state, and an analysis of the solution showed the plutonium concentration to be 25.4 g/l, the aluminum concentration 0.15 g/l, and the nitric acid 1.2 g/l.

The second and third batches of the FDP solution (800 ml each) were evaporated too far in the small flask. It is believed that the dry walls of the flask became over-heated, converting some of the plutonium nitrate to the oxide. This material dissolved only very slowly in hot nitric acid and appeared to reprecipitate on continued evaporation. Spectroscopic analysis of the apparently acid insoluble solid showed that it contained primarily plutonium and silicon with traces of aluminum, calcium, chromium, magnesium, nickel, and sodium.

Evaporation studies are now being analyzed at various points during the runs to obtain a relation between aluminum, plutonium, and the HNO_3 concentrations. The concentrate is now being heated in an oil bath and the low temperature evaporation is again being assisted by an air stream.

II. RECOVERY OF PLUTONIUM FROM SLAG AND CRUCIBLE (C. Groot, H. E. Hopkins, Jr., H. W. Schulz)

A status report on the recovery of plutonium from slag and crucible

(HW-20817) is now being prepared for publication and includes studies of three methods of obtaining a nitric acid solution of slag and crucible and four methods of separating plutonium from such solutions. The three methods of solution preparation are (1) leaching slag and crucible with nitric acid, (2) complete dissolution of slag and crucible (except for a SiO_2 residue) with nitric acid, and (3) complete dissolution (except for SiO_2) by nitric acid in the presence of aluminum nitrate. The leaching and dissolution studies have been carried out using a plant size crucible and its associated slag. This work may be summarized as follows:

1. The preparation of a plutonium solution by leaching slag and crucible with nitric acid has not proven effective. Leaching solutions are difficult to filter because of suspended fines, and high plutonium recoveries cannot be obtained without dissolution of most of the solid material.
2. The Los Alamos method of nitric acid dissolution in the presence of aluminum nitrate appears to be a satisfactory procedure for obtaining a solution of slag and crucible and the associated plutonium.
3. Extraction of plutonium from leaching solution into TBP-AMSCO 125-90W cannot be readily accomplished with aluminum nitrate as salting agent because of emulsion formation. The use of calcium nitrate, however, enables good phase separations with high distribution coefficients. In one experiment where the leaching solution was 1.2 M HNO_3 and 2.7 M $\text{Ca}(\text{NO}_3)_2$ excess, 99% of the plutonium was extracted in three 1/10 volume contactings of 30% TBP-AMSCO 125-90W.
4. Solutions obtained by dissolution in the presence of aluminum nitrate, or leaching solutions which have been digested 18 hours in the presence of aluminum nitrate can be filtered and extracted without emulsion difficulties. A solution from dissolution, 0.16 M $\text{Al}(\text{NO}_3)_3$ and 5.0 M HNO_3 , was contacted three times with 1/10 volumes of 30% TBP-AMSCO 125-90W, and 99% of the plutonium extracted.

5. To obtain a reasonably pure product, the TBP-AISCO phases contacted with leaching solution 3 M in calcium nitrate must be scrubbed to remove calcium. Scrubbing also offers a convenient step for removal of nitric acid from the organic phase prior to stripping. The acidity of an organic phase can easily be reduced by neutralization to a value of 0.09 M HNO_3 , with the aqueous phase at $\text{PH} \approx 0.8$.

6. Stripping with three 1/10 volumes of 0.1 M hydroxylamine sulfate effectively removes 99% of the plutonium from 30% TBP-AISCO 125-90W solution, 0.1 M in HNO_3 . Evidence has been obtained which indicates removal of nitric acid from the organic phase is not necessary when using 0.1 M hydroxylamine sulfate as a stripping agent.

7. Plutonium(III) oxalate can be precipitated from the aqueous strip solution. A solubility of 22 mg/l was obtained. The purity of the precipitate has not been determined.

8. Small scale experiments indicate that leaching solutions can be recycled to the IIA column in the Redox Plant in amounts up to 10% of IIAF by volume.

9. It appears possible to recycle nitric acid solution of slag and crucible obtained in the presence of $\text{Al}(\text{NO}_3)_3$ to the second BiPO_4 precipitation step in the present Bismuth Phosphate Process. The action of small amounts of aluminum, carried by the BiPO_4 , in the lanthanum fluoride cycle remains to be investigated.

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III. P-11 ASSISTANCE (P. M. Brown)

A. STABILITY OF DILUTED AT MATERIAL IN THE PRESENCE OF PHOSPHORIC ACID AND BISMUTH NITRATE

In assisting P-11 personnel carrying out some critical mass measurements in the presence of phosphoric acid and bismuth ion, laboratory scale studies were made to determine the stability of plutonium nitrate solutions

containing (1) phosphoric acid up to concentrations of 250 g $\text{PO}_4^{3-}/\text{l}$, and (2) bismuth nitrate up to concentrations of 450 g Bi^{+++}/l .

Critical mass measurements can be performed in the presence of phosphoric acid only if the plutonium is first oxidized to Pu(VI) to prevent precipitation of Pu(IV) phosphate. It was found that the rate of oxidation of Pu(IV) nitrate solutions (50 g Pu/l) in 1.5 M HNO_3 by 0.1 M $\text{H}_2\text{Cr}_2\text{O}_7$ is extremely slow at 25°C., viz., 52%, 86%, and 98% oxidized after one, eight, and twenty days, respectively. At 90°C. and at the same reagent concentrations, the plutonium is completely oxidized in one hour and the solutions are stable with respect to precipitation for at least five weeks in the presence of 60, 125, 190, or 250 g $\text{PO}_4^{3-}/\text{l}$.

Since it is inconvenient to heat the large volume of product solution in the critical mass assembly, laboratory work was performed to determine the rate and extent of oxidation of cut sample can material before dilution and introduction into the equipment. Plutonium nitrate (320 g Pu/l) in 2.25 M HNO_3 is 83%, 95%, and 98% oxidized by 0.5 M $\text{H}_2\text{Cr}_2\text{O}_7$ at 65°C. after 80, 150, and 220 minutes, respectively. Using the same reagent concentrations at a temperature of 85°C., greater than 99% of the plutonium is oxidized after one hour. Experiments carried out simulating the high temperature evaporation of AT material as performed in the 231 Building in the presence of excess $\text{H}_2\text{Cr}_2\text{O}_7$ show that only 90-95% of the plutonium is oxidized after six hours. Furthermore, virtually all of the excess dichromate (50% excess in one experiment) had been reduced to chromic ion after the six-hour evaporation, thus explaining to some extent the incompleteness of the plutonium oxidation.

The oxidation of plutonium (50 g/l) in 1.5 M HNO_3 by 0.1 M KMnO_4 at 25°C. is 98.3% complete after one hour; however, some manganese dioxide is formed and should be removed before the solution is used for critical mass experiments.

Critical mass measurements in the presence of bismuth nitrate required that conditions be found to prevent the hydrolysis and subsequent precipitation of basic bismuth nitrate compounds. It was found that plutonium solutions (50 g/l) in 2.0 M HNO_3 containing 100, 215, 330, or 450 g Bi^{+++} /l are stable with respect to precipitation for at least one week providing Baker and Adamson bismuth nitrate salt, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, is used.

Vessels fabricated of 317 stainless steel were used for all the experiments.

B. THE SEPARATION OF LITHIUM FROM PLUTONIUM BY PLUTONIUM(IV) PEROXIDE PRECIPITATIONS

In assisting P-11 personnel carrying out critical mass measurements in the presence of lithium nitrate, laboratory scale experiments were performed to determine the feasibility of returning the lithium poisoned solutions to the 231 Building for product isolation and purification. The composition of the solution to be used in the critical mass assembly is ca. 40 g Pu/l and ca. 1 g Li/l. The solution will be diluted about four fold upon return to the 231 Building for recycle.

Of the two laboratory experiments performed, one was carried out adhering as closely as possible to the 231 Building operations as described in the Technical Manual. The remaining experiment differed only in that the plutonium peroxide precipitates were centrifuged rather than using a settling and decantation technique. The results of these experiments are presented in Table VI.

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Table VI

SEPARATION OF LITHIUM FROM PLUTONIUM NITRATE SOLUTION
THROUGH PEROXIDE PRECIPITATION

Scale: 200 mg Pu/run

Starting solution: 40 g Pu/l, 1 g Li⁺/l, 1.25 M HNO₃,
5 ml totalPreroduction: 10 g Pu/l, 0.25 g Li⁺/l, 2 M HNO₃, 0.2 M
(NH₄)₂SO₄, 0.05 M (NH₄)₂SO₃, 20 ml totalPrecipitation: Solution made 10% in H₂O₂.

	I		Settling Time, hrs.	II	
	Vol., ml	Li ⁺ , g/l		Vol., ml	Li ⁺ , g/l
First precipitate supernatant	28.0	0.2	2.0	27.0	0.4
First wash, 2% H ₂ SO ₄	3.5	0.1	0.5	3.5	0.07
Second " " "	3.5	0.04	0.5	3.5	0.02
Third " " "	3.5	0.01	0.5	3.5	0.005
Fourth " " "	3.5	0.001			
Second precipitate supernatant	13.0	5 x 10 ⁻⁵	2.0	13.0	1 x 10 ⁻⁴
First wash, 6% HNO ₃	3.5	3 x 10 ⁻⁵	0.5	3.5	6 x 10 ⁻⁵
Second " " "	3.5	1 x 10 ⁻⁵	0.5	3.5	5 x 10 ⁻⁴
Third " " "	3.5	<3 x 10 ⁻⁶	1.0	3.5	1 x 10 ⁻⁴
Fourth " " "	3.5	<3 x 10 ⁻⁶			
Final peroxide cake dissolved	2.3	<2 x 10 ⁻⁶		10.0	1 x 10 ⁻⁵

It can be seen from the data for the second experiment of Table VI which is more representative of plant conditions, that 10⁻⁴ mg of lithium is associated with 200 mg of plutonium. The lithium content expressed in parts per million of plutonium metal is 0.5. This value is far below the allowable limits for lithium and is, therefore, negligible.

The product losses in the various operations, although not presented in the table, were all normal. The lithium material balance which may be calculated from the above data is not precise, but does not influence the final interpretation of the experimental data.

It is concluded, therefore, that the lithium poisoned plutonium solutions may be returned to the 231 Building for purification without the hazard of subsequently producing impure plutonium metal. It is recommended, although seemingly unnecessary, that the final purified product from 231 be analyzed for lithium before being shipped to 234-5 for metal reduction.

IV. HEAD-END STUDIES (W. H. Reas, Group Leader)

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A. CENTRIFUGATION OF MANGANESE DIOXIDE SLURRIES IN THE PRESENCE AND ABSENCE OF INSOLUBLE "COAGULANTS" (C. G. McCormack)

Some considerable difficulty has been encountered in the Semi-works in the centrifugation of MnO_2 precipitates. It has been difficult to get complete removal of the MnO_2 and, under some conditions, appreciable carry-over of MnO_2 into the solvent extraction columns has resulted. In order to obtain conditions which may result in a more handleable precipitate an investigation has been begun, on the laboratory scale, of the handling of MnO_2 formed in synthetic dissolver solution. This study includes, not only the centrifugation of MnO_2 precipitates as formed, but also the effect of certain additives, including filter aids and "coagulants". The latter term is meant to imply the use of gelatinous or "sticky" precipitates in small quantities which may serve to scavenge the solution of small particulate matter in a manner similar to that employed in water treatment.

A series of settling runs has been made centrifuging MnO_2 -Filtrol and MnO_2 -alumina mixtures, and some preliminary work has been done on the effect of zirconium phosphate on the settling characteristics of MnO_2 under one G. The results of the work with MnO_2 -Filtrol mixture are summarized below in Table VIII.

Using 50 ml samples of 1.7 M UNH and centrifuging in the clinical centrifuge at approximately 1700 G, nine MnO_2 -Filtrol runs were made with mixtures listed below. All mixtures should produce nearly equal cake volumes upon centrifugation. Light transmission of the supernatant, as measured on the Cary spectrophotometer at 600 $m\mu$ is listed in the right hand column.

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Table VII

SOLUTION CLARITIES OF CENTRIFUGED FILTROL- MnO_2 SLURRIES
Centrifuged at 1700 G.

	<u>$\text{KMnO}_4(\text{M})$</u>	<u>Filtrol (g/l)</u>	<u>L.T.(%)</u>
1	0.078	0	85.6
2	0.06825	2.5	95.0
3	0.0585	5	90.6
4	0.04875	7.5	97.3
5	0.039	10	77.5
6	0.02925	12.5	76.7
7	0.0195	15	74.8
8	0.00975	17.5	93.7
9	0	20	99

The supernatant solutions were clear, and showed little, if any, visible difference. Thus, almost no MnO_2 remained in the supernatant. The data indicate, however, that the centrifuging characteristics of the MnO_2 can be enhanced by addition of small amounts of Filtrol. The main disadvantage in the use of Filtrol is that it is insoluble.

Five runs were made using alumina- MnO_2 mixtures. Operating conditions were identical to those described above for Filtrol. Data are listed in Table VIII in the same manner.

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TABLE VIII

SOLUTION CLARITIES OF CENTRIFUGED ALUMINA-MnO₂ SLURRIES

	<u>KMnO₄ (M)</u>	<u>Alumina (g/l)</u>	<u>L.T. (%)</u>
1	0.078	0	85.6
2	0.06825	2.5	100
3	0.04875	7.5	99
4	0.02925	12.5	98
5	0.00975	17.5	97
6	0	20	100

These data would indicate alumina to be superior to Filtrol for clarification. It was observed that the coarser particles of the alumina settled to the bottom of the container almost at once, and, apparently, did not participate in coagulation with MnO₂. Thus, substantially smaller amounts of ultra-fine alumina might be expected to accomplish satisfactory results. Alumina suffers from the same disadvantage as Filtrol in that it is not readily soluble. Small quantities of ultra-fine material might, however, be acceptable, providing they made sufficient improvement in MnO₂ removal.

A series of samples from a single slurry was allowed to settle under one G, with varying quantities of 0.1 M zirconium phosphate added. The influence of the additive seemed negligible, however further work is still to be done. One might be inclined to speculate that the gelatinous nature of zirconium phosphate at even low concentrations might well aid the coherence of the MnO₂ cake. This is to be investigated further.

To investigate centrifuging characteristics of the MnO₂ resulting from the permanganate kill-off with chromic ion, a 5-inch solid bowl centrifuge (no baffle plates) was set up with a gravity feed at constant hydrostatic pressure.

This was designed to allow three throughput volumes of the centrifuge (288 ml each; total 864 ml) to be heated to 95°C., titrated electrometrically with 2 M chromic ion, cooled to 50°C., and fed into the centrifuge at varying flow rates as desired.

Two runs have been made using the five inch solid bowl centrifuge. Both were made using 0.078 M KMnO_4 and no additive, titration to a slight excess with chromic ion at 95°C., and centrifuging. In the first run the slurry was cooled to 45°C. before centrifuging, and the hold-up time was 20 minutes. In the second run the slurry was not cooled below 75°C., and the hold-up time was one hour.

In the first of the two runs the effluent stream was alternately turbid and clear depending upon flow rates. No cake or effluent stream analyses were made.

In the second run the effluent stream was generally clear, but the apparatus was not sufficiently sensitive to maintain the low flow rate. Samples of the effluent stream were taken over a wide range of time during the three hour run and the hold-up times actually vary from one hour to one hour and a half. It was found that the samples contained from 0.00003 to 0.00011 M manganese as MnO_2 . A Cary spectrophotometer was used to obtain these data, and although the accuracy may be suspect, the pertinent point is that the MnO_2 in the effluent stream is less than 0.1% of that in the feed. This is within desirable limits.

The cake from this run was found to contain 0.1 g MnO_2 /cc, which is of the same magnitude as that given by 20 g/l of Filtrol. Nevertheless, it is considered to be unsatisfactory, as this cake density would require batchwise centrifugation of the MnO_2 slurry in the plant.

Digestion time after titration has yet to be checked for an optimum value. It is believed that if the titration is carried out over a ten to twenty minute period, and the slurry stirred in the feed tank, that no digestion time would be required for satisfactory results, thus providing for additional saving of time.

B. RUTHENIUM, ZIRCONIUM, AND NIOBIUM DECONTAMINATION (W. E. Roake)

Several experiments concerned with Redox head-and feed treatment (ruthenium volatilization and fission product adsorption on manganese dioxide) have been carried out at the so-called "Junior Cave scale", i.e., 33 ml Hanford Dissolver solution (429 MWD) per charge. The initial experiment of this series which was reported in the Chemical Research Section Progress Report for December, 1950 (HW-20053), is included in this report for comparison purposes. Items of particular interest in this investigation are the reduction of permanganate during ruthenium volatilization and the ultimate fate of the volatilized ruthenium.

1. RUTHENIUM VOLATILIZATION

The ruthenium volatilization steps of the five runs reported here were all carried out at 95°C. using a sparge gas: solution volume ratio of one-half cc min⁻¹ ml⁻¹. Ozene and permanganate concentrations were varied. The data are recorded in Table IX. The values of k_{A_2} (cf. HW-18415) were estimated graphically from the data obtained by hourly analyses of the oxidizer pot during ozonization. The initial permanganate concentration listed in Table IX indicates the amount added. A reducing substance in the dissolver solution decreased the permanganate concentration in each case by about 0.008 molar immediately upon addition of the permanganate. Further reduction of permanganate to manganese dioxide occurred at 95°C. during ozonization. This is discussed in the next section.

On the basis of the data reported here, no decrease in rate of ruthenium volatilization is observed as the concentration of ozone in the sparge gas is reduced from three weight per cent to zero, permanganate concentration being the same in all cases. The one dependent variable observed was the quantity of volatilized ruthenium reaching the scrubber trap. In the cases where ozone was included in the sparge gas on the order of forty per cent of the original ruthenium was observed in the scrubber trap.

Table IX
REDUX HEAD-END FEED TREATMENT

Hanford dissolver solution, 0.03 M HNO_3 as received made appropriate molarity of MnO_4^- , subjected to ruthenium volatilization at 95°C . and MnO_2 scavenging in stainless steel equipment. Ratio cc. gas min^{-1} : ml solution = $1/2 \text{MnO}_4^-$ which was not reduced to MnO_2 during ruthenium volatilization was then reduced to MnO_2 by $\text{Cr}(\text{NO}_3)_3$.

Run	Initial Molarity KMnO_4	Spurge Gas	% O_3	Estimated k_{A_2}	Ruthenium Volatilization						Log Decontamination Factor		
					1	2	3	4	5	6	Zr	Nb	Ru
1	0.078	O_3 in air	3	ca. 0.013	4.1	1.16	0.63	0.34*	0.31*	0.32*	1.89	2.56	2.49
2	0.078	O_3 in air	3	0.014	9.2	1.4	0.40	--	--	--	2.00	3.00	2.01
3	0.038	O_3 in air	3	0.009	20.5	7.7	3.9	3.7*	3.4*	--	1.53	3.09	1.54
4	0.078	Air	0	0.013	10.0	1.6	0.62	0.36	0.19	0.23	2.05	2.60	2.64-2.74
											0**	0**	2.00**
5	0.068	O_3 in air	2	0.012	6.0	1.1	0.31	0.16	0.13	0.12	2.16	2.60	2.93-3.10

* MnO_4^- completely reduced

** MnO_2 reduced to Mn^{++} by excess Cr^{+++}

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The remainder (ca. 60%) was in each case not clearly accounted for. Suffice it to say it was not found in the oxidizer pot residue or in the scrubber trap. In Run 4 in which air alone was used as a sparge gas only three-tenths of one per cent of the original ruthenium was carried to the scrubber trap, about ninety-nine per cent remaining unaccountable.

A decrease in the original permanganate concentration was accompanied by a decrease in the rate of ruthenium volatilization as indicated in Table IX. Whereas the ultimate decontamination achievable at the end of six hours might have approached that obtained using increased permanganate concentration, the reduction of permanganate during ozonization proceeded at such a rate as to leave no permanganate in solution shortly after three hours, following which very little ruthenium was volatilized.

2. PERMANGANATE REDUCTION

Reliable hourly permanganate analyses were obtained only during Runs 3, 4, and 5. The rates of reduction to MnO_2 during sparging at 95°C. were roughly first order with half lives of 57 minutes, 180 minutes, and 400 minutes for Runs 3, 4, and 5, respectively.

3. ZIRCONIUM AND NIOBIUM ADSORPTION

The final decontamination factors obtained in the various runs are listed in Table IX. The Freundlich adsorption isotherm has been fitted to zirconium and niobium adsorption data from Runs 3, 4, and 5 by the method of least squares. The fitted equations are

for zirconium(see Figure 1):

$$\log\left(\frac{\% \text{ adsorbed}}{g/l \text{ } MnO_2}\right) = 1.3775 + 0.456 \log(\% \text{ not adsorbed})$$

root mean square deviation ± 0.197

for niobium(see Figure 2):

$$\log\left(\frac{\% \text{ adsorbed}}{g/l \text{ } MnO_2}\right) = 1.5724 + 0.2883 \log(\% \text{ not adsorbed})$$

root mean square deviation ± 0.188

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Figure 1

ADSORPTION OF ZIRCONIUM FROM 429 MWD
HANFORD DISSOLVER SOLUTION ON
CO-FORMED MANGANESE DIOXIDE

MnO_2 formed on reduction of MnO_4^- at initial acidity
of 0.03 M HNO_3 , at 95°C.

$$-\log\left(\frac{\% \text{ adsorbed}}{\text{g/l MnO}_2}\right) = 1.3775 + 0.456 \log(\% \text{ not adsorbed})$$

..... root mean square deviation of

$$\log\left(\frac{\% \text{ adsorbed}}{\text{g/l MnO}_2}\right) = \pm 0.197$$

Per Cent Zr Not Adsorbed

Figure 2

ADSORPTION OF NIOBIUM FROM 429 MWD
HANFORD DISSOLVER SOLUTION ON
CO-FORMED MANGANESE DIOXIDE

MnO_2 formed by reduction of MnO_4^- at initial acidity
of 0.03 M HNO_3 , at 95°C.

$$\log\left(\frac{\% \text{ adsorbed}}{\text{g/l MnO}_2}\right) = 1.5724 + 0.2883 \log(\% \text{ not adsorbed})$$

----- root mean square deviation of

$$\log\left(\frac{\% \text{ adsorbed}}{\text{g/l MnO}_2}\right) = \pm 0.188$$

Per Cent Nb Not Adsorbed

1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

100
90
80
70
60
50
40
30
20

10
9
8
7
6
5
4
3
2
1

0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

g/l MnO_2

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These data were obtained by sampling the slurry at various stages of MnO_2 reduction at 95°C ., supernatant sampled after centrifugation at room temperature.

4. SOLVENT EXTRACTION STUDIES (H. G. Hicks)

Following head-end treatment, Run 4 (Table IX), excess chromic nitrate was added to the manganese dioxide slurry at 95°C . sufficient to reduce all manganese present to Mn^{++} . By doing so the log decontamination factors attained for zirconium, niobium, and ruthenium were reduced respectively from 2.05, 2.60, and 2.7 to 0, 0, and 2.0. The resulting solution was subjected to a batch extraction and two scrubbing conditions at the feed plate of the IA Redox column in the manner which has been described in previous reports (HW-20053). The resulting data are compared in Table X with similar data (previously reported HW-20053) obtained using in one case untreated dissolver solution and in the other case dissolver solution which had received complete head-end treatment (Run 1; see Table IX). It should be pointed out here that the decontamination factors reported in Table X for the extraction-scrub measurements involving ozonized and scavenged dissolver solutions represent a minimum decontamination due to insufficient activity remaining in the final solution for accurate zirconium and niobium analyses. In the single experiment in which MnO_2 had been reduced the distribution of ruthenium in the scrub stages appears low. Certainly the total "column" decontamination is no greater in this case than for unozonized solution. Two factors were present in Run 4 (cf. Table IX) which may individually or collectively account for this adverse behavior. These are (1) no ozone was present in the air sparge during ruthenium volatilization, and (2) 1.05 per cent of the original ruthenium which had been presumably adsorbed on the MnO_2 was returned to solution upon reduction of the MnO_2 by Cr^{+++} . This ruthenium might be a species with undesirable solvent extraction characteristics.

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Table X

DECONTAMINATION FACTORS OF ZIRCONIUM, NIOBIUM, AND RUTHENIUM
OBTAINED BY SOLVENT EXTRACTION

Preparation of IAFS: Dissolver solution (both before and after head-end treatment) made 0.1 M $\text{Na}_2\text{Cr}_2\text{O}_7$, heated 1 hour at 95°C. (if not treated), made 0.2 M acid deficient and diluted with an equal volume (6 ml) of scrub solution.

Extractant: Hexone equilibrated with aqueous solution of composition: 1.0 M ANN, 0.2 M NaOH, 0.2 M UNH.

Scrub: 2.0 M ANN, 0.2 M NaOH, 0.04 M UNH.

Phase ratios: IAFS:IAX = 1:2; IAS:IAX = 1:4.

Fission Product	Decontamination Factor						Feed
	Extraction	Scrub 1	Scrub 2	Total "Column"	Head-end	Over-all	
Zr	3.4×10^4	6.6	1.2	2.7×10^5	--	2.7×10^5	Untreated dissolver solution
	4.3×10^2	14	3.2	$2.0 \times 10^{4*}$	77	1.5×10^6	Head-end treated solution
	5.4×10^3	10	2.1	1.1×10^5	1	1.1×10^5	Head-end treated MnO_2 reduced
Nb	1.7×10^5	3.4	1.4	8.0×10^5	--	8.0×10^5	Untreated dissolver solution
	4.5×10^2	9.7	2.0	$8.7 \times 10^{3*}$	360	2.9×10^6	Head-end treated dissolver sol'n
	6.9×10^4	6.8	2.0	8.6×10^5	1	8.6×10^5	Head-end treated MnO_2 reduced
Ru	110	7.3	2.8	2.3×10^3	--	2.3×10^3	Untreated dissolver solution
	67	11	11	8.3×10^3	311	2.6×10^6	Head-end treated diss. sol'n.
	294	4.5	1.7	2.3×10^3	78	1.8×10^5	Head-end treated MnO_2 reduced

* Because of low activity, these values represent the minimum decontamination only.

V. REDOX IIA COLUMN STUDIES (W. H. Adams)A. RECYCLE OF PLUTONIUM PEROXIDE SUPERNATANT SOLUTIONS

Several experiments have been performed to determine the feasibility of recycling plutonium peroxide supernatant solution to the IIA column in the Redox plant for product recovery. Since the plutonium peroxide precipitations can be carried out at ca. 5 M HNO_3 or at ca. 2 M HNO_3 after reducing the acidity with sodium hydroxide, two separate synthetic peroxide supernatant solutions were used in the recycle experiments. One solution was 2.8 - 3.3 M HNO_3 , 0.12 M $(\text{NH}_4)_2\text{SO}_4$, 0.01 M $\text{Al}(\text{NO}_3)_3$, and 10 to 15% H_2O_2 ; the other contained 1 M HNO_3 , 0.1 M $(\text{NH}_4)_2\text{SO}_4$, 1.0 M NaNO_3 , 0.004 M $\text{Fe}(\text{NO}_3)_3$, and 10 to 15% H_2O_2 . Each supernatant was subjected to a heat-kill of the hydrogen peroxide and then diluted 1:10 with synthetic IIAFS and contacted for five minutes with hexone containing 0.5 M HNO_3 . Values of the plutonium distribution coefficients were ca. 7.5 in the presence of recycle material. Although plutonium distribution coefficients in the absence of recycle material are somewhat higher (ca. 10), these data indicate that recycle of heat-killed peroxide supernatants to the IIA column is feasible.

B. EFFECT OF SULFATE ON IIA COLUMN OPERATION

Experiments are being carried out to evaluate the effect of replacing ferrous sulfamate by ferrous ammonium sulfate and sulfamic acid in the IIA column of the Redox plant. Synthetic IBP solutions were used in this study and contained 0.19 g Pu^{+3}/l , 1.25 M $\text{Al}(\text{NO}_3)_3$, 0.10 M HNO_3 , and either (1) 0.05 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ or (2) 0.05 M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and 0.1 M $\text{NH}_2\text{SO}_3\text{H}$. The IBP solution was then diluted with an equal volume of IIAS solution which was ca. 1.25 M in ANN and 0.04 M in $\text{Na}_2\text{Cr}_2\text{O}_7$ to form a IIAFS solution. This procedure was used to insure that all plutonium would be in the (IV) state at the time of extraction with hexone. Five ml of the IIAFS solution was contacted with an equal volume of hexone containing 0.5 M HNO_3 for 5 minutes. Anomalous results were obtained using this procedure, and,

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therefore, the plutonium extraction into the hexone phase was measured as a function of time. The results obtained are presented in Table XI.

Table XI

EXTRACTION OF PLUTONIUM INTO HEXONE AS A FUNCTION OF TIME
UNDER IIA CONDITIONS

IIAFS Containing Ferrous Sulfamate		IIAFS Containing Ferrous Ammonium Sulfate and Sulfamic Acid	
Time (min.)	E_a^*	Time (min.)	E_a^*
2	2.99	2	2.76
4	4.55	4	3.66
6	5.09	6	4.22
8	5.66	8	4.84
10	5.39	10	5.37
20	6.62	20	6.67
40	8.15	40	8.84
60	8.70	65	8.78
120	9.30	120	7.87

It can be seen from the data in Table XI that the value of the plutonium distribution coefficients are still changing markedly after twenty minutes of contacting. Previous data taken at the end of five minutes could not be relied upon since a small variation in contacting time would produce a large change in the extraction coefficient. It can also be seen from the table that the plutonium extraction coefficients are nearly identical after one hour's contacting, thus indicating no appreciable sulfate effect. However, the values of these plutonium distribution coefficients indicate that virtually all the plutonium is in the +6 oxidation state. Previous studies⁽²⁾ have shown that the oxidation of Pu(IV) to Pu(VI) is at least an order of magnitude slower than that found in this investigation. Laboratory work is being continued to determine the cause(s) of this rather rapid Pu(IV) - Pu(VI) oxidation.

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(2) R. L. Moore, HW-16053, Continuous Crossover Oxidation Study, February 18, 1950.

VI. REDOX STUDIES (C. M. Slansky, Group Leader)A. SOLUBILITY OF ALUMINUM NITRATE IN HEXONE (I. M. Rehn)

The solubility in hexone of aluminum nitrate from either 1.3 or 2.5 M aqueous aluminum nitrate solution containing 0.2 M HNO_3 was measured by direct evaporation and ignition. In either case the residue was less than 0.001 g Al_2O_3 /100 ml hexone, the limit of analytical sensitivity. Assuming aluminum nitrate solubility to be unaffected by plutonium, the aluminum impurity in the Redox IIBP stream, neglecting entrainment, should not exceed 0.003 g Al/g Pu from 400 g/T material.

B. PLUTONIUM(VI) DISTRIBUTION IN REDOX (I. M. Rehn)

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In the course of measuring the temperature dependence of extraction of Pu(VI) and Pu(IV) in the Redox system, the Pu(VI) concentration dependence in the acid deficient region and a possible photochemical reduction effect suggested by KAPL studies were investigated.

Experimental techniques were the same as described by Matheson and Rehn in HW-13760. Pre-treated hexone was used and $\text{Na}_2\text{Cr}_2\text{O}_7$ and Pu(VI) nitrate added to the pre-equilibrated aqueous phase. All contactings were thermostated at 25.0°C. All lights were turned out for experiments labeled "zero light exposure"; sampling was assisted by the aid of a flashlight. Analyses were made specifically for Pu(IV) and Pu(VI) by the Berkeley method in order to distinguish between the reduction of Pu(VI) and a change in the extraction properties of Pu(VI) itself.

The results are presented in Table XII. The E_a° values for Pu(VI) in the neutral to 0.6 M HNO_3 aqueous solutions are in close agreement to those reported in HW-13760. Any Pu(VI) concentration effect or photochemical reduction was very slow.

The 0.2 M acid deficient data showed some disagreement with our previous data and hence E_a° Pu(VI) was measured in 0 to 1.0 M UNE and 1.0 and 1.3 M $\text{Al}(\text{NO}_3)_3$ solutions. The results for acid deficient solutions are summarized in Figure 3.

Table XII

SUMMARY OF PU(VI) DATA

0.14 g/l Pu in aqueous before Pu contacting, except as noted

0.10 M $\text{Na}_2\text{Cr}_2\text{O}_7$ in all solutions

Expt.	Light Exposure 30-40 ft. Candles Hours	Aqueous Composition after Equilibration					Total Pu(IV) Aq and Org ₄ g/m/ml($\times 10^{-4}$)	E _a , Pu(VI)
		UNH M	HNO_3 M	$\text{Al}(\text{NO}_3)_3$ M	$\text{Z}(\text{NO}_3)_2$ M	pH		
W14-1	0	0	-0.155	0.982	2.944	2.3		0.633
2	0.25	"	"	"	"	"		0.604
3	1.75	"	"	"	"	"		0.539
W14dil-1*	0	0	"	"	"	"		0.587
2	0.25	"	"	"	"	"		0.34
W12B-1	0	0	-0.17	1.27	3.80	1.95	14.5	1.96
2	0.25	"	"	"	"	"		1.88
4	1.5	"	"	"	"	"	39.2	1.81
W7-1	0	0	0	1.35	3.84	0.82	4.90	4.82
2	0.25	"	"	"	"	"	6.53	4.80
3	1.0	"	"	"	"	"	7.50	4.75
W8-1	0	0	+0.23	1.30	4.06	0.14		12.56
W15-1	0	0.0033	-0.173	0.987	2.97	2.30		0.437
2	0.25	"	"	"	"	"		0.408
W15dil-1*	0	"	"	"	"	"		0.406
2	0.25	"	"	"	"	"		0.221
3	0.50	"	"	"	"	"		0.149

* 0.006 g/l Pu

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Table XII (Cont'd.)

Expt.	Light Exposure 30-40 ft. Candles Hours	Aqueous Composition after Equilibration					Total Pu(IV) Aq and Org ₄ d/m/ml(x10 ⁻⁴)	E _a , Pu(VI)
		UNH <u>M</u>	HNO ₃ <u>M</u>	Al(NO ₃) ₃ <u>M</u>	Σ(NO ₃) <u>M</u>	pH		
W13-1	0	0.0022	-0.165	1.294	3.89	1.96	20.5	1.47
2	0.25	"	"	"	"	"	22.0	1.40
3	2.50	"	"	"	"	"	32.6	1.44
W16-1	0	0.117	-0.165	1.01	1.90	2.38		0.458
W16a11-1*	0	"	"	"	"	"		0.428
2	0.25	"	"	"	"	"		0.389
W1B-1	0	0.115	-0.16	1.30	4.13	1.85	14.2	1.51
2	0.25	"	"	"	"	"	14.5	1.48
3	1.25	"	"	"	"	"	15.9	1.33
W5-1	0	0.0914	+0.35	1.32	4.27	-1.48		4.06
2	18	"	"	"	"	"		3.50
W2-1	0	1.02	-0.17	1.32	5.82	0.85		1.32
3	1.25	"	"	"	"	"		1.12
W3-3	0	1.06	0	1.30	5.94	-1.58		1.22
5	2	"	"	"	"	"		1.04
6	19	"	"	"	"	"		0.86

* 0.006 g/l Pu

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DISTRIBUTION OF Pu_6 IN THE REDOX SYSTEM IN THE ABSENCE OF LIGHT

0.3 M HNO_3
0.0 M HNO_3
0.2 M $NaOH$

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The apparent decrease in Pu(VI) distribution caused by exposure to laboratory light was slow for macro plutonium concentrations of 0.2 g Pu/l in 0.2 acid deficient solutions but was appreciable for concentrations of 0.006 g Pu/l and 0 and 0.0025 M UNH. In the latter case 15 minutes' exposure to laboratory light dropped the apparent E_a° of Pu(VI) (i.e., based on Pu(VI) analyses) to ca. 50% of its value in the dark. The cause of this drop in E_a° has not been determined. The E_a° of Pu(VI) in 0.2 M acid deficient solutions when measured in the dark was independent of concentration over the range trace to 0.2 g/l.

Besides the change in Pu(VI) distribution upon exposure to light, a reduction to Pu(IV) was followed as shown in Figure 4. The build-up of Pu(IV) is approximately linear for the first few hours and varies inversely with UNH concentration.

The new values for the E_a° of Pu(VI) are applicable largely to the ORNL #1 flowsheet for Redox. Interpolation of these data indicate that the flowsheet can attain a 99.8% recovery of Pu in the IA column with a maximum H.T.U. of two feet. Abnormal H.T.U. values could be taken care of by a slight change in $Al(NO_3)_3$ concentration.

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VII SOLVENT RESEARCH (C. M. Slansky, Group Leader)

A. SYNTHESIS OF 2,2-DIETHYLTRIMETHYLENE OXIDE (R. M. Wagner)

Research has been initiated (HW-20053) on the extraction behavior of various organic solvents with basic oxygen included in their structure. The properties of particular interest are stability to nitric acid oxidation, uranium extractability, viscosity, water solubility, flash point, volatility and boiling point.

Several classes of compounds under consideration include furans, tetrahydrofurans, pyrans, tetrahydropyrans, substituted trimethylene oxides, and spirotrimethylene oxides.

Figure 4

Pu^4 FORMED ON EXPOSURE TO LIGHT

- 0 M UNH, 0.2 M NaOH, 1.3 M $Al(NO_3)_3$
- △ 0.0022 M UNH, " "
- 0.115 M UNH, " "

Hours, Exposure to light (30-40 foot candles fluorescent "Daylight")

The trimethylene oxides were chosen for study because of the fact that they are reported to be more stable to ring cleavage than three-membered rings and should be equal to or superior to five-membered conjugated ring oxygen compounds in stability. The first member of this series to be studied is 2,2-diethyltrimethylene oxide. Its synthesis and properties are given by the following preliminary data.

2,2-diethyltrimethylene oxide

The method of synthesis involved the cyclization of 1,1-diethyl-3-bromo-propanol with KOH⁽³⁾ according to the reactions represented by the following equations:

Properties:

Molecular weight	114
Density 25/4	0.845
Boiling point	128-130°C/750 mm
Refractive index (25°C.)	1.4150
Color	None
Odor	Mint
Water solubility	Same order as hexone

Extraction behavior, chemical stability and other properties are being investigated.

Two similar compounds are in the process of being synthesized in order to study the effect of other substituents on the trimethylene oxide ring. These two compounds are

2,2-dibutyltrimethylene oxide

2,2-diethyl-4,4-dimethyltrimethylene oxide.

(3) R. Dallmeyer, Bull. Soc. Chim. de France, 29, p. 156-158 (1906)

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B. EXTRACTION BEHAVIOR OF DIETHYLISOBUTYL PHOSPHATE AND Di-n-BUTYLETHYL PHOSPHATE (B. R. Jones and L. L. Burger)

Modification of the physical properties of tributyl phosphate by substitution of other alkyl groups for one or more of the butyl groups can be qualitatively predicted. The resulting effect on other properties such as solvent power is of equal or greater importance and in general cannot be accurately predicted. Data recently obtained by Baldwin, Higgins and Ruth⁽⁴⁾ indicated little difference in uranium extraction between various tri-alkyl phosphates. To obtain further information tri-substituted phosphates containing mixed alkyl groups have been considered.

Di-n-butylethyl phosphate (DBEP) was synthesized by reacting dibutylchloro phosphate with an excess of anhydrous ethyl alcohol in the presence of pyridine at 15°C.⁽⁵⁾ Diethylisobutyl phosphate (DEBP) was prepared in the same manner using diethylchloro phosphate and anhydrous butyl alcohol as the starting materials.

Table XIII lists some of the physical properties of the two compounds, compared with tributyl phosphate.

Table XIII

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	<u>DEBP</u>	<u>DBEP</u>	<u>TBP</u>
Specific Gravity, 25°C.	1.0209 g/ml	0.9984 g/ml	0.9730 g/ml
η (millipoises), 24.9°C.	18.9	25.5	33.2
n _D ²⁵	1.40744	1.41681	1.4226
bp _{2-4 mm}	82-87°C.	95-101°C.	127°C.
Solubility in H ₂ O, 24°C., g/l	14	3.4	0.4

(4) W. H. Baldwin, C. E. Higgins, and J. M. Ruth, ORNL-870, Quarterly Progress Report for Period Ending September 30, 1950, p. 76.

(5) C. R. Dutton and C. R. Noller, Inorganic Syntheses, Collective Volume III, Ed. A. H. Blatt, p. 109, Wiley, New York, 1953.

A solution of 0.495 M diethylisobutyl phosphate in Super Sol was contacted with an aqueous feed 0.20 M in uranyl nitrate and 2.98 M in nitric acid at 24.9°C. When the phases were allowed to separate, it was observed that a second organic layer containing nearly all of the uranyl nitrate present had been formed. Increasing the nitric acid in the aqueous feed to 5.00 moles/l gave the same results after contacting. In the absence of free nitric acid and other salting agents no second organic phase was produced. Previous experiments using 0.5 M tributyoxyethyl phosphate as extractant and Super Sol as diluent showed the same results after contacting with 0.20 M uranyl nitrate and 5.00 M nitric acid, but not when the nitric acid was 2.98 M. Substituting carbon tetrachloride for Super Sol as diluent eliminated the formation of a second organic layer.

Table XIV compares the data for the extraction of uranyl nitrate by dibutylethyl phosphate.

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Table XIV

EXTRACTION OF URANYL NITRATE BY 0.5 M DIBUTYLETHYL PHOSPHATE IN
CARBON TETRACHLORIDE AT 24.9°C.

<u>UNH, g/l</u>		<u>E_a</u>	<u>HNO₃, g/l</u>		<u>E_a</u>	<u>Specific Gravity</u>		<u>Refractive Index</u>		<u>K</u>
<u>Organic</u>	<u>Aqueous</u>		<u>Organic</u>	<u>Aqueous</u>		<u>Organic</u>	<u>Aqueous</u>	<u>Organic</u>	<u>Aqueous</u>	
13.4	87.4	0.15				1.5273	1.0546	1.45350	1.33880	6
72.5	29.0	2.50	5.54	188.0	0.03	1.5582	1.1117	1.45554	1.35659	5.7
80.1	24.7	3.24	7.70	317.0	0.03	1.5605	1.1731	1.45564	1.37008	3.8
0.3	19.2	0.015				1.5210	1.0098	1.45314	1.33400	10
18.9	2.12	8.92	12.07	180.0	0.07	1.5285	1.0914	1.45300	1.35399	5.0
18.5	1.54	18.50	19.93	297.0	0.07	1.5274	1.1527	1.45528	1.36748	4.0

Table XV summarizes the data for the extraction of uranyl nitrate by diethylisobutyl phosphate.

Table XV

EXTRACTION OF URANYL NITRATE BY DIETHYLISOBUTYL PHOSPHATE (0.495 M)
IN CARBON TETRACHLORIDE AT 24.9°C.

UNH, g/l		E_a°	HNO ₃ , g/l		E_a°	Specific Gravity		Refractive Index	
Organic	Aqueous		Organic	Aqueous		Organic	Aqueous	Organic	K
16.0	85.0	0.19				1.5339	1.0521	1.45291	8.5
76.3	27.4	2.78	7.17	187.0	0.04	1.5638	1.1105	1.45472	7.2
84.8	25.1	3.38	13.0	314.0	0.04	1.5647	1.1717	1.45390	5.1
0.13	20.2	0.0064				1.5232	1.0099	1.45217	4.0
17.6	2.36	7.5	15.5	182.0	0.08	1.5323		1.45206	4.8
21.6	1.25	17.3	22.6	306.0	0.07	1.5318	1.1551	1.45163	3.0

K is defined by the following equilibrium expression

$$K = \frac{E_a^\circ}{(\text{Free Solvent})^2 (\text{NO}_3^-)^2}$$

The K for 20 volume per cent TBP in CCl₄ at 25°C. has been given⁽⁶⁾ as 7.7 which is very similar to the values obtained here for the mixed esters. The distribution coefficient, E_a° , of uranium should be nearly the same for the three solvents under the same UO₂⁺⁺ and total NO₃⁻ concentration in the aqueous phase and the same fraction of saturation of the solvent in a constant molarity dilution by CCl₄. Solvent capacity for uranium then becomes primarily dependent on the molecular weight since the densities are practically the same. A comparison of the three phosphates at uranium saturation is given in Table XVI at several dilutions by carbon tetrachloride.

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Table XVI

VOLUMETRIC EFFICIENCIES FOR SOLVENT EXTRACTION OF URANYL NITRATE

		M UNH for various vol. % in CCl ₄				
	M.W.	d 25/4	100	20	30	15
TBP	266	0.9730	1.83	0.92	0.55	0.27
DBEP	238	0.9984	2.10	1.05	0.63	0.32
DEBP	200	1.0209	2.55	1.28	0.77	0.38

(6) R. L. Moore, HW-15230, Extraction of Uranium in the TBP Metal Recovery Process, September 1, 1949.

Further criteria for a good solvent with respect to column behavior is a low viscosity and a low coefficient of viscosity with increasing uranium concentration. The data in Table XVII show that both of the new solvents have an appreciably lower viscosity than TBP, and the increase in viscosity with uranium concentration is nearly the same as for the TBP system.

Table XVII

VISCOSITIES OF ORGANIC PHOSPHATE SOLVENTS
IN CARBON TETRACHLORIDE AT 25°C.

Conc. Ester	Viscosity (Millipoises)		
	TBP	DBEP	DEBP
0.5 M	10.8	10.1	9.6
1.0 M	13.3	11.5	10.4
2.0 M	19.7	14.8	12.2
2.0 M with 0.5 M $\text{UO}_2(\text{NO}_3)_2^*$	36	25	18

* Reflux IAP is 0.476 M $\text{UO}_2(\text{NO}_3)_2$; Purex #2 IAP is 0.38 M $\text{UO}_2(\text{NO}_3)_2$

In conclusion it appears that differences in uranium extractability for a fixed volume per cent of the various phosphate esters are quite small. However, on the basis of volumetric efficiency and improved physical properties there would be some advantage to the lower molecular weight esters, particularly if higher concentrations of the ester in a diluent were being considered.

VIII. TRIBUTYL PHOSPHATE METAL RECOVERY PROCESS (C. M. Slansky, Group Leader)

A. THE SOLUBILITY OF TRIBUTYL PHOSPHATE IN AQUEOUS SOLUTIONS (L. L. Burger, R. C. Forsman)

The solvent tributyl phosphate (TBP) has a lower solubility in water than most uranium solvents that have been employed. However because it is potentially hydrolyzable to non-volatile species, the amount that is carried with the various aqueous streams in an extraction process has greater importance. The solubility relations are also of theoretical interest in that they represent a

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balance between the highly polar oxygen which favors miscibility with water and the alkyl groups which are hydrophobic in nature.

The solubility of TBP in water is reported in the industrial literature as about 0.6% or 6 grams per liter. This is considerably higher than values obtained by the Chemical Research Section which were of the order of 0.1 to 0.6 grams per liter (HW-16076). The availability of TBP containing P^{32} , a convenient α -emitter, made possible more accurate analytical determinations than were previously possible and the solubilities of TBP in various aqueous solutions were re-examined. The sample of TBP containing the tracer phosphorus was obtained from W. H. Baldwin of the Oak Ridge National Laboratories. At the time the material was used the activity was about 0.1 mc/ml. Before using the TBP it was washed with a sodium carbonate solution and then washed several times with water.

Solubilities were determined in water and in solutions of nitric acid of various concentrations. Measurements were also made in solutions typical of various processes, e.g., a solution 0.2 M in uranyl nitrate and 0.06 M in nitric acid corresponding roughly to a uranium "strip" solution such as the Metal Recovery RCU stream and in a simulated "waste" solution containing phosphates and sulfates and small concentrations of other ions.⁽⁷⁾ A few measurements were also made using more concentrated uranyl nitrate solutions.

The organic phase consisted of the pure TBP or of TBP diluted with AMSCO-125-90W, a paraffinic hydrocarbon diluent of average molecular weight of about 160. Dilutions to 16% and 33% were employed and in the case of the determinations in pure water dilutions of 8%, 50% and 75% were also employed.

Solubility determinations were carried out by adding 200 μ l of the organic solution to about 2 1/2 ml of the aqueous phase. This was stirred or shaken for 2-3 hours at 25°C., centrifuged and the excess of organic phase removed.

(7) R. E. Smith, HW-18169, TBP Waste Metal Recovery Process Flowsheet No. 4.

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from the surface. A measured sample of the aqueous phase, the size depending on the solubility and the specific activity of the TBP, was then removed and placed in a 3 ml centrifuge cone. The dissolved TBP was extracted with four 200 % fractions of n-hexane and the hexane transferred directly to a 25 mm watch glass where it was evaporated for 10-30 minutes at room temperature. The watch glass was mounted on an aluminum tray, covered with a layer of cellophane and counted. Standardization of the method was provided by making up known concentrations of the TBP in n-hexane and evaporating aliquots on the watch glasses. Frequent standardization was required because of the relatively short (14.3 days) half life of the P^{32} . Tests showed no loss by volatilization during the evaporation for times up to several hours at room temperature. However, attempts to carry out the evaporation under a heat lamp produced appreciable losses.

Table XVIII lists the solubility data for TBP in pure water. The mol fractions are based on an assumed molecular weight of 160 for the hydrocarbon diluent. It will be seen that the solubility increases rapidly as the concentration of TBP in the diluent increases and at a mol fraction of 0.2, the solubility is 70% of that of pure TBP. The data are shown graphically in Figure 5.

Table XVIII

THE SOLUBILITY OF TBP IN H_2O AT $25^\circ C$.

<u>Vol.% TBP in Diluent</u>	<u>Mol Fraction TBP in Diluent</u>	<u>Solubility g/l</u>	<u>Relative Solubility</u>	<u>Activity Coef. TBP in Diluent*</u>
100	1.00	0.39	1.00	1.00
75	0.700	0.33	0.865	1.24
50	0.436	0.29	0.737	1.7
33.3	0.280	0.28	0.721	2.6
16.6	0.134	0.24	0.622	4.6
8.3	0.066	0.17	0.436	6.6

* Standard state as pure TBP

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0.0 0.1 0.2 0.3 0.4

Solubility, gm/l

SOLUBILITY OF TBP IN H₂O AT 25°C.

Figure 5

% TBP in ANSGO 125-90W

Solubilities of TBP corresponding to typical extraction process conditions are listed in Table XIX. Solubility falls off rapidly as the concentration of electrolyte rises. The amount of TBP dissolved in the RAW solution is only 1/20 of that dissolved in pure water. This is lower than one would predict from the simple decrease in water activity.

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Table XIX

SOLUBILITY OF TBP IN PROCESS SOLUTIONS AT 25°C.
16.6% and 33.3% TBP in AMSCO 125-90W

Organic Phase	H ₂ O	Solubility of TBP in Aqueous Phase, g/l			
		0.2 M UO ₂ (NO ₃) ₂ 0.06 M HNO ₃	3 M HNO ₃	2 M UO ₂ (NO ₃) ₂	RAW*
Vol % TBP					
33.3	0.28	0.19	0.21		0.0097
16.6	0.24	0.17	0.17	0.01	0.0097

* RAW consisted of 2.6 M HNO₃, 1.0 M NaNO₃, 0.2 M Na₂SO₄, 0.2 M Na₃PO₄, 0.03 M NH₄NO₃, 0.02 M FeCl₃, 0.03 M NH₂SO₂OH

Several experiments were carried out in which the TBP-saturated aqueous solutions were concentrated by evaporation. It was found that for solutions containing electrolytes, e.g., uranyl nitrate, the TBP content drops in accordance with the decreased water activity and no build-up of TBP or its decomposition products occurs. When excess TBP was added prior to the evaporation, the excess distilled out rapidly. That this would be expected is evident from the following considerations: The ratio of the vapor pressures of TBP to water is about 1.2×10^{-3} . Multiplying by the molecular weight ratio 266/18 gives 3.5×10^{-2} or the weight ratio of TBP to H₂O expected on steam distillation. Thus a ten-fold concentration of an aqueous solution by evaporation at 130°C. would remove an excess of TBP equivalent to greater than 3% of the original aqueous volume.

Examination of the residue from these evaporations was carried out, after hexane extraction, by adding carrier PO₄³⁻ and precipitating ammonium

phosphomolybdate using a modified molybdate citrate reagent. Negligible activity was found indicating no appreciable hydrolysis of the TBP. When uranium was present, interference of its daughter products during counting was prevented by carrying out a preliminary lanthanum fluoride precipitation. Boric acid was then added to complex the fluoride ion and the ammonium phosphomolybdate precipitation carried out as above. Residues were also examined for organic phosphates by this procedure after refluxing a 1 ml sample with 15 ml of fuming nitric acid to decompose the organic compounds. The maximum amount found corresponded to a total phosphate of less than 0.004 g/l of PO_4^{3-} .

The decreased solubility of TBP in salt solutions (i.e., 0.01 g/l in RAW) together with the apparently easy stripping of TBP by distillation is significant in the concentration of the RCU and RAW solutions.

The solubility of pure TBP in nitric acid solutions was found to decrease to about 0.1 g/l as the acid concentration increased up to 9-10 M HNO_3 . At this concentration, the solubility begins to increase rapidly and at 15 M HNO_3 it is about 1.3 g/l. In the higher acid concentrations the strong attraction of the acid molecules more than balances the decreased water activity. It is probable that TBP is very soluble in pure HNO_3 .

The analytical method for small amounts of TBP that has previously been employed consists of decomposition of the ester with boiling fuming nitric acid for 3 hours followed by the molybdenum blue colorimetric procedure for phosphate. A check on this method using the tracer TBP with a known amount of carrier PO_4^{3-} present was carried out by analyzing the resulting solution by ammonium phosphomolybdate precipitation followed by counting and titration of the precipitate by dissolving in NaOH and titrating with standard HCl. A recovery of 93-100% of the carrier PO_4^{3-} was found but only 60-80% of the TBP. Due to the low recovery by the nitric acid decomposition method and the general scatter of the results, an alternate decomposition scheme that had been investigated by C. W. Pollock⁽⁸⁾

(8) C. W. Pollock, unpublished work.

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was tested. This method involved heating the TBP sample contained in CCl_4 with a small amount of concentrated sulfuric acid at $175-200^\circ\text{C}$. for 3 minutes followed by digestion for a few minutes with HNO_3 and ammonium persulfate to decompose the residual organic matter. The ammonium phosphomolybdate precipitation was then carried out. The precipitate was counted and the recovery was checked by titration as before. TBP recoveries were found to be 98-100% in agreement with the work of Pollock.

Combination of the sulfuric acid decomposition procedure with the molybdate blue colorimetric method should result in improvement over the existing chemical method for small amounts of TBP, e.g., in aqueous solutions, and with the cooperation of the analytical group under E. W. Christopherson the details of such a method are being delineated.

The analytical work together with a more detailed description of the solubility data will be discussed more thoroughly in a terminal report on the solubility of TBP in aqueous solutions which will be published soon.

B. STABILITY OF TRIBUTYL PHOSPHATE AT 105°C . (R. M. Wagner)

Previous studies in this laboratory have indicated that the hydrolysis of tributyl phosphate proceeded with an over-all rate constant of 0.0004 fraction per day, following either zero or first order kinetics, in the presence of 3 M nitric acid at 76°C . with the aqueous/organic volume ratio equal to unity.

Additional data have been obtained concerning (1) the effect on the rate of hydrolysis of variance of acid concentration and organic/aqueous volume ratios, (2) determination of the rate constant for the hydrolysis in each phase at 105°C . and (3) the stability of diluent (AMSCO 125-90W) at 105°C . in the presence of 3 M and 6 M nitric acid.

1. AMSCO 125-90W Stability at 105°C . in Nitric Acid

A two phase system of 15% TBP-85% AMSCO 125-90W and aqueous 3 M HNO_3 (100 ml:100 ml) was refluxed at 105°C . for a period of six days. Decomposition

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of the nitric acid started as soon as the boiling point was reached and proceeded rapidly until the nitric acid concentrations had changed after six days in the organic phase from 2.0 M to 0.07 M and in the aqueous phase from 1.5 M to 0.5 M.

A nitrogen balance on the two phase system is summarized in Table XX.

Table XX

NITROGEN BALANCE ON 3 M NITRIC ACID - R-LX SYSTEM

% Original Nitrogen Combined with Organic	28.6
% Original Nitrogen Remaining as Nitric Acid	21.9
% Original Nitrogen Lost to Atmosphere (by difference)	49.5

It is shown by Table XX that the AMSCO 125-90W suffered heavy deterioration at 105°C. and as a result no data for TBP hydrolysis were derived from this experiment. The high per cent of nitrogen lost to the atmosphere is attributed to removal as oxides of nitrogen. Previous stability tests on diluents had indicated⁽⁹⁾ that diluents which were high in both aromatic and olefin content would be expected to undergo oxidation by nitric acid at temperatures from 70 to 105°C. However, the high per cent of nitrogen which combined with the AMSCO 125-90W, which is a relatively pure paraffinic hydrocarbon (HW-19065), was unexpected.

2. TBP Kinetics

To determine simultaneously the effect on the hydrolysis rate of variance of acid concentration and phase volume ratio, and also the hydrolysis rate itself at elevated temperatures, pure tributyl phosphate and aqueous 3 M and 6 M nitric acid were refluxed at 105°C. for extended periods of time with phase volume ratios (organic/aqueous) of 1:1 and 1:200. The TBP hydrolyzed was calculated from measurement of orthophosphate determined by the phosphomolybdate method. Data for these studies are tabulated below in Table XXI.

(9) R. M. Wagner, HW-19959, The Hydrolysis Products of Tributyl Phosphate and Their Effect on the Tributyl Phosphate Process for Uranium Recovery.

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Table XXI

HYDROLYSIS OF TBP AT 105°C.

Run	Initial Phase Volume, ml		Time, days	M HNO ₃		TBP Fraction Remaining
	Aqueous	Organic		Aqueous	Organic	
I	100	100	0	1.5	1.5	1.000
			6	1.0	1.5	0.993
			8	0.9	1.5	0.987
			13	0.8	-	0.978
II	100	100	0	2.5	3.5	1.0000
			1	2.5	3.5	0.9996
			2	2.5	3.0	0.9967
			6	1.5	3.0	0.9775
III	200	1	0	3.0	-	1.000
			6	3.0	-	0.400
			13	3.0	-	0.050

TBP hydrolyzes stepwise: $\text{TBP} \longrightarrow \text{Bu}_2\text{HPO}_4 \longrightarrow \text{BuH}_2\text{PO}_4 \longrightarrow \text{H}_3\text{PO}_4$, and the rate determining step has been shown⁽⁹⁾ to be $\text{TBP} \longrightarrow \text{Bu}_2\text{HPO}_4$; thus the H_3PO_4 determined is a direct measure of the TBP hydrolyzed. In a two phase system the TBP concentration in the aqueous phase is considered constant with time since measurements by L. L. Burger have shown only a slight drop in TBP solubility in going from 3 to 6 M HNO₃ solutions (see Section A, above).

The rate of hydrolysis of TBP at 105°C. in either the aqueous or organic phase can be calculated from the data of Table XXI by solving six equations with six unknowns. A graph of the data in Runs I and II of Table XXI gives a rate which is first order with respect to HNO₃. It is reasonable to assume first order dependence of hydrolysis on the TBP concentration. We then get the expression

$$\frac{-d(\text{TBP})}{dt} = k(\text{TBP})(\text{H}^+)$$

Integrating

$$\ln \frac{(\text{TBP})_t}{(\text{TBP})_i} = -k(\text{H}^+)(t)$$

where $(\text{TBP})_i$ and $(\text{TBP})_t$ represent the amounts of TBP initially present and

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remaining after time t , respectively. By expanding in a power series and neglecting terms of second order or greater, the expression can be re-written

$$(TBP) = k(H^+)(t)(TBF)_i$$

where (TBP) now represents the amount of TBP reacted in time t . This expression is general for either phase; a rate constant k_o resulting in the organic and k_a for the aqueous phases.

The solubility of TBP in 3 M nitric has been determined in this laboratory as 0.2, 0.35 and 0.40 g/l at 25, 76 and 105°C., respectively. Thus, e.g., $(TBP)_i$ for the aqueous phase in Run III is $0.4 \times 2 = 0.08$ g and the resulting equations for Run III in Table XXI are

$$\begin{aligned}(TBP)_a &= k_a(0.08)(3)(13) \\ (TBP)_o &= k_o(< 0.97)(4.0)(13)* \\ (TBP)_a + (TBP)_o &= 0.95 \quad (\text{In 13 days})\end{aligned}$$

* The nitric acid solubility in the organic phase is 4.0 M. The volume of the organic phase, and thus the amount of TBP, decreased appreciably from its initial value, of course. This is the only such case in this series of experiments, and the resulting uncertainty in this equation has little influence on the reaction rate constant calculation since the organic phase contribution is so small in this instance.

The corresponding experiment in Run II is with 6 M HNO_3 where the equilibrium HNO_3 in the aqueous phase is 2.5 M. Thus,

$$\begin{aligned}(TBP)_a &= k_a(0.04)(2.5)(5) \\ (TBP)_o &= k_o(97)(3.5)(5) \\ (TBP)_a + (TBP)_o &= 2.2 \quad (\text{In 5 days, allowing one day for an apparent induction period})\end{aligned}$$

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By solving these six equations simultaneously, one obtains values for k_o and k_a of 0.0012 and 0.28/day/mole per liter of acid, respectively.

These values of k were substituted into the rate expression for 1 ml TBP: 200 ml 3 M HNO_3 and the amount of TBP decomposed in 13 days found to be 0.87 and 0.06 g in aqueous and organic phases, respectively. Similarly, the 100 ml 6 M HNO_3 decomposed 100 ml of TBP in five days to the extent of 0.14 and 2.1 g TBP in aqueous and organic phases, respectively.

Data previously obtained at 76°C.⁽⁹⁾ showed a 1% hydrolysis of TBP in an equivolume (5 ml - 5 ml) two phase system of 3 M HNO_3 - TBP in 22 days. Substitution of experimental data in the equations previously used yields a temperature coefficient for the hydrolysis of TBP of 1.63/10°C. Using this temperature coefficient, the amount of hydrolysis at 25°C. in a similar system was calculated to be 0.00004 in fraction/day.

A direct comparison of the over-all rate (both phases) at 76 and 105°C. yielded a calculated energy of activation for the hydrolysis of TBP by 3 M nitric acid of 14,700 cal/mole; the energy of activation for the hydrolysis of MBP to H_3PO_4 was previously determined⁽⁹⁾ to be ca. 11,400 cal/mole. This activation energy for TBP can be compared to that for ordinary esters which have an energy of activation of the general magnitude of ca. 10,000 cal/mole.

The experimental and extrapolated rate constants for hydrolysis in either phase are summarized in Table XXII.

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Table XXII

VARIATION OF HYDROLYSIS CONSTANTS WITH TEMPERATURE
(Units of k in Fraction Decomposed per day per M Nitric Acid)

<u>Temperature (°C.)</u>	<u>k_a</u>	<u>k_o</u>
105	2.8×10^{-1}	1.2×10^{-3}
76	6.4×10^{-2}	2.7×10^{-4}
25	5.6×10^{-3}	2.4×10^{-5}

Obviously this study of the hydrolysis of TBP is not an exhaustive one and the results are of low precision. However, the data can be used to determine TBP stability suitable for engineering calculations and to correlate with the previous studies on the butyl acid phosphates. Conversion of TBP stability from these data to a system in which a diluent is present is uncertain, but it is reasonably safe to say that a rate calculated from Table XXII would

give the upper limit. In general at temperatures of the order of 25° to 50°C. neither TBP nor diluent in an RAX should undergo any appreciably rapid decomposition by nitric acid.

C. RECOVERY AND DECONTAMINATION OF URANIUM FROM COMBINED AGED AND CURRENT METAL WASTES (R. I. Sperling)

The Bismuth Phosphate Process may remain in operation for some time following the start-up of the Redox plant. It is possible to combine the current metal waste (CMW) from Bismuth Phosphate canyon with aged uranium waste (AMW) as feed to the TBP Metal Recovery Process, thus affecting savings in chemicals needed to adjust the pH of both solutions and in storage space.

This investigation was undertaken to furnish decontamination factors and losses in a batch-countercurrent extraction run using a simulated combined feed whose fission product spectrum was due to dissolver solution. Uranium from the combined waste was compared with that recovered from aged metal waste.

A batch-countercurrent run with four extraction and one scrub stages, and with a feed whose activity was due to dissolver solution, resulted in total α and γ decontamination factors of 7×10^4 and 1×10^5 , respectively. Decontamination was not appreciably affected by the use of two extraction and three scrub stages. Uranium recovery was good, with losses of approximately 0.2%. Beta contamination of the extracted uranium amounted to 46% of that associated with natural uranium, even without a stripping section which has been shown to give some further decontamination. (10) Plutonium was retained in the waste stream by the addition of ferrous sulfamate to the feed which gave a plutonium separation factor of 2500 or an uranium stream which contained 4×10^{-8} g Pu/g U.

In a run employing aged metal waste and using one scrub and four extraction stages the total α and γ decontamination factors of 3.1×10^4 and

(10) T. G. Runion, GEH-17,412, Counter Current Decontamination Runs on TBP Process Using Shell Deodorized Spray Base as a Diluent, September 25, 1950.

2.4×10^3 , respectively, were somewhat lower than for the combined waste run, possibly due to a lower fission product level. Beta contamination of the uranium product was equivalent to 14% of that in natural uranium, and plutonium amounted to 3×10^{-8} g Pu/g U.

The results are described and discussed in detail in report HW-20556.

IX. PULSE COLUMN RESEARCH (C. M. Slansky, Group Leader)

A. PUREX STRIPPING COLUMN STUDIES (W. A. Burns, W. F. Johnson)

Purex IC column runs were made in the 1" x 65" pulse column on a feed solution containing 195 g/l UNH, 6.55 g/l HNO_3 , 30% by volume TBP in Shell Spray Base. The extractant was tap water and a feed to extractant ratio of 1 to 1.5 was used. Five plate assemblies were tried with 1" spacings: (a) 0.077" diameter hole, 10% open area compound plates; (b) 0.079" diameter hole, 10% open area stainless steel plates; (c) 0.079" diameter hole, 10% open area dri-filmed stainless steel plates, (d) 0.079" diameter hole, 10% open area plastic fluorothene plates; and (e) 0.046" diameter hole, 23% open area, compound plates. In addition, a series of runs was made using 0.125" diameter hole, 23% open area, dri-filmed stainless steel plates at 2" spacing. The data for these runs are given in Table XXIII and Figure 6.

Flooding with the compound plates in the column, aqueous or organic phase continuous, occurred at slightly below 1250 gal/ft²/hr total flow both phases for pulsing conditions of 1/2" liquid displacement and 50 cycles per minute. With the 0.079" diameter hole stainless steel plates, flooding occurred at 740 gal/ft²/hr for continuous aqueous phase and the same pulsing conditions. The flood point using the dri-filmed 0.079" diameter hole stainless steel plates, and fluorothene plates with organic phase continuous was 540 gal/ft²/hr and 300 gal/ft²/hr, respectively, for the above pulsing conditions. However, the flooding capacity of the plastic plates was raised to ca. 600 gal/ft²/hr by lowering the pulse

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frequency to 28 cycles/minute. Flooding with 0.125" hole dri-filmed stainless plates occurred above 1650 gal/ft²/hr with 85 cycles/minute and half-inch liquid displacement.

H.T.U. values were calculated using the simplified procedure of Colburn. The lowest H.T.U. values (ca. 0.6 feet) were obtained with the 0.079" hole dri-filmed stainless steel plates with aqueous continuous at 90 cycles/minute and 1" displacement and the 0.046" hole compound plates with continuous organic phase at 50 cycles/minute and 1/2" displacement. At approximately 500 gal/ft²/hr the H.T.U. values for the compound plates and stainless steel plates, aqueous phase continuous, were, respectively, 1.6 and 1.9 feet. For the same flow rate but organic phase continuous the H.T.U. values for the compound plates, 0.079" hole dri-filmed stainless steel plates, plastic plates, 0.125" dri-filmed stainless plates, and 0.046" compound plates were 1.2, 1.0, 1.3, 2.0 and 0.6 feet, respectively.

With the exception of the runs with 0.079" hole stainless steel plates aqueous phase continuous, the waste losses and H.T.U. values increased with increasing flow rate.

An attempt to run the column with stainless steel plates and continuous organic was unsuccessful. The aqueous phase channeled and the column tended to invert to aqueous continuous. The operation was so unstable that no samples of the streams were taken for analysis. Dri-filmed plates with 0.079" holes with aqueous continuous channeled badly at a pulse rate of 50 cycles/minute and 1/2" strokes, but at 90 cycles and one inch displacement, the column showed good dispersion and a very low H.T.U. of 0.7 feet.

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Table XXIII

PUREX IC RUNS 1" x 65" PULSE COLUMN

30 Volume Per Cent TBP in Shell Spray Base

Run No.	Cont. Phase	Frequency	Stroke (inches)	Flow Rate gal/ft ² /hr	Volumetric Phase Ratio Aq/Org	Analyses (g/l)				H.T.U. (ft)	
						UNH		HNO ₃			
						ICW	ICU	ICW	ICU		
0.077" diameter hole compound plates, 10.5% open area, 1" spacing											
1C-1	Aq.	50	1/2	470	1.45	25.8	118	< 0.026	5.02	1.6	Flooding
1C-2	Org.	50	1/2	490	1.49	10.1	125	< 0.023	5.23	1.2	
1C-3	Org.	50	1/2	940	1.50	32.8	104	0.083	5.39	2.0	
1C-X1	Org.	50	1/2	1250	1.5	--	--	--	--	--	
1C-4	Aq.	50	1/2	1002	1.50	50	100	-0.11	4.74	2.7	Flooding
1C-5	Aq.	100	1/4	730	1.50	16.1	128	0.55	5.18	1.5	
1C-6	Aq.	100	1/2	250	1.32	9.08	140.0	0.77	6.67	1.1	
1C-7	Aq.	50	1/2	1250	1.5	47	105	0.52	5.05	2.6	
0.079" diameter hole stainless steel plates (non-dri-filmed), 10% open area, 1" spacing											
1C-8	Aq.	50	1/2	525	1.45	32.4	115	0.2	5.39	1.9	Flooding
1C-9	Aq.	50	1/2	738	1.5	--	--	--	--	--	
1C-10	Aq.	50	1/2	650	1.43	13.8	120	< 0.027	4.73	1.3	
0.079" diameter hole dri-filmed stainless steel plates, 10.5% open area, 1" spacing											
1C-11	Org.	50	1/2	500	1.35	7.99	142	0.64	5.19	1.0	Flooding
1C-X2	Org.	50	1/2	540	1.5	--	--	--	--	--	
1C-12	Org.	50	1/2	295	1.49	5.49	128	1.20	4.66	0.9	
1C-13	Aq.	50	1/2	520	1.50	33.7	110	--	--	1.9	
1C-14	Aq.	90	1	555	1.48	2.27	131	< 0.032	4.65	0.7	

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Table XXIII (Cont'd.)

Run No.	Cont. Phase	Frequency	Stroke (inches)	Flow Rate gal/ft ² /hr	Volumetric Phase Ratio Aq/Org	Analyses (g/l)				H.T.U. (ft)	
						UNH		HNO ₃			
						ICW	ICU	ICW	ICU		
0.079" diameter hole fluorothene plates, 10.5% open area, 1' spacing											
1C-15	Org.	28	1/2	308	1.54	7.20	122	<0.03	7.20	1.0	
1C-16	Org.	28	1/2	560	1.55	14.8	115	<0.7	4.21	1.3	Near flood.
1C-X3	Org.	50	1/2	300	--	--	--	--	--	--	Flooding
0.125" diameter hole tri-filmed stainless steel plates, 23% open area, 2" spacing											
1C-17	Org.	85	1/2	520	1.46	30.9	114	0.18	4.97	2.0	
1C-18	Org.	85	1/2	1000	1.47	47.2	103	0.19	5.05	2.7	
1C-19	Org.	85	1/2	1640	1.30	86	84	0.69	5.13	4.5	
0.046" diameter hole compound plates, 23% open area, 1" spacing											
1C-20	Org.	50	1/2	515	1.55	1.25	125	0.18	4.67	0.6	

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B. VALVE-ACTUATED PULSE COLUMN (L. L. Burger, L. H. Clark)

The synchronized, valve-actuated pulse column described in HW-20053 has been applied to the stripping of uranyl nitrate from 12 1/2% TBP - 87 1/2% MIBK 125-90W. Column operability and extraction behavior was followed at room temperature for various valve "open" and "closed" times and at several throughput rates. The column was also operated at 40° and 60°C. in order to note any beneficial effect of lowered viscosity on transfer rates.

The compositions and flow ratio of RCF and RCX were taken from Metal Recovery Process Flowsheet EW #4. The column was jacketed and thermostated to the desired temperature and the inlet streams were preheated with nichrome heaters. Equilibrium data for RC column operation over the range of 0 to 60°C. obtained previously, were employed for the calculation of H.E.T.S. values. The column is 1" diameter x 17" packed length, compound plates with 0.039" diameter holes and 8.7% free area and spaced 1" apart.

In Table XXIV are presented data from 31 experiments using the apparatus as a "RC" column, of which 10 were run at 35-40°C. and 21 at 25°C. The results are not conclusive, since the variables have not been thoroughly investigated, but rather show typical run conditions which have been found reasonably satisfactory. The flow rate is proportional to the pressure on the valves, even for short open times. Flooding capacity has not been evaluated, nor has hole size, per cent free area, or other variables.

The data presented in Table XXV show the effect of increasing the temperature on uranium extraction. Experiments conducted with nearly the same operating variables are compared.

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Table XXIV

OPERATING DATA FOR VALVE-ACTUATED RC PULSE COLUMN

Run No.	Flow Ratio Aq/Org	Flow(Total) gal/ft ² /hr	Cycles per Min.	Valve "On" Time (sec.)		Valve "Off" Time (sec.)		Op. Press. (psig)		Cp. Temp. (°C.)	Mat. Bal. (%)		Waste Conc. UNH(g/l)	H.E.T.S. (in.)
				Organic	Aqueous	Org-Aq	Aq-Org	Org	Aq		UNH	HNO ₃		
4-g	0.39	526	26	0.27	0.21	1.05	0.82	20	13	40	87	81	17.9	19.5
3-1	0.47	440	28	0.15	0.15	1.05	0.80	32	23	R.T.	78	66	19.1	27.0
4-o	0.55	600	26	0.27	0.18	1.05	0.82	25	16	25	102	102	20.9	17.7
3-1	0.68	290	28	0.10	0.14	1.05	0.82	27	16	R.T.	96.2	83	17.3	22.1
4-a	0.72	500	43	0.10	0.13	0.57	0.59	25	12	25	102	107	18.5	23.6
4-p	0.73	830	22	0.51	0.28	1.05	0.82	24	17	25	108	109	21.9	34.0
4-b	0.76	500	43	0.10	0.13	0.57	0.59	25	12	25	103	107	18.7	27.9
2-a	0.78	410	28	0.10	0.15	1.05	0.82	28	15	R.T.	107	110	20.7	32.1
4-1	0.80	490	43	0.10	0.13	0.57	0.59	24	12	35	103	98	12.5	21.0
2-b	0.82	408	28	0.10	0.15	1.05	0.82	28	15	R.T.	92	104	21.3	32.7
4-c	0.83	500	43	0.10	0.13	0.57	0.59	24	12	35	111	108	13.1	20.2
3-1	0.84	483	26	0.25	0.23	1.05	0.80	19	17	R.T.	102	95	16.8	24.3
4-j	0.85	567	25	0.27	0.30	1.05	0.82	19	13	40	92	94	9.35	22.7
4-e	0.86	463	43	0.10	0.13	0.57	0.59	22	12	40	111	114	10.3	17.3
3-j	0.86	612	27	0.16	0.18	1.05	0.80	32	23	R.T.	90.5	83	17.1	32.7
3-a	0.89	384	28	0.10	0.14	1.05	0.82	35	15	R.T.	105	102	19.4	36.2
3-h	0.92	610	28	0.15	0.16	1.05	0.80	33	23	R.T.	98	84	19.2	39.5
4-1	0.94	576	27	0.17	0.17	1.05	0.82	28	18	40	98	97	11.5	29.3
4-q	0.975	524	28	0.15	0.15	1.05	0.82	27	19	25	86	81	14.2	37.0
4-n	0.984	700	25	0.27	0.25	1.05	0.82	25	17	25	93.4	118	18.4	40.5

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Table XXIV (Cont.d)

Run No.	Flow Ratio Aq/Org	Flow(Total) gal/ft ² /hr	Cycles per Min.	Valve "On" Time (sec.)		Valve "Off" Time (sec.)		Op. Press. (psig)		Op. Temp. (°C.)	Mat. Bal. (%)		Waste Conc. UNH(g/l)	H.E.T.S. (in.)
				Organic	Aqueous	Org-Aq	Aq-Org	Org	Aq		UNH	HNO ₃		
3-m	1.00	394	28	0.10	0.14	1.05	0.82	26	17	R.T.	101	87	16.1	29.8
3-f	1.00	677	28	0.15	0.16	1.05	0.80	33	22	R.T.	103	99	19.4	40.5
4-m	1.00	394	25	0.27	0.25	1.05	0.82	20	16	R.T.	105	70	13.1	29.8
4-k	1.08	600	28	0.15	0.16	1.05	0.82	27	18	40	98	100	10.6	31.5
3-e	1.08	642	28	0.15	0.18	1.05	0.80	35	20	R.T.	99.2	79.5	17.5	39.5
3-c	1.16	362	28	0.10	0.145	1.05	0.82	25	15	F.T.	87.8	33	12.4	30.3
3-b	1.19	428	28	0.10	0.14	1.05	0.82	25	15	F.T.	106	96	16.4	35.5
4-h	1.77	710	23	0.27	0.52	1.05	0.82	19	13	40	110	117	6.2	27.8

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Table XXV

EFFECT OF TEMPERATURE ON "RC" COLUMN EXPERIMENTS

Run No.	Flow Ratio Aq/Org	Flow gal/ft ² /hr	UNH Mat.Bal.(%)	HNO ₃ Mat.Bal.(%)	Temp. (°C.)	RCW UNH (g/l)	H.E.T.S. (in.)
2-a	0.78	410	107	110	25	20.7	32.1
4-a	0.80	490	103	98	35	12.5	21.0
2-b	0.82	408	92	104	25	21.3	32.7
4-c	0.83	500	111	108	35	13.1	20.2
3-j	0.86	612	90.5	83	25	17.1	32.7
4-j	0.85	567	92	94	40	9.4	22.7
3-h	0.92	610	98	84	25	19.2	39.5
4-l	0.94	576	98	97	40	11.5	29.3
3-f	1.00	677	103	77	25	19.4	40.5
4-k	1.08	600	98	100	40	10.6	31.5

It should be pointed out that the equilibrium curve at 40°C. falls below that of the 25°C. curve. Therefore, the beneficial effects of operating at the higher temperature are lower stage heights as well as fewer number of stages for a given loss. For example, in the RC column with a flow ratio (aq/org) of 0.785 and a composition of feed of 41.7 g/l UNH, 12.5 volume per cent TBP in Shell Spray Base, 6.3 g/l HNO₃ the number of theoretical stages to reduce the RCW to 0.1 g/l UNH would be 3.0 and 2.3 stages at 25 and 40°C., respectively. For the same throughput and waste loss, the column heights are 8.9 and 4.8 feet at 25 and 40°C., respectively.

C. PULSE COLUMN FOR PLUTONIUM STUDIES (W. A. Burns, W. F. Johnson)

The start-up and operation of the Redox plant for the continuous separation of plutonium and uranium from the fission products will very probably present many heretofore unanswered questions regarding the behavior, reactions, and path of plutonium in the various column contactors of the Redox Process. Also, the need for a study of plutonium extraction in alternate processes, both future and

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currently contemplated (Purex), together with the possibility of utilizing continuous solvent extraction as a step in the recovery of plutonium from slag and crucibles is readily apparent.

It is with these considerations in mind that an apparatus has been designed which should provide adequate facilities for the necessary studies. The apparatus (Figures 7 and 8) is of sufficient size and capacity to provide data of significance from the standpoint of the plant scale process. The extraction pulse column is to be 1" I.D. precision bore Pyrex glass pipe approximately 6 feet long, including 3" I.D. phase disengaging bells at each end. Pump and tank capacities have been chosen to permit variations in liquid flow rate up to 2000 gal/ft²/hr for periods of 1 hour or longer. All equipment will be fabricated from Pyrex glass and stainless steel, with suitable connections for easy removal and replacement of worn out parts, plugged filters, valves, lines, etc. Use will be made of the Zenith gear pump unit with speed control for feeding the various liquids to the columns. The pipe and valve arrangement has been designed to allow operation of the column as Redox IA, IB, IIA, or IIB, and Purex IA, IC, IIA, or IIR.

The entire column with all of its auxiliary apparatus with the exception of the cold extractant and scrub tanks will be enclosed in a large glove box comprising two units. One unit will contain the column, flow meters, pumps and sampling apparatus; the other will contain the hot feed and waste tanks (Figure 8). This separation of equipment is intended to facilitate the operation of the apparatus by isolating the column operation and sampling activities from the tank filling and waste dumping operation. The arrangement would also prevent large scale contamination of apparatus in the event of a leak or spill, and it would facilitate the handling of the apparatus in the event it must be moved for any reason.

The fact that the column is a pulsed type contactor should in no way lessen its usefulness in the study of current processes and operations being conducted

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NOTE: GLOVE PORTS TO BE
ON BOTH SIDES

Figure 7

PULSE COLUMN
GLOVE BOX ARRANGEMENT

Figure 8

SCHEMATIC
PULSE COLUMN GLOVE BOX

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in packed columns, since all the essential features of solvent extraction operations are common to each type of column. The pulse column was a natural choice for this application since it can provide the necessary transfer units in a minimum of height.

X. PUREX DECONTAMINATION STUDIES (R. L. Moore and J. S. Kane)

Earlier extraction and scrub studies (HW-18880, HW-19155, HW-19503) as well as recent Oak Ridge experience (ORNL-936) have indicated that ruthenium and zirconium are the principal fission products which are extracted into the organic phase in the Metal Recovery or Purex Process. Cerium and niobium are extracted to a lesser extent but are apparently removed by scrubbing. It is thus expected that ruthenium and zirconium may impose a limitation on the decontamination achievable in a single cycle Purex process.

To determine the effect of Hanford head-end treatment (which removes most of the ruthenium, zirconium and niobium) on subsequent decontamination in the Purex process a program of extraction and scrub studies to compare the behavior of head-end treated feed with that of untreated feed was undertaken. In these studies, a feed solution, 1.4 M UNH, 2.0 M HNO₃, was extracted once with 30 volume per cent TBP-AMSCO 125 and scrubbed three times with 3.0 M HNO₃. Extractant to feed to scrub ratios were ten to three to two. Table XXVI gives pertinent information concerning the experimental conditions for a number of runs involving treated and untreated feeds. Table XXVII gives the results obtained in these runs. The feed solutions used in these experiments were all prepared from the same sample of dissolver solution (designated as DS-18 by W. E. Roake). Pretreatment had removed 97, 96.7 and 99.9 per cent of the ruthenium, zirconium and niobium, respectively, from the solution used to prepare the feed for Experiments SC-1, -4, -6, -7 and -10. The pretreatment was considered to be inferior in that only about half of the usual amount of permanganate was used.

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Table XXVI

PUREX EXTRACTION AND SCRUB STUDIES - CONDITIONS

Expt.	Age of Feed - Days			Pretreatment	Experimental Conditions
	Since Pushed	Since Dissolved	Since Treated		
SC-1	149	83	27	Yes	500 λ dissolver solution used.
SC-2	151	85	29	No	500 λ dissolver solution used, one-sixth full level activity.
SC-4	169	103	47	Yes	500 λ dissolver solution used, 0.05% DBP in extractant.
SC-5	175	109	53	No	500 λ dissolver solution used, 0.05% DBP in extractant, one-sixth full level activity.
SC-6	190	124	68	Yes	2.5 ml dissolver solution used.
SC-7	192	126	70	Yes	2.5 ml dissolver solution used, not centrifuged to separate phases.
SC-8	197	131	75	No	2.5 ml dissolver solution used, feed had been stored in glass.
SC-9	199	133	77	No	2.5 ml dissolver solution used, one-sixth full level activity, feed had been stored in stainless steel.
SC-10	199	133	77	Yes	500 λ dissolver solution used, Pu valence state in feed adjusted to (IV) by 0.01 M ferrous sulfamate followed by 0.02 M NaNO_2 and digestion at 60°C. for one hour.

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Table XXVII

PUREX EXTRACTION AND SCRUB STUDIES - RESULTS

Expt.	Activity	Extr'n.	E _a			Decontamination Factor		% Natural Uranium Activity in Product ⁽²⁾
			1st Scrub	2nd Scrub	3rd Scrub	Extr'n. and Scrubs	Over-all ⁽¹⁾	
SC-1	U	0.0024	0.004	0.011	0.08	7.3×10^5	9×10^5	22
	Y	0.0025	0.014	0.03	0.045	1.4×10^5	1.3×10^6	122
	Ce	0.0026	0.0022	0.006	0.038		3.8×10^6	
	Ru	0.0024	0.026	0.02	0.02	1.2×10^5	3.2×10^6	
	Zr	0.0027	0.13	0.08	0.16	3.9×10^3	7×10^4	
SC-2	U	0.0018	0.006	0.06	0.17	1.1×10^5		156 ⁽³⁾
	Y	0.0018	0.012	0.09	0.55	1.4×10^4		9924 ⁽³⁾
	Ce	0.0015	0.0019	0.058	0.029	1.23×10^6		
	Ru	0.0023	0.026	0.044	0.057	3.7×10^5		
	Zr	0.0045	0.015	0.014	0.14	7×10^4		
SC-4	U	0.0022	0.005	0.05	0.12	1.24×10^5	1.5×10^5	110
	Y	0.0036	0.064	0.29	0.43	1.4×10^3	1.3×10^4	12350
	Ce	0.0023	0.0021	0.0029	0.036		9.5×10^5	
	Ru	0.0021	0.08	0.35	~1	1.6×10^3	5.3×10^4	
	Zr	0.028	0.13	0.26	0.40	118	3.54×10^3	
SC-5	U	0.0025	0.054	0.17	0.12	5.3×10^3		495
	Y	0.0074	0.18	0.32	0.37	360		52900
	Ce	0.0012	0.0021	0.024	0.07	1.43×10^6		
	Ru	0.0013	0.03	0.17	0.09	2.1×10^4		
	Zr	0.021	0.17	0.27	0.33	141		
SC-6	U	0.0025	0.0036	0.01	0.063	9.9×10^5	1.2×10^6	12
	Y	0.0024	0.018	0.03	0.05	1.4×10^5	1.3×10^6	107
	Ce	0.0024	0.0023	0.0032	0.0028	8.4×10^7		
	Ru	0.0012	0.029	0.15	0.85	1.9×10^4	6.4×10^5	
	Zr	0.012	0.046	0.046	0.014	1.8×10^4	5.3×10^5	

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Table XXVII (Cont'd.)

Expt.	Activity	E _a				Decontamination Factor		% Natural Uranium Activity in Product ⁽²⁾
		Extr'n.	1st Scrub	2nd Scrub	3rd Scrub	Extr'n. and Scrubs	Over-all ⁽¹⁾	
SC-7	β	0.0067	0.0031	0.0081	0.039	8×10^5	1×10^6	13
	γ	0.0059	0.0064	0.030	0.038	1.3×10^5	1.2×10^6	114
	Ce	0.0022	0.0008	0.0056	0.0022	2.2×10^7		
	Ru	0.0026	0.0064	0.24	0.44	1.7×10^4	5.5×10^5	
	Zr	0.018	0.022	0.043	0.059	7.3×10^3	2.2×10^5	
SC-8	β	0.0017	0.0048	0.021	0.07	5×10^5		35
	γ	0.0012	0.018	0.034	0.07	1.4×10^5		661
	Ce	0.0020	0.0018	0.0050	0.0058	4.1×10^7		
	Ru	0.0031	0.019	0.045	0.045	5.7×10^4		
	Zr	0.0017	0.023	0.024	0.035	7.1×10^4		
SC-9	β	0.0017	0.0088	0.024	0.07	2.4×10^5		60 ⁽³⁾
	γ	0.0034	0.017	0.025	0.08	6×10^4		1662 ⁽³⁾
	Ce	0.00083	0.0019	0.071	1.33	3.1×10^5		
	Ru	0.0041	0.010	0.056	0.098	1.7×10^5		
	Zr	0.011	0.013	0.036	0.060	2.1×10^4		
SC-10 ⁽⁴⁾	β	0.00084	0.0023	0.017	--	3.9×10^6	4.9×10^6	
	γ	0.00052	0.020	0.042	--	1.6×10^5	1.5×10^6	
	Ce	0.00039	0.00068	0.012	--	2.0×10^7		
	Ru	--	--	--	--	1.7×10^5	5.5×10^6	
	Zr	0.0061	(0.21)	0.0071	--	9.8×10^3	2.9×10^5	

(1) Including head-end treatment.

(2) Per cent natural uranium activity and D.F.'s were not corrected for uranium and plutonium contribution to beta and gamma activity.

(3) Observed values multiplied by six to correct for dissolver solution dilution.

(4) Only two scrubs made.

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It will be noted by comparing the results of Experiments SC-1 and SC-2 that the treated material gives higher solvent extraction decontamination factors for both gross beta and gamma activity than does the untreated feed. This is reflected in the lower distribution ratios, E_a^* , for these activities in the scrub steps and implies that additional scrubs would accomplish even further decontamination with the head-end treated feed whereas the non-treated feed is already "in a pinch" after three scrubs. The over-all D.F.'s for these two runs indicate that head-end treatment improves the over-all gamma decontamination by a factor of about 100 and the beta by about 10. Specific fission product analyses indicated that most of the activity extracted from the treated feed was cerium and that the extraction and scrub behavior of ruthenium was the same in both cases, i.e., the E_a^* values were the same. The zirconium decontamination factors are suspect since the analytical material balances were low.

The activity level employed in these first experiments was scaled up as in Experiments SC-6 to SC-9 in an effort to obtain more reliable analyses. Even in these larger scale experiments the activity remaining in the organic after the last scrub was so low that the individual fission product analyses, and hence the corresponding decontamination factors, are very uncertain. The gross beta and gamma factors are probably more reliable. Much of the analytical data for these latter runs is not yet available.

Over-all beta and gamma decontamination factors obtained in the larger scale experiments in which a treated feed was used (Experiments SC-6 and SC-7) check closely those obtained in SC-1. However, when Experiment SC-2 (untreated feed) was repeated on a larger scale as in Experiments SC-8 and SC-9, over-all decontamination factors obtained were higher than for SC-2 although still two to twenty fold lower than obtained for treated feeds. It is noteworthy that the dissolver solution was somewhat older when Experiments SC-8 and SC-9 were performed than for SC-2. This suggests that aging may improve the extraction and scrub behavior of feeds

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prepared from untreated dissolver solution. Whether the dissolver solution was stored in glass or in stainless steel seems to have little effect on that improvement.

Experiments SC-6 and SC-7 differed only in that centrifugation was employed to insure clean phase separation in the case of SC-6 whereas five minutes of gravity settling was employed with SC-7. In the latter case, entrained droplets of aqueous gave a turbid appearance to the organic phase. The nearly identical decontamination factors obtained in the two experiments indicates that, under the conditions of these experiments, entrainment did not affect the results.

Studies SC-4 and SC-5 show that dibutyl phosphate has an adverse effect on decontamination whether or not the feed is treated. It will be noted that both the beta and gamma decontamination factors are about thirty-fold greater for the treated than for the untreated feeds, i.e., the same as the zirconium decontamination achieved in the head-end treatment. Fission product analyses showed that zirconium accounted for essentially all of the gamma activity remaining in the organic phase in both cases.

Study SC-10, in which the plutonium was adjusted to the (IV) state by ferrous sulfamate reduction followed by digestion with nitrite, indicates that this adjustment has no adverse effect on decontamination and may, indeed, cause an improvement, possibly by insuring that all the cerium is in the tervalent state.

XI. KINETICS OF PLUTONIUM REDUCTION IN THE REDOX IB COLUMN (R. L. Moore)

Recent semi-works runs at SPRU employing head-end treated feed have demonstrated that the required degree of decontamination of the product uranium with respect to beta and gamma activities may be realized in one cycle. There is some uncertainty however as to whether or not the Hanford IB column as presently designed will also decontaminate the uranium adequately from plutonium, particularly if there is any slowness in either the rate of reduction or transfer of plutonium. Earlier investigations have suggested that the reduction is not instantaneous and that appreciable

Pu(V) may be formed as an intermediate in the reduction of Pu(VI) to Pu(III).

These experiments were, however, performed with trace amounts of plutonium and in solutions not typical of the present flow sheet. A re-examination of the problem at full flowsheet concentration of plutonium has been made.

In these studies the reduction of plutonium was followed by means of a Cary spectrophotometer. The instrument was calibrated by determining the absorption curves for Pu(III), (IV) and (VI) in 1.3 M $\text{Al}(\text{NO}_3)_3$, 0.04 M HNO_3 solutions. To determine how effectively the Pu(V) could be "seen" by the instrument, hydroxylamine (a reducing agent known to produce appreciable Pu(V)) was added to a 1.3 M $\text{Al}(\text{NO}_3)_3$, 0.04 M HNO_3 , 0.4 g/l Pu(VI) solution and the absorption spectrum scanned repeatedly. The prominent Pu(V) absorption at about 569 millimicrons reached a maximum in about five minutes and then decreased. In a similar experiment in which 0.05 M ferrous sulfamate was added to a solution of the above composition, no detectable quantity of Pu(V) was observed at any time even though the first scanning was made within 45 seconds after the addition of ferrous sulfamate. At that time the Pu(III) spectrum appeared fully developed and did not change with time.

Similar experiments with hexone-saturated aqueous solutions containing less ferrous sulfamate (0.025 and 0.01 M) gave the same results even when scanned as soon as 15 seconds after the addition of sulfamic acid. These results indicate that the reduction of Pu(VI) to Pu(III) in the aqueous phase of the IB column is practically instantaneous even in the presence of one-fifth of the flowsheet concentration of ferrous sulfamate.

Two-phase experiments were then performed in which a hexone phase containing 0.4 grams of Pu(VI) per liter was contacted with an equal volume of IBP aqueous solution of the composition 1.3 M $\text{Al}(\text{NO}_3)_3$, 0.04 M HNO_3 , 0.05 M ferrous sulfamate. Samples of the hexone phase were analyzed for plutonium after various agitation times. When agitation was by means of a motor driven stirrer, plutonium E_a values decreased for about ten minutes. With more vigorous agitation (shaking by hand)

the E_a had reached a constant value within 15 seconds contact time. These experiments indicate that plutonium reduction and extraction in the IB column is essentially instantaneous provided the agitation is sufficiently vigorous.

Complete details of this work may be found in a summary report HW-20580.

XII. BISMUTH PHOSPHATE EXTRACTION PROCESS STUDIES (H. S. Gile)

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For some time the bismuth phosphate plant processed uranium of increasing grams of plutonium per ton of uranium (g/T). Since a plant run is based on a given amount of plutonium, decreasing volumes of dissolver solution were used per run. However, the total amount of bismuth phosphate precipitated per run in the extraction step was not changed. Previous work has suggested that, in the g/T range currently processed by the plant, the amount of bismuth phosphate which is necessary to precipitate in the extraction step to insure adequate carrying of plutonium is dictated by the initial concentration of bismuth rather than by the bismuth to plutonium mole ratio. These studies were undertaken to determine the feasibility of reducing the amount of bismuth phosphate precipitated in the extraction step consistent with increasing the g/T level of the uranium processed.

Plutonium losses in the extraction step were determined as a function of g/T when precipitating 2.5 and 1.8 grams of bismuth per liter. Also, plutonium losses as a function of the Bi/Pu mole ratio were determined for the first decontamination cycle product precipitation. Complete details of the experimental procedures and analytical methods may be found in HW-20687.

When precipitating 2.5 grams of bismuth per liter in the extraction step, plutonium losses were essentially constant and low ($< 0.5\%$) for g/T values from 250 to 1400. Higher g/T levels were not studied. At 1.8 grams of bismuth per liter, plutonium losses were constant and low for g/T values to about 500. Above this value the losses were very erratic and sometimes quite high. It is possible that when precipitating 1.8 grams of bismuth per liter, plutonium carrying becomes sensitive to other process variables such as agitation at Bi/Pu ratios < 30 .

In laboratory studies of the first decontamination cycle product precipitation (wherein 1.8 grams of bismuth per liter are precipitated in the plant) plutonium losses were low ($\approx 0.5\%$) at Bi/Pu mole ratios down to about 15. Assuming that the volumes of post-extraction-step solutions are determined by the amount of bismuth phosphate precipitated in the extraction step, a Bi/Pu ratio of 15 in the first decontamination cycle precipitation step corresponds to 850 and 600 g/T when precipitating 2.5 and 1.8 grams of bismuth per liter, respectively, in the extraction step.

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XIII. WASTE TREATMENT STUDIES (R. F. Burns, Group Leader)

A. DECONTAMINATION OF AGED FIRST CYCLE SUPERNATANTS BY SCAVENGING
(H. S. Gile and C. R. McMullen)

Plutonium and fission product analyses of first cycle supernatants from the six oldest first cycle tanks in each COO area are shown in Table XXVIII. Gross salt analyses show the supernatants to be about 1.5 M in NO_3^- , 2.2 M in Na^+ , 0.21 M in PO_4^{3-} , 0.05 M in SO_4^{2-} and 0.2 M in F^- and to have a pH of about 9.5. Of the principal activities remaining in wastes as old as these, ruthenium and zirconium can be expected to decay to a considerable extent in the ten to twenty years estimated for ground water adjacent to cribbing areas to reach the Columbia River; decay alone would decontaminate ruthenium by factors of 10^3 and 10^6 while factors for zirconium and its daughter, niobium, would be even higher. The principal activities remaining in these wastes which would be of concern after such a decay period are plutonium, strontium, cesium and promethium. Of these, plutonium and strontium probably represent the greatest hazard biologically because of their tendency to become fixed in body tissue.

Decontamination of these aged first cycle supernatants by a variety of scavenging agents has been studied. Emphasis was given to procedures which, because of simplicity of operation, low cost of reagents and small volumes of residues to be stored, could compete economically with evaporation as a means of reducing the volume of these wastes.

Table XXVIII

ACTIVITIES IN FIRST CYCLE SUPERNATANTS

Plutonium analyses based on ferric hydroxide - lanthanum fluoride analyses of 5 ml samples.

All fission product samples counted on 2nd shelf, assumed geometry: 7.5% for α and 0.075% for γ .

Tank	Date Filled	Pu $\mu\text{g/cc}$	Gross α $\mu\text{c/cc}$	Gross γ $\mu\text{c/cc}$	Str $\mu\text{c/cc}$	Cs $\mu\text{c/cc}$	Ru $\mu\text{c/cc}$	RE+Y-Ce $\mu\text{c/cc}$	Ce $\mu\text{c/cc}$	Nb $\mu\text{c/cc}$	Zr $\mu\text{c/cc}$	Te $\mu\text{c/cc}$
107B	8-45	17×10^{-3}	0.16	0.055	0.011	0.10			0.017			
107T	7-45	1.5×10^{-3}	0.18	0.077	0.0013	0.20			0.0065			
108B	12-45	20×10^{-3}	0.18	0.036	0.022	0.12						
108T Top	12-45	20×10^{-3}	0.18	0.062	0.012	0.17	0.0066	0.047	0.007	0.0018	10^{-3}	1.2×10^{-5}
109T	3-46	2.6×10^{-3}	0.15	0.067	0.00036	0.15						
109B	4-46	18×10^{-3}	0.16	0.042	0.01	0.11			0.013			
104T Top	7-46	3×10^{-3}	0.42	0.130	0.00013	0.13	0.058	0.004	0.051	0.028		2.4×10^{-5}
110C	8-46	2×10^{-3}	0.14	0.056	0.00026	0.11						
111C	11-46	4.2×10^{-3}	0.16	0.058	0.01	0.13						
111X	4-47	3.1×10^{-3}	0.14	0.053	0.006	0.13						
110U	4-47	0.21×10^{-3}	0.13	0.058	0.00011	0.17						
111U	10-47	0.34×10^{-3}	0.12	0.050	0.00023	0.14						
109TX	9-49	2.7×10^{-5}	2.91	2.23	0.00087	0.27	0.34	0.0085	0.0035	0.34	1.2×10^{-5}	

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Table XXIX presents the experimental conditions used and the results obtained for the scavenging agents so far studied. These experiments were meant to be exploratory and it is recognized that the particular conditions used were probably not optimum for any one scavenger.

Experiments M-1, -1A, -2, -2A and -5 indicate that tannic acid is a good plutonium scavenger, moderately good for cerium and strontium but poor for cesium. The apparently anomalous behavior, that the carrying is better at lower tannic acid concentration (M-1 and M-2), has been observed before in connection with 231 wastes. Precipitation of the tannic acid appears to be incomplete at the higher concentration. Experiments M-3, -4 and -4A show that, in these wastes, ferric iron is only moderately efficient as a scavenger for plutonium and cerium and poor for strontium and cesium. The presence of considerable phosphate in the solutions probably explains the increase in plutonium scavenging with increase in pH since the precipitate is largely ferric phosphate at the lower pH.

The use of calcium nitrate as in Experiments M-6 and M-7 was suggested by the work of Lauderdale on the scavenging of fission products by calcium phosphate.⁽¹¹⁾ At the increased pH, carrying of plutonium, strontium and cerium was good. Cesium is apparently not carried. The two experiments performed do not determine whether or not the initial reduction in pH is necessary to obtain good carrying.

Ferrous ferrocyanide as a scavenger for wastes of similar gross salt content has been studied at Mound Laboratory.⁽¹²⁾ As applied to these particular wastes, at high pH (ca. 9.5), scavenging was moderate for plutonium and strontium and poor for cesium (M-15). At medium pH (ca. 6) plutonium and cerium removal were very good, cesium good and strontium moderate (M-12, -14, -17). At low pH (0.4) cesium carrying was very good but scavenging of other activities was very

(11) R. A. Lauderdale, Jr., ORNL-932, Studies on the Removal of Radioisotopes by Coagulation, January 23, 1951.

(12) Quarterly Reports for Liquid Waste Disposal, MLM-369, -380, -406, -441, -466, -487, -515, April 1, 1949 to November 13, 1950.

Table XXIX

SCAVENGING OF FIRST CYCLE SUPERNATANTS

Expt.	Supernatant	Reagents and Conditions	Decontamination Factors						RE+Y -Ce	Volume Solution Volume Solid
			Gross ϕ	Pu	Sr	Cs	Ce			
M-1	107B	Add tannic acid to 0.01 M. Raise pH to 12.3. Stir 1 hour. Centrifuge.	1.7	9	2	1.5	6	--	25	
M-2	104T	As M-1 except pH not changed.	--	63	8	--	--	--	25	
	107B	As M-1 except made 0.001 M in tannic acid.	1.5	275	7	1.1	92	--	125	
M-2A	104T	As M-2 except pH not changed.	--	2.3	3.25	--	--	--	125	
M-5	107B	As M-2 except pH lowered to 5 before tannic acid added.	1.3	4	3	1	4	--	125	
M-3	107B	Add Fe^{+++} to 0.01 M. Raise pH to 12. Stir 1 hour. Centrifuge.	1.2	17	2.2	1	17	--	--	
M-4	107B	As M-3 except 0.001 M in Fe^{+++} .	1.2	9	2.4	1	18	--	--	
M-4A	104T	As M-4 except pH not changed.	--	1.2	9.5	--	--	--	--	
M-6	107B	Add $\text{Ca}(\text{NO}_3)_2$ to 0.01 M. Stir 1 hour. Centrifuge.	1	1.7	1.5	1	1.6	--	50	
M-7	107B	Reduce pH to 0. Add $\text{Ca}(\text{NO}_3)_2$ to 0.01 M. Raise pH to 12. Stir 1 hour. Centrifuge	1.8	123	59	1.2	160	--	25	
M-10	110C	Reduce pH to 3. Make 0.005 M NaHSO_3 and 0.01 M $\text{K}_4\text{Fe}(\text{CN})_6$. 5 minutes. Make 0.01 M Fe^{++} . Stir 15 minutes. Centrifuge.	5	140	4.3	90	--	--	27	

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Table XXIX (Cont'd.)

Expt.	Supernatant	Reagents and Conditions	Decontamination Factors						Volume Solution Volume Solid
			Gross α	Pu	Sr	Cs	Ce	RE+Y -Ce	
M-11	110C	As M-10 except 0.01 M in Fe^{4+} .	1.55	140	2	2.3	--	--	166
M-12	110C	As M-10 except pH reduced 5.5 to 6.	5.5	>145	11	480	--	--	25
M-13	108T	As M-10 except pH reduced to 0.4.	5.1	2.4	2	2080	1	--	50
M-14	108T	Reduce pH to 6. Make 0.01 M NaHSO_3 . Stir 10 minutes. Make 0.005 M $\text{K}_4\text{Fe}(\text{CN})_6$. Stir 10 minutes. Make 0.01 M Fe^{4+} . Stir 1 hour. Centrifuge.	18.5	1450	24	170	1100	--	31
M-15	108B	As M-10 except pH not changed	1.3	14	13	1.8	--	--	23
M-16	108B	Make 0.01 M $\text{K}_4\text{Fe}(\text{CN})_6$. Stir 1 hour. Make 0.01 M Fe^{4+} . Stir 1 hour. Centrifuge.	1	8	2.6	1.2	--	--	--
M-17	108B	As M-14	13	1450	16	290	--	--	--
M-18	108B	Reduce pH to 6. Make 0.005 M $\text{K}_4\text{Fe}(\text{CN})_6$. Stir 1 hour. Make 0.01 M $\text{Fe}(\text{NO}_3)_3$. Stir 1 hour. Centrifuge.	6.5	1450	27	7.5	1390	--	--
M-19	108B	As M-18 except reduce pH to 3.	1.5	725	2.6	1	1390	--	--
B-2	109B	Add 0.05 moles solid $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ per liter. Stir 1 hour. Centrifuge	1.1	1.6	1.4	1.1	1.5	1.2	--
B-4	109B	Reduce pH to 4. Make 0.01 M $\text{H}_2\text{C}_2\text{O}_4$ and 0.002 M $\text{Ca}(\text{NO}_3)_2$. Raise pH to 12. Stir 1.5 hour. Centrifuge.	1.8	490	41	1.3	550	23	50

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Table XXIX (Cont'd.)

Expt.	Supernatant	Reagent and Conditions	Decontamination Factors						Re+Y -Ce	Volume Solution Volume Solid
			Gross $\mathcal{A}$	Pu	Sr	Cs	Ce			
B-5	109B	As B-4 except heated at boiling point for 2 hours.	1.5	420	205	1.1	> 2000	--		50
B-7	109B	0.14 moles solid $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ per liter. Make 0.005 M $\text{H}_2\text{C}_2\text{O}_4$. Raise pH to 12. Stir 3 hours R.T. Let settle 1 hour.	1.65	--	--	--	--	--		3.5
		Let settle 21 hours	1.7	3000	800	1.5	~2000	18		8.3
B-8	109B	As B-4 except pH not changed.								
		Let settle 1 hour.	1.3	--	--	--	--	--		--
		Let settle 21 hours.	1.4	1.8	2.8	1.25	--	--		--
B-3	109B	0.5 g Attaclay/25 ml waste. Stir 1 hour. Centrifuge.	1.8	1.4	2.1	2.2	1.9	1.8		25
B-6	109B	1.5 g Attaclay/25 ml waste. Heat at b.p. 2 hours. Centrifuge.	4.7	160	140	4.6	550	115		8.3
B-11	109B	As B-6	5.1	2500	1600	6.9	--	--		8
B-12	109B	1.5 g Fuller's earth/25 ml waste. Stir 2 hours at 95-100°C. Centrifuge.	4.7	145	410	7.0	730	--		8
B-9	109B	0.5 g KH_2 tartrate/25 ml waste. Stir 1 hour. Centrifuge.	--	--	--	1.9	--	--		50
B-18	112C	Reduce pH to 4. Add 10 g $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ per 25 ml waste. Heat to clear solution. Cool to crystallize. Centrifuge.	--	--	--	73	--	--		--

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Table XXIX (Cont'd.)

Expt.	Supernatant	Reagent and Conditions	Decontamination Factors					Volume Solution	
			Gross $\mathcal{S}$	Pu	Sr	Cs	Ce	Re+Y -Ce	Volume Solid
B-19	112C	As B-18 except no change in pH	--	--	--	3100	--	--	--
B-13	109B	Add 0.5 g Fuller's earth and 0.5 g $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}/50$ ml waste. Make 0.005 M $\text{H}_2\text{C}_2\text{O}_4$. Increase pH to 12. Stir 2 hours. Settle 2 hours	2.8	197	--	2.7	--	--	8.3

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greatly reduced. Ferric ferrocyanide at pH 6 appears to work as well for plutonium, strontium and cerium as the ferrous compound but less efficiently for cesium (M-18 and M-19).

Calcium oxalate appears to be a very good scavenging agent for plutonium, strontium and the rare earths provided the separation is carried out at high pH (ca. 12). Cesium is not efficiently removed (B-2, -4, -5, -7 and -8). The oxalate is crystalline in form and settles readily.

Attaclay and Fuller's earth both appear to be good scavengers for plutonium, strontium and the rare earths without pH change provided the slurry is heated during contact. Attempts to operate columns of Attaclay and Fuller's earth at elevated temperatures failed because of extremely low flow rate. Apparently these materials are disintegrated somewhat by the supernatants at high temperature, the fines produced effectively plugging the columns. Successive additions of these materials to the wastes without intervening phase separation were not effective in increasing activity removal. A study is currently underway involving countercurrent batch contacting of waste with Attaclay.

The use of potassium alum as a carrier for cesium has been studied by Gresky at ORNL.⁽¹³⁾ As can be seen from experiments B-18 and B-19 carrying of cesium was good when the contact was made at pH 4. At pH 9.5 cesium scavenging was very good for the one successful experiment performed. Attempts to repeat this experiment have failed in that heating apparently converted the alum to alumina as one would expect at this pH. Because the alum is relatively soluble and an appreciable amount is lost to the supernatant at each contacting, this procedure is likely to be prohibitively expensive for use on these wastes.

Of the scavengers so far studied, calcium oxalate, the iron ferrocyanides and Attaclay appear the most promising. Experiments are now underway to define optimum conditions for these reagents and to obtain settling rate data for the solids concerned.

(13) A. T. Gresky, ABCD-2999, The Recovery of Cs¹³⁷ from ORNL Radiochemical Waste, October 12, 1950.

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B. IODINE IN DISSOLVER SOLUTION (C. H. Holm)

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1. Removal of Iodine by Sparging

Studies of the removal of iodine from simulated dissolver solutions were continued to firm up and complete data previously reported.⁽¹⁴⁾ The variables studied were found to have the following effect on the efficiency of sparging:

1. Temperature. The rate of removal of iodine, added as iodide, iodine or iodate, from simulated dissolver solution in contact with metallic uranium by air sparging is markedly increased with increase in temperature. At a spargant flow rate of 1.7 cc/min/ml of solution about 90% of the iodine was removed in three hours at 95°C. regardless of the oxidation state in which the iodine was added.

2. Spargant. The rate of evolution of iodine is affected to a small degree by the spargant used. Oxygen, air and nitrogen are of increasing effectiveness in the order given when the iodine is added as iodine or iodate. The order is reversed for iodide.

3. Spargant flow rate. Increasing the spargant flow rate increases markedly the rate of evolution of iodine when added in any of the three oxidation states studied. For example, air sparging a simulated dissolver solution in contact with metallic uranium for three hours at 95°C. and at spargant flow rates of 0.4, 1.2 and 3.4 cc/m/ml removed 70, 90 and 97 per cent, respectively, of the iodine added as iodide. Similar variations were shown for iodine added as iodine and iodate.

4. Presence or absence of metallic uranium. Iodine, added as iodine or iodate, is more rapidly evolved at a given spargant flow rate when the solution is in contact with metallic uranium; iodide removal is slower when metallic uranium is present.

5. Nitric acid concentration. Curves relating per cent iodine remaining after three hours of air sparging at 1.7cc/m/ml to acidity show a broad

(14) HW-18880, -19155, -19503, -19739, -20053. Chemical Research Section Monthly Progress Reports August through December, 1950.

minimum for each oxidation state ranging from 0.5 to 2.0, 0.1 to 0.7 and 0.0 to 0.5 M HNO_3 , respectively, for iodide, iodine and iodate.

6. Uranyl nitrate concentration. The rate of iodine evolution is not influenced by uranyl nitrate concentration for any of the three oxidation states studied.

The foregoing is a brief summary of the sparging investigations which have been carried out. A detailed discussion of the work may be found in HW-20803.

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2. Retention of Iodine by Complexing with Mercuric Nitrate

Previous work on this problem has been reported in HW-19739 and HW-20053. The material in those reports may be summarized as follows:

1. Of several complexing agents tried, Hg^{++} , Cd^{++} , Zn^{++} , Pb^{++} and Bi^{+3} , only Hg^{++} was effective in preventing the evolution of iodine from simulated dissolver solution by sparging. Less than 0.05 per cent of the iodine in a simulated dissolver solution was removed during one hour of air sparging at a spargant flow rate of 1.7 cc/m/ml, when 10^{-4} M Hg^{++} was present.

2. Air sparging at 8.5 cc/m/ml for at least 30 minutes after each process step prior to bismuth phosphate precipitation removed a total of 0.5, 7.0 and 1.74 per cent of the iodine from simulated dissolver solution containing 10^{-4} M mercury when the iodine was added as iodide, iodine and iodate, respectively.

3. In the extraction step, iodide, iodine and iodate are carried on bismuth phosphate to a greater extent in the absence of mercury than in its presence; about three, two and eight per cent, respectively, being carried from an extraction solution containing mercury equivalent to 10^{-4} M in dissolver solution.

4. Considerable iodine was evolved during a simulated slug dissolving when mercury was present at 10^{-4} M. Increasing the mercury concentration appears to reduce the iodine evolution.

5. Data indicate that 10^{-4} M is about the minimum concentration of mercury in simulated dissolver solution which will effectively prevent evolution of I_2 by sparging. Iodide and iodate are effectively retained at 10^{-5} M.

The following phases of the problem were investigated during the period covered by this report. Previously reported experiments were all performed in glass equipment. Sparging experiments carried out with stainless steel (T-304) present indicated that the presence of the steel had no appreciable effect on the ability of mercury to prevent evolution of iodine. Experiments in which radioactive mercury was used showed that the mercury does not plate out either on stainless steel or on metallic uranium when in contact with dissolver solution. Dissolver solution at its boiling point and containing 10^{-3} M mercury corroded T-309-SCB stainless steel at a rate of 2×10^{-5} inches per month, an essentially negligible corrosion rate.

To determine whether or not the presence of mercury would have any effect on the rate of dissolution, solutions were prepared simulating the solution at various points during the dissolving. One set of these solutions contained 10^{-3} M mercuric nitrate while a second set contained no mercury. The solutions were heated to boiling and pieces of metallic uranium introduced. After five minutes the uranium was removed, weighed and measured to determine, approximately, its macro surface area. Table XXX shows the dissolving rates obtained with and without mercury. The variations between the rates obtained with and without mercury are probably within experimental error indicating that the presence of mercury has little effect on the dissolving rate.

The effect of mercury on the carrying of plutonium in the extraction step was studied by performing the reduction and extraction steps (approximating plant procedures) on simulated dissolver solutions containing plutonium, varying amounts of mercury and 10^{-5} M iodine added as iodide, iodine and iodate. The extraction residue was washed twice with water. Table XXXI shows the plutonium

losses obtained. Because of the erratic data for iodate, reruns at 0 and 10^{-4} M mercury were made and losses of 0.4 and 0.5, respectively, were obtained. The data do indicate that there may be a trend toward slightly higher plutonium losses in the presence of mercury. Iodine used in these experiments was traced with I^{131} such that the carrying of iodine by bismuth phosphate under these conditions could be observed. These results are shown in Table XXXII. The presence of mercury appears to have little effect on iodine carrying when the iodine is added as iodine or iodide and reduces the carrying slightly when added as iodate. Low material balances for iodine indicated iodine evolution during the runs. Further reduction and extraction runs were made under conditions to allow trapping of any evolved iodine in a caustic scrub solution. Results presented in Table XXXIII show that, for these laboratory experiments, iodine initially as iodide is, to a large extent, evolved during reduction and extraction. The evolution is reduced somewhat by the presence of mercury. Iodate evolution is not appreciable.

The carrying of mercury on bismuth phosphate in the extraction step was determined by performing experiments similar to those just discussed except that no I^{131} or plutonium was present while the mercury was traced with radioactive mercury. Results of these runs are shown in Table XXXIV. About 20 per cent of the mercury was carried under all conditions studied.

Since most of the mercury added to dissolver solution remains in the extraction supernatant or metal waste an investigation was made of the effect which its presence in the feed might have on the TBP process. Since a report covering the work done on the use of mercury to complex iodine in dissolver solution is in preparation and will appear shortly, only a summary of the results obtained will be given here.

1. The presence of mercury in the aqueous had no significant effect on disengaging times when feeds simulating RAF prepared from current and aged metal wastes were shaken with 12.5 per cent TBP-Shell Spray Base as an extractant.

2. Distribution coefficients for uranium and nitric acid in extraction studies simulating the RA column were unaffected by the presence of mercury.

3. Mercury is not extracted into the TBP phase.

4. Iodine, added as iodide, strongly favors the organic phase.

After three extractions more than 98 per cent of the iodine added had been removed from the aqueous phase whether or not mercury was present. This is of little interest in connection with the TBP process but might be of interest in the Purex process. The behavior of iodine in the Redox process is under investigation.

A preliminary investigation was made of the carrying of iodine in the presence of mercury on MnO_2 as formed in the proposed head-end treatment for Redox feed. Simulated dissolver solutions containing 10^{-4} M mercury and 10^{-5} M iodine added as iodide, iodine or iodate were made 0.078 M in KMnO_4 . MnO_2 was formed by reduction with $\text{Cr}(\text{NO}_3)_3$. After centrifuging and washing the MnO_2 was found to contain 88, 74 and 71 per cent of the iodine added as iodide, iodine and iodate, respectively.

In summary, addition of mercuric nitrate in the range of 10^{-4} M to dissolver solution prevents the evolution of iodine by sparging through all process steps to reduction and bismuth phosphate precipitation. Iodine evolution during these latter steps is reduced by the presence of mercury but is still appreciable in the case of iodide and iodine. Addition of mercury to dissolver solution has no deleterious effects on corrosion of stainless steel or on the carrying of plutonium by bismuth phosphate in the subsequent extraction step. It does not plate out on stainless steel or uranium and its presence does not affect the dissolving rate of uranium. The presence of mercury in metal waste solution appears to have no deleterious effects on the TBP process for metal recovery.

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Table XXX

EFFECT OF MERCURY ON DISSOLVING RATE

Dissolving Time, Hrs.	Composition of Solution		Rate of Dissolving, mg/hr/cm ²	
	<u>M UNH</u>	<u>M HNO₃</u>	<u>Without Hg</u>	<u>With Hg</u>
0	0.0	13.0	1200	1200
2	0.6	10.0	1750	1800
4	1.72	4.4	1300	1200
6	2.35	1.0	350	310
0(1)	0.0	13.0	1400	1400

(1) Uranium pitted by previous partial dissolution

Table XXXI

EFFECT OF MERCURY ON PLUTONIUM LOSSES IN THE EXTRACTION STEP

Hg, <u>M</u> ⁽¹⁾	Plutonium Loss to Supernatant and Washer		
	<u>I⁻</u>	<u>I₂</u>	<u>IO₃⁻</u>
0	0.39	0.28	0.97
10 ⁻⁵	0.54	0.49	3.90
10 ⁻⁴	0.79	0.53	3.50
10 ⁻³	0.58	0.77	1.50

(1) Refers to M of mercury in dissolver solution

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Table XXXII

EFFECT OF MERCURY ON CARRYING OF IODINE BY BISMUTH PHOSPHATE

Hg, <u>M</u>	Iodine in Precipitate, %			Iodine in Supernatant and Washes, %		
	<u>I⁻</u>	<u>I₂</u>	<u>IO₃⁻</u>	<u>I⁻</u>	<u>I₂</u>	<u>IO₃⁻</u>
0.0	2.8	2.8	11	2.2	12	75
10 ⁻⁵	(7.1)	2.9	9.2	5.6	12	75
10 ⁻⁴	2.8	2.3	8.0	22	31	80
10 ⁻³	0.69	2.1	7.5	78	82	84

Table XXXIII

EVOLUTION OF IODINE DURING REDUCTION AND EXTRACTION

Hg, <u>M</u>	Iodine	Iodine, %			
		<u>Precipitate</u>	<u>Supernatant</u>	<u>Scrub</u>	<u>Material Balance</u>
10 ⁻⁴	10 ⁻⁵ M I ⁻	6.1	33	61	99
0.0	10 ⁻⁵ M I ⁻	3.0	3.1	89	94
10 ⁻⁴	10 ⁻⁵ M IO ₃ ⁻	11	88	1.2	100

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Table XXXIV

CARRYING OF MERCURY ON BiPO_4 IN THE EXTRACTION STEP

Hg, M	Iodine	Mercury, %		Material Balance
		Precipitate	Supernatant	
10^{-4}	10^{-5} M I^-	19	79	98
10^{-4}	10^{-5} M IO_3^-	19	79	98
10^{-4}	None	19	80	98

XIV. DOCUMENTED REPORTS ISSUED DURING QUARTER, JANUARY, FEBRUARY, MARCH, 1951

Document No.	Date of Document	Author(s)	Title
HW-19065	10-6-50	LL Burger	Comparison of Diluents for TBP
HW-19303	12-1-50	C Groot, IM Rehn, CM Slansky	Properties of the System: $\text{UO}_2(\text{NO}_3)_2$ - $\text{Al}(\text{NO}_3)_3$ - HNO_3 - H_2O - Hexone. Part VI. Distribution of Pu(IV)
HW-19696	12-12-50	IM Rehn CM Slansky	Batch-Countercurrent Equilibria of U and HNO_3 in the TBP Process for Waste Uranium Recovery
HW-20053	1-19-51	OF Bill FJ Leitz	Progress Report for December, 1950 - Chemical Research Section
HW-20195	2-5-51	RE Burns	Radioactive Content of Stored BiPO_4 First Cycle Waste Supernatants
HW-20224	2-7-51	PM Brown WH Reas	Chemical Assistance to P-11
HW-20287	9-1-50	WE Roake HG Hicks	Decontamination of Redox Feed Solutions by Filtrol Scavenging
HW-20556	3-16-51	CM Slansky RI Sperling	Recovery and Decontamination of U from Combined Aged and Current Metal Wastes
HW-20580	3-20-51	RL Moore	Kinetics of Plutonium Reduction in the Redox IB Column
HW-20649	3-28-51	WH Reas PM Brown	The Separation of Lithium from Pu by Pu(IV) Peroxide Precipitations
HW-20587	3-20-51	C Groot	Trip to Los Alamos - March 5 and 6, 1951

<u>Document No.</u>	<u>Date of Document</u>	<u>Author(s)</u>	<u>Title</u>
HW-20687	3-30-51	HS Gile	Carrying of Plutonium on BiPO_4 as a Function of the Bismuth to Plutonium Ratio
HW-20688	3-30-51	JS Kane RE Burns	Bismuth Phosphate Concentration Process Studies. Recycle of Lanthanum Fluoride By-Product Precipitation Rework Solution

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