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CHEMICAL RESEARCH

by

O. F. Hill and F. J. Leitz
Separations Technology Unit
TECHNICAL SECTION

January 15, 1952

Nucleonics Division
Richland, Washington

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TABLE OF CONTENTS

	<u>Page No.</u>
I. THE RECUPLEX PROCESS	4
A. Summary of Flowsheet Studies	4
B. Recovery of Plutonium from Silica Filter Cake	5
C. Decomposition of Recuplex Solvent Due to Alpha Irradiation	6
II. PROCESS STUDIES	8
A. Pulse Column Glove Box Program	8
B. Recuplex Process - Pulse Column Studies	9
C. Pulse Column Surface Investigations	14
III. SINGLE CYCLE PROCESS STUDIES	15
A. Sulfide Scavenging of Ruthenium Activity	15
B. Purex Decontamination as a Function of Acidity	20
C. Alternate Aqueous Media for Solvent Extraction of Uranium and Plutonium	24
D. Adsorption of Fission Products from Hexone Solutions	26
E. Decontamination of Uranium Solutions from Fission Products by Ion Exchange Methods	30
IV. SOLVENT EXTRACTION MECHANISM	30
A. Pulse Column Studies	30
B. Solvent Studies	34
C. Thermodynamics of Uranyl Nitrate Solutions	36
V. RUTHENIUM CHEMISTRY	40
VI. 234-5 PROCESS STUDIES	41
A. Resin Column Coupling	41
B. Alternate Fluorinating Agents	43
VII. WASTE TREATMENT STUDIES	47
A. Evolution of Heat from Fission Product Decay in Process Wastes	47
B. Ion Exchange Decontamination of Redox Distillates	49
C. Decontamination of Bismuth Phosphate Process Second Cycle Waste	54
D. Removal of Activity from Uranium Recovery Process Aqueous Wastes	60
VIII. DOCUMENTED REPORTS ISSUED DURING QUARTER, OCTOBER, NOVEMBER, DECEMBER, 1951	64

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QUARTERLY REPORT OCTOBER THROUGH DECEMBER 1951CHEMICAL RESEARCHI. THE RECUPLEX PROCESS (H. H. Hopkins, Jr., Problem Leader)A. SUMMARY OF FLOWSHEET STUDIES

(W. H. Adams, H. L. Greenberg, H. H. Hopkins, C. Groot)

Research investigations on the Recuplex process reported last quarter (HW-22138) are nearing completion and final reports on the Recuplex process and on Recovery of Plutonium from Slag and Crucible are in preparation.

1. Summary and Conclusions from Final Report on Recovery of Plutonium from Slag and Crucible are as follows: (see HW-23343)

- a. The dissolution of slag and crucible is best done by the "nitric acid" method which yields 86 per cent of the charged plutonium. The "aluminum nitrate-nitric acid" dissolution procedure, while less corrosive to equipment, leads to low recovery of the charged plutonium in the dissolution step and necessitates further treatment of the silica to recover held-up plutonium.
- b. The plutonium can be quantitatively extracted from slag and crucible solution (containing aluminum nitrate) into 30 per cent tributyl phosphate in AMSCO 125-90W by using six stages of countercurrent extraction with one-tenth volume of organic phase.
- c. After scrubbing with an equal volume of water the organic phase can be stripped of plutonium in four stages of countercurrent extraction with one-fifth volume of 0.4 M ammonium sulfate solution.
- d. Plutonium can be precipitated from the strip solution as the peroxide or oxalate. The compound is of good purity (ca. 99.8%). A button prepared from an oxalate showed satisfactory purity although the low reduction yield indicates the need for counting development work.

2. Summary and Conclusions from Final Report on the Recuplex Process are as Follows: (see HW-23344)

- a. Flowsheets have been developed for the isolation of plutonium from IIBP concentrate, F-10-P, SN-3 oxalate supernates, slag and crucible solution and other recycle streams. The proposed processes involve ca. seven stages of extraction into fifteen per cent tributyl phosphate in carbon tetrachloride, scrubbing of the organic phase, and ca. six stages of stripping into an aqueous phase.

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- b. Demonstration of these flowsheets showed that the extraction process produces plutonium nitrate at a high concentration (ca. 50-60 g/l Pu), of high purity (99.9 + per cent) and in good yield (ca. 99.9 per cent). The concentration is attained either by the use of a high reflux of plutonium between the extraction and stripping sections, or by the use of sulfate in the stripping section.
- c. The plutonium isolated by the process can be precipitated as the oxalate with ca. 99.9 per cent yield. After hydrofluorination the fluoride can be reduced to the metal in satisfactory yield. The purity of the buttons was good.

B. RECOVERY OF PLUTONIUM FROM SILICA FILTER CAKE (H. L. Greenberg)

The recovery of plutonium from the silica filter cake has been investigated, so that a method will be available should this recovery prove necessary. Leaching of the cake with nitric acid is in-effective, it is necessary to attack the silica. The silica cake is attacked rapidly by hydrofluoric acid. Silica dissolves as fluosilicate and plutonium remains with the insoluble residue. The silica may be separated either by (1) volatilization of silicon tetrafluoride or (2) by filtration of the non-silicon residue.

The volatilization of silicon tetrafluoride proceeds readily upon heating the system. One problem is the design of a trap to receive the silicon tetrafluoride, yet which will not plug when the gas hydrolyzes to silicic acid.

The separation of fluosilicate from the residue by filtration or centrifugation is satisfactory. One per cent or less of the plutonium follows the filtrate. Plutonium in the residue is present as the fluoride, since it can be dissolved in aluminum nitrate solution, or methathesized with caustic to the hydroxide and then dissolved in nitric acid. The insoluble residue from these treatments retained approximately eight per cent of the plutonium. Thus overall recovery of plutonium from the silica would be ca. 90 per cent.

The experimental results are presented in Table I.

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Table I

RECOVERY OF PLUTONIUM FROM SILICA FILTER CAKE

Silica Cake g	Pu in Silica mg	HF Added ml	% Pu Lost to HF Solution	Treatment of Fluoride Insoluble Residue	% Pu Dissolved	% Pu Lost to Residue
ca. 5 (wet)	78	40	1	Added 40 ml 1 M $\text{Al}(\text{NO}_3)_3$ 20 hrs. contact.	98	--
40 (dried)	315	70	1.2	50%: Added 80 ml 1 M $\text{Al}(\text{NO}_3)_3$ 6 hrs; then 40 ml wash.	95	4
				50%: methathesize w. KOH, dissolve in HNO_3	87	12
25 (dried)	167	50	0.4	Added 134 ml 1 M $\text{Al}(\text{NO}_3)_3$	85	14

C. DECOMPOSITION OF RECUPLEX SOLVENT DUE TO ALPHA IRRADIATION (W. H. Adams)

Under prolonged exposure to alpha bombardment from plutonium, tributyl phosphate is partially decomposed to dibutyl phosphate, and carbon tetrachloride decomposes yielding either chlorine or hydrogen chloride. This behavior is evidenced by an increasing concentration of non-strippable plutonium in the organic phase with time, and by the increased formation of water soluble chloride. Over a 24 hour period the effect is pronounced in a 15 per cent TBP carbon tetrachloride phase containing about 20 g/l Pu but is unimportant in an organic phase containing only 1 g/l Pu. Thus in Recuplex operation these effects will occur in those few stages in which the plutonium concentration in the organic is high.

The experimental data are summarized in Table II.

Light was shown to have no significant effect on the decompositions.

The reason for the drop in the concentration of non-strippable plutonium in the organic phase over the first hour or two is not known. One possibility is a change in valence state in the organic phase, the species formed being more readily stripped than the species which was originally extracted.

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Table II

FORMATION OF NON-STRIPPABLE PLUTONIUM AND OF
CHLORIDE IN RECUPLEX SOLVENT DUE TO ALPHA IRRADIATION

Organic: 15% TBP in CCl_4
Treatment: Stripped at intervals with five
equal volumes 0.1 M HNO_3

Organic Composition	1 g/l Pu* 32 g/l HNO_3		17 g/l Pu* 21 g/l HNO_3		22 g/l Pu 20 g/l HNO_3	
	mg/l Pu	mg/l Cl	mg/l Pu	mg/l Cl	mg/l Pu	mg/l Cl
Time, hours	Not Stripped	Formed	Not Stripped	Formed	Not Stripped	Formed
0-0.1	1.4	--	--	--	3.7	0.05
0.7-0.8	0.7	0.02	0.9	--	--	--
1.5-1.8	0.45	0.02	1.05	--	2.0	0.075
2.5-3.3	0.37	0.03	1.26	--	2.6	0.085
24	0.67	0.1	31	0.23	35.	0.35
96	--	--	--	--	215.	1.0

* Organic phases maintained in contact with 1 M $\text{Al}(\text{NO}_3)_3$, 1 M HNO_3 .

The effect of dibutyl phosphate was investigated in order to correlate the amounts of non-strippable plutonium with DBP concentration. The data are presented in Table III.

On comparing these data with the data of Table II, it is seen that ca. 0.008 volume per cent of dibutyl phosphate is necessary to produce the same effect on stripping as the radiation effects of 17 g/l Pu residing in the organic solution for 24 hours. The implication is that $\frac{0.0008}{0.15} = 0.05$ per cent of the TBP has decomposed to DBP in the 24 hour period. The decomposition of TBP in the organic phase when only 1 g/l Pu is present for 24 hours is less by a factor of at least eight.

The above numbers are only approximate as the decomposition of TBP to other products is not considered.

Investigations have started on the removal of the non-strippable plutonium from the organic phase. The approach is to remove the DBP from the organic phase by a wash with carbonate solution. The plutonium should then strip as a hydroxide into the same caustic. In one experiment in which the organic was originally 0.03 g/l Pu successive scrubbing for one minute with five half volumes of 0.5 M Na_2CO_3 solution reduced the plutonium concentration in the organic to 2.2 mg/l, 0.9 mg/l, 0.4 mg/l, 0.4 mg/l, and 0.4 mg/l respectively. Evidently a small amount remained non-strippable even with the carbonate treatment. This study will be continued employing longer contacting times.

Table III

EFFECT OF DIBUTYL PHOSPHATE ON PLUTONIUM (IV) STRIPPABILITY

Organic: 15% TBP in CCl_4
0.479 g/l Pu (from stock solution 99% Pu IV)

Treatment: Added DBP, stripped five times with equal
volume 0.1 M HNO_3

60.

<u>Vol. % DBP</u>	<u>Pu in Organic After 5th strip mg/l</u>	<u>E_a Pu (5th strip)</u>
0.	0.66	1.0
0.001	0.73 (ave.)	0.6 (ave.)
0.00125	2.51	0.8
0.0025	6.3	1.9
0.00375	11.4	2.7
0.005	14.6	3.1
0.010	46. (ave.)	5.0 (ave.)

II. PROCESS STUDIES (C. M. Slansky, Problem Leader)

A. PULSE COLUMN GLOVE BOX PROGRAM (W. S. Figg and C. M. Slansky)

The construction of the two pulse columns for use in Redox start-up assistance and for other extraction process studies such as the Recuplex process, is approximately 50% complete.

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The high-alpha glove box column which has been described in HW-20863, is being completed first and will be used initially to test the Recuplex extraction and stripping columns under full plutonium concentration. The packed height of the column has been increased to 12 feet. The column itself, its water jacket and heaters, glove box, tanks, pulser and control panel have been completed and installed. The water jacket was made of two 1/2" thick lucite and two 1/2" dural panels which have withstood temperatures up to 60°C. without undue expansion or warping. Higher temperatures are considered undesirable due to softening of the lucite. At the present time the wiring of the Skinner solenoid valves and piping of the tanks is being undertaken.

The principal problem remaining to be solved for successful column operation is the procurement of corrosion resistant, positive displacement, non-pulsating pumps for the feed tanks and interface control. The original choice of Zenith gear pumps coupled to a Graham drive and explosion-proof motor has been shown to be undesirable because of 1) jamming of gears, 2) seal surface failure, 3) air leakage past the seal. A Maisch metering pump (Mechanical Products Co.) has been tested for column application. The original gears, after hardening by the Malcomizing process, corroded very rapidly in dilute nitric acid. However, plain 18-8 stainless steel gears have given very satisfactory performance over a period of 300 hours. Maisch pumps have been ordered for installation to the alpha pulse column.

B. RECUPLEX PROCESS-PULSE COLUMN STUDIES (L. E. Kattner and W. H. Swift)

The applicability of the pulse column to the Recuplex Process has been successfully demonstrated and detailed operating characteristics are being obtained with uranium as a stand-in for plutonium.

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These experiments are preliminary to full scale activity in the alpha, glove-box column.

The column work to date has been done in a 1" diameter x 65" column with the plates spaced 1" apart. Plates of 0.027 and 0.040" diameter holes of 18 and 23% open area, respectively, have been tried. The conventional double-faced plate made of separate stainless steel and fluorothene plates was used as well as a new plate in which the perforated stainless steel plate is coated with Kel-F dispersion, a fluorothene dispersion in an organic liquid.

Effort to date has been primarily directed toward determining the effect of the variables; volume velocity, plate material, and plate hole size, on the HETS values in the "C" column, where the greatest difficulty in transfer is expected. The results of these "C" column studies are presented in Figure 1.

A total of fourteen "C" runs were made in accordance with flowsheet 12A (HW-22409) with samples taken on all influent and effluent streams. In all runs, the frequency and amplitude of the pulse were maintained constant at 65 cycles/min and 0.5 inches respectively. This particular combination of pulse conditions is not necessarily optimum but was felt to be a good average value at which to evaluate extraction as a function of thruput. All HETS values were calculated using EP-17 Equilibrium data obtained from Chemical Development personnel and in accordance with the procedure adopted by Chemical Development regarding HNO_3 concentration. These data are presented in Table IV.

The effect of making the organic phase continuous is shown in a greatly increased value of the HETS and larger dependency of HETS on volume velocity which may be explained by the extreme lack of aqueous holdup and of poor coalescence between plates. Runs made with the aqueous phase continuous yielded a substantially lower value in the HETS and less dependence on thruput.

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URE 1

Recuplex C Column - Flowsheet 12A
H.E.T.S. vs Volume Velocity

1" x 65" glass column
Pulse amplitude = 0.5"
Pulse frequency = 65 cyc./min.
Plate spacing = 1"

Again, this may be explained by increased dispersed phase holdup and a higher degree of coalescence between plates at the end of each pulse.

The use of the Kel-F dispersion coated plates with the aqueous phase continuous gave very encouraging results. The thruput capacity of the column was increased approximately 30% over the capacity of even the compound fluorothene-stainless steel plates, probably due to a less restricted free area. Increased extraction efficiency is indicated, but further work must be done to demonstrate its significance. However, the lack of dependence of extraction efficiency on volume velocity promises great column versatility.

HETS values with 0.040" diameter hole plates were approximately 30% higher than those for 0.027" diameter holes when both sizes were coated with fluorothene.

Two Recuplex "A" column runs have been made with the organic phase continuous and .046" diameter, 23% open area double plates at 1" spacing. This operation appeared to give better dispersion than with aqueous continuous. At 500 gal/(hr)(ft²) with 30 cycles/min. frequency and 0.5 inches displacement the column operated smoothly. Flooding appeared to be near 850 gal/(hr)(ft²). Operation at 800 gal/(hr)(ft²) resulted in a condition at the center portion of the column that was very near flooding with a tendency for the phases to invert.

The results at 600 gal/(hr)(ft²) and CAFF'S:CAX::3:1 flow ratio are given below.

<u>Run</u>	<u>Frequency cyc/min</u>	<u>Amplitude inches</u>	<u>Waste loss %</u>	<u>HTU ft.</u>
1	36	0.75	0.6	1.0
2	52	0.75	0.9	--

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Table IV

RECUPLEX C COLUMN
Flowsheet 12A
1" x 65" Pulse Column

Flow Ratio AQ:ORG = 2:3;

Frequency = 65 cyc/min.

Amplitude = 0.5"

Run No.*	Volume Velocity gal/(hr)(ft ²) (sum of both phases)	Continuous Phase	UNH in CF g/l	CU Composition		UNH Loss % of Feed	H.E.T.S. ft.	H.T.U. _{oo} ft.
				UNH	HNO ₃			
1-27-A	400	Organic	52.0	83.5	20.4	42	4.2	--
2-27-A	1000	Organic	52.0	73.2	22.3	23	3.2	--
3-27-A	1000	Organic	54.4	77.5	21.8	22	3.0	--
4-27-A	1000	Aqueous	54.4	87.0	23.5	8.1	1.9	--
5-27-A	700	Aqueous	56.0	80.0	20.0	5.7	1.8	--
6-27-A	700	Organic	57.0	80.4	23.0	24	2.89	--
1-27-B	1000	Aqueous	55.0	90.7	7.8	2.6	1.45	1.06
2-27-B	700	Aqueous	56.3	90.7	7.3	4.1	1.54	0.95
3-27-B	400	Aqueous	58.2	94.2	9.1	3.3	1.42	0.92
4-27-B	1200	Aqueous	58.8	85.1	7.8	4.9	1.85	0.97
5-27-B	100	Aqueous	53.3	91.6	6.02	3.6	1.42	0.97
6-27-B	1431	Aqueous	54.6	93.9	6.27	5.7	1.54	1.15
1-40-C	1200	Aqueous	55.0	71.0	5.59	9.1	2.7	2.00
2-40-C	300	Aqueous	56.3	91.1	5.67	6.9	1.8	1.40
3-40-C	700	Aqueous	56.4	90.0	5.84	9.9	1.9	1.24

* Second Number indicates perforation hole size in 1/1000" Series A: Double plates (stainless steel-fluorothene) Series B, C: Kel-F coated plates.

C. PULSE COLUMN PLATE SURFACE INVESTIGATIONS (W. S. Figg and L. E. Kattner)

Previous laboratory pulse column investigations on Purex and Waste Metal Recovery Systems (HW-19145 and HW-20863) have demonstrated the desirable qualities of plates constructed so that one exposed surface is stainless steel and one is fluorothene; such plates have been generally called "two-faced", compound, or double plates. The results of these studies may be briefly summarized as follows:

1. In aqueous continuous systems, at volume velocities up to the flooding point of similar all stainless steel plates, the two-faced plates give mass transfer efficiencies about equivalent to those obtained using the all stainless steel plates. On the otherhand, the maximum flooding velocity of the two-faced plates is roughly twice that of the stainless steel plates.
2. In organic continuous systems all stainless steel plates caused excessive channeling of the aqueous phase at all volume velocities and gave poor mass transfer efficiencies. The two-faced plates gave a maximum flooding capacity about twice that obtained with all fluorothene plates and gave H.T.U.'s about one-half the height of those given by the all fluorothene plates.
3. Two-faced plates made by flame spraying polyethylene onto stainless steel plates exhibited wetting and operating characteristics that were visually the same as those of the all stainless steel plates.

From the above data it seems reasonable to conclude that the advantages of the double plates derive from their causing the rapid coalescence of the dispersed phase, regardless of which phase is continuous.

In the past the two-faced plates have been constructed from perforated stainless steel plates held against fluorothene plates that had been drilled with holes corresponding in size and location to those in the steel plates. This construction was both tedious and costly and considerable trouble was experienced in maintaining the positions of the holes relative to each other. The latter problem was especially important in plates with small holes, because a slight rotation of the plates relative to each other resulted in a large reduction of the free area.

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Recently a possible solution to the above problems was discovered by coating the perforated stainless steel plates with a fluorothene film (Kel-F dispersion), of about 0.001" thickness, which seems to give a relatively permanent organic wet surface, while the uncoated side retains its aqueous wetting characteristics. These plates will be called coated plates to differentiate them from the double plates.

The current Recuplex column studies employing uranium as a stand-in for plutonium, as reported above, have indicated that the performance of these coated plates is at least as good as, and possibly significantly better than, that achieved with the double plates. The coated plates have shown excellent adherence of the fluorothene film to the metal after three weeks installation under Recuplex column conditions. The application of this coating to larger plates should not be difficult.

III. SINGLE CYCLE PROCESS STUDIES (R. L. Moore, Problem Leader)

A. SULFIDE SCAVENGING OF RUTHENIUM ACTIVITY (R. L. Moore)

Benwell, Lever, and Powell¹ have investigated the chemistry of ruthenium in nitric acid solutions and have reported that ruthenium was precipitated from such solutions by hydrogen sulfide. The removal was improved and a more easily handled precipitate obtained by the simultaneous precipitation of copper sulfide or some other heavy metal sulfide. The solutions employed by these investigators were prepared by dissolving ruthenium-nickel or ruthenium-uranium alloys in nitric acid. Only macro-concentrations of ruthenium were employed and no radioactive species were present.

It accordingly seemed worthwhile to determine whether ruthenium activity could be scavenged from aqueous Redox or Purex solutions, such as the feed or final uranium streams, by means of sulfide precipitation.

(1) February, 1950, (2) June, 1950 AERE-499

The Chemistry of Ruthenium in Nitric Acid Solutions.

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A series of experiments was carried out under essentially the conditions recommended by the British investigators, but with Hanford dissolver solution activity present. Hydrogen sulfide was bubbled at room temperature (ca. 25°C.) for two hours through uranyl nitrate - nitric acid solutions containing initially 0.025 M $\text{Cu}(\text{NO}_3)_2$ and 2% Hanford level dissolver solution. The results of several experiments are shown in Table V.

Table V

COPRECIPITATION OF RUTHENIUM WITH COPPER SULFIDE

Initial Composition: Indicated UNH
 Indicated HNO_3
 0.025 M $\text{Cu}(\text{NO}_3)_2$
 2% Hanford level Fission Products
 Time of H_2S Passage - 2 hours
 Temperature - ca. 25°C.

<u>M UNH</u>	<u>M HNO_3</u>	<u>% Ru Removed</u>	<u>Ru D.F.</u>
1	0.5	99.8	580
1	0.5	99.8	600
1	0.5	99.6	260
1	0	99.78	450
2	0	99.47	190

It will be noted that the precipitation of 1.6 g/l Cu^{++} carried down from 99.5 to greater than 99.8% of the ruthenium activity. It also appears that neither the uranium or nitric acid concentration is critical. However additional experiments revealed that there was danger, at higher temperatures or greater nitric acid concentrations, of oxidation of hydrogen sulfide to free sulfur. It was also observed that there is some apparent reduction of uranium (VI) to uranium (IV) in that the supernatant takes on a greenish tinge upon prolonged passage of hydrogen sulfide. Any uranium (IV) may be readily reconverted to uranium (VI), however, by warming the solution to the boiling point after sparging out dissolved hydrogen sulfide.

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I. KINETICS OF RUTHENIUM PRECIPITATION

The precipitation of copper sulfide appears to be essentially complete within several minutes after the passage of hydrogen sulfide is commenced. That of ruthenium is much slower, however, as shown by the data in Table VI.

Table VI

RATE OF RUTHENIUM PRECIPITATION ON COPPER SULFIDE

Initial Composition: 1 M UNH, 0.5 M HNO₃, 0.025 M Cu(NO₃)₂,
2% Hanford Fission Product Activity.

Temperature: 25°C.

<u>Time of Passage of H₂S</u>	<u>Ru Activity in Supernatant, c/m/ml</u>	<u>% Initial Ru Remaining</u>	<u>Ru D.F.</u>
0	1.5 x 10 ⁶	100	--
5 min.	110,000	7.3	14
15 min.	33,000	2.2	45
30 min.	13,000	0.87	115
1 hr.	5,400	0.36	280
2 hr.	2,500	0.17	600

It is seen that a ruthenium decontamination factor of only 14 was obtained at the end of five minutes and that this increased slowly to a value of 600 at two hours, suggesting that some chemical process such as a slow reduction of higher ruthenium valence states or the destruction of a nitroso or nitrate complex may be rate limiting. This, and other similar data, are not found to fit any simple rate equation.

2. PLUTONIUM BEHAVIOR DURING COPPER SULFIDE SCAVENGING

Hydrogen sulfide was passed at room temperature through a solution containing 0.5 g/l Pu (IV) in 1 M HNO₃. The color of Pu(IV) persisted after half an hour, however at one hour there was evidence of production of some Pu(III) and at the end of one and one-half hours Pu(III) predominated.

A slight hazy appearance was presumably due to the formation of a small amount of colloidal sulfur. Analysis of the initial solution, the solution after passage of hydrogen sulfide, and the supernatant after centrifugation showed that there had been no change in the plutonium concentration and indicated no appreciable precipitation of plutonium.

Another experiment was carried out to determine whether plutonium coprecipitated with the copper sulfide. Hydrogen sulfide was passed for two hours at room temperature through a solution containing both plutonium and copper, as well as uranium. Hydrogen sulfide was passed through the solution for two hours, the copper sulfide precipitate allowed to settle and the supernatant pipetted off. The precipitate was washed three times by stirring up with 2 ml portions of 1 M HNO_3 , allowing to settle, and decanting. The precipitate was dissolved in potassium cyanide solution and all solutions analyzed. The results are shown in Table VII.

The fraction of the plutonium associated with the precipitate is seen to be 3.6%, which corresponds well with the bulk volume of the precipitate (3 to 4% of the volume of the solution). The amounts left after the first, second, and third washes are 0.6, 0.09, and 0.017% respectively, and these are found to obey dilution law expectations, i.e. a plot of the logarithm of the amount associated with the precipitate versus the number of washes is a straight line.

It might be noted that some earlier experiments indicated an apparent plutonium loss after prolonged passage of hydrogen sulfide. This was found to be due to uranium (IV) interference with the lanthanum fluoride analysis.

3. Effect of Washing on Adsorbed Ruthenium

Since it is necessary to wash the precipitate to remove entrapped plutonium (and uranium) in event sulfide scavenging were used as a head-end treatment, analyses were run to determine how much ruthenium might be desorbed by washing.

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Table VII

BEHAVIOR OF PLUTONIUM DURING COPPER SULFIDE PRECIPITATION

Solution Composition: 1 M UNH, 0.5 M HNO₃,
0.2 g/l Pu(IV), 0.3025 M
Cu(NO₃)₂

Solution Volume: 10 ml
Wash: 1/5 vol. 1 M HNO₃
Temperature: 25°C.

<u>Sample</u>	<u>Pu d/m/ml</u>	<u>Total</u>	<u>%</u>
Initial Solution	2.74×10^7	2.74×10^8	100
Supernatant after 2 hrs. Passage of H ₂ S	2.67×10^7	2.67×10^8	97.4
First wash	4.11×10^6	8.22×10^6	3
Second wash	6.48×10^5	1.3×10^6	0.47
Third wash	93,000	1.86×10^5	0.07
CuS Precipitate	--	4.53×10^4	0.017

Analysis of the washings from scavenging experiments showed that ruthenium was not removed from the copper sulfide cake by washing with 1 M HNO₃, that found in the washes corresponding to the concentration in the supernatant after scavenging and to dilution law considerations. Thus in one experiment the supernatant contained 0.38% of the initial ruthenium (D.F. - 260) and the washes 0.058, 0.015, and 0.0028%, respectively. In another experiment the supernatant contained 0.11% (D.F. - 930) and the washes 0.0092, 0.006, and 0.0023%.

4. Effect of Pretreatment

If the slowness in the precipitation of ruthenium is due to slow reduction of the higher oxidation states, pretreatment with a reducing agent might be expected to improve the kinetics and perhaps the degree of subsequent scavenging. In one experiment the feed solution (1 M UNH, 0.5 M HNO₃, 0.025 M Cu(NO₃)₂, 2% Hanford F.P.) was heated for one hour at 70°C. with 5 vol. % formic acid, cooled to room temperature and copper sulfide precipitated.

Two hours passage of hydrogen sulfide yielded a ruthenium decontamination factor of 930.

5. Homogeneous Precipitation of Copper Sulfide

It was thought that the use of conditions of homogeneous precipitation might lead to better scavenging. Uranyl nitrate - nitric acid solutions containing cupric ion were heated with thiourea, however the expected copper sulfide precipitate was not obtained. It appeared that thiourea was oxidized to sulfur dioxide, rather than hydrolyzing to sulfide, by heating in nitrate solutions.

6. Miscellaneous Experiments

Scavenging experiments have been carried out to compare other heavy metal sulfides, such as lead, mercury, and bismuth, to copper as scavenging agents. Other experiments have been performed to determine the effectiveness of adding the sulfide as a soluble sulfide (Na_2S) and also to determine how much additional decontamination may be secured by a second copper sulfide strike. However, results on these experiments are not yet available.

It is planned to carry out scavenging experiments on full Hanford level dissolver solution and to determine the solvent extraction behavior of the residual ruthenium under both Redox and Purex conditions. Scavenging of ICU is also contemplated.

B. PUREX DECONTAMINATION AS A FUNCTION OF ACIDITY (R. A. Watts)

A series of extractions were made at 5% Hanford activity level to determine if operation of the Purex extraction column under acid deficient conditions using aluminum nitrate as a salting agent would improve decontamination. The distribution behavior of uranium, plutonium (IV), plutonium (VI), gross beta activity, and gross gamma activity, as well as certain specific fission products (ruthenium, zirconium, niobium, and cerium) into 30% TBP-AMSCO 125 was determined as a function of acidity and salting strength.

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Aluminum nitrate concentrations ranged from 0.50 to 1.50 M for acidities of 0.5, 0.2, 0, -0.1, and -0.2 M.

The results indicated that the distribution of ruthenium into the organic phase decreased with decreasing acidity and with decreasing aluminum nitrate concentration. Cerium was not improved to any extent. The niobium and zirconium counts came out too low for accurate analysis due to their low starting concentrations in the old dissolver solution used for the extractions. Separation factors, defined as the uranium or plutonium (VI) distribution ratios divided by the corresponding fission product distribution ratios, are tabulated for ruthenium in Table VIII.

Table VIII

SEPARATION FACTORS FOR RUTHENIUM

Aqueous Composition: 0.8 M UNH Indicated
 $\text{Al}(\text{NO}_3)_3$
 Indicated HNO_3
 5% Hanford Level
 Fission Products

Organic Composition: 30% TBP in AMSCD 125
 2/1 org/aq volume ratio
 10 min. stirring time

<u>M</u> $\text{Al}(\text{NO}_3)_3$ \ <u>M</u> HNO_3						
		0.5	0.2	0.0	-0.1	-0.2
S.F. UNH	0.50	1,670	1,220	4,520	2.12×10^4	1.28×10^5
	0.75	2,240	5,320	6,250	3.30×10^4	1.12×10^4
	1.00	11,700	4,200	12,000	4.71×10^4	6.30×10^4
	1.25	--	4,800	10,600	5.68×10^4	1.31×10^5
	1.50	54,200	34,000	25,200	1.14×10^5	7.25×10^5
S.F. Pu(VI)	0.50	200	206	550	1,300	1.58×10^4
	0.75	489	629	620	733	1.41×10^3
	1.00	1,050	880	1,420	1,040	1.84×10^4
	1.25	--	1,020	2,970	2,810	1.48×10^5
	1.50	5,490	3,780	4,520	11,200	6.25×10^5

In order to supplement and corroborate the above results, extraction and scrub studies at full Hanford activity level was carried out simulating an acid deficient IA column.

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The extractant was 30% TBP-AMSCO 125. The results from these studies are tabulated in Table IX.

Table IX

EFFECT OF DICHROMATE ON DECONTAMINATION

(One Extraction and Three Scrubs)

Conditions: Feed: 0.8 M UNH
 -0.2 M HNO₃
 1.0 M Al(NO₃)₃
 2/1 org/aq volume
 ratio
 Full Hanford Level
 Fission Products

Scrubs: 1.0 M Al(NO₃)₃
 -0.2 M HNO₃

Expt. No.	M Na ₂ Cr ₂ O ₇ in feed	M Na ₂ Cr ₂ O ₇ in scrub	Decontamination Factors			
			<u>U</u>	<u>B</u>	<u>Ru</u>	<u>Ce</u>
1	0.1	0.01	138	111	37.3	89.1
2	0	0	2.88 x 10 ⁴	5070	4.52 x 10 ⁴	1.16 x 10 ⁴

Since the run containing 0.1 M Na₂Cr₂O₇ showed such poor decontamination, it was suspected that dichromate was somehow causing trouble. A run using organic pretreated with dichromate followed by a carbonate and water wash, in the hope of removing some degradation product, failed to improve the results and gave decontamination factors almost identical to those obtained without this treatment. The possibility of a dichromate reaction with AMSCO was also investigated by using carbon tetrachloride as diluent; however, this gave slightly poorer results than comparable AMSCO experiments.

Extraction-scrub studies at full Hanford level activity were made at varying acidities with and without dichromate present. The beta and gamma results from these experiments are tabulated in Table X.

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Analytical results of fission products are incomplete, but the beta and gamma results seem to indicate a definite detrimental effect upon dichromate addition. Since oxidation of plutonium to the (VI) state is essential in acid deficient Purex, this detrimental effect of dichromate makes acid deficient conditions very unattractive. However, final judgment is to be deferred until complete analytical results are tabulated for troublesome fission products; and until some oxidation studies using ceric ion have been conducted.

Table X

EFFECT OF DICHROMATE AT VARYING ACIDITIES

(One Extraction and Three Scrubs)

Conditions: Feed - 0.8 M UNH
1.0 M $\text{Al}(\text{NO}_3)_3$
2/1 org/aq
Full Hanford Level
Fission Products

Scrubs: - 1.0 M $\text{Al}(\text{NO}_3)_3$, except where indicated.
 HNO_3 - Same as feed except where indicated.

<u>M HNO_3 in Feed</u>	<u>$\text{Na}_2\text{Cr}_2\text{O}_7$ Present*</u>	<u>Decontamination Factors</u>	
		<u>α</u>	<u>β</u>
-0.2	No	8.07×10^4	8.93×10^4
-0.2	Yes	1460	2.10×10^4
0	No	8.67×10^4	6.30×10^4
0	Yes	51.5	1470
0.3	No	2.70×10^3	2.65×10^4
0.3	Yes	48.1	30.4
2.4**	No	5.54×10^4	5.97×10^5
2.4**	Yes	12.6	4.65

* When present, 0.1 M $\text{Na}_2\text{Cr}_2\text{O}_7$ in feed and 0.01 M $\text{Na}_2\text{Cr}_2\text{O}_7$ in scrub.

** No $\text{Al}(\text{NO}_3)_3$ in feed or scrub; 3.0 M HNO_3 scrubs.

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C. ALTERNATE AQUEOUS MEDIA FOR SOLVENT EXTRACTION OF URANIUM AND PLUTONIUM
(W. W. Schulz)

The extractability of uranium from CF_3COOH and CCl_3COOH solutions into 30% TBP-AMSCO 125 has been determined. Trichloro and trifluoro acetic acid solutions containing uranium were prepared by dissolving UO_3 in the respective acids. These solutions were then contacted with an equal volume of 30% TBP-AMSCO 125. The results obtained are given in Table XI.

Table XI

EXTRACTION OF URANIUM FROM CCl_3COOH AND CF_3COOH SOLUTIONS
Equal Volume Contactings with 30% TBP-AMSCO 125

Acid	Initial U Conc., M	Initial Acid Conc., M:	E_a° U					
			0.5	1.0	2.0	3.0	5.0	7.0
Trichloro Acetic	0.20		7.66	6.53	1.23	0.563	--	--
Trichloro Acetic	0.50		--	6.14	1.26	0.604	--	--
Trifluoro Acetic	0.20		--	1.16	--	0.134	0.129	0.154
Trifluoro Acetic	0.50		--	1.41	--	0.171	0.173	0.216

As the results show, uranium is more extractable from CCl_3COOH than from CF_3COOH . The results also show that the extraction of uranium is greater at lower concentrations of CCl_3COOH and CF_3COOH . The E_a° values for uranium at 0.5 M CCl_3COOH appear promising.

The extractability of plutonium (IV) and plutonium (VI) from CCl_3COOH and CF_3COOH solutions into 30% TBP-AMSCO 125 was determined by spiking plutonium (IV) or plutonium (VI) from plutonium nitrate stock solutions into the desired CCl_3COOH or CF_3COOH solution and contacting five minutes with an equal volume of 30% TBP-AMSCO 125. The results for plutonium (IV) are listed in Table XII and those for plutonium (VI) in Table XIII.

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Table XII

EXTRACTION OF Pu (IV) FROM CCl_3COOH AND CF_3COOH SOLUTIONS
 Equal Volume Contactings with 30% TBP - AMSCO 125
 Aqueous Phase Initially 0.03 M HNO_3

<u>Initial Acid Conc., M</u>	<u>E_a° Pu (IV)</u>	
	<u>CCl_3COOH</u>	<u>CF_3COOH</u>
0.5	21	3.8
1.0	21	3.7
3.0	21	0.24
5.0	5.2	0.30
7.0	0.40	0.37
9.0	0.14	0.06

Table XIII

EXTRACTION OF Pu (VI) FROM CCl_3COOH AND CF_3COOH SOLUTIONS
 Equal Volume Contactings with 30% TBP-AMSCO 125
 Aqueous Phase Initially 0.03 M HNO_3 , 0.001 M $\text{Na}_2\text{Cr}_2\text{O}_7$

<u>Initial Acid Conc., M</u>	<u>E_a° Pu (VI)</u>	
	<u>CCl_3COOH</u>	<u>CF_3COOH</u>
0.5	4	0.52
1.0	4.2	0.11
3.0	0.67	0.15
5.0	0.47	0.29
7.0	0.091	0.11

As in the case with uranium, extraction of both plutonium (IV) and plutonium (VI) from either CCl_3COOH or CF_3COOH is greater at lower acid concentrations. Plutonium (IV) extracts better than plutonium (VI) from both CCl_3COOH and CF_3COOH and both plutonium (IV) and plutonium (VI) extract more readily from CCl_3COOH than from CF_3COOH . The E_a° value (ca. 20) for plutonium (IV) from 0.5 M CCl_3COOH is encouraging in view of the fact that uranium also extracts well at this CCl_3COOH concentration.

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D. ADSORPTION OF FISSION PRODUCTS FROM HEXONE SOLUTIONS (I. M. Rehn)

A. M. Gaudin, et al,⁽²⁾ have found that an adsorption technique similar to chromatography is very effective in removing impurities from an ether solution of uranium. Applying a similar technique involving passage of hexone solutions through an alumina bed (not activated) has proven to give promising decontamination of the fission products not eliminated by the Redox IA column.

Preliminary experiments with a simulated fission product-free Redox IAP indicated, as expected, that UNH and plutonium (VI) passed readily through an alumina bed whereas plutonium (IV) was adsorbed. Although some UNH was retained by the bed, equilibrium with respect to UNH was attained after passage of only a few bed volumes of IAP and that retained was readily removed by rinsing with a few bed volumes of hexone.

Subsequent experiments were conducted with simulated IAP containing fission product activity at ca. 20% and 100% Hanford level to determine gross and specific fission product decontamination factors and give some indication of the fission product capacity. In the first of these experiments, IAP resulting from one extraction and one scrub was prepared by contacting four ml of hexone with two ml of 20% Hanford level IAFS (0.8 M UNH, 20% from DS-19, i.e., dissolver solution from 7 month cooled U; 0.85 M $\text{Al}(\text{NO}_3)_3$; 0.2 M acid deficient). After extraction the hexone was scrubbed once with one ml of 0.85 M $\text{Al}(\text{NO}_3)_3$, 0.2 M acid deficient, this scrub having been pre-equilibrated with a fission product-free hexone phase containing uranium to prevent undue uranium loss to the scrub phase. The resultant active hexone was passed through a 1.2 cm³ alumina bed (5.8 cm x 0.2 cm²) at a flow rate of 1.0 ml per minute. Sixteen effluent samples were taken, the last three of which were collected after a 1.2 ml hexone rinse was added to the column. The analytical results are given in Table XIV.

(2) Gaudin, et al, Lyometallurgy: A New Method of Extracting Uranium from its Ores, Reactor Science and Technology, Vol. 1, No. 2, August 1951 (TID-72).

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Table XIV

DECONTAMINATION OF REDOX IAP (20% LEVEL) BY ALUMINA

Adsorption Bed: Chromatographic grade alumina,
not activated 5.8 cm x 0.2 cm².

IAP Feed Composition: ca. 150 g/l UNH
ca. 8000 d/m/ml Pu
2.33 x 10⁵ c/m/ml gross beta FP

Flow Rate: 1.0 ml IAP/min

Effluent Sample		Volume Ratio Total Effluent/Al ₂ O ₃ Bed	Effluent Composition		
No.	Vol., ml.		Gross β , c/m/ml	Pu, c/m/ml	UNH, g/l
1	0.15	0.13	<10	~0	<1
2	0.15	0.26	-	~0	<1
3	0.30	0.52	<10	-	<1
4	0.30	0.78	-	2300	<1
5	0.30	1.0	70	-	<1
6	0.15	1.2	-	-	<1
7	0.15	1.3	75	-	<1
8	0.15	1.4	-	2890	U appears
9	0.30	1.7	314 (84) ⁽¹⁾	-	U appears
10	0.30	1.9	-	-	150 g/l UNH
11	0.30	2.2	330 (90)	-	-
12	0.30	2.5	-	-	-
13 ⁽²⁾	0.30	2.7	280 (90)	-	-
14	0.30	3.0	-	2630	-
15	0.70	3.6	330 (100)	4590	-
16	0.40	3.9	200 (100)	3090	~50 g/l UNH

(1) Values in parentheses are corrected for UX₁ and UX₂ activity.

(2) Hexone rinse (1.2 ml containing 0.1 M HNO₃) added to column near end of Sample #13.

The plutonium concentration of the IAP was low because no oxidation was performed on the IAFS before extraction. After passage of enough IAP to bring the UNH and plutonium concentrations essentially to equilibrium, the beta activity content of the effluent was ca. 300 c/m/ml, a value which is reduced to ca. 90 c/m/ml, on correction for UX₁ and UX₂ activity which grew in before counting. Thus, a fission product decontamination factor of 250 was obtained under these conditions.

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The succeeding experiment was designed to give decontamination factors for full level activity and also some estimate of the capacity of the bed for fission products. Forty ml of hexone was contacted with 20 ml of IAFS (0.85 M UNH, 100% from DS-19; 1.3 M $\text{Al}(\text{NO}_3)_3$; 0.2 M acid deficient; 0.1 M $\text{Na}_2\text{Cr}_2\text{O}_7$; 0.065 g/l Pu) and then scrubbed once with 10 ml of 1.35 M $\text{Al}(\text{NO}_3)_3$, 0.2 M acid-deficient, which had been pre-equilibrated with a similar hexone solution of inactive uranium. The resulting IAP was then passed through a 0.03 cm³ alumina bed (1.0 cm x 0.03 cm²) at a flow rate of 0.3 ml per minute to a total throughput of 1080 bed volumes with the results given in Table XV. The high flow rate, apparently too high for attainment of equilibrium, was obtained by pressurizing the hexone.

As expected, the decontamination factor decreased with increasing passage of IAP, being ca. 60 for the first 65 bed volumes, ca. 40 for the cumulative 125-190 bed volumes fraction. After approximately 250 bed volumes had passed through the alumina column, the effluent activity rose to a value approximating that for the feed. This breakthrough was found due to cesium which was present in the IAP at an abnormally high concentration due presumably to the limited scrubbing in this experiment. Although decontamination factors were less promising than those observed at the 20% level, it is worth noting that the concentrations of several of the fission products particularly troublesome in solvent extraction, viz., Ce, Zr and Nb, were low in the effluent throughout the entire 1080 bed volumes. Future experiments will give attention to ruthenium behavior as well.

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Table XV

DECONTAMINATION OF REDOX IAP (FULL LEVEL) BY ALUMINA

Adsorption bed: Chromatographic grade alumina,
not activated 1.0 cm x 0.03 cm².

IAP feed composition: 320 g/l UNH
2.96 x 10⁵ c/m/ml gross beta FP

Flow rate: 0.3 ml IAP/min

Effluent Sample		Volume Ratio Total Effluent/Al ₂ O ₃ Bed	Effluent Composition		
No.	Vol., ml.		Gross β , c/m/ml	FP, c/m/ml	UNH, g/l
1	2.0	64	5500 (4800)	-	~320 ⁽¹⁾
2	2.0	127	8400 (7700)	-	-
3	7.0	191	8700 (8000)	-	-
4	2.02	255	150,000	Ce-55	323
5	2.0	318	335,000	Cs-323,000	-
6	2.0	382	303,000	-	-
7	2.0	446	254,000	Zr-5, Nb-5	-
8	2.0	519	276,000	Cs-165,000	-
9	2.0	573	388,000	-	-
10	2.0	637	340,000	Zr-12, Nb-25	-
11	2.0	700	299,000	Ce-160	-
12	2.0	764	294,000	-	-
13	2.0	828	284,000	Nb-0	-
14	2.0	892	118,000(3)	Zr-5 to 30	-
15	2.0	955	118,000(3)	-	-
16	2.0	1020	124,000(3)	Ce-65	-
17	2.0	1083	134,000(3)	-	320

(1) Column pretreated with uranyl nitrate in hexone.

(2) Values in parentheses are corrected for UX₁ and UX₂ activity.

(3) Values uncertain, possible counting error.

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E. DECONTAMINATION OF URANIUM SOLUTIONS FROM FISSION PRODUCTS BY ION-EXCHANGE METHODS (W. W. Schulz)

Experiments are in progress to investigate the application of ion-exchange techniques for the tail-end decontamination of uranium solutions from fission products. In the first experiments completed, uranium solutions were spiked with dissolver solution to simulate a Purex ICU composition (0.2 M U, 0.05 M HNO_3) and then passed through a bed of Dowex 50 cation exchanger. The effluent uranium stream was passed through a bed of Amberlite IRA 400 anion exchanger.

Incomplete results indicate a gross beta D. F. of ca. 7 for the effluent from the Dowex 50 exchange resin and no additional beta decontamination upon passage of the effluent through the anion exchange resin. A further experiment in which the feed stream contained only 0.05 M HNO_3 and a spike of dissolver solution gave beta D. F. of ca. 20 for the Dowex 50 exchanger and again, no appreciable further decontamination upon passage of the effluent through the Amberlite IRA 400 resin. Analyses have not yet been completed to determine the amount of uranium held up on the Dowex 50 resin, the specific fission products which are being adsorbed, or the volume of uranium solution which can be passed through the Dowex 50 column before break-through of activity occurs. The specific fission product adsorption data are of particular interest in order to estimate expected decontamination from an actual ICU solution where the fission product spectrum is changed from that used in this experiment since the ICU stream would have undergone some decontamination via solvent extraction.

IV. SOLVENT EXTRACTION MECHANISM (L. L. Burger and W. F. Johnson, Co-Problem Leaders)

A. PULSE COLUMN STUDIES (L. H. Clark)

In the last quarterly report (HW-22138) Purex IA runs at 28°C. and 57°C. were compared using a pulse column packed with 17 double-faced (stainless-fluorothene plates containing 0.026" diameter holes, an open area of 15.7% and spaced at one inch intervals.

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Considerable improvement in extraction efficiency was noted at the higher temperature. With the same column conditions, the effect of temperature on the stripping (Purex IC) operation has now been studied. Experimental data are listed in Table XVI. Waste losses of ca. 40 g/l of UNH at 26°C. were reduced to ca. 4 g/l when the column was operated at 52°C. It should be noted that the improvement in stripping is due not only to more favorable distribution into the aqueous phase but also to reduced stage heights at the elevated temperature. The increased ease of operation at the higher temperature was again noticed.

In Table XVII similar sets of data are compared except that the plates in the column were spaced two inches apart. Nine plates were used in the 17" section. As will be seen the extraction was ~~somewhat~~ poorer than found with 1" spacing. It was noted however that frequency and thruput could be varied more easily with the greater plate separation. With the two inch spacing a very noticeable improvement in extraction resulted when the frequency was increased.

The possibility of using flame-sprayed polythene on stainless steel plates was examined in an experiment in which plates flame sprayed on one side were alternated with double-faced plates. It was found that the polythene surface was not organic-wetted as is required for good coalescence but instead was preferentially wetted by the aqueous phase. Column thruput was rather low although fair uranium extraction was achieved.

More promising results were obtained by coating one side of the stainless plates with Kel-F dispersion. This gave a surface which was organic-wetted and appeared to be stable under column operation. These plates have been tested more extensively by Figg et al, p. 15.

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Table XVI

OPERATING DATA FOR VALVE-ACTUATED IC PUREX PULSE COLUMN

Condition B Purex ORNL #2 Flowsheet

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)		Mat.Bal(%)		ICW UNH(g/l)	HETS* (in)
				Org	Aq	Org-Aq	Aq-Org	Org	Aq	UNH	HNO ₃		
Operating Temperature = Room Temperature (26°C)													
VI-PC-1g	1.18	640	34.3	.13	.12	.71	.79	50	52	101	110	59.5	8.5
VI-PC-1L	1.22	241	28.7	.10	.12	1.05	.82	16	15	105	113	51.1	7.9
VI-PC-1e	1.47	457	28.4	.10	.12	1.07	.82	43	45	102	104	42.2	8.5
VI-PC-1d	1.49	468	30.3	.10	.12	1.05	.71	42	45	103	116	39.0	8.3
VI-PC-1c	1.58	528	38.7	.10	.12	.62	.71	40	41.5	99	109	29.0	8.1
VI-PC-1a	1.66	415	30.7	.10	.12	.92	.81	40	40	107	120	39.4	8.5
VI-PC-1b	1.80	407	30.7	.10	.12	.92	.81	40	40	112	121	31.8	8.5
VI-PC-1f	2.34	610	39.5	.10	.12	.48	.82	42	47	115	127	17.0	8.4
Operating Temperature = 52°C													
VII-PC-2g	1.37	701	47.6	.12	.23	.50	.41	17.5	33	110	111	4.49	2.3
VII-PC-2d	1.40	650	39	.12	.23	.66	.53	21.5	38.5	99	100	4.50	2.6
VII-PC-1c	1.41	364	27.4	.10	.25	1.05	.79	11	16.5	107	115	7.50	2.7
VII-PC-2a	1.41	586	41	.10	.25	.63	.48	17	27	101	98	3.75	2.5
VII-PC-2e	1.42	625	39	.12	.23	.66	.53	21	38.5	100	103	4.35	2.7
VII-PC-2b	1.47	437	35.1	.10	.21	.74	.66	19.5	35	101	96	1.00	2.5
VII-PC-2c	1.52	445	35.1	.10	.21	.74	.66	20	35	109	104	3.05	3.0
VII-PC-2f	1.53	724	47.6	.12	.23	.50	.41	17	34	110	105	2.51	3.0
VII-PC-2h	1.56	752	48.4	.12	.23	.48	.41	18	31	112	103	1.19	2.8
VII-PC-1f	1.57	405	43.8	.10	.19	.63	.45	29.5	24	108	98	.08	2.7
VII-PC-1e	1.62	386	43.8	.10	.19	.63	.45	10.5	19	102	109	1.93	3.5
VII-PC-1b	1.63	400	26.8	.10	.30	1.05	.79	10	16	104	132	5.8	4.0
VII-PC-1d	1.70	554	41.1	.10	.28	.63	.45	10	18	108	105	4.1	4.0

* HETS values are based on 25° equilibrium line. From calculations based on equilibrium data at 25°C and higher temperatures in studies on the Metal Recovery RC column, it is estimated that the HETS values reported here for the higher temperature runs might be increased about 50% if calculated on the basis of the higher temperature equilibrium line.

Table XVII

OPERATING DATA FOR VALVE-ACTUATED IC PUREX PULSE COLUMN

Condition B-2" Spacing Purex ORNL #2 Flowsheet

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)		Mat.Bal(%)		ICW UNH(g/l)	HETS* (in)
				Org	Aq	Org-Aq	Aq-Org	Org	Aq	Org	HNO ₃		
Operating Temperature = Room Temperature (26°C)													
IX-PC-1e	1.35	780	46	.10	.17	.74	.29	37	27	97.6	98	67.4	13.1
IX-PC-1j	1.42	570	40	.10	.12	.83	.45	23	15	94.5	78	53.0	10.0
IX-PC-1i	1.44	652	40	.10	.12	.83	.45	25	20	100	103	48.4	8.5
IX-PC-1L	1.45	750	52	.10	.12	.74	.20	17	18	95.5	61	58.8	11.3
IX-PC-1b	1.53	505	28	.10	.23	1.05	.79	35	22	93.5	87	52.4	11.0
IX-PC-1k	1.53	745	52	.10	.12	.74	.20	17	18	96.2	62	55.6	11.3
IX-PC-1f	1.56	765	46	.10	.17	.74	.29	35	28	107.8	113	67.0	13.7
IX-PC-1c	1.60	574	27	.10	.25	1.05	.79	34	21	104.5	101	52.2	10.5
IX-PC-1g	1.60	550	29	.10	.12	1.05	.82	30	25	104	100	41.1	8.4
IX-PC-1d	1.62	534	27	.10	.25	1.05	.79	34	21	104	101	60.3	13.0
IX-PC-1a	1.80	470	28	.10	.23	1.05	.79	33	21	104	100	60.7	14.9
Operating Temperature = 59°C													
X-PC-1b	1.44	640	27	.10	.25	1.05	.82	14	13	104	98	23.0	4.25
X-PC-1f	1.48	625	48	.10	.13	.74	.29	16	7	101	111	2.75	2.71
X-PC-1a	1.62	570	28	.10	.15	1.05	.82	18	14	110	105	26.5	6.6
X-PC-1c	1.65	750	39	.10	.14	.83	.45	16.5	11	100	99	15.0	5.3
X-PC-1e	1.68	740	39	.10	.14	.83	.45	16	11.5	106	112	5.75	4.25
X-PC-1d	1.69	710	39	.10	.14	.83	.45	17	11	99	92	7.52	4.45

* HETS values are based on 25° equilibrium line. From calculations based on equilibrium data at 25°C and higher temperatures in studies on the Metal Recovery RC column, it is estimated that the HETS values reported here for the higher temperature runs might be increased about 50% if calculated on the basis of the higher temperature equilibrium line.

B. SOLVENT STUDIES (B. R. Jones and R. M. Wagner)

The investigation of physical properties and extraction behavior of phosphates, phosphonates and phosphinates has been continued. A long chain phosphate, diethyl decylphosphate, has been synthesized as well as three new phosphonates. The physical properties are listed in Table XVIII and a comparison of uranium extraction behavior in Table XIX. The effect of the electronegative chlorine atoms in decreasing the solvent power is quite apparant. Diethyl hydrogen phosphonate showed no tendency to extract uranyl nitrate into a CCl_4 phase; the distribution of the phosphonate itself was not determined. That this compound was a true phosphonate and not a phosphite was shown by its infrared pattern.

The infrared pattern of about 25 phosphates and phosphonates have been obtained and a correlation of the P^+-O^- stretching frequency with extraction behavior is being examined as indicated in HW-22138. Present indications are:

- (1) The band maximum shifts from about 1270 cm^{-1} for phosphates to about 1255 cm^{-1} for phosphonates and 1160 cm^{-1} for phosphine oxides, in qualitative agreement with the extraction behavior.
- (2) Presence of electronegative groups such as chlorine shifts the band to higher frequencies indicating more double-bond, less ionic character.
- (3) There is little correlation within a class of compounds such as the phosphates, between P^+-O^- stretching frequency and extraction of uranyl nitrate.

These results will be compared in detail in a subsequent report.

Several silicones were examined as diluents for phosphate type esters. The heavy oils have been found to give a third liquid phase with uranyl nitrate solutions. Two lighter silicones with the properties indicated in Table XX were tested as diluents for tributyl phosphate. Extraction behavior appeared about normal but the silicones were unstable towards nitric acid and on prolonged contact began to polymerize.

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Table XVIII

PHYSICAL PROPERTIES OF SOLVENTS AT 25°C.

Compound	Index of Refraction n_D^{25}	Density g/cc	Boiling Point °C/mm	Viscosity Millipoise	Solubility in H_2O g/l
Diethyl-decyl- phosphate	1.4266	0.966	136/3	59	0.1
Diethyl-trichloro- methanephosphonate	1.4597	1.3622	83/1.5	62	--
Diethyl- benzoylphosphonate	1.50532	1.1558	130/1	99	--
Diethyl- hydrogen phosphonate	1.4060	1.0704	47/2	--	miscible

Table XIXEXTRACTION OF URANYL NITRATE BY 0.5 M ESTER IN CCl_4 AT 25°C.

Compound	HNO_3 , g/l		UNH , g/l		E_a U
	Org	Aq	Org	Aq	
Diethyl-decylphosphate	0	0	91.3	10.5	0.11
	0	0	91.9	11.9	0.13
	10.4	173	72.0	37.9	1.6
Diethyl- trichloro-methanephosphonate	0	0	0.12	89.3	.0013
	5.4	205	3.4	106	.033
Diethyl-benzeylphosphonate	0	0	1.2	93.0	0.013
	16.8	190	18.2	89.5	0.204
Diethyl- hydrogen phosphonate	No extraction of $UO_2(NO_3)_2$ into CCl_4 solution.				

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Table XX

PHYSICAL PROPERTIES OF SILICONES AT 25°C

Type and Structure	Index of Refraction n_D^{25}	Density g/cc	Flash Point °F	Viscosity Millipoise
M ₂ D ₂ -M ₂ D ₅ (linear)	1.3878	0.8541	172	13.5
D ₄ -D ₅ (cyclic)	1.3941	0.9493	157	21.9

The phosphinates, R⁰R¹R²P^OOR, should have somewhat stronger solvent properties than the phosphonates, being intermediate between the phosphine oxides and the phosphonates. The first of these compounds prepared, dibutyl-ethyl phosphinate, looks very attractive. It is a good solvent for uranyl nitrate and does not have the undesirable property of the phosphine oxides of being hygroscopic.

C. THERMODYNAMICS OF URANYL NITRATE SOLUTIONS (R. L. Dillon)

Studies have been made on the distribution at 25°C of UNH between an organic phase composed of 30% TBP by volume in an AMSCO 125-90W diluent and an aqueous phase containing Al(NO₃)₃, Ca(NO₃)₂ or NaNO₃ as salting agent. A series of aqueous solutions of varying salting strength was equilibrated with the same organic solution of uranyl nitrate and the concentration of the uranyl nitrate (U) in the aqueous phase determined. Plotting log (U) against the concentration of nitrate ion from the salting agent the following empirical relation was obtained:

$$\log (U) = \log (U_0) + \alpha(\text{NO}_3^-) \quad (1)$$

Where (U) is the molar concentration of uranium in the salted solution in equilibrium with a particular organic phase; (U₀) is the molar uranium concentration in the unsalted aqueous solution in equilibrium with the same organic phase; α is a function of (U₀); (NO₃⁻) is the molar nitrate ion concentration from the salting agent.

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Plotting $\log \phi$ vs $\log (U_0)$ gave the following expression:

$$\phi = - \frac{0.18}{(U_0)^{.90}} \quad (2)$$

Examples of these plots are presented in Figures 2 and 3.

From published values of molal activity coefficients⁽³⁾ and densities of pure aqueous uranyl nitrate solutions, molar activity coefficients can be obtained. Since the activities of uranyl nitrate in aqueous solutions in equilibrium with the same organic phase are assumed to be the same, by a simple extension of equation (1) the molar activity coefficients of uranyl nitrate in salted solutions may be calculated.

$$\log f_{\pm} = \log f_{\pm}^{\circ} - \frac{\phi}{3} (\text{NO}_3^-) \quad (3)$$

Where $f_{\pm}$ is the mean molar activity coefficient for uranyl nitrate in salted solutions, $f_{\pm}^{\circ}$ is the mean molar activity coefficient of unsalted uranyl nitrate solution in equilibrium with the same organic phase.

The applicability of expressions (1) and (2) was investigated over a concentration range 0.04 - 0.5 M in $\text{UO}_2(\text{NO}_3)_2$ and 0-4.8 M in nitrate ion concentration from the salting agent for each of the three salting agents. On the basis of present work the salting ability of non-extractable salting agents appears to be a function of nitrate ion concentration alone. It may be surmised that relations (1) and (2) are independent of the organic phase so long as a uranium compound is the only extractable species.

(3) Robinson and Lim, J. Chem. Soc. 1840 (1951).

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FIGURE 2

Aqueous solutions of $\text{UO}_2(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ in equilibrium with same organic phase of uranyl nitrate in 30% TBP-70% AMSCO 125-90W.

FIGURE 3

α as a function of U_{NH_4}

REF ID: A62555

V. RUTHENIUM CHEMISTRY (A. S. Wilson, Problem Leader, and J. L. Swanson)

Two techniques are being used to study the stability of Ru(IV) -nitrate complexes. The spectrophotometric method will employ J. Bjerrum's⁽⁴⁾ idea of corresponding solutions. Preliminary results as to the feasibility of this method are inconclusive because of the slowness of equilibration in these systems. The second method which is being used in these studies is the distribution of radio-ruthenium between an aqueous phase and organic phase in the presence of a chelating agent, TTA. Equipment is being set up to prepare tracer ruthenium in perchloric acid or nitric acid media. In the distribution studies it will be of interest to know the extent of formation of any aqueous soluble Ru(IV)-TTA complexes. Several experiments were conducted in which 50 ml of a solution, 8×10^{-5} M Ru(ClO₄)₄ and 2.6 M HClO₄ was equilibrated at room temperature with 50 ml of a benzene solution of TTA. In separate experiments the initial concentration of TTA in the benzene varied from 0.02 M to 0.3 M. The equilibration time was ten days after which time the aqueous phase was examined by means of a Cary recording spectrophotometer to detect any absorption peaks which might be related to an aqueous soluble Ru(IV)-TTA species. No peaks of this kind were detected in the range, 250 mμ to 800 mμ.

The rate of equilibration in Ru(IV)-Cl⁻ systems is slow. This rate can be increased 20 to 25 fold by the use of powdered activated decolorizing charcoal. The amount of charcoal used does not affect the position of the equilibrium nor does the charcoal remove more than 0.02% of the total ruthenium present in a solution of the following composition: 2.2×10^{-4} M Ru(IV), 1.15 M ClO₄⁻, 1.25 M Cl⁻ and 2.40 M H⁺ plus 36 mg charcoal. The rate of equilibration is increased by increasing the amount of charcoal. When charcoal is shaken with equilibrating Ru(IV)-NO₃⁻ solutions a change in the absorption spectrum of Ru(IV) is observed.

(4)

J. Bjerrum, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. 21, No. 4 (1944).

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The change has not been interpreted, but it appears likely that nitrites are formed, thus making unattractive the use of charcoal as a catalyst in the nitrate system.

VI. 234-5 PROCESS STUDIES (W. H. Reas, Problem Leader)

A. RESIN COLUMN COUPLING (W. H. Reas, P. M. Brown)

The feasibility of employing a Dowex 50 resin bed column for the concentration, purification, and decontamination of Hanford Works plutonium bearing streams is being investigated. Much of the development work for application of the resin column system to the Purex process has already been carried out at Oak Ridge (CF-51-10-131). The initial resin column experiments performed at this site have been carried out using solution compositions and flow rates recommended by Oak Ridge.

Two resin column runs have been made, however neither is satisfactory for making an accurate or reliable evaluation of the resin system. The data which have been collected are presented in Tables XXI and XXII. It should be noted that the plutonium feeds do not correspond to any current Hanford plutonium streams, nevertheless these experiments are useful in testing the apparatus and control system.

It can be seen from Table XXI that the plutonium concentration in Elution Cut #1 is ca. 50 g/l Pu while a concentration of ca. 90 g/l Pu was expected based on Oak Ridge results. Further, the plutonium waste loss is quite high while losses of less than 0.1% were expected. These results are probably due to three factors: 1) the iron present on the resin was not removed prior to the plutonium adsorption; 2) air was inadvertently admitted to the resin column and thereafter extensive channelling of the feed through the resin bed probably occurred; 3) the flow rates used were likely too high for efficient operation using resin of 40-60 mesh.

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Table XXI

RESIN COLUMN RUN #1

Dowex-50 resin: 40-60 mesh^(a); Packed section volume: 110 cm³;
 Column cross section: 3.9 cm²; Column length: 29 cm.
 Adsorption flow rate: 6.4 ml/min/cm²; Elution flow rate: 0.6 ml/min/cm²
 Plutonium feed composition: 1.365 g/l Pu, 0.3 M HNO₃, 0.3 M NH₂SO₃H,
 0.1 M (NH₄OH) · 1/2 H₂SO₄.
 Plutonium feed volume: 4.5 liters (6.149 g Pu total).
 Plutonium wash: 0.25 M H₂SO₄.
 Plutonium Elution Solution: 6 M HNO₃, 0.3 M NH₂SO₃H.

<u>Elution Cut No.</u>	<u>ml</u>	<u>Pu(g/l)</u>	<u>Pu(mg)</u>	<u>Pu(mg) Cumulative</u>
0	50	0.695	34.8	34.8
1	50	54.5	2725	2760
2	50	28.4	1420	4180
3	50	14.1	705	4885
4	50	9.63	481	5366
5	50	3.62	181	5547
6	50	2.26	113	5660
7	50	1.57	78.5	5738
8	50	1.11	55.5	5794
9	50	0.775	38.8	5833
10	50	0.585	29.3	5862
11	450	0.218	98.1	5960

Plutonium feed effluent waste: 121.0 mg (1.97%)
 Plutonium wash effluent waste: 27.9 mg (0.454%)
 Total plutonium recovered: 6109 mg (99.35%)

(a) The resin had not been washed with 6 M HCl to remove iron.

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The data of Run 2 (Table XXII) shows much lower plutonium waste losses even though one and one-half times as much plutonium was put through the column. The lower plutonium loss is probably a result of removing iron from the resin prior to the plutonium adsorption.

During the elution of plutonium from the resin with 6 M HNO_3 and 0.1 M $\text{NH}_2\text{SO}_3\text{H}$, gas formation became excessive and completely plugged the column. It seems reasonable, therefore, that the sulfamic acid concentration lower limit is ca. 0.3 M. The column volume was 155 cm^3 in this experiment as compared to 110 cm^3 in Run 1.

Table XXII

RESIN COLUMN RUN #2

Dowex-50 Resin: 40-60 mesh^(a); Packed section volume: 155 cm^3 ; Column cross section: 5.06 cm^2 ; Column length: 30.6 cm.
 Adsorption flow rate: 6.5 $\text{ml}/\text{cm}^2/\text{min}$; Elution flow rate: 0.6 $\text{ml}/\text{cm}^2/\text{min}$.
 Plutonium feed composition: 1.031 g/l Pu, 0.3 M HNO_3 , 0.3 M $\text{NH}_2\text{SO}_3\text{H}$, 0.1 M $(\text{NH}_2\text{OH}) \cdot 1/2 \text{H}_2\text{SO}_4$.
 Plutonium feed volume: 9.0 liters (9.3 gr Pu).
 Plutonium wash: 0.25 M H_2SO_4 .
 Plutonium elution solution: 6 M HNO_3 , 0.1 M $\text{NH}_2\text{SO}_3\text{H}$.
 Plutonium feed effluent waste: 9.88 mg (0.106%)
 Plutonium wash effluent waste: 0.476 mg (0.051%)

(a) The Dowex-50 had been washed repeatedly with 6 M HCl to remove iron from the resin.

Studies with actual or synthetic Hanford Works plutonium streams will be made as soon as a few preliminary equipment testing runs have been made.

B. ALTERNATE FLUORINATION AGENTS (W. E. Roake, R. C. Smith)

The use of gaseous hydrofluoric acid in 234-5 operations for converting Pu(III) oxalate to plutonium tetrafluoride leads to many corrosion problems.

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An investigation into the feasibility of replacing hydrofluoric acid with a less corrosive fluorinating agent such as Freon 12 has been initiated. Freons are chemically inert at room temperature but are quite active fluorinating agents at temperatures of 500°C. Freons 12, 22, 113, and 114 are being investigated with uranium trioxide and ceric oxide as plutonium "stand-ins".

The experimental data which has been collected using uranium and cerium as "stand-ins" are presented in Tables XXIII and XXIV.

A comparison of Tables XXIII and XXIV show that a substantial difference in the nature of the final fluoride is found with cerium and uranium "stand-ins". The cerium (III) fluoride is generally a fine powder which can be "poured" from the reaction boat while the uranium (IV) fluoride is usually quite badly caked. On the basis of the limited number of experiments performed Freon 12 seems to be the best fluorinating agent of the Freons studied.

It should be noted that the behavior of plutonium need not correspond to either that of uranium or cerium; nevertheless, the data do indicate to some extent the Freons which are likely to be of use in the fluorination of plutonium compounds. These data further suggest that the product of fluorination should be plutonium (III) fluoride.

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Table XXIII

FLUORINATION OF CERIC OXIDE WITH FREONS

Run	Pretreatment			Freon Used	Furnace Conditions		Product Characteristics (d)				Material Balance, %
	Time, hr	Temp, °C	Gas		Time, hr	Temp., °C	Color	Ce	F	Cl %	
CeO ₂ -1	1	400	O ₂	12	5	400	White	68.0	27.1	2.97	98.07
CeO ₂ -2	0.5	425	O ₂	12	3.6	400	White	75.4	23.1	1.1	99.7
	1.0	425	A								
CeO ₂ -3	1.5	400	O ₂	12	1	400	White	76.1	24.0	0.8	100.9
CeO ₂ -4	1	400	A	114	0.5	700	White	--	--	--	--
	0.67	500	A								
CeO ₂ -5	1	400	A	60% 114 40% O ₂	0.3	700	White	--	--	--	--
	0.6	500	A								
CeO ₂ -6	0.67	500	A	113 (a)	2.5	500	No Reaction	--	--	--	--
					0.5	700	White (b)	--	--	--	--
CeO ₂ -7	0.5	500	A	113 (a)	0.5	700	White (b)	--	--	--	--
CeO ₂ -8	--	200	A	22	ca. 2	ca. 400	Black (c)	--	--	--	--

(a) Argon Saturated with Freon 113 at room temperature.

(b) Slight tendency to cake.

(c) Black color most likely due to free carbon. Some tetrafluoroethylene polymer (white in color) also formed.

(d) All products were free flowing powders.

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Table XXIV

FLUORINATION OF URANIUM TRIOXIDE WITH FREONS

Run	Time, hr	Temp, °C	Gas	Freon Used	Furnace Conditions		Product Characteristics ^(b)				Material Balance, %
					Time, hr	Temp, °C.	Color	U	F	Cl	%
UO ₃ -2	0.67	400	A	12	4.5 2.0	400 500	Dark Green to Black	--	--	--	--
UO ₃ -3	1	475	A	12	5	470	Dark Green & Black	--	--	--	--
	0.75	475	O ₂	12	4	450	Dark Green	80.0	15.6	1.83	--
UO ₃ -4	1.5 0.5	400 400	O ₂ A	12	4.67	400	Dark Green	73.0	13.1	3.1	89.2
UO ₃ -5	3.5	400	A	12	3.75	400	Dark Green	78.5	18.6	1.9	99.16
UO ₃ -6	1.5	400	A	12	1	400	Bright Green	76.9	9.35	4.2	90.5
UO ₃ -7,8, 9,10	1	500	A	114 60% 114 40% O ₂	--	700	Black	--	--	--	--
							Black	--	--	--	--
UO ₃ -11	1	500	A	113 ^(a)	20-30 min	720	Black	--	--	--	--
UO ₃ -12,13	0.5	500	A	113 ^(a)	1	720	Black	--	--	--	--

(a) Air saturated with Freon 113 at Room Temperature.

(b) All products were badly caked.

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VII. WASTE TREATMENT STUDIES (R. E. Burns, Problem Leader)

A. EVOLUTION OF HEAT FROM FISSION PRODUCT DECAY IN PROCESS WASTES(J. S. Kane)

To supplement material previously published concerning heat evolution by decay of radioactive nuclides^(5,6,7), curves showing total curies and heat evolution as a function of cooling time for uranium irradiated for a total of 600 megawatt days per ton have been derived by calculation. With the aid of these data, other curves showing heat evolution in Redox aqueous waste storage tanks during and following filling have been constructed assuming different production rates and modes of operating the plant. The objective was to determine under what conditions, if any, quantities of heat sufficient to evaporate significant amounts of water from the tanks will be generated by radioactive decay within the tanks.

In calculating the amount of water which may be evaporated by a tank of waste, consideration was given to the loss of heat from the tanks to the surrounding soil. This quantity is not accurately known. R. E. Tomlinson states a value of 250,000 Btu. per hour as the heat lost from a 500,000 gallon tank containing Bismuth Phosphate Process Metal Waste at near its boiling point⁽⁸⁾. That value was obtained by relating calculated heat evolution to tank temperature for certain Metal Waste tanks whose contents have approached boiling. For the present study, 300,000 Btu. per hour was taken as a reasonable heat loss to the ground for a 750,000 gallon tank of Redox waste at its boiling point. Total heat available for evaporating water was considered to be that in excess of 300,000 Btu. per hour from the time the tank is filled until the heat evolution within the tank has decreased to 300,000 Btu. per hour.

(5) J. L. Schwennesen, Calculations of Expected Heat Evolution and Radiation Intensity in Redox Waste Storage Tanks, HW-14388, September 8, 1949.

(6) H. J. Kamack, Fission Product Activities in Irradiated Uranium Cooled for Long Periods, (H)CN-S-3475, January 4, 1946.

(7) Hanford Engineer Works Technical Manual, Section C, May 1, 1944.

(8) R. E. Tomlinson, Purex Process Evaluation, HW-22888, December 10, 1951.

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The calculations show that Redox wastes will generate sufficient heat to evaporate significant amounts of water from the waste tanks. The total quantity of heat available for evaporation of water will be a function of the MWD/T irradiation of the uranium processed, the power level at which it is irradiated, the rate at which it is processed, and the mode of operation of the plant (number of uranium and plutonium cycles). For the most favorable case considered it was calculated that available heat from a 750,000 gallon tank of waste would evaporate 360,000 gallons of water; while for the least favorable case considered, 150,000 gallons of water would be evaporated. Similar considerations, by R. E. Tomlinson⁽⁸⁾ of expected heat generation in Purex Process waste tanks indicate that a peak heat evolution rate more than twice that calculated here for Redox wastes will be reached, with a consequent longer period for generation of "available" heat. Thus, the prospect of evaporating water from Purex waste tanks is even more promising than for Redox wastes.

The availability of heat within the tanks in amounts sufficient to evaporate appreciable quantities of water is of no value unless it is possible to concentrate the stored wastes by a significant factor before they solidify. Preliminary experiments with simulated stored wastes showed that, when the wastes are concentrated by a factor of two, solids begin to form when the concentrated solution is cooled to about 60°C. and that at room temperature, the slurry contains about 50% solids. When concentrated by a factor of 2.5, the freezing point is about 100°C. and at room temperature the slurry contains about 65% solids. Thus, considerable concentration of the stored wastes is possible. If the water evaporated by heating within the tanks could be removed and disposed of by cribbing instead of being returned to the tanks by reflux as is now planned, considerable saving in storage space could be effected.

(8) R. E. Tomlinson, Purex Process Evaluation, HW-22888, December 10, 1951.

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The decontamination factor which may be obtained by evaporation within the tanks is not known. However, because of the low vapor velocities involved, decontamination factors of 10^4 or greater should be realized. Although such distillates might well contain more activity than is desirable in cribbed solution, they would be low in salt content and further decontamination by an ion exchange procedure should be economical.

Complete details of these studies may be found in a report, HW-23477, to be issued shortly.

B. ION EXCHANGE DECONTAMINATION OF REDOX DISTILLATES (C. R. McMullen)

The various concentrators in the Redox plant will produce large volumes of distillates all of which will be combined, stripped of hexone and reevaporated. The condensate from this second evaporation will be discharged to the ground through cribs and the still bottoms will be returned to the waste concentrator. A Redox plant operating three uranium and three plutonium cycles will produce about 5,000 gallons of concentrator distillates (after hexone stripping) containing about 50 and 10 curies of beta and gamma activities, respectively, per ton of uranium processed, (HW-18700, Figure X-5). Further decontamination by a factor of about 400 is expected in the second stage of evaporation.

Because of the low salt content of the concentrator distillates and of the relatively small decontamination factor required to produce a solution which can be cribbed it is possible that the second stage of evaporation could be replaced, to an economic advantage, by an ion exchange process. Studies of ion exchange decontamination of the concentrator distillates are in progress.

Gross salt composition of a solution simulating the combined concentrator distillates was obtained by calculations based on the salt content of the streams concentrated and the deentrainment factors quoted for the various concentrators.

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Composition of this solution is shown in Table XXV. In practice, a relatively concentrated stock solution containing the chemicals in the proportions shown in Table XXV was prepared and diluted to volume for use as feed to ion exchange columns.

As previously stated, it is estimated that the combined concentrator distillates will contain about 2.5 microcuries of beta and 0.5 microcuries of gamma activities per ml. To simulate these activities, the feed solution used was spiked with dissolver solution to a beta activity of about 3×10^5 counts per minute per ml. (7.5% Geometry), corresponding to 1.8 microcuries per ml.

Table XXV

COMPOSITION OF SIMULATED COMBINED
REDOX CONCENTRATOR DISTILLATES

<u>Chemical</u>	<u>mg/l</u>	<u>M</u>
$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	19	5×10^{-5}
HNO_3	2	3.2×10^{-5}
NaNO_3	1	1.2×10^{-5}
$\text{Na}_2\text{Cr}_2\text{O}_7$	0.2	7×10^{-7}
$\text{Fe}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$	0.3	9×10^{-7}
$\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	0.07	1.7×10^{-7}
NH_4HSO_4	0.2	1.7×10^{-6}
UNH*	130.	2.6×10^{-5}

* Relatively high because much of the combined distillate results from concentration of uranium streams. Deentrainment factors quoted for these uranium stream concentrators are relatively low.

The feed solution so prepared was passed through a hydrogenform Dowex-50 resin bed (57 cm. x 0.28 cm^2 , > 40 < 60 mesh) at a flow rate of 1.5 ml. per minute.

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Gross beta activity in the effluent rose immediately to 15,000 counts per minute per ml. and has remained at about that value since the column was started. To date about 1,260 column volumes of the feed have been passed through the bed without further breakthrough of activity.

Analysis of the effluent from the column showed that the activity present was principally ruthenium. The effluent was passed through a bed of hydroxyl-form IRA-400 resin (20 cm. x 0.8 cm², as received) at a flow rate of 2.5 ml. per minute. Effluent from this column averaged about 150 counts per minute per ml. for 810 column volumes after which break through of activity occurred. Thus, a decontamination factor of about 20 was obtained in the cation exchanger (Dowex-50) and an additional beta decontamination factor of about 100 was obtained in the anion exchanger (IRA-400) giving an overall decontamination factor for the two columns in series of about 2000. This is larger by a factor of five than the decontamination factor expected in the second stage of evaporation in the Redox plant.

The pH of the above feed solution as prepared was 4.5. To determine the effect of pH on decontamination by and the capacity of these ion exchangers, the above experiment was repeated, using as feed the simulated concentrator distillate previously described adjusted to a pH of 2 with nitric acid. Beta activity in the effluents from the two columns was about the same as with the high pH feed, decontamination factors of 20 and 100 being obtained over the Dowex-50 and IRA-400 columns, respectively. To date, 440 column volumes of feed have been passed through the Dowex-50 column without further increase in effluent activity. However, a sharp increase in effluent activity occurred in the IRA-400 column when only 140 column volumes of effluent from the Dowex-50 column had been passed through it. The results of these runs are summarized in Table XXVI.

Regeneration of the IRA-400 column used in Run A was attempted with NaOH and NaNO₃ as regenerants. Table XXVII shows the results obtained. No explanation is apparent for the increase in activity removed after each change in regenerant.

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Table XXVI

DECONTAMINATION OF REDOX CONCENTRATOR DISTILLATES BY ION EXCHANGE

	Resin	Feed	Effluent β Activity, c/m/ml	β DF	Break Through Point	
					Column Vols.	Tons U (2) Processed per ft ³ resin
Run 1	Dowex-50 >40 <60 mesh	Simulated Distillates pH 4.5(1)	~ 15,000	~ 20	>1260	>1.9
Run 1A	IRA-400 As received	Effluent from Run 1	~ 150	~ 100	810	1.2
Run 2	Dowex-50 >40 <60 mesh	Simulated Distillates pH 2(1)	~ 15,000	~ 20	> 440	> 0.66
Run 2A	IRA-400 As received	Effluent from Run 2	~ 150	~ 100	140	0.21

(1) Contained ca. 300,000 c/m/ml activity.

(2) Assuming 5000 gallons of combined distillates per ton of uranium processed.

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Total activity removed represents about 60% of the activity calculated to have been on the column. The first 200 ml of 4 M NaOH used removed about 40% of the activity present. Following the regeneration, effluent from the Dowex-50 Run A column was again passed through the IRA-400 column. Again, a gross beta decontamination factor of about 100 was obtained. However, breakthrough of activity occurred when about 100 column volumes of effluent had passed through the column as compared to 140 column volumes in the first pass.

Since regeneration of the anion exchange column was not completely successful, attention is being given to adsorbents for ruthenium sufficiently inexpensive to discard without regeneration. Some of the effluent from the Dowex-50 Run 2A column was passed through a column (dimensions similar to the resin columns used), containing 6.9 grams of steel wool (American Steel Wool Mfg. Co., Grade No. 2) at a flow rate of 2.5 ml per minute. A beta decontamination factor of only five was obtained. Other adsorbents such as charcoal, stainless steel, and clays will be considered.

Table XXVII

REGENERATION OF IRA-400 COLUMN (RUN 2A)

<u>Fraction*</u>	<u>Eluate</u>	<u>Effluent c/m/ml</u>
1	4 M NaOH	84,000
2	4 M NaOH	43,000
3	H ₂ O	3,200
4	H ₂ O	320
5	4 M NaNO ₃	28,000
6	4 M NaNO ₃	3,500
7	H ₂ O	490
8	H ₂ O	270
9	4 M NaOH	7,600
10	4 M NaOH	1,300
11	2 M NaOH	5,400
12	2 M NaOH	2,500
13	H ₂ O	12
14	H ₂ O	10

* Each fraction volume 100 ml.

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C. DECONTAMINATION OF BISMUTH PHOSPHATE PROCESS SECOND CYCLE WASTE
(H. S. Gile)

Activities for this report period have included studies of several carriers as general scavenging agents for Second Cycle wastes and of the effectiveness of copper sulfide as a scavenging agent for ruthenium in these wastes. Table XXVIII shows gross beta decontamination factors obtained by adding various carriers to acidic Second Cycle waste, adjusting to the specified pH, digesting, and separating the resulting solids by centrifugation. Since Second Cycle waste contains an appreciable fraction of short-lived activities, the fission product spectrum of any particular sample of the waste will vary considerably with time. One must, then, either obtain one large sample to use throughout the studies and recognize that, due to radioactive decay, it becomes less representative of the actual wastes as time increases or obtain successive small samples in order to have, always, material closely resembling actual solutions as processed. In these studies, the latter course was followed. As obtained, samples of the acidic wastes involve two different solutions which are mixed in the laboratory in the proper proportions to represent the total waste. Since there is some variation from sample to sample, it is, for comparison purposes, necessary to know what combination of waste samples was used for any particular experiment. The first column in Table XXVIII was included to aid in comparing experiments.

Some decontamination is obtained on neutralization of the wastes without added carriers due to the alkaline insoluble constituents present (iron, bismuth and chromium). Consequently, what is sought in these studies is an improvement in decontamination, over and above that currently obtained by neutralization by the addition of carriers and by variations in the procedure for precipitating these carriers. Entered first in Table XXVIII is a series of experiments in which various waste sample combinations were neutralized without addition of carriers.

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These may be used to evaluate the results of the remainder of the experiments in which carriers were added. None of the carriers tried gave a large improvement in gross beta decontamination. Copper and calcium produced the best improvement in decontamination. To obtain the maximum benefit from the addition of copper or calcium it was necessary to digest the slurry at an elevated temperature. The use of a combination of copper and calcium gave little better decontamination than the addition of copper alone. Maximum decontamination improvement with copper added was obtained when the slurry was digested at a pH of about 7.

Beta decontamination under the conditions of the experiments shown in Table XXVIII was, in general, limited by the failure to carry ruthenium. Means of removing ruthenium from Second Cycle wastes were, accordingly, sought. Benwell, Lever, and Powell⁽⁹⁾ have found copper sulfide to be a very effective carrier for ruthenium. A series of experiments was performed to determine the effectiveness of copper sulfide in removing ruthenium from Second Cycle wastes. Copper sulfate was added to the acidic waste, the pH was adjusted with sodium hydroxide, and hydrogen sulfide was bubbled through the solution for a given time. Ruthenium decontamination obtained in a series of these experiments is shown in Table XXIX. Adjustment of the pH of the wastes to two or three prior to hydrogen sulfide addition was necessary to obtain effective carrying of ruthenium. Ruthenium decontamination increased somewhat with increased contact with the sulfide, particularly at elevated temperature. Bismuth, present in the waste is precipitated as the sulfide under the experimental conditions and is, itself, a fairly effective ruthenium carrier. However, ruthenium carrying was improved considerably by the presence of copper.

(9) Benwell, N. R. W., Lever, F. M., Powell, A. R., Chemistry of Ruthenium in Nitric Acid Solutions, AERE-X/R-499, (1) February 1950, (2) June 1950.

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Since the sulfide precipitation carried ruthenium very well, combinations of copper sulfide followed by calcium phosphate scavenging of the wastes was tried with the view that calcium phosphate would carry other activities such as rare earths and strontium. Results of these experiments are also shown in Table XXIX. After the precipitation of sulfides at low pH, the solutions were neutralized to pH 7 and digested to remove calcium as phosphate. Solid-liquid separation was by centrifugation. Gross beta decontamination factors of about 2,000 as obtained in these experiments represent a decontamination improvement factor of about 15 over that obtained on neutralization of the same waste combination with no added carriers and digestion at room temperature (see Table XXVIII). The supernatant obtained in these experiments contained about three microcuries of beta activity per liter. The two attempts made to add the sulfide as sodium sulfide instead of hydrogen sulfide gave such varied results that it is impossible to say at this time whether or not sulfide addition in this fashion is practical. Preliminary settling studies indicate that the volume of the settled sludge is less when the waste is treated as indicated in the latter experiments in Table XXIX than when neutralized to pH 7 without added carriers or sulfide precipitation.

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Table XXVIII

DECONTAMINATION OF SECOND CYCLE WASTE BY VARIOUS SCAVENGING AGENTS

Waste (1) Combination Used	Carriers Added		pH	Digestion		Gross Beta DF
	Ion	M		Time, hrs.	Temp., °C.	
A	--	--	5.6	1	R.T.	61
A	--	--	8	1	R.T.	23
A	--	--	10	0.5	R.T.	17
A	--	--	10	1	80	101
B	--	--	12	2	80	520
B	--	--	12	2	R.T.	300
C	--	--	5.6	2	80	326
C	--	--	8.6	2	80	350
C	--	--	10	2	80	202
D	--	--	8.6	2	R.T.	130
C	Fe ⁺⁺⁺	0.005	8	2	R.T.	320
C	Fe ⁺⁺⁺	0.028	8	2	R.T.	400
C	Ni ⁺⁺	0.028	8	2	R.T.	350
C	Zn ⁺⁺	0.005	8	2	R.T.	350
C	Zn ⁺⁺	0.028	8	2	R.T.	310
C	Fe(CN) ₆ ⁻⁴	0.01	7	2	R.T.	200
C	Ca ⁺⁺	0.01	8.6	2	R.T.	250
C	Ca ⁺⁺	0.01	8.6	2	80	480
C	Cu ⁺⁺	0.024	5	2	R.T.	350
C	Cu ⁺⁺	0.024	6	2	R.T.	520
C	Cu ⁺⁺	0.0024	7	2	R.T.	108
B	Cu ⁺⁺	0.024	7	2	R.T.	1150
B	Cu ⁺⁺	0.024	7	2	80	1400

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Table XXVIII (Cont'd)

Waste (1) Combination Used	Carriers Added		pH	Digestion		Gross Beta DF
	Ion	M		Time, hrs.	Temp., °C.	
B	Cu ⁺⁺	0.024	8	2	80	2400
B	Cu ⁺⁺	0.024	10	2	R.T.	710
B	Cu ⁺⁺	0.024	10	2	R.T.	330
B	Cu ⁺⁺	0.024	10	2	80	450
B	Cu ⁺⁺	0.024	12	2	R.T.	320
C	Cu ⁺⁺	0.028	--	--	--	--
	Ca ⁺⁺	0.028	7	2	R.T.	790
C	Cu ⁺⁺	0.028	--	--	--	--
	Ca ⁺⁺	0.028	7	2	80	930
C	Cu ⁺⁺	0.028	--	--	--	--
	Ca ⁺⁺	0.028	7	2	R.T.	720
C	Cu ⁺⁺	0.024	7	2	R.T.	570
C	Cu ⁺⁺	0.028	7	0.25	R.T.	700
				1.25	R.T.	720
				3.25	R.T.	750
				5.25	R.T.	820
				7	R.T.	880

(1) Refers to particular waste samples used and is included here for comparison purposes.

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Table XXIX

RUTHENIUM AND GROSS BETA REMOVAL FROM SECOND CYCLE WASTE BY PRECIPITATION OF COPPER SULFIDE

Waste Combination Used	Carriers Added	M	Addition of H ₂ S			Digestion at pH 7		Decontamination Factors	
			pH	Temp., °C	Time, hrs	Time, hrs	Temp., °C.	Gross β	Ru
B	--	--	<0	R.T.	0.5	--	--	6	1.8
B	Cu ⁺⁺	0.024	<0	R.T.	0.5	--	--	6	34
D	Cu ⁺⁺	0.024	2	R.T.	1	--	--	--	130
				R.T.	2	--	--	--	200
				R.T.	4	--	--	--	160
				R.T.	6.5	--	--	--	260
D	Cu ⁺⁺	0.024	2	80	1	--	--	--	70
				80	2	--	--	--	220
				80	4	--	--	--	400
				80	6.5	--	--	--	730
D	Cu ⁺⁺	0.024	2	80	6.5	--	--	--	150
D	Cu ⁺⁺ Ca ⁺⁺	0.028 0.028	3	R.T.	0.5	2	80	1800	--
D	Cu ⁺⁺ Ca ⁺⁺	0.028 0.028	3	R.T.	0.5	2	80	1600	50
D	Cu ⁺⁺ Ca ⁺⁺	0.028 0.028	2	R.T.	0.5	2	80	2300	700
D*	Cu ⁺⁺ Ca ⁺⁺	0.028 0.028	2	R.T.	0.5	2	80	1300	700
D*	Cu ⁺⁺ Ca ⁺⁺	0.028 0.028	2	R.T.	2	2	80	810	8

* A solution of sodium sulfide was added instead of bubbling hydrogen sulfide through the waste solution.

D. REMOVAL OF ACTIVITY FROM URANIUM RECOVERY PROCESS AQUEOUS WASTES

(C. H. Holm)

In the recovery of uranium from Bismuth Phosphate Process Metal Wastes, large volumes of aqueous wastes will be produced which will, because of its radioactive content, have to be stored. Mound Laboratory has expended considerable research effort on means of decontaminating these wastes sufficiently to permit their discharge to ground⁽¹⁰⁾. These studies have resulted in a procedure which will achieve the necessary 10^4 to 10^5 gross beta and gamma decontamination factors necessary to produce a supernatant comparable in radioactive content to wastes currently cribbed at Hanford. However, the procedure is relatively costly and would require considerable equipment. Consideration is being given to other means of decontaminating these wastes.

The raffinate from the RA column, the RAW waste, will be about 2.4 M in NaNO_3 , 1.7 M in HNO_3 , 0.16 M in H_3PO_4 and 0.16 M in H_2SO_4 , and will contain small amounts of ferrous iron and sulfamic acid. The fission product spectrum in the wastes will, because of ageing, be somewhat simpler than that of currently processed material. In the two-year-old wastes, about 65% of the beta and gamma activity is due to rare earths (Ce^{144} and Pm^{147}), 18.5% to Sr^{90} and its short-lived daughter Y^{90} , 8.5% to Cs^{137} and 4% to Ru^{106} . The remaining few per cent is due to Sr, Zr, Nd, Ru, Sn, Sb, Te, Sm, and Eu isotopes. Total activity in two-year-old wastes will be about 0.5 and 0.2 curies per liter of beta and gamma activity, respectively. Since wastes containing about 10 microcuries of beta activity per liter are currently being cribbed at Hanford a decontamination factor of approximately 10^5 would be required to produce a cribbable supernatant from RAW.

(10) Liquid Waste Disposal Research Reports
MLM-515, August 21, to November 13, 1950.
MLM-554, November 13, 1950 to March 5, 1951.
MLM-579, March 5, 1951 to June 4, 1951.
MLM-614, June 4, 1951 to September 3, 1951.

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Table XXX

DECONTAMINATION OF SIMULATED RAW BY VARIOUS SCAVENGERS

<u>Expt.</u>	<u>Carriers Added, M</u>	<u>pH</u>	<u>βDF</u>
2	0.01 M Cu^{++}	8	6
3	0.01 M Ca^{++} 0.01 M Cu^{++}	9.1	5
4	0.01 M La^{+++}	8.0	9
5	0.01 M Zr^{+4} , Cu^{++} , $\text{SiF}_6 =$, Sn^{++} , Pb^{++} , Bi^{+++} , La^{+++} , Ca^{++}	10	8
6	0.01 M Cu^{++} , La^{+++} , Sn^{++} , 0.03 M $\text{Fe}(\text{CN})_6^{-4}$	1	3
		2	7
		3	5
		4.8	25
		7	60
		10	8
7	0.01 M Cu^{++} , La^{+++} , 0.03 M $\text{Fe}(\text{CN})_6^{-4}$	11.8	6
		4.6	36
		6.0	60
		6.5	90
		7.0	92
		7.5	94
8	0.01 M Cu^{++} , 0.01 M La^{+++} Unk. Amt. Dipicrylamine	8.5	76
		9.5	16
		5	5.7
9	0.01 M Cu^{++} , 0.03 M $\text{Fe}(\text{CN})_6^{-4}$	7	4.8
		9	51
10	0.01 M La^{+++} , 0.03 M $\text{Fe}(\text{CN})_6^{-4}$	7	37
11	Hg^{++} , I^-	7	43
		1	1
		3	3
		5	4
		7	6
		9.5	4
		11.5	7

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Neutralization of the waste precipitates first ferric phosphate and, at higher pH, ferric hydroxide. Samples of simulated, acidic RAW spiked with fission product activities from five-year-old metal waste were brought to various pH values, stirred at the given pH for a few minutes and centrifuged to separate the solid and liquid phases. Gross beta decontamination factors of about seven were obtained in the pH range from six to twelve. At a pH below six the beta decontamination dropped significantly. At best the decontamination obtainable by neutralization is probably limited by the presence of cesium activity since cesium is not known to carry on ferric phosphate or hydroxide.

In Table XXV the results of a series of exploratory experiments are presented in which a number of carriers known to be effective for certain fission products were tried on spiked, simulated RAW. In general the gross beta decontamination is in the same range as when the waste is neutralized without added carriers. However, in those cases where ferrocyanide was added with consequent precipitation of one or more of the "iron blues" gross beta decontamination was markedly improved. Since iron ferrocyanides are known to carry cesium, the improved decontamination when ferrocyanide was added is probably due to cesium removal.

The scavenging of strontium from solution (distilled water spiked with Oak Ridge radioactive strontium) by various carriers including aluminum hydroxide, calcium sulfate, calcium phosphate, ferric hydroxide, calcium hydroxide, and calcium oxalate was studied. Of these, ferric phosphate and hydroxide and calcium oxalate gave the best decontamination. In a more detailed study of ferric iron and phosphate as a carrier for strontium it was found that the carrying was pH sensitive, decontamination factors increasing from six at pH 4.3 to a maximum of 94 at pH 8.5 and decreasing to 12 at pH 10 when 0.01 M Fe^{+++} was precipitated with 0.3 M phosphate. Decontamination at the optimum pH (8.5) showed little increase with contact time, the decontamination factors ranging from 83 at eight minutes to 94 at five hours.

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Digestion at elevated temperature increased the carrying somewhat; decontamination factors of about 130 being obtained when a solution containing 0.01 M Fe^{+++} , 0.3 M H_3PO_4 and spiked with Sr^{90} activity was brought to pH 7 and digested at 80°C. No significant change in decontamination was observed as digestion time, at the elevated temperature, was increased from two minutes to five hours. Decontamination at room temperature was adversely affected by an increase of either sodium nitrate or sodium sulfate concentration, being decreased by 60% as the salt concentration was increased from 0 to 5 M NaNO_3 or from 0 to 0.5 M Na_2SO_4 .

Similar studies on the carrying of strontium by calcium oxalate showed the optimum pH to be about 10, a decontamination factor of 450 being obtained when a solution containing 0.01 M $\text{Ca}(\text{NO}_3)_2$, 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ and Sr^{90} was brought to pH 10 and stirred 15 minutes at room temperature. Relatively good carrying (DF's ca. 300) was obtained under these conditions over a pH range from 4 to 10 but carrying decreased at higher pH. Digestion at elevated temperature decreased the carrying markedly. Under conditions for optimum carrying at room temperature, but with the solution digested at 80°C. following pH adjustment, strontium decontamination factors varied from 20 to 26 as digestion time was increased from five minutes to three hours. As with ferric iron and phosphate, carrying of strontium by calcium oxalate decreased with increased sodium nitrate and sodium sulfate concentration. When precipitating 0.01 M Ca^{++} at pH about 10 with 15 minutes contact time at room temperature, strontium decontamination factors decreased from 450 to 16 as the salt concentration was increased from 0 to 5 M NaNO_3 and from 450 to 6 as the salt concentration was increased from 0 to 0.7 M Na_2SO_4 . The fact that the carrying of strontium by calcium oxalate and by ferric phosphate decreases as the gross salt content of the solution increases indicates that the strontium is not carried by these solids as a colloid.

When simulated RAW containing only Sr^{90} activity was brought to pH 8.4 and the resulting solid (FePO_4) removed by centrifugation a decontamination factor of 60 was obtained.

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The decontamination factor was increased to about 150 when the Sr-spiked, simulated RAW was made 0.01 M in $\text{Ca}(\text{NO}_3)_2$ and 0.05 M in $\text{H}_2\text{C}_2\text{O}_4$ before raising the pH to 8.6. These results bear out qualitatively the above observation that calcium oxalate is a more effective carrier for strontium than ferric phosphate in solutions similar to RAW.

VIII. DOCUMENTED REPORTS ISSUED DURING QUARTER, OCTOBER, NOVEMBER, DECEMBER, 1951

<u>Document No.</u>	<u>Date of Document</u>	<u>Author(s)</u>	
HW-22138	10-1-51	O. F. Hill, F. J. Leitz	Quarterly Report - July through September
HW-22425	10-5-51	W. S. Figg	Trip Report - ANL, Sept. 17-18; KAPL, Sept. 19; and BNL, Sept. 20-21, 1951
HW-22434	10-15-51	W. H. Reas, P. M. Brown	Report of Invention - 234-5 Operations - The Replacement of Hydriodic Acid by Hydrogen Peroxide or Other Reducing Agents
HW-22573	10-26-51	W. S. Figg	Report of Invention - Apparatus for Separations by Solvent Extraction - The Turbo-Extractor
HW-22919	12-6-51	R. L. Moore	Report of Invention - The Use of Mono-Substituted Phosphates Such as Monobutyl Phosphate for the Purification and Isolation of Tetravalent Metal Ions Such as Plutonium (IV), Cerium (IV) or Zirconium(IV)
HW-22920	12-6-51	R. L. Moore	Report of Invention - The Removal of Ruthenium from Redox or Purex Type Aqueous Solutions by Carrier Precipitation on Metal Sulfide Precipitates, Such as Copper Sulfide

O. F. Hill

O. F. Hill

F. J. Leitz

F. J. Leitz