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Report Compiled by Leslie Burris, Jr.

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S U M M A R Y

Redox Process Studies - Semi-Works Column Operations

With the completion of two first cycle runs in the past quarter, acid-deficient extraction conditions have now been tested in eight semi-works runs at ANL (results in Table A, page 12). Ten pilot plant runs have been completed at ORNL. At both sites, plutonium has been decontaminated from beta and gamma activities by average factors of 1.6×10^4 and 7.4×10^3 , respectively. At ANL, uranium was decontaminated from beta and gamma activities by average factors of 6.3×10^3 and 3.3×10^3 , respectively. Higher decontamination of uranium was obtained in the larger scale ORNL runs because decontamination from ruthenium, the principal activity associated with the uranium, was unaccountably poorer at ANL.

The demonstration of plutonium decontamination and recovery in the second cycle continued during this quarter using plutonium product solutions from ORNL first cycle runs. Three runs were made at 30 per cent of the Hanford radiation level and were followed by four runs at the full Hanford radiation level. Through two cycles, decontamination factors varied only from 2×10^6 to 6×10^6 for gamma activity, and from 1.5×10^6 to 4×10^6 for beta activity (Table H, page 22). The required decontamination factor of 10^7 for plutonium will be achieved in a third cycle, and may be achieved in the second cycle with slightly improved operations. Plutonium losses in these runs averaged about 0.7 per cent.

Mixer-Settler Extractors

The two 20-stage sealed mixer-settler units, equipped with provision for simultaneous sampling of all stages, were operated routinely during the quarter for the purpose of obtaining approximate uranium equilibrium data under Redox process conditions and variations from these. The units have operated satisfactorily under conditions of all flowsheets tested and over a wide range of throughputs. Therefore, no further developmental work is planned at this time. The units are now being installed behind shielding for active operation with fission products and plutonium.

Redox Laboratory Studies

Experiments were made to determine the potential value in the Redox process of tributyl phosphate-hexane solvent mixtures, since work at ORNL showed this solvent to have considerable promise for recovering uranium from waste metal solutions. The ready extractibility of uranium from an unsalted system was confirmed, but neither plutonium-IV nor VI was very extractible at high uranium concentrations. In laboratory batch tests made under oxidizing conditions and simulating column operation, cerium and zirconium decontamination factors were poor, whereas the ruthenium decontamination factor of about 370 is at least tenfold better than previously obtained under acid flowsheet conditions.

While the use of this solvent in the first cycle is not promising, its use in the second uranium cycle is attractive. In this cycle ruthenium is the principal fission product, and since uranium is being decontaminated from plutonium, the relative inextractibility of the plutonium is an advantage.

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Consistent removal in the laboratory of over 99 per cent of the ruthenium activity present in dissolver solutions has been achieved by ozonization of the solution for times of about 10 hours. For the 50-milliliter scale laboratory experiments, an ozone-oxygen mixture, 4 per cent in ozone, has been employed at a rate of 100 ml./min. Nitrite ion (0.01 M) and silver ion (0.025 M) catalysts and solution temperatures of near 100°C have been shown to be necessary. Testing on a semi-works scale is now contemplated.

Laboratory Studies of Ruthenium Chemistry

Ruthenium chemistry studies have shown that large changes occur in the spectra of ruthenium-IV nitrate solutions when a molar excess of nitrite ion is added to the solution. A large increase in the distribution of ruthenium into hexone accompanied these changes, the distribution ratio (hex./aq.) increasing from the order of 10^{-5} to about 0.02 as the molar ratio of nitrite to ruthenium was increased from 1:4 to 10:1 or 100:1.

The study of the polarography of ruthenium-IV in 1 M perchloric acid using a platinum microelectrode has revealed reduction waves at approximately 0.2 and 0.4 volts, and an oxidation wave at around 0.9 volts.

The development of a colorimetric analytical procedure for analysis of micro amounts of ruthenium in nitrate solutions has been completed and is described herein (page 49). Testing of this procedure has shown no detectable interference by aluminum nitrate, uranyl nitrate, sodium nitrate, potassium dichromate, ferrous sulfamate, or nitrite ion. Results accurate to ± 2 per cent have been demonstrated.

Plutonium Chemistry

In hexone solutions of plutonium-VI, nitric acid was found to convert part of the plutonium-VI to the trinitrato complex, but to a smaller extent than does the same concentration of tetrabutyl ammonium nitrate. Formation of this stable complex serves to retard reduction of the hexavalent plutonium to the quadrivalent state. In solutions containing both uranyl and plutonyl ions, the trinitrato-plutonyl complex was found to be about twice as strong as the corresponding trinitrato-uranyl complex.

Neptunium Chemistry

Studies are now in progress to determine the effect of Redox process variations on the extraction of neptunium. It has been found that, under the acid-deficient conditions now employed for uranium extraction, extraction by hexone of neptunium in either the quadrivalent or hexavalent state is very slight.

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Americium Isolation

Two runs for the separation from plutonium solutions of americium-241, the decay product of plutonium-241, were made in the past quarter. Approximately 16 mg of americium associated with 22 mg of plutonium was separated from 155 grams of plutonium. In these runs, the americium was separated from plutonium by factors of 6×10^3 and 10×10^3 . In neither run was there a measured loss of either plutonium or americium of greater than 1 per cent. Final purification of the americium is being made in the laboratory.

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Testing of Hexone Extraction Step of Kellex Waste Recovery Process

The solvent extraction step of a process proposed by Kellex for recovering uranium from Hanford metal waste has been tested in Argonne laboratory and semi-works equipment. With a feed simulating the product of a sodium diuranate precipitation step and containing activity provided by 3-year-aged Hanford slugs, the required decontamination factors of 10^4 for beta and gamma activities and of 10^3 for plutonium were achieved in two column solvent extraction cycles, the latter of which was made under acid-deficient conditions as the phosphate concentration in the second cycle feed is negligible. Uranium losses of about 0.1 per cent obtained in ten mixer-settler stages (1 per cent in column operation) indicate that low uranium losses are readily obtainable. No unusual difficulties of operation were noted in either the column or mixer-settler runs.

Purification of Heavy Water in ANL Pile

An ion exchange process has been developed for purification of the heavy water in the ANL reactor. The anion exchange resin is Nalcite SAR (Dowex 2); the cation resin: Nalcite HCR (Dowex 50). Satisfactory purification of one gallon of heavy water with no decrease in the isotopic purity of the heavy water was demonstrated. The original activity in the water, amounting to 4 alpha and 6,000 combined beta and gamma cts./min./ml., was reduced to zero.

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I. REDOX PROCESS DEVELOPMENT STUDIES

A. Uranium Plutonium Separation -- First Cycle Semi-Works Column Operations under Acid-Deficient Extraction Conditions

(Rodger, Schraidt, Feder, Natale, Shor, King, Jonke, Coleman, Aikens, Gaumer, Hykan, Yasui, Casler, Levitz, Loeding, Rosenthal, Seefeldt, Trice, Lee, Brown, Dorsey, and West)

With the completion of two first cycle runs in the past quarter, acid-deficient extraction conditions⁽¹⁾ have now been tested in eight semi-works runs at ANL. Ten pilot plant runs have been completed at ORNL. At both sites, plutonium has been decontaminated from beta and gamma activities by average factors of 1.6×10^4 and 7.4×10^3 , respectively, the mean deviation from these values being 30 per cent. At ANL, uranium was decontaminated from beta and gamma activities by average factors of 6.3×10^3 and 3.3×10^3 , respectively, the mean deviation being 45 per cent. Higher decontamination of uranium was obtained in the larger scale ORNL runs because decontamination from ruthenium, the principal activity associated with the uranium, was unaccountably poorer in ANL runs.

Results from the completed series of ANL runs are given in Table A, page 12. Complete data and conditions for these runs are given in Table I, attached.

Laboratory work has shown that nitric acid may be present in the solvent to the extent of a few tenths molar without affecting decontamination. This acid is rapidly neutralized in the lower stages of the column, but its presence in these stages increases uranium and plutonium distribution in favor of the solvent and thus helps reduce product losses. In general, the use of acidified solvent in Runs 114-2, 115, 117, and 118 produced lower product losses without affecting decontamination.

Use of ammonium persulfate instead of sodium dichromate, at a concentration of 0.1 M in the feed as the plutonium oxidant and at a concentration of 0.01 M in the scrub as a holding oxidant, proved of no advantage (Run 112), a high plutonium loss of 2.4 per cent occurring. However, in this run, the zirconium decontamination factor obtained in the IA or extraction column increased from around 2000 to 5000, indicating that the presence of the persulfate may have improved decontamination from zirconium.

-
- (1) Acid-deficient conditions are produced by neutralizing a portion (0.2 of a mole per liter) of the hydrogen ion concentration resulting from the hydrolysis of uranyl and aluminum nitrates in feed and scrub streams.

Table A

Results of Redox First Cycle Runs Made Under Acid-Deficient Conditions

Acid-deficient conditions employed:

<u>Feed (IAF) - 1 vol.</u>	<u>Scrub (IAS) - 1 vol.</u>	<u>Solvent (IAX) - 4 vols.</u>
2 M uranyl nitrate	2 M aluminum nitrate	Recovered hexone
0.2 M Acid-deficient	0.2 M Acid-deficient	Acidity as noted in table
0.1 M sodium dichromate		

Run No.	HNO ₃ in Solvent (M)	Extraction Column Losses (%)		Average Decontamination Factor (log)			
		Pu	U	Plutonium		Uranium	
				Beta	Gamma	Beta	Gamma
112	0	1.0	2.8	4.3	4.1	3.9	3.4
113*	0	1.2	0.5	4.1	3.9	3.9	3.6
114-1	0	1.2	3.9	4.4	3.9	3.9	3.5
114-2	0.1	0.8	1.4	4.4	4.0	4.1	3.8
115**	0.2	0.4	0.6	4.1	3.8	4.1	3.7
116**	0	0.7	2.0	4.2	3.8	3.9	3.6
117	0.1	0.8	2.2	4.1	3.6	3.7	3.5
118***	0.1	2.4	0.2	4.2	3.9	3.7	3.4

* Scrub-to-feed ratio was 1.3 instead of 1. No significant effect on decontamination or losses is apparent.

** Sodium dichromate to 0.01 M was present in scrub as plutonium holding oxidant. Plutonium losses appear to be lowered slightly and decontamination unaffected.

*** Ammonium persulfate (0.1 M) used instead of sodium dichromate in feed; 0.01 M ammonium persulfate used in scrub.

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Prior to Run 118, the semi-automatic interface control system previously used on Column IA was discarded in favor of a completely automatic pneumatic system. In an inactive test run made under acid-deficient conditions, but with no dichromate present, uranium losses were considerably lower and more uniform than in previous runs. An average uranium loss of 0.24 per cent was obtained, almost an order of magnitude lower than values obtained in preceding runs. This uranium loss was further confirmed in the following active run, 118, in which the uranium loss was 0.2 per cent. It is possible that the higher uranium losses previously obtained were caused by the larger interface fluctuations.

Previously reported plutonium losses may also be high because of this same reason. However, the substitution of the less effective ammonium persulfate plutonium oxidant for sodium dichromate in Run 118 masks any effect that better control of the interface may have had on plutonium loss.

The separation of uranium from plutonium in the IB or uranium-plutonium separation column continues to be adequate in the acid-deficient system. The amount of uranium in the first cycle plutonium product solution has been approximately 5×10^{-5} per cent of the uranium originally in the feed (Table I, attached).

It has been found that increasing the nitric acid content of the hexone scrub stream in the IB or plutonium-uranium separation column from 0.01 M to either 0.05 or 0.1 M is desirable for increasing the stability of the plutonium product solution, i.e., preventing formation of a precipitate in the product solution. No untoward effects have been observed either in ANL or ORNL operation.

B. First Cycle Laboratory Studies

1. Elimination of Ruthenium from Process Solutions by Ozonization
(S. Vogler and M. Beederman)

As a result of the laboratory demonstration in the previous quarter that 99 per cent or more of the ruthenium in dissolver solutions could be removed by ozonization, semi-works investigation of this process is planned. Laboratory work was therefore directed toward establishing conditions to be followed in semi-works operations.

This work may be summarized as follows:

- (1) In ozonization times of the order of ten hours and in the presence of silver catalyst (0.025 M), slightly more ruthenium is volatilized in the presence of 0.05 to 0.1 M nitrite than in the presence of 0.001 or 0.01 M nitrite (about 99.8 versus 99.5 per cent).
- (2) Ozone in the ozone-oxygen or ozone-air gas mixtures is the active oxidizing agent, air or oxygen by themselves being much less effective, despite the use of nitrite and silver catalysts.

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- (3) In the presence of nitrite ion (0.01 M), both silver ion (0.025 M) and dichromate ion (0.05 M) further improve the rate of removal of ruthenium, with the silver catalyst appearing to be slightly more effective. No improvement in rate of ruthenium volatilization was noted in the presence of ceric ion.
- (4) High solution temperatures of 95-100°C are required for rapid ruthenium volatilization.
- (5) The rate of ruthenium volatilization increased with ozone concentration over the investigated range of 1.5 to 4.0 per cent.

Additional details of the experiments and data supporting these contentions follow.

Effect of Nitrite Concentration on Ruthenium Volatilization. Preliminary work reported in ANL-4292 showed that ruthenium volatilization with ozone was markedly enhanced in the presence of nitrite ion (0.1 M). This work was extended to determine the effect of nitrite concentration on ruthenium removal. Over the range investigated, 0.001 M to 0.1 M, it was found that at the higher concentrations of 0.05 and 0.1 M slightly more ruthenium was volatilized in times of about ten hours than at nitrite concentrations of 0.001 and 0.01 M and that the rate of ruthenium removal was initially faster at the higher concentrations (Table B). When the concentration of nitrite was 0.001 or 0.01 M, 99.3 to 99.5 per cent of the ruthenium was removed in ten hours as compared to about 99.6 to 99.9 per cent for nitrite concentrations of 0.05 and 0.1 M. This difference represents approximately a twofold difference in decontamination.

Table B

Effect of Nitrite Concentration on Volatilization of Ruthenium
with Ozone

Conditions: 10 ml. of dissolver solution diluted to 50 ml with 2 M uranyl nitrate. Solution made 0.3 M in nitric acid, and 0.025 M in silver ion. Temperature of solution maintained at 95°C. Gas rate — 100 ml/min (4% by volume ozone in oxygen).

Nitrite Conc. (M)	Per Cent Ruthenium Volatilized after:						
	2 to 2½ hrs.	3 to 3½ hrs.	4 hrs.	6 hrs.	7 to 7½ hrs.	10 to 10½ hrs.	12 to 13 hrs.
0.001	87.2	96.9	-	98.1	98.5	99.5	-
0.01	97.5	98.6	-	-	99.3	99.5	-
0.01*	93.9	97.4	97.7	-	98.8	99.3	-
0.05	95.9	99.3	-	99.8	-	99.9	-
0.05	99.3	-	99.0	-	99.7	-	99.8
0.1	95.8	-	99.3	-	99.6	-	99.7

* Additional nitrite (equivalent to 0.01 M) added after 3 hours. Solution allowed to stand overnight before ozonization was resumed.

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Substitution of Air and Oxygen for Oxone-Oxygen Mixture. Because of the effectiveness of nitrite in promoting oxidation and volatilization of the ruthenium by ozone-oxygen mixtures (4 per cent or less in ozone), the question was raised of whether ozone was actually necessary to produce ruthenium removal. In identical experiments (conditions in Table B) except that air and oxygen were substituted for the ozone (4%)-oxygen mixture, about ten per cent of the ruthenium was removed in ten hours with either air or oxygen as compared with a 99.5 per cent removal in the same time with ozone-oxygen. This shows the necessity of ozone for rapid volatilization of the ruthenium.

Catalysts. Besides silver ion, ceric IV ion and dichromate have shown effectiveness as catalysts in the ozonization process, in conjunction with 0.01 M nitrite ion which also functions as a catalyst. The use of these catalysts, as well as 0.01 M instead of 0.025 M silver, was examined in experiments made under conditions given in Table B, page 14.

Results in Table C indicate silver ion (0.025 M) to be superior to ceric ion (0.05 M), 99.5 per cent ruthenium being removed in the presence of silver versus about 97 per cent removed in the presence of ceric ion, in ten hours of ozonization. The latter is of the same order as the 98 per cent removal accomplished in 10 hours with only nitrite present. Dichromate ion appears to be virtually as efficacious as silver ion, producing 99.4 to 99.5 per cent ruthenium removal in 12 to 14 hours. A strict comparison between dichromate (0.05 M) and silver ions cannot be made since a value for dichromate was not obtained for 10 hours of ozonization. However, for comparable times of less than ten hours, the amounts removed in the presence of silver exceeded those removed in the presence of dichromate. Silver ion at a concentration of 0.01 M was ineffective, a ruthenium removal of 97 per cent occurring, about equal to that with only nitrite present.

Table C

Effect of Catalyst on Ruthenium Removal by Ozonization

Conditions: See Table B, page 14. Nitrite ion concentration was 0.01 M in all tests.

Catalyst and Conc.	Per Cent Ruthenium Volatilized after:						
	2 hrs.	2½ to 3 hrs.	4 hrs.	7 to 7½ hrs.	10 hrs.	12 hrs.	14 hrs.
None	-	84	-	94.5	98	-	-
0.01 M Ag ⁺	-	79.5	-	96.9	97.0	-	-
0.025 M Ag ⁺	97.5	98.6	-	99.3	99.5	-	-
0.05 M Ce ⁴⁺	59.9	-	84.5	96.0	-	96.8	97.4
0.05 M Cr ₂ O ₇ ⁼	91.9	-	95.8	98.7	-	99.4	99.5

Effect of Temperature on Ruthenium Removal by Ozonization. Previous experiments had indicated that elevated temperatures were necessary for rapid removal of ruthenium by ozonization. Experiments of the past quarter have confirmed this, the higher the temperature the greater the percentage of ruthenium removed in a given time. Negligible ruthenium is volatilized in ten hours at room temperature as compared with volatilization of 99.5 per cent at 95°C (Table D).

Table D

Effect of Temperature on Ozonization of Ruthenium

Conditions: See Table B, page 14. Nitrite ion concentration of 0.01 M employed in all tests.

Temperature (°C)	Per Cent Ruthenium Volatilized after:					
	2 hrs.	3 hrs.	4 hrs.	7 to 7½ hrs.	10 hrs.	11½ hrs.
Room Temp.	Negligible					
50	37.8	-	77.3	88.5	-	92.8
75	74.4	-	93.2	97.0	-	97.4
95	97.5	98.6	-	99.3	99.5	-

Effect of Ozone Concentration on Rate of Ruthenium Removal. The concentration of ozone produced by the Welsbach ozonator can be varied by changing the rate of flow of oxygen through the apparatus. When the rate is 100 ml/min, the percentage, by volume, of ozone produced is about 4 per cent; when the rate is 1000 ml/min, the percentage produced is 2.0 per cent. Table E shows the effect of ozone concentration at the same total gas flow rate. The speediness of ruthenium removal is dependent on the concentration of ozone: for instance, after 10 hours, 99.5 per cent was removed when a mixture 4 per cent in ozone was used as compared with 90.7 per cent when the ozone concentration was 1.5 per cent.

Table E

Effect of Ozone Concentration on Ruthenium Volatilization

Conditions: See Table B, page 14. Nitrite ion concentration was 0.01 M in all tests.

Conc. of Ozone in Oxygen (% by vol.)	Gas Rate (ml/min)	Per Cent Ruthenium Volatilized after:				
		2 hrs.	3 hrs.	4 hrs.	7½ hrs.	10 hrs.
1.5	100	36.5	-	63.5	-	90.7
2.0	100	72.6	-	92.8	98.7	98.8
2.5	100	95.0	96.9	-	-	99.3
4.0	100	97.5	98.6	-	99.3	99.5

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Effect of Gas Flow Rate on Rate of Ruthenium Removal. To ascertain the effect of gas flow rate (ozone-oxygen mixture 4 per cent in ozone), decreasing the rate from 100 ml/min to 50 and 25 ml/min was tried. It was not possible to obtain rates higher than 100 ml/min with the present Welsbach ozonator and at the same time maintain an ozone concentration of 4 per cent. Decreasing the rate to 25 ml/min lowered the amount of ruthenium volatilized from 99.5 to about 95 per cent, while at a rate of 50 ml/min nearly the same amount of ruthenium (99.4 per cent) was volatilized as that for a rate of 100 ml/min (Table F). This suggests that, even if available, high gas rates of oxygen 4 per cent in ozone would not be advantageous. Very high gas rates of 600 and 1100 ml/min obtained by diluting the 4 per cent ozone-oxygen at a rate of 100 ml/min with air, did not prove beneficial, the amount of ruthenium volatilized actually dropping 2 to 3 tenths of a per cent under that produced by using the 4 per cent ozone-oxygen directly at 100 ml/min.

It should be borne in mind that the optimum gas flow rate is a function of the geometry of the container. Since a negligible amount of ozone is consumed in oxidation of the ruthenium or in side reactions, it is possible that for the same flow rate, equal rates of ruthenium removal would prevail over a wide range of solution depth.

Apparatus is now being constructed to permit the ozonization of solutions in packed towers or similar contacting vessels, both batchwise and with countercurrent flow. It is hoped that more efficient and economical ruthenium volatilization can be demonstrated with improved contacting equipment.

Table F

Effects of Gas Flow Rate in Ruthenium Volatilization

Conditions: Same as in Table B, page 14. Nitrite ion concentration was 0.01 M in all tests.

Gas Rate (ml/min)		Ozone Conc. (% by vol.)	Per Cent Ruthenium Volatilized after:					
			2 hrs.	3 hrs.	4 hrs.	7 hrs.	10 hrs.	11 hrs.
25		4	9	-	62.4	91.3	-	95.7
50		4	80.6	-	96.6	98.5	99.4	-
100		4	97.5	98.6	-	99.3	99.5	-
600	100	4 } Air	= 0.7	95.2	97.5	-	98.9	99.3
	500							
1100	100	4 } Air	= 0.36	79	-	76.3	-	99.2
	1000							

2. Tributyl Phosphate as a Redox Solvent (S. Vogler and R. Hildebrandt)

The use of tributyl phosphate diluted with hexane, an inert solvent, has been shown in preliminary work at ORNL to have considerable promise in the recovery of uranium from metal waste solutions. Tributyl phosphate possesses the advantage that it is very stable at high concentrations of nitric acid, which alone provides adequate salting strength in the aqueous phase. The elimination of the aluminum nitrate salting agent now used in the Redox process would simplify markedly the problems of waste treatment and storage. Dilution of the tributyl phosphate with hexane or a similar inert solvent is necessary since the tributyl phosphate has a high viscosity and high density which result in poor phase separation from aqueous solutions.

Experiments were therefore made at ANL to determine the potential value of tributyl phosphate as a solvent in the Redox process. A solvent consisting of 15 per cent by volume of tributyl phosphate and 85 per cent by volume of hexane was employed. These experiments confirmed the ready extractibility of uranium from an unsalted system, but in the presence of high concentrations of uranium (1 - 2 M), neither plutonium-IV nor plutonium-VI was very extractible. Also, under oxidizing conditions decontamination from cerium was very poor (a factor of less than 10 after one extraction and five scrubs). Zirconium decontamination was also rather poor (120 after one extraction and five scrubs), but ruthenium decontamination was 370 after one extraction and 440 after five scrubs, at least tenfold better than the decontamination obtained for this element under Redox Column IA conditions of the June, 1948 flowsheet.

While the use of this solvent combination in the first Redox cycle is not at all promising, its value in the second uranium cycle is strongly indicated. Ruthenium is the principal fission product in this cycle, and since in this cycle uranium is being decontaminated from plutonium, the relative inextractibility of the plutonium is an advantage.

Extraction of Uranium by Tributyl Phosphate - Hexane Solvent. First examined was the distribution of uranium between the solvent mixture and aqueous solutions containing between 0.01 and 2.0 M uranyl nitrate and 0 to 8 M added nitric acid. The solvent mixture was found to be saturated with uranium at a uranium concentration of about 0.25 moles/liter, so that uranium distribution coefficients, while high at aqueous uranium concentrations of 0.1 M or lower, were fixed by this saturation of solvent at aqueous uranium concentrations of above 0.5 M (Table G, 19).

At aqueous uranium concentrations of below 0.5 M, the uranium coefficient was strongly dependent on the aqueous nitric acid concentration (Figure A, page 20). For example, for extraction from an aqueous solution initially 0.1 M in uranium, the uranium distribution coefficient in favor of the solvent decreased from 5.3 to 0.2 when the initial aqueous nitric concentration was decreased from 8.0 M to 0 M (Figure A). This dependence on acidity is not apparent at high uranium concentrations (above 1 M) because saturation of the solvent would occur even at low uranium distribution coefficients. However, it should be realized that at the high uranium concentrations, considerable nitric acid will be present through hydrolysis of the uranyl nitrate.

Table G

Distribution of Uranium between Aqueous Nitric Acid Solutions
and a Tributyl Phosphate-Hexane Solvent Mixture

Solvent: Tributyl phosphate, 15 vol. per cent; Hexane, 85 vol. per cent.
 Method: Solutions (approximately equal in volume) equilibrated for ten minutes; after settling, phases were sampled and analyzed colorimetrically for uranium. Asterisk indicates twice the volume of solvent was used.

Uranyl Nitrate (M)	Nitric Acid (M)	Uranium Concentration after Phases were Equilibrated (M)		Uranium Distribution Ratio (Solvent/Aqueous)
		Organic	Aqueous	
2.0	2.0	0.268	1.83	0.15
2.0	1.4	0.271	1.82	0.15
2.0	1.0	0.249	1.72	0.15
2.0	0.5	0.249	1.80	0.14
2.0	0.0	0.273	1.76	0.16
1.0	8.0	0.230	0.826	0.28
1.0	4.0	0.256	0.764	0.34
1.0	2.0	0.245*	0.556*	0.44*
1.0	1.0	0.252	0.740	0.34
1.0	0.5	0.239	0.790	0.32
1.0	0.0	0.246	0.812	0.30
0.5	8.0	0.222	0.285	0.78
0.5	4.0	0.245	0.260	0.94
0.5	2.0	0.222	0.291	0.76
0.5	1.0	0.213	0.288	0.74
0.5	0.5	0.203	0.296	0.69
0.5	0.0	0.157	0.340	0.46
0.25	8.0	0.186	0.880	2.32
0.25	4.0	0.190	0.064	2.97
0.25	2.0	0.168	0.080	2.10
0.1	8.0	0.101	0.019	5.3
0.1	2.0	0.091	0.022	4.1
0.1	1.0	0.080	0.038	2.1
0.1	0.0	0.020	0.099	0.2
0.01	8.0	0.012	0.0001	100
0.01	2.0	0.012	0.0013	10
0.01	1.0	0.011	0.003	4
0.01	0.0	0.0001	0.012	0.01

Fig. A

DISTRIBUTION OF URANIUM BETWEEN AQUEOUS NITRIC ACID SOLUTIONS
AND A TRIBUTYL PHOSPHATE-HEXANE SOLVENT MIXTURE

Solvent: Tributyl phosphate, 15 vol. per cent; hexane,
85 vol. per cent.

Equal volume, ten-minute equilibrations

At saturation of the solvent, the solvent-to-uranium ratio corresponds to between 2 and $2\frac{1}{2}$ moles of tributyl phosphate per mole of uranium. This partially confirms Oak Ridge information, which indicated that a complex molecule is formed between the uranium, tributyl phosphate, and nitric acid, the ratios being two moles of tributyl phosphate to one of uranium to two of nitric acid.

Extraction of Plutonium with Tributyl Phosphate. The distribution ratio of plutonium-IV between the tributyl phosphate (15%)-hexane (85%) solvent and a 4 M nitric acid solution was 0.5 (solvent/aqueous) using a solvent-to-aqueous ratio of 8. However, when the aqueous phase was made about 1.5 M in uranyl nitrate and 0.5 M in nitric acid, the plutonium-IV distribution coefficient dropped to 0.06. Oxidation of the plutonium to the plutonyl or hexavalent state increased the distribution coefficient only to 0.09, still much too low to be useful in a solvent extraction process. Evidently, the uranium complex is much stronger than any corresponding plutonyl complex.

Decontamination with Tributyl Phosphate. Decontamination data were obtained in one test simulating first cycle conditions. For this test the feed was 2 M in uranyl nitrate, 0.5 M in nitric acid, 0.1 M in sodium dichromate and contained 4.5×10^5 plutonium-VI cts./min./ml. A 4 M solution of nitric acid, equilibrated with respect to uranium, was the scrub. The feed/scrub/solvent ratio was 1:1:8. The following decontamination was effected:

	<u>Decontamination Factors</u>				
	<u>Gamma</u>	<u>Beta</u>	<u>Zr</u>	<u>Ce</u>	<u>Ru</u>
After Extraction	29	5.2	8	1.8	370
After Five Scrubs	60	25	120	8.8	440

The low beta and gamma factors can be attributed to the poor decontamination from cerium and zirconium. Of considerable importance, however, is the fact that the ruthenium decontamination factor is over tenfold greater than that obtained with hexone under Redox Column IA conditions of the June, 1948 flowsheet.

Since ruthenium activity comprises about 90 per cent of the total activity present in the second uranium cycle, the tributyl phosphate-hexane solvent may be superior to hexone in the second uranium cycle. This application will be investigated in the near future.

C. Decontamination of Separated Plutonium in Second Cycle Column Operations

The demonstration of plutonium decontamination and recovery in the second cycle continued during this quarter using plutonium product solutions from ORNL first cycle runs. Three runs were made at 30 per cent of the Hanford radiation level. The overall beta and gamma decontamination factors

obtained through two cycles of operation, as well as those obtained in each cycle, were very consistent. Through two cycles, gamma decontamination factors varied from 2×10^6 to 6×10^6 ; beta factors from 1.5×10^6 to 4×10^6 (Table H).

Table H

Plutonium Decontamination through Two Cycles of Operation

ORNL 1st Cycle Run No.*	ANL 2nd Cycle Run No.**	Decontamination Factors (log)					
		First Cycle		Second Cycle		Overall	
		Beta	Gamma	Beta	Gamma	Beta	Gamma
39	45	4.3	3.8	2.2	2.8	6.5	6.6
44	46	4.0	3.5	2.2	2.8	6.2	6.3
46	47	4.5	3.9	1.9	2.6	6.4	6.5
48	48	4.4	4.1	2.0	2.7	6.4	6.8
49	49	4.4	3.95	1.95	2.65	6.4	6.6
50	50	4.4	3.9	2.15	2.8	6.6	6.7
51	51	4.4	3.9	2.0	2.6	6.4	6.5

* Made under acid-deficient conditions of the ORNL No. 1 flowsheet.

** Made under acid conditions of the June, 1948 ANL flowsheet.

It may be noted that the desired decontamination factor of 10^7 for plutonium has been very nearly achieved in two cycles. Accordingly, it is possible that routine operation of the third plutonium cycle in the full scale plant may be unnecessary if slightly greater efficiency is achieved in such equipment.

Plutonium losses in these runs averaging, with the exclusion of Run 50, about 0.7 per cent are listed in Table J, page 23. An explanation for the high loss in Run 50 (2.4 per cent) cannot be given. Laboratory work with the raffinate from this run is now being conducted to determine the cause of this loss.

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Table J

Plutonium Losses in Second Cycle Column Operations

<u>Run No.</u>	<u>Extraction Loss (%)</u>	<u>Stripping Loss (%)</u>	<u>Total Loss (%)</u>
45	0.58	0.17	0.75
46	0.45	0.13	0.62
47	0.43	0.10	0.53
48	0.62	0.06	0.68
49	0.86	0.16	1.02
50	2.4	0.19	2.6
51	0.4	0.24	0.64

Specific Fission Product Decontamination Factors. Specific fission product decontamination factors for both the first cycle ORNL runs and the second cycle ANL runs are given in Table K, page 24, together with the distribution of the beta activity in the product solutions of the two cycles. From these tables the following may be noted:

1. Cerium decontamination although poor in the second cycle (a factor of about 10 to 30) is essentially complete in two cycles (a factor of 10^7 to 10^8) because of the very high decontamination from this element in the first cycle. Cerium beta activity usually comprised only a few per cent of the total beta activity in the final product.
2. A decontamination of between 10^5 and 10^6 was obtained for ruthenium, with values for the later runs being near 10^6 . Factors of about 2000 and 400 were obtained in first and second cycle operations, respectively. The percentage of the total beta activity due to ruthenium in the final product varied widely, from 12 to 58 per cent. Lower values of around 20 per cent in the last four runs appear to be normal.
3. Through two cycles of operation, zirconium decontamination factors were very consistent, varying between 2×10^6 and 4×10^6 , of which a factor of about 400 was obtained in second cycle operation (near 10^4 in first cycle operation). Zirconium beta activity constituted between 6 and 15 per cent of the total beta activity in the final solutions.

A large portion of the total beta activity in the final solution was from the plutonium itself — between 30 and 70 per cent.

Table K

Two Cycle Decontamination of Plutonium from Specific Fission Products

		First Cycle		Second Cycle		Overall Two-Cycle Decontamination Factor (log)
		Decontamination Factor (log)	Per Cent of Total Activity	Decontamination Factor (log)	Per Cent of Total Activity	
ORNL 1st Cycle Run No.	ANL 2nd Cycle Run No.					
Cerium:						
39	45P	6.6	0.3	1.1	2	7.7
44	46P	5.8	1	1.4*	12*	7.2
46	47P	5.7	5			7.1
48	48P	7.0	0.1	0.9	2	7.9
49	49P	6.3	0.5	1.2	4	7.5
50	50P	6.5	0.3	1.5	1	8.0
51	51P	6.8	0.2	0.9	3	7.7
Ruthenium:						
39	45P	3.2	75	2.2	50	5.4
44	46P	3.0	59	2.0*	58*	5.0
46	47P	3.4	56			5.4
48	48P	3.3	90	2.9	12	6.2
49	49P	3.2	79	2.7	15	5.9
50	50P	3.3	59	2.6	19	5.9
51	51P	3.3	63	2.4	28	5.7
Zirconium:						
39	45P	3.7	26	2.6	6	6.3
44	46P	3.5	32	2.9*	4*	6.4
46	47P	3.8	38			6.7
48	48P	4.2	13	2.1	12	6.3
49	49P	3.9	36	2.4	15	6.3
50	50P	3.8	20	2.6	6	6.4
51	51P	4.0	20	2.6	6	6.6

* Fission product analyses were made on the combined product solutions.

D. Decontamination of Separated Plutonium in Third Cycle Column Operations

According to the ANL June, 1948 flowsheet, the procedure for preparing the third cycle feed requires the addition of 2.2 M aluminum nitrate solution to the second cycle product solution to make the final feed 1.3 M in aluminum nitrate. During this quarter, a tracer run was made in which the second cycle product solution was used as feed directly without the addition of any aluminum nitrate. The required salting strength was obtained by using 2.0 M aluminum nitrate in the scrub and increasing the scrub flow rate. The conditions for the run were as follows:

	<u>Composition</u>	<u>Flow Rate (ml/min)</u>
Feed	0.6 M nitric acid	27
Scrub	2.0 M aluminum nitrate	50
Hexone Extractant	0.5 M in nitric	77
Strip	0.1 M nitric acid	16

The following losses were obtained:

Extraction loss - 5.6 per cent,
Stripping loss - 0.1 per cent.

It is believed that the high extraction loss obtained in this run may be due to inadequate mixing of the feed and scrub in the column. Additional work on this flowsheet is contemplated.

E. Decontamination of Separated Uranium

1. Semi-Works Column Operations

In the one second uranium cycle run made, the feed was refluxed with urea (0.25 M) and nitrite ion (0.1 M) for thirty hours, a treatment designed to improve ruthenium decontamination. In this run, the beta and gamma decontamination factors were both 20, making the overall two cycle decontamination 10^5 for beta activity and 6×10^4 for gamma activity, which values are consistent with previously obtained uranium second cycle decontamination values. The uranium loss was low -- 0.03 per cent. No improvement in the ruthenium decontamination as a result of the nitrite-urea feed pretreatment was apparent, the ruthenium decontamination factor being 15. Of the total activity in the final product, 93 per cent was due to ruthenium. Complete data and conditions for this run are given in Table III, attached.

2. Laboratory Studies of Decontamination of Separated Uranium (S. Vogler and C. DeZeh)

Previous laboratory studies of the second uranium cycle have indicated that pretreatment of the feed by refluxing with urea was beneficial in increasing decontamination. However, lack of reproducibility of results indicated that other variables may be involved, such as urea and acid concentrations during reflux, reflux time, and also the effect of possible intermediate or hydrolysis byproducts of urea or hexone.

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The effect of acidity during the urea refluxing was such that over an acidity range of -0.2 M acid-deficient to 1.0 M free nitric and with twelve hours of refluxing the gross beta decontamination factor varied from 90 to 225 and the ruthenium decontamination factor from 110 to 375 (Table L). However, these variations are irregular, and tend to show that the aqueous acidity during refluxing is not critical. Gamma decontamination values vary more widely in these tests, but their reliability is questionable because of the low number of gamma counts in the feed solution - 350 cts/min/ml.

Decreasing the time of refluxing from 12 to 8 and then to four hours, as was done in tests 5, 6, and 7, Table L, caused a corresponding decrease in beta decontamination factors from 225 to 160 to 50, with a similar decrease occurring in the ruthenium decontamination factors, from 375 to 110 overall. These results show that a minimum refluxing time of about 8 hours is required. The upward trend of decontamination with time of refluxing indicates that refluxing time of longer than twelve hours may be beneficial.

Table L

Second Cycle Urea Feed Pretreatment Tests - Effects of Time of Refluxing and Acidity During Refluxing

(Product solution from column run 116-U was concentrated to 2 M uranyl nitrate and refluxed with 0.25 M urea.)

Acidity during Refluxing (M)	Reagent Reflux Time (hrs.)	Acidity during Extraction (M)	Decontamination Factors**		
			Beta	Gamma	Ruthenium
-0.2	No reagent	-0.2	15	10	10
-0.2	12	-0.2	150	No γ cts.*	275
0.3	12	0.3	130	10	195
0.3	12	-0.2	95	20	135
0.5	12	0.5	225	No γ cts.*	375
0.5	8	0.5	160	95	—
0.5	4	0.5	50	35	110
1.0	12	1.0	90	55	215
		-0.2	150	No γ cts.*	275

* Gamma activity level was low, about 300 to 400 cts/min/ml, so that knowledge of gamma decontamination factors in excess of 100, as indicated by "No γ cts.", was not possible.

** Obtained in column simulated batch extraction procedure: Feed combined with an equal volume of scrub; resultant solution was extracted with double volume of neutral hexone. The extract was scrubbed with two one-quarter volumes of scrub.

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Because it was thought that the lack of reproducibility of the urea feed pretreatments might be traceable to differences in the second cycle feeds employed, duplicate experiments were conducted with product solutions from first cycle column runs 117-U and 118-U. Non-uniformity in feeds might be produced by differences in feed preparations, either for the first or second cycle, or in slug dissolving conditions. The gamma decontamination values obtained are not sufficiently different to indicate that there were differences in these particular feeds (Table M).

Table M

Effect of Second Cycle Feed Pretreatment Procedure on Decontamination

Procedure: Feed combined with an equal volume of scrub; resultant solution was extracted with double volume of neutral hexone. The extract was scrubbed with two one-quarter volumes of scrub.

Feed Refluxed* twelve hours with:	Reagent Conc. (M)	Aqueous Feed Acidity (M)	Gamma Decontamination Factors	
			Feed from First Cycle Run 117-U	Feed from First Cycle Run 118-U
No reagent	-	-0.2	5	5
Urea	0.25	-0.2	20; 30*	10; 30.
Nickel and urea	0.3 (as powder)	-0.2	120	55; 40**
Urea	0.25	0.5***	-	15

* The refluxed aqueous feed was re-extracted 19 days later at which time a decontamination value of 120 was obtained.

** Feed allowed to stand one month before check run was made.

*** Feed neutralized to 0.1 M acid-deficient before extraction.

With both feeds, the addition of a small amount of nickel powder during refluxing appeared to benefit decontamination further. In these tests, gamma decontamination factors were measured in a high pressure argon ionization chamber, a method which gives results more reliable than does direct counting.

Refluxing of acid-deficient feed solutions with nitrite ion (0.1 M) either in combination with urea (0.25 M) or acetone (17% by weight) proved ineffective in the tests made in increasing decontamination. (Under acid conditions, the nitrite-acetone reflux has been reported by Oak Ridge to be effective in ruthenium decontamination.)

The effectiveness of urea in aiding decontamination suggested the use of other amines. Those tested were glycine, alanine, and guanidine nitrate. Of these, only alanine produced decontamination appreciably higher than runs with no reagent present (the gamma decontamination increased from 5 to 125). The effect of alanine in improving decontamination will warrant further investigation.

The use of possible intermediate or decomposition products of hexone or urea during the reflux period did not help the decontamination through a subsequent solvent extraction cycle. Materials tried were cyanate ion, 3-isonitroso-2-methyl pentanone (the oxime of hexone), salicyldioxime, and biacetyl.

F. Chemistry of Neptunium in Redox Process (H. Evans and K. Schoenemann)

During the past two years the Redox flowsheet has undergone several important modifications which may affect the distribution of neptunium through the Redox system. Work is now underway to extend the existing information on the solvent extraction behavior of neptunium to conditions of the present Redox process, and for certain modifications of that process that have been suggested in the last two years.

There are two major differences between current operation and the former Redox flowsheet. The first is substitution of ferrous sulfamate for the ferrous ammonium sulfate-hydrazine combination formerly used in the IB or uranium-plutonium separation column of the first Redox cycle. The second is the suggested use of acid-deficient conditions in the first column of each uranium cycle.

As to the first of these, the extraction of neptunium-IV nitrate into hexone was enormously enhanced by the presence of hydrazine. Counteracting this was the fact that the extraction into the aqueous phase was highly favored by the complexing effect of sulfate introduced with the ferrous ammonium sulfate used as the reducing agent. Substitution of ferrous sulfamate for both these reagents has eliminated both effects and made the distribution of neptunium in the IB column dependent on the usual variables of salt concentration, nitric acid concentration, and the volume ratio. Formerly, conditions could be established whereby the neptunium could be directed either with the plutonium or uranium stream by altering the hydrazine and acid concentrations in the solvent phase without too seriously affecting the other requirements of the IB column.

On the basis of very preliminary results now available, it appears that even if the oxidation of neptunium to the hexavalent state can be readily effected under the same conditions now employed for the oxidation of plutonium in acid-deficient systems, the extraction coefficient for neptunyl nitrate does not appear to be adequate in an acid-deficient system to permit its extraction.

Neptunium Distribution Coefficient Measurements. Neptunium distribution coefficient measurements were made employing neptunium-239 tracer, prepared by bombarding uranium oxide depleted in uranium-235 in the Argonne reactor. The exact mixture of valence states making up this solution was not determined. When neptunium-VI was desired, sodium dichromate was added to the aqueous solution and the solution kept at near boiling from four to six hours (past work has shown that neptunium-VI is formed under these conditions -- Report CC-3623). When neptunium-IV was desired, it was assumed that the presence of ferrous sulfamate in the system would guarantee the production of neptunium-IV.

The neptunium distribution coefficient data obtained so far has been summarized in Figures B, C, and D, pages 30, 31, and 32, where the neptunium-IV or VI distribution ratio is plotted as a function of the aqueous phase acidity, aluminum nitrate, or uranyl nitrate concentration (as measured before equilibration). Although the data are meager and are being expanded, present indications from these graphs are as follows:

1. The sensitivity of the neptunium-IV distribution coefficient to acidity is illustrated in Figure B, page 30. A decrease in acidity below 0.1 M in an aqueous phase 1.3 M in aluminum nitrate causes the neptunium-IV distribution coefficient to drop very sharply from 0.3 to the order of 0.0001 (hexone/ aqueous) for acid-deficient systems. Above an acidity of 0.1 M the coefficient increases gradually to 2 to 3 for an acidity of 0.6 M. It is apparent that neptunium-IV would not be extracted under present Redox acid-deficient conditions.

In the plot, pH values are used for acidities below 0.1 M. While the exact relation between pH and acidity is not known, the resultant scale change is small.

2. For an aqueous phase 0.2 M in nitric acid, the logarithm of the neptunium-IV distribution coefficient increased linearly from 0.007 to 8 (hexone/ aqueous) with the aluminum nitrate concentration over the investigated concentration range of 0.5 to 1.7 M (Figure C, page 31).
3. In an acid-deficient, 1 M aluminum nitrate system, the neptunium-VI distribution coefficient increased from 0.003 to about 0.3 as the uranyl nitrate concentration was increased from 0.05 to 1 M (Figure D, page 32), indicating that neptunium-VI as well as the IV will be but slightly extracted under acid-deficient conditions. Investigation of the effect of uranyl nitrate on the neptunium-IV distribution under acid conditions has been measured only up to uranyl nitrate concentrations of 0.35 M, with a slight increase in neptunium distribution into hexone being noted (from 0.4 to 0.6 M -- Figure D).

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Fig. C
DISTRIBUTION OF NEPTUNIUM-IV UNDER REDOX EXTRACTION
CONDITIONS--EFFECT OF AQUEOUS PHASE
ALUMINUM NITRATE CONCENTRATION

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G. Volatilization of Ruthenium in Process for Converting Redox Uranyl Nitrate Product to Uranium Metal (S. Vogler and H. Tyler)

The principal residual activity present with the uranyl nitrate product of the Redox process, although decontaminated to a prescribed low level of activity, will be that due to ruthenium. This uranyl nitrate must be converted to uranium metal before it can be fabricated into new pile fuel rods and reused.

Preliminary data, previously reported in ANL-4292, indicated that in a roasting step of this process, in which step uranyl nitrate is ignited at approximately 210 - 250°C to form uranium trioxide, around 80 per cent of the ruthenium associated with the uranium is volatilized. Several further experiments have confirmed these results, between 72 and 86 per cent of the ruthenium being volatilized in 11 tests in which the ignition temperature was varied from 205 to 500°C (Table N). Over this temperature range, the ignition temperature had no effect on the amount of ruthenium volatilized. The percentage of gamma activity volatilized in these tests was essentially equal to the percentage of ruthenium activity volatilized, as would be expected since most of the gamma activity is attributable to 42-day ruthenium. Because of this volatilization of activity and the possibility that it may be concentrated at some point in process equipment, provision may be required in the conversion process for caring for the volatilized activity.

Table N

Volatilization of Activity, Ruthenium and Gamma, in Igniting
Uranyl Nitrate to Uranium Trioxide

(Original samples contained 200-300 ruthenium cts/min/mg of uranium and about 1 gamma ct/min/mg of uranium.)

<u>Samples Heated for</u> <u>Two Hours at:</u> <u>(°C)</u>	<u>Per Cent Uranium</u> <u>in</u> <u>Product*</u>	<u>Per Cent of Activity Volatilized</u>	
		<u>Gamma</u>	<u>Ruthenium (beta)</u>
205	74.6	77	86
205	86.2	84	76
205	80.6	80	76
230	75	68	72
275	79.7	76	80
350	84.0	74	86
350	80.0	89	85
350	81.0	78	82
350	83.3	—	81
400**	84.0	82	76
500**	84.5	74	72

* Per cent of uranium in uranium trioxide is 83.2.

** These samples were dried to uranyl nitrate hexahydrate and then ignited in muffle furnace at stated temperature for one hour.

This volatilization of residual activity in the uranyl nitrate product is such that, to a first approximation, about 0.2 of a curie of gamma activity per metric ton of uranium metal would be volatilized in the roasting step of the conversion process.

In the laboratory, the roasting was carried out by heating the uranyl nitrate in a stainless steel beaker by means of an oil bath. The solution was stirred while heating with a slow speed, high torque stirrer. After crystallization, the heating was usually continued for approximately two hours.

Analysis of several batches of residual solids which had been ignited at 205 - 275°C showed high values for nitrogen, indicating that possibly not all of the uranyl nitrate had been decomposed. Accordingly, several samples of the previously prepared solids were further ignited in the muffle furnace for four hours at approximately 350°C. Very little more ruthenium was volatilized. Nor was more ruthenium volatilized when samples were ignited in a muffle furnace for one hour at 400 - 500°C. However, at these higher ignition temperatures the percentages of uranium found in the solid products generally agreed more closely with the theoretical value of 83 per cent for uranium in uranium trioxide than the percentage found in samples ignited at 205 to 275°C.

H. Operation of Multi-Stage Mixer-Settler Extractors (M. Levenson and B. Devine)

The two 20-stage sealed mixer-settler units were operated routinely during the quarter for the purpose of obtaining approximate uranium equilibrium data for several alternate Redox flowsheets. Since the units have operated satisfactorily under conditions of all flowsheets tested and over a wide range of throughputs, no further developmental work is planned at this time.

At the end of this quarter, the units were completely disassembled, cleaned, and inspected in preparation for installation in a shielded area for active operation with fission products and plutonium. The molded polythene stirrers which have been in contact with uranyl nitrate-hexone-nitric acid-aluminum nitrate solutions for approximately 5000 hours showed no signs of deterioration.

1. Equipment Operation and Performance

The mixer-settler units are operated in a manner similar to column operation. All incoming streams are fed to open standpipes and organic streams leave via fixed spillovers. The control variable is the aqueous effluent rate which is controlled in the same manner as in column operation. The aqueous exit stream is restrained by air pressure, the amount of pressure determining the exit rate through a v-notched weir. As in column operation, the "box" units are operated by cascading from one unit to the next throughout a cycle.

Operation of the multiple samplers has been revised this quarter. Because of the wide range in viscosities of the solutions involved in the flowsheet variations, sample sizes would vary considerably. To overcome this one sampler box is now used for samples of one phase. Both phases of all stages are still sampled simultaneously, but by controlling the vacuum in the samplers equal size samples of organic and aqueous phases can be obtained. Figure E, page 36, is a photograph of one of the sampler units with the door open showing the sample vials in position.

2. Equilibrium Data for Uranium Extraction in the Redox Process

The series of scouting runs to obtain approximate uranium equilibrium data for various Redox flowsheets started last quarter was completed this quarter. Samples from runs made in the past quarter were analyzed at Hanford Engineer Works. Acid-deficient conditions in these runs were obtained by neutralization with ammonium hydroxide.

Equilibrium data for the acid-deficient flowsheet known as ORNL No. 1 (Run 17-Y) are plotted in Figure F, page 37, and recorded in Table IV, appended. As in previous runs with this flowsheet, the uranium losses are 1 - 2 per cent in ten extraction stages.

Run 18-Y was designed to show that very low uranium losses were obtainable with only a slight modification in flowsheet conditions. The hexone stream was made 0.2 N in nitric acid while acid-deficient scrub and feed solutions were still employed. In ten extraction stages, the uranium loss was less than 0.1 per cent. As compared with the equilibrium curve of the previous run, a shift in the equilibrium line occurs at the uranium - poor end while the rich end remains about the same since the acid extracts in the bottom stages of the unit (Figure F, data in Table V, appended). On this basis it would be predicted that small quantities of acid added to the solvent stream would not effect decontamination. Subsequent work in columns has borne this out.

On the basis of the results of Run 18-Y a flowsheet was devised to give 0.1 per cent uranium loss in ten stages. This was done by reducing the salt concentration in the scrub stream from 2.0 M to 1.65 M aluminum nitrate. The uranium loss which actually occurred was 0.3 per cent. Equilibrium data are plotted in Figure G, page 38, and recorded in Table VI, appended. The data for this run are erratic.

Run 20-Y was also made under modified acid-deficient conditions, selected to give a uranium loss of 0.1 per cent in ten extraction stages. The conditions used were those of the nominal ORNL No. 1 flowsheet except that the aluminum concentration in the scrub stream was increased from 2.0 to 2.1 M. The results of this run are shown in Figure G, and Table VII, appended. An actual uranium loss of 0.15 per cent occurred. In this run, the two phases from each stage were further equilibrated at Hanford prior to analysis. They were improperly equilibrated in the ratio of the volumes of the samples sent to Hanford instead of the ratio of the flow rates. Since attainment of equilibrium in a box extractor stage has been shown to be approached very closely (better than 90 per cent - ANL-4292), accuracy of the results was probably not greatly impaired.

Fig. E

MULTIPLE SAMPLE UNIT FOR SIMULTANEOUSLY WITHDRAWING

SAMPLES FROM BOX EXTRACTORS

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The results of these four runs as well as those of previous runs in the mixer-settler units now comprise sufficient available information on the uranium-aluminum nitrate-hexone system to enable reasonable choices of flow-sheet conditions and the prediction of the uranium loss under these conditions. Because of this, work on this system has been stopped. Future operation with plutonium and fission products is planned.

J. Spectrophotometric Studies of Plutonium in Hexone (M. Berkman)

Previous reports (ANL-4266 and ANL-4292) have presented spectrophotometric evidence for the formation of the complex anion, $\text{Pu}(\text{NO}_3)_6^-$, and the corresponding acid, $\text{H}_2\text{Pu}(\text{NO}_3)_6$, upon the addition of tetrabutyl ammonium nitrate and nitric acid, respectively, to a hexone solution of plutonium-IV nitrate. The formation of $[\text{PuO}_2(\text{NO}_3)_3]^-$ from plutonium-VI and tetrabutyl ammonium nitrate was similarly demonstrated.

Work of the past quarter dealt with the effect of nitric acid on plutonium-VI in hexone, and with a study of the relative effect of tetrabutyl ammonium nitrate on plutonyl and uranyl nitrates. Nitric acid was found to convert part of the plutonium-VI to the trinitrato complex, $[\text{PuO}_2(\text{NO}_3)_2]^-$, but to a smaller extent than does the same concentration of tetrabutyl ammonium nitrate. It was erroneously reported in the last quarterly, ANL-4292, that the uranyl nitrate complex is the stronger of the two.

Effect of Nitric Acid Concentration on the Spectrum of Plutonium-VI in Hexone. In a hexone solution of plutonium-VI nitrate, the nitric acid concentration was varied by the addition of concentrated aqueous nitric acid to the hexone solution. Absorption spectra were measured in a 1 cm. cell with the Beckman Model DU spectrophotometer. The spectra of three such solutions are plotted in Figure H, page 41, together with the curve for plutonium-VI nitrate in the presence of excess tetrabutyl ammonium nitrate.

It may be noted that an increase in nitric acid concentration produces pronounced changes in the solution spectrum. These changes are in the same direction as those produced by the addition of tetrabutyl ammonium nitrate, but are smaller in magnitude than those produced by equal concentrations of tetrabutyl ammonium nitrate. Since the ratio of the nitric acid effect to that of tetrabutyl ammonium nitrate is the same over the entire spectrum, it appears that the only effect of nitric acid at the concentrations studied is to convert part of the plutonium to the trinitrato complex ion, $\text{PuO}_2(\text{NO}_3)_3^-$, the corresponding acid being $\text{HPuO}_2(\text{NO}_3)_3$.

The Extent of Complexing of Plutonium-VI by Nitric Acid. An experiment was carried out to estimate the degree of complexing of plutonium-VI in hexone solution as a function of the nitric acid concentration. To a hexone solution, about 0.002 M in plutonium-VI, nitric acid was added in small increments, and the absorption at 813 mμ, the characteristic peak for uncomplexed plutonium-VI, determined after each addition. The extinction coefficient for uncomplexed $\text{PuO}_2(\text{NO}_3)_2$ was taken as that obtained by extrapolation to zero nitric acid concentration; the extinction coefficient for the complex, $\text{HPuO}_2(\text{NO}_3)_3$, was assumed to be that of the $[\text{PuO}_2(\text{NO}_3)_2]^-$ obtained in the presence of excess tetrabutyl ammonium nitrate. With these

values and the observed optical density, the concentration of complexed and uncomplexed plutonium nitrate was calculated for each nitric acid concentration. The apparent equilibrium constant, K , for the reaction:

was then calculated from these values. The data and results are given in Table VIII, appended, and plotted in Figure J, page 42.

The mean value for the association constant obtained is 10.7. (It should be noted that these measurements were not made at constant water concentration, since water was introduced with the concentrated nitric acid.)

Relative Stabilities of the Uranyl and Plutonyl Nitrate Complexes.

Uranyl and plutonyl nitrates in hexone form analogous, very stable complexes, $\text{UO}_2(\text{NO}_3)_3^-$ and $\text{PuO}_2(\text{NO}_3)_3^-$, with tetrabutyl ammonium nitrate. The formation of the uranyl complex may readily be followed by the increase in absorption at 454 and 469 $\text{m}\mu$, and the formation of the plutonyl complex by the decrease in absorption at 813 $\text{m}\mu$. The comparison of the association constants for the reactions: $\text{UO}_2(\text{NO}_3)_2 + \text{Bu}_4\text{NNO}_3 \rightarrow \text{Bu}_4\text{N UO}_2(\text{NO}_3)_3$ and $\text{PuO}_2(\text{NO}_3)_2 + \text{Bu}_4\text{NNO}_3 \rightarrow \text{Bu}_4\text{N PuO}_2(\text{NO}_3)_3$, can be obtained by determining the amount of each complex formed in a mixture of uranyl, plutonyl, and tetrabutyl ammonium nitrates.

Increments of uranyl nitrate hexahydrate were added to a 0.005 M plutonium-VI hexone solution, 0.0025 M in tetrabutyl ammonium nitrate, and absorption of the solution determined in the regions 454, 469, and 813 $\text{m}\mu$ after each addition. The concentrations of the uranyl nitrate complex and the plutonium-VI nitrate complex were calculated from the optical density values at the above wavelengths and from known extinction coefficients. The ratio of the association constants, for the two complexes was calculated by the formula

$$\frac{K_{\text{Pu}}}{K_{\text{U}}} = \frac{[\text{Bu}_4\text{N PuO}_2(\text{NO}_3)_3] [\text{UO}_2(\text{NO}_3)_2]}{[\text{Bu}_4\text{N UO}_2(\text{NO}_3)_3] [\text{PuO}_2(\text{NO}_3)_2]}$$

The results in Table IX, appended, indicate that plutonyl trinitrato complex is about twice as strong as the corresponding uranyl trinitrato complex.

FIG. H ABSORPTION SPECTRA OF PLUTONIUM-VI NITRATE IN HEXONE.

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FIG. J EFFECT OF NITRIC ACID CONCENTRATION
ON DEGREE OF COMPLEXING OF
PLUTONIUM-VI.

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II. CHEMISTRY OF RUTHENIUM

A. Absorption Spectra of Trivalent and Quadrivalent Ruthenium Solutions
(H. Baxman and L. Deutsch)

Preparation of Ruthenium-III Nitrate. In studying the chemistry of ruthenium-III nitrate, it was deemed advisable to prepare pure ruthenium-III nitrate free from any nitrite or other possible complexing agents, since nitrite or nitroso complexing effects might complicate the study of ruthenium-III.

Accordingly, various reducing agents were examined for their effect on nitric acid. With two, hydroxylamine sulfate and methyl alcohol (each 0.1 M), nitrite was not produced when nitric acid was refluxed with these reagents. However, when ruthenium was present with hydroxylamine sulfate, nitrite ion and nitrogen dioxide were produced in fairly large amounts. (Although not tested, a similar reaction with methyl alcohol is considered likely.) With two other reducing agents tried, formaldehyde and formic acid, nitrite ion was formed in refluxing a nitric acid solution.

Since previous attempts to reduce ruthenium-IV nitrate have also resulted in the formation of nitrite ion (see ANL-4292), it was concluded that at present there seems to be no method whereby ruthenium-IV nitrate can be reduced to the (III) state in nitric acid without the co-formation of nitrite ion. The presence of ruthenium-III whether as an ion or in a complex has not been established.

Effect of Nitrite Ion on Spectra of Ruthenium-IV Nitrate Solutions. Since all attempts to produce ruthenium-III nitrate resulted in the simultaneous production of nitrite ion, the reaction between ruthenium-IV and nitrite ions was studied in a series of experiments in which the nitrite ion concentration was controlled and varied. Large changes were found to occur in the spectra of ruthenium-IV nitrate solution when a molar excess of nitrite ion was added to the solution. These changes were accompanied by a large increase in the distribution of ruthenium into hexone.

Four samples of ruthenium-IV nitrate tracer in 0.5 M nitric acid were prepared with ruthenium-to-nitrite molar ratios of 4:1, 2:1, 1:10, and 1:100. For each, the spectrum was obtained after a 15-minute shaking period following the nitrite addition. The sample was then contacted with an equal volume of hexone and shaken for 15 minutes after which the spectrum and distribution ratio were obtained. To complete an experiment, the distribution ratio was again obtained following a 20-hour shaking period.

The spectra of the ruthenium-IV nitrate solutions before and after addition of nitrite are plotted in Figure K, page 44. It may be seen that very little change occurred in the spectra of solutions in which the molar ratio of ruthenium-to-nitrite exceeded one, i.e., in solutions containing a two-fold and twentyfold molar excess of ruthenium. Large changes in solution spectra occurred in the two solutions having an excess of nitrite, ten- and one hundred-fold. Absorption of the solution was generally lowered except around 300 $m\mu$; the peak at 400 $m\mu$ disappeared; and a peak at 660 $m\mu$ appeared. In all cases, there was very little change in the absorption spectra of the solutions after extraction with hexone.

Fig. K

EFFECT OF NITRITE ION ON
SPECTRA OF RUTHENIUM-IV NITRATE SOLUTIONS

(All solutions about 0.5 M in nitric acid)

Wavelength--mμ

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Evidence that a reaction occurred is indicated by the large increase in the distribution of the ruthenium into hexone as the proportion of nitrite was increased, the distribution ratio increasing from about 10^{-5} (hexone/aqueous) to the order of 0.02 as the ratio of ruthenium-to-nitrite was changed from 4:1 to 1:10 or 1:100 (Table 0). There was essentially no difference in distribution ratio obtained after 15 minutes of shaking, and 20 hours of shaking, indicating the reaction or reactions had gone to completion in a short time.

Table 0

Effect of Nitrite Ion Concentration on Distribution of Ruthenium,
Originally in Quadrivalent State, into Hexone

Ruthenium-to-Nitrite Molar Ratio*	Ruthenium Conc. (M)	Ruthenium Distribution Ratio (hexone/aqueous)	
		After 15 min. of Shaking	After 20 hours of Shaking
4:1	0.0028	ca. 10^{-5}	ca. 10^{-5}
2:1	0.0028	5×10^{-4}	5×10^{-4}
1:10	0.0023	0.02	0.023
1:100	0.00058	0.026	-

* Aqueous solution 0.5 M in nitric acid. Equal volume extractions.

The disappearance of the 480 $m\mu$ peak and appearance of a peak at 660 $m\mu$ provided a basis for further spectrophotometric study. Further examination was therefore made of the changes in molar extinction coefficients taking place at these wavelengths upon the successive addition of small increments of nitric acid to a ruthenium-IV nitrate solution. Figure L, page 46, a plot of the percentage change in extinction coefficient versus the nitrite-to-ruthenium molar ratio shows that the molar extinction at each wavelength decreases until a nitrite-to-ruthenium ratio of about 14 is reached. Probably the reaction taking place has been forced to completion by a mass action effect.

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As an indication of the change in absorption at $660\text{ m}\mu$, due only to the ruthenium species formed by reaction of the ruthenium-IV nitrate and nitrite and characterized by this peak, the differences between the percentage changes in absorption at 660 and $480\text{ m}\mu$ were determined and are plotted in Figure L, page 46. This concept is based on the assumption that the absorption of the ruthenium species in the original ruthenium nitrate solution, which species is characterized by the $480\text{ m}\mu$ peak, comprises a constant percentage of the absorption at any wavelength. The difference curve, showing net change in molar extinction coefficient attributable to a reaction product, builds up until a nitrite-to-ruthenium molar ratio of six is reached, and then drops slightly and levels off.

The interpretation of this data is somewhat clouded by kinetic uncertainties, and as yet no further conclusions can be drawn from these observations. The kinetics of the nitrite-ruthenium reaction is being studied.

B. Ruthenium-IV Polarographic Studies (E. Turk)

The study of the polarography of ruthenium-IV in 1 M perchloric acid using a platinum microelectrode continued to reveal the same reduction waves as reported previously in ANL-4292, one at approximately 0.4 volts, and another at approximately 0.2 volts. (All voltage measurements in this work are referred to a saturated calomel electrode.) One oxidation wave at around $+0.9$ volts was also observed.

Polarograms were made at various ruthenium-IV concentrations (from 10^{-4} to 10^{-2} molar) to find out if all the half waves observed were due to ruthenium (a change in diffusion current for a half wave usually would occur only if the half wave were due to the ruthenium). As shown in Table P, page 48, the change in diffusion current is roughly linear with concentration for each of the half waves, a strong indication that these half waves are those of ruthenium and not of impurities.

The diffusion current for a platinum microelectrode is directly proportional to the number of electrons transferred, the concentration of the wave species involved, and the diffusion coefficient of that species. Since each electrode has its own proportionality constant, calibration of each electrode is necessary. A solution of 0.001 M silver perchlorate in 1.0 M perchloric acid was chosen for calibrating the electrodes, the process involved being a one electron reduction process. For all of the electrodes employed the diffusion current was about 4 microamperes.

The diffusion current for 0.001 M ruthenium in 1.0 M perchloric acid was approximately only 1 microampere. If it is assumed that a one electron change is taking place at each of the reported potentials, the diffusion coefficients for the ruthenium series involved is about one quarter of that for the monovalent silver ion. While this is not an unreasonable value for a hydrated tetravalent ruthenium ion, it does not constitute evidence for the existence of any particular ruthenium species. Calibration of the electrodes with other ions may yield more information on this question, and the reduction of uranium-IV to uranium-III in a perchlorate medium will be investigated in the near future.

Table P

Effect of Ruthenium-IV Concentration on Half Wave Diffusion Currents -Ruthenium-IV Polarographic Studies

<u>Half Waves* and Corresponding Diffusion Currents</u>						
<u>Ruthenium-IV Concentration (M)</u>	<u>Half Wave (volts)</u>	<u>Diffusion Current (micro- amperes)</u>	<u>Half Wave (volts)</u>	<u>Diffusion Current (micro- amperes)</u>	<u>Half Wave (volts)</u>	<u>Diffusion Current (micro- amperes)</u>
1.36×10^{-4}	-	-	+0.42	0.13	+0.96**	0.2
6.8×10^{-4}	+0.22	0.4	+0.41	0.5		
1.36×10^{-3}	+0.24	0.9	+0.42	1.2	+0.97**	0.76
6.8×10^{-3}	+0.24	4.8	+0.43	6.0		
1.36×10^{-2}	+0.24	7.2	+0.42	12.4	+0.99**	8.4

* All half wave voltages referred to saturated calomel half cell at midpoint of wave.

** Actually an oxidation wave since it appears below the galvanometer zero of a reduction curve run.

The polarograms were made with various forms of a 1 M perchloric acid bridge between the solution and a saturated potassium chloride junction bottle. None were particularly satisfactory because chloride ions diffused through the bridge into the solution. Therefore, some development work on agar - perchlorate bridges was undertaken, and resulted in the adoption of a 0.05 M sodium perchlorate - agar bridge for future work.

A subsequent study of the effect of chloride ion on ruthenium polarography revealed that, in concentrations of 0.01, 0.001, and 0.0001 M, it had no effect on half-wave potentials of a 0.001 M ruthenium-IV - 1 M perchloric acid solution. Information later obtained indicated that a chloride concentration of 1 molar may be necessary to produce a sufficient quantity of chloride - ruthenium-IV complex to cause a detectable wave shift.

One run was made at a temperature of -8°C to see if the reduction wave of ruthenium-III could be stabilized or magnified since it had been reported that ruthenium-III in perchloric acid was stable only at temperatures around -8°C . The results obtained were not appreciably different from those at room temperature.

C. Analysis for Ruthenium in Nitrate Solutions (B. Kaplan)

The development of a colorimetric analytical procedure for analysis of micro amounts of ruthenium in nitrate solutions has been completed. Testing of this procedure has shown no detectable interference by aluminum nitrate, uranyl nitrate, sodium nitrate, potassium dichromate, ferrous sulfamate, or nitrite ion. Results accurate to ± 2 per cent have been demonstrated.

The use of hydroxylamine hydrochloride, to prevent ruthenium oxidation and loss by nitrite ion in the evaporation steps for conversion of the nitrate sample to a sulfate sample, was found to interfere in the subsequent oxidation and distillation of the ruthenium. In trials of alternative procedures, it was discovered that loss of ruthenium in the presence of nitrite could be avoided if samples were evaporated to dryness to remove excess nitric and nitrous acids on a steam bath rather than at elevated temperatures, and the residue of ruthenium nitrate dissolved in a solution of 1 ml of sulfuric acid in 8 ml of water. No loss of ruthenium occurred with this procedure, and samples prepared in this manner were found to distill quantitatively with periodic acid. Furthermore, any nitrate which may have distilled into the hydrochloric acid-peroxide absorbing solution did not interfere with the analysis. (The absorbing solutions were not tested for traces of nitrate.)

Data on a blank run indicated the necessity for evaporating the aliquot of absorbing solution to be used for the colorimetric analysis, in order to get rid of the traces of iodine which distill. Slightly high results are obtained if this is not done. (In distillation, the bulk of the periodate is reduced to iodate.) Results of the analyses of 35 microgram samples were approximately 4 per cent high in the presence of 10^{-4} M iodine.

The final procedure was tested and found successful for solutions containing sodium nitrite, aluminum nitrate, ferrous sulfamate, and potassium dichromate in concentrations of the same order as in process solutions. Ruthenium analyses for these solutions and solution compositions are given in Table Q, page 50. When iodine was removed by evaporation of the aliquot of the ruthenium tetroxide absorbing solution, the errors in ruthenium analyses varied between 1 and 2 per cent, being both positive and negative. When iodine was not so removed, all errors were positive, varying from 0 to 4.2 per cent. This shows that traces of iodine should be removed before development of the thiourea color.

No interference by aluminum nitrate, uranyl nitrate, sodium nitrate, potassium dichromate, or ferrous sulfamate was detectable. In testing for interference by dichromate ion, a standard dichromate-containing ruthenium solution was not prepared because it was felt that oxidation of ruthenium to the volatile tetroxide with a resultant unknown change in the ruthenium concentration might occur. So that errors in analysis made in presence of dichromate would be attributable only to interference by dichromate and not be due to an unknown change in the ruthenium concentration of the original solution, samples of the uranium-containing stock solution were diluted with an equal volume of a solution 0.1 M in potassium dichromate and 0.5 M in nitric acid. The dichromate was immediately destroyed by addition of a five-fold excess of 3 M ferrous sulfamate, and the analysis carried out in the usual manner. No interference in the analysis by dichromate was apparent.

Table Q

Accuracy of Colorimetric Analyses of Ruthenium in Nitrate Solutions —Necessity of Removing Introduced Iodine*

<u>Composition of Solution Analyzed</u>	<u>Sample Size (micro- liters)</u>	<u>Fraction of Sample Analyzed**</u>	<u>Ruthenium Conc. of Solution (mg/ml)</u>		<u>Per Cent Error</u>	
			<u>Iodine not Removed</u>	<u>Iodine Removed</u>	<u>Iodine not Removed</u>	<u>Iodine Removed</u>
1.82 mg Ru/ml	300	0.04	1.90	1.81	+4.2	-0.5
0.01 M NaNO ₃	250	0.08	1.87	1.82	+2.8	0.0
1.35 M HNO ₃	100	0.16	1.87	1.81	+2.8	-0.5
	50	0.16	1.86	1.86	+2.2	+2.2
	50	0.16	1.84	1.84	+1.1	+1.1
1.21 mg Ru/ml						
1 M Al(NO ₃) ₃	450	0.04	1.23	1.22	+1.7	+0.9
0.9 M HNO ₃	200	0.12	1.21	1.19	0.0	-1.7
0.01 M NaNO ₃	75	0.16	1.24	1.22	+2.4	+0.9
0.606 mg Ru/ml						
1.3 M Al(NO ₃) ₃	800	0.04	0.623	0.608	+2.8	+0.3
0.05 M Fe(NH ₂ SO ₃) ₂	150	0.16	0.628	0.614	+3.6	+1.3
0.05 M HNO ₃						
0.605 mg Ru/ml***						
0.5 M Al(NO ₃) ₃	800	0.04	0.623	0.617	+3.0	+2.0
1 M UO ₂ (NO ₃) ₂	150	0.16	0.621	0.594	+2.6	-1.8
0.005 M NaNO ₂	800	0.04	0.608	0.597	+0.5	-1.3
0.45 M HNO ₃	150	0.16	0.608	0.601	+0.5	-0.7

* One hundred milligrams of periodic acid used in all ruthenium distillations.

** Corresponds to aliquot taken of 25 ml of ruthenium tetroxide absorbing solution. Aliquot size chosen so that fraction analyzed contained between 15 and 40 milligrams of ruthenium.

*** These samples were diluted with an equal volume of solution 0.1 M in potassium dichromate and 0.5 M in nitric acid to test for interference by dichromate ion.

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The following is the recommended procedure for the analysis of ruthenium in nitrate solutions:

1. Transfer a sample containing between 90 and 550 micrograms of ruthenium to a watch glass using a minimum of wash water in pipetting. Evaporate to dryness over a steam bath.

Notes:

- a. If the evaporation is performed at a higher temperature an insoluble residue results, and in the presence of nitrite ion loss of ruthenium occurs.
 - b. If too much water is added to the sample before evaporation or if the nitric acid concentration of the solution is very low ($<0.1\text{ M}$), a residue of insoluble oxide instead of soluble nitrate will result. This can easily be avoided by the addition of a small amount of nitric acid to the sample before evaporation.
 - c. For solutions containing aluminum nitrate which melts at 70°C , evaporation on a steam bath to apparent dryness is not feasible. Therefore, after an appropriate length of time, depending on the volume of the sample, the watch glass should be cooled to see if solidification occurs.
2. Dissolve the residue on the watch glass in a solution of sulfuric acid (1 volume of concentrated sulfuric to 8 volumes of water), and transfer to a distilling flask; add 50 mg of periodic acid dissolved in 2 ml of water, and distill the ruthenium tetroxide into an absorbing solution composed of a 30 per cent hydrogen peroxide solution. A convenient receiver is a 25 ml mixing cylinder.

Notes:

- a. For samples containing chromic or ferrous ion, the quantity of periodic acid used must be increased appropriately.
 - b. The distillation should be performed for one-half hour at boiling and with bubbling of a gentle but continuous stream of air through the solution.
3. Decompose excess peroxide in the absorbing solution by heating until bubbling stops.

Note: If the solution is analyzed before bubbling due to hydrogen peroxide decomposition has stopped, slightly low results are obtained. A large excess of peroxide will prevent the formation of a blue color.

4. Dilute the absorbing solution to 25 ml after cooling.
5. (If the accuracy sought is not very high, this step may be omitted and the small correction for distilled iodine ignored.) Evaporate an aliquot (1 - 4 ml) of the absorbing solution to dryness to remove traces of iodine, dilute the residue with 3 M hydrochloric acid, transfer to a 5 ml volumetric flask, add 2 drops of a 30 per cent hydrogen peroxide solution and heat until bubbling stops (see note under Step 3. above).
6. To the aliquot in the 5 ml volumetric flask, add 5 drops of a 2.5 per cent thiourea solution and 3 M hydrochloric acid to 5 ml. Heat on a steam bath for 2½ minutes and then cool rapidly in an ice bath. After allowing the blue solution to warm to room temperature note the optical density at 630 mμ on a Beckman spectrophotometer using 1 cm cells. The ruthenium content, in micrograms is 162 times the optical density.

The Analysis of Solutions other than Nitrate. The method described above for ruthenium nitrate solutions has been successfully applied to sulfate and perchloric acid samples. These samples were distilled directly, without first evaporating. The sulfate sample was analyzed gravimetrically and found to contain 0.847 mg/ml. Colorimetric analysis gave 0.852 mg/ml. The perchloric acid sample was analyzed by P. Wehner by an independent colorimetric procedure involving the absorption of the tetroxide, and was found to contain 1.38 mg/ml. Analysis by the thiourea method gave 1.39 mg/ml.

D. Hexone Extraction of Ruthenium Compounds (R. Wagner)

Distribution ratio studies have shown that ruthenium-IV in nitric acid reacts with sodium nitrite to form at least one hexone-soluble species having a distribution ratio in favor of the hexone of probably greater than five. An attempt is being made to obtain the hexone-soluble substance and characterize it in solid form.

A small quantity of a solid possessing the hexone-soluble property was isolated by concentrating hexone which had been contacted with an aqueous ruthenium-IV solution, 0.5 M in nitric acid, 0.1 M in nitrous acid, 1 - 2 M in aluminum nitrate, and less than 10^{-4} M in chloride ion. The hexone solution was concentrated under vacuum at room temperature to about one fifth volume, washed with a tenth-volume water, again concentrated and washed and so on until the volume of hexone was reduced about one- to four-hundredfold. Then toluene or benzene added to the hexone residue in the proportions about 90 to 1 caused the precipitation of a yellow-brownish flocculent solid.

The absorption spectrum of a hexone solution of this solid showed no character; nor did a water solution made from contacting with the hexone solution. Analysis for ruthenium, C and N gave the following results.

$$\text{Ru} = 27.6\% \pm 1\%$$

$$\text{C} = 20.0\% \pm 2\%$$

$$\text{N} = 8.7\% \pm 1\%$$

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No analysis for hydrogen or oxygen was made. Ignition of the sample at 700°C in nitrogen showed that the material contained 14 per cent water.

It is planned to obtain a greater amount of this solid in order to know with more certainty that it is homogeneous before more characterization work is undertaken.

III. WASTE TREATMENT

(H. G. Swope, P. Fineman, M. J. Nagy, M. Klein,
R. Peters, C. Hoffman)

Glass laboratory scale apparatus for the recovery of aluminum nitrate from aqueous Redox waste streams has been fabricated. The apparatus will be installed as soon as the performance of individual components has been tested. This equipment is designed for the handling of one liter of active waste.

Development and testing of methods of analysis for waste solution constituents, namely, aluminum nitrate, nitric acid, chromic nitrate, and sodium dichromate, are now in progress.

V. SPECIAL SERVICE WORK

A. Americium Recovery (W. Walters, M. Ader, A. Fitch)

Two runs for the recovery of americium were made in the past quarter, in which approximately 16 mg of americium associated with 22 mg of plutonium was separated from 155 grams of plutonium.

In the first of these runs, 11 milligrams of americium was obtained from approximately 100 grams of plutonium. The factor by which americium was separated from plutonium was 6×10^3 . In the second 5 milligrams was obtained from approximately 55 grams of plutonium, the americium-plutonium separation factor being 1×10^4 . In neither run was there a measure loss of either plutonium or americium of greater than 1 per cent.

Complete details of these runs are shown in Table X, attached.

B. Testing of Hexone Extraction Step of Kellex Waste Recovery Process
(S. Vogler and R. Hildebrandt)

At the request of the Kellex Corporation, the solvent extraction step of a process proposed by Kellex for recovering uranium from Hanford metal waste has been tested in Argonne laboratory and semi-works' equipment. With synthetic feeds simulating the product of a preliminary sodium diuranate precipitation step, (1.1 M in uranyl nitrate, 1.4 M in sodium nitrate, 0.175 M in sodium phosphate, and 2 M in nitric acid), containing activity provided by 3-year-aged Hanford slugs, the required decontamination factors of 10^4 for beta and gamma activities and of 10^3 for plutonium were achieved in two column solvent extraction cycles, the latter of which was made under acid-deficient conditions as the phosphate concentration in the second cycle feed is negligible.

The first cycle was studied in mixer-settler equipment to obtain equilibrium data (ANL-SL-150). With a neutral scrub solution 1.3 M in aluminum nitrate and a hexone solvent 0.8 M in nitric acid (one volume of feed to one volume of scrub to four volumes of solvent), uranium losses of about 0.1 per cent were obtained in ten mixer-settler stages (1 per cent in column operation) indicating that low uranium losses are readily obtainable. No unusual difficulties of operation were noted in either the column or mixer-settler runs.

A complete report of this work has been prepared and issued as ANL-SL-175.

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C. Purification of Heavy Water Used in Argonne CP-3 Reactor (H. G. Swope, P. Fineman, and M. J. Nagy)

Experimental studies have been completed on the selection of anion and cation exchange resins and on the development of a process for purification of the heavy water (D₂O) in the Argonne CP-3 reactor. With the anion exchange resin, Nalcite SAR (Dowex 2) and the cation resin Nalcite HCR (Dowex 50), satisfactory purification of one gallon of heavy water with no decrease in its isotopic purity was demonstrated. The original activity in the water, amounting to 4 alpha and 6000 combined beta and gamma cts/min/ml, was reduced to zero.

The analysis of the gallon sample of heavy water as received and after passage through the ion exchange columns is shown in Table S.

Table S

Analysis of Heavy Water Before and After Passage Through

Nalcite HCR and Nalcite SAR Resins

(Concentration of all constituents given in parts per million.)

Ion	As Rec'd		After Purification		Ion	As Rec'd		After Purification	
Ag	L*	0.1	L	0.02	Na	L	0.1		0.02
Al		0.2		0.01	Ni		0.5	L	0.04
Ba	L	0.1	L	0.05	Pb		5		0.1
Be	L	0.002	L	0.001	Pt	L	0.3	L	0.1
Bi	L	0.2	L	0.04	Si		1		0.09
Ca		0.5		0.05	Sn	L	0.5	L	0.1
Cb	L	0.2	L	0.1	Sr		0.005		0.002
Co	L	0.2	L	0.1	Th	L	0.5	L	0.2
Cr	L	0.05	L	0.01	Ti	L	0.05	L	0.02
Cu		0.3		0.04	U	L	2	L	1
Fe		0.01		0.02	V	L	0.05	L	0.01
K		0.5		0.08	W	L	3	L	0.3
La	L	0.05	L	0.01	U	L	0.01	L	0.02
Li		0.01		0.003	Zn	L	2	L	0.4
Mg		0.05		0.01	Zr	L	0.2	L	0.04
Mn		0.1		0.004	NH ₃ as N		170		2
Mo	L	0.05		0.03	NO ₃ as N		162		0
*L = less than									
Isotopic Purity				99.71 - .72				99.70	
Activity: Alpha				4				0 c/min/ml	
Beta and Gamma				5.66 x 10 ³				0	
pH				6.0				9.8	
Conductivity				1.43 x 10 ⁻⁴				103 x 10 ⁻⁶	
				mhos at 27°C				mhos at 27.2°C	

The resins investigated were: cation resins, Nalcite HCR (Dowex 50), Amberlite IR-100H, and Ionac C-200; anion resins, Nalcite SAR (Dowex 2), Amberlite IR-4B, and Ionac A-300. Choice of the Nalcite SAR and HCR resins was based on their high capacity and stability. The two anion resins, Amberlite IR-4R and Ionac A-300 packed before becoming exhausted (solution flow restricted). Ionac C-200 and Amberlite IR-4B were unstable to nitric acid. The cation resin, Amberlite IR-100A had satisfactory stability, but its capacity is only about one-half that of the Nalcite HCR.

The laboratory purification of the heavy water was carried out in short ion exchange columns fabricated from 7/8-inch diameter soft glass tubing. The cation bed was 6 inches in depth; the anion bed 9 inches in depth. Upward solution flow was employed.

Conditioning of the cation resin was accomplished by exhausting with calcium chloride (0.4 per cent) and regenerating with nitric acid (10 per cent) or hydrochloric acid (5 per cent). This cycle was repeated once with the excess acid finally being washed out with distilled water. The anion resin was similarly conditioned except that 0.01 M hydrochloric acid was used for exhausting and 2 to 4 per cent sodium hydroxide for regenerating.

After the resins had been conditioned, they were deuterized to prevent dilution of the heavy water with water (to avoid isotopic dilution with moisture of the air, the equipment and solutions were maintained under a helium atmosphere). The resins were first dried under vacuum for 2½ hours, then flushed with helium, and finally covered with heavy water for about 12 hours. This heavy water was then replaced with fresh heavy water for 12 hours, and after similar contact with a third portion the resins were considered deuterized. This was confirmed when no isotopic dilution of the gallon sample of heavy water occurred in passage through the columns.

D. Production of Hafnium-Free Zirconium

At the request of the Naval Reactor Division, the Chemical Engineering Division has undertaken the production of enough hafnium-free (less than 0.1 per cent hafnium) zirconium oxide (about 7 kilograms) to yield at least 1 kilogram of crystal bar zirconium metal. This is being done to insure the production of enough hafnium-free zirconium for immediate testing requirements in the event that delivery schedules of other producers of this material are not met.

E. Shipping (J. Natale)

Total shipments from Chicago to Oak Ridge, Tennessee during the quarter were as follows:

<u>Type of Container</u>	<u>No. of Units</u>
4300 - lb. lead shipping pots	13 (waste)
2000 - lb. lead shipping pots	21 (waste)
1500 - lb. Sugarman slug pots	10 (slugs)
ORNL solution transfer pots	7
55-gal. stainless steel drums	14
Total no. of units	65

This was equivalent to approximately 80,800 ton-miles of shipping.

TABLE I

SUMMARY OF FIRST CYCLE REDOX OPERATIONS

Columns (IA and IB): 1-inch Pyrex pipe packed with 1/4-inch Raschig rings.

(IC): 1-1/2-inch Pyrex pipe packed with 1/4-inch Raschig rings.

OPERATING CONDITIONS

PRODUCT QUALITY AND DISTRIBUTION

			Column IA Feed(A)			Column IA Scrub				Column IA Extractant		Column IB Extractant			Column IB Scrub		Column IC Extractant	Activity in Waste Solvent		Average Recovery and Losses (% of Quantity in Feed)								Average Decontamination (Log D.F.)									
Run No.	Grams of Pu Per Metric Ton of Uranium	Duration (Hours)	Aqueous			Aqueous				Recovered Hexone		Aqueous			Recovered Hexone		Water, 0.1 M in HNO ₃	% of Feed		Plutonium				Uranium				Plutonium				Uranium					
			Rate ml/min	Uranium (M)	Acid Deficiency (M)	Rate ml/min	Aluminum Nitrate (M)	Sodium Dichromate (M)	Acid Deficiency (M)	Rate ml/min	Nitric Acid (M)	Rate ml/min	Aluminum Nitrate (M)	Ferrous Sulfamate (M)	Rate ml/min	Nitric Acid (M)		Beta	Gamma	Recovery(B)	Loss With F.P.	Loss With U	Loss In Solvent	Recovery	Loss With F.P.	Loss With Pu (x 10 ⁵)	Loss In Solvent	Beta	Gamma	Ru	Ce(F)	Zr(F)	Beta	Gamma	Ru	Ce(F)	Zr(F)
Stream Designation:			IAF			IAS				IAX		IBX			IBS		ICX	ICW		IBP	IAW	ICU	ICW	ICU	IAW	IBP	ICW	IBP				ICU					
ORNL No. 1 Acid-Deficient Flowsheet			1 Vol.	2	0.2	1 Vol.	2.0	None	0.2	4 Vols.	None	0.4 Vol.	1.3	0.05	2 Vols.	0.01	2 Vols.	0.025	0.025	99.8	0.1	0.1	Neg.	99.9	0.1	2.5	0.01	-	-	-	-	-	-	-	-	-	
112	13.7	30	29.2	1.98	0.18	29.1	2.0	None	0.22	117	None	11.4	1.3	0.05	58.6	0.01	59.4	0.005	0.015	80	1.0	0.6	0.02	95	2.8	11	0.01	4.3	4.1	3.0	5.5	3.7	3.9	3.4	2.6	4.6	3.3
113	12.4	35	25.8	2.07	0.22	33.8	2.0	None	0.25	120	None	11.8	1.3	0.05	58.8	0.01	61.2	0.003	0.005	87.5	1.2	0.6	0.04	106	0.5	9	0.01	4.1	3.9	3.6	5.7	3.8	3.9	3.6	2.9	5.2	3.4
114-1	11.5	33	29.1	1.93	0.22	31.2	2.0	None	0.18	117	None	12.2	1.3	0.05	60.2	0.01	60.9	0.03	0.01	92	1.2	0.5	0.03	104	3.9	2.2	0.03	4.4	3.9	3.3	5.5	3.8	3.9	3.5	2.9	5.9	3.4
114-2	11.5	22	29.1	1.93	0.22	31.2	2.0	None	0.18	117	0.10	12.2	1.3	0.05	60.2	0.01	60.9	0.003	0.10	92	0.8	0.8	0.03	104	1.4	3.6	0.03	4.4	4.0								
115-1	14.0	19	30.9	2.07	0.20	31.1	2.0	None	0.19	118	0.20	12.1	1.3	0.05	57.5	0.01	60.1	0.01	0.02	88	1.8	0.9	0.02	101	0.9	5.6	0.03	(C)				(C)					
115-2	14.0	20	30.9	2.07	0.20	31.1	2.0	0.01	0.19	118	0.20	12.1	1.3	0.05	57.5	0.01	60.1	0.01	0.02	88	0.4	0.8	0.02	101	0.6	2.7	0.03	4.1	3.8	3.0	4.0	3.3	4.1	3.7	2.1	5.2	3.4
116	15.3	39	29.1	1.0	0.20	31.3	2.0	0.01	0.22	117	None	11.8	1.3	0.05	61.5	0.02	60.3	0.007	0.01	99	0.7	0.6	0.01	96	2.0	8.3	0.03	4.2	3.8	3.1	4.8	3.6	3.9	3.6	2.6	6.1	3.6
117	13.0	35	29.7	1.98	0.22	30.0	2.0	0.01	0.21	124	0.09	12.5	1.3	0.05	57.0	0.10	60.0	0.004	0.007	57(D)	0.6	0.2	0.04	76(D)	2.2	2.1	0.03	4.1	3.6	2.8	5.4	3.5	3.7	3.5	2.6	5.7	3.6
118	10.0	41	30.0	2.11	0.15	31.0	2.0	(E)	0.19	119	0.10	12.2	1.3	0.05	63.0	0.09	60.0	0.01	0.02	81	1.8	0.6	0.03	97	0.2	1.3	0.03	4.2	3.9	3.1	5.1	4.1	3.7	3.4	2.5	6.4	3.9

(A) A sodium dichromate concentration of 0.1 M was present in all Column IA feed solutions, except in the feed solution for Run 118 where ammonium persulfate (0.1 M) was used.

(B) Low plutonium recoveries are due to interference by aluminum in analyses.

(C) Equilibrium with respect to fission products was not established in part of run from which these samples were taken.

(D) Low plutonium and uranium recoveries in Run 117 are due to loss of solution between Columns IA and IB.

(E) Contained ammonium persulfate, 0.01 M.

(F) Decontamination values for cerium and zirconium were erroneously reversed in previous quarterly, ANL-4292.

TABLE II

SUMMARY OF REDOX SECOND PLUTONIUM CYCLE OPERATIONS

Columns (IIA and IIB): 1-inch Pyrex pipe packed with 1/4-inch Raschig rings

OPERATING CONDITIONS											PRODUCT QUALITY AND DISTRIBUTION													
Run No.	Source of Feed (ORNL 1st Cycle Run No.)	Duration (Hours)	Column IIA Feed			Column IIA Scrub		Column IIA Extractant		Column IIB Extractant		Average Pu Recovery and Losses (% of that in Feed)			Average Pu Decontamination (Log D.F.)					Overall Plutonium Decontamination (Log D.F.)				
			Aqueous			Aqueous		Recovered Hexone		Water, 0.1 M in HNO ₃														
			Rate ml/min	Aluminum Nitrate (M)	Sodium Dichromate (M)	Nitric ^(A) Acid (M)	Rate ml/min	Aluminum Nitrate (M)	Rate ml/min	Nitric Acid (M)	Rate ml/min		Recovery	Loss With F.P.	Loss In Solvent	Beta	Gamma	Ru	Ce	Zr	Beta	Gamma	Ru	Ce
Stream Designation:			IIAF			IIAS		IIAX		IIBX		IIBP	IIAW	IIBW										
Flowsheet ^(B) -		-	1 Vol.	1.22	0.02	0.5	0.95 Vol.	1.3	1.9 Vols.	0.5	0.4 Vols.	99.7	0.2	0.02	2	2	-	-	-	5.3	5.3	-	-	-
45P	39	16	43.5	~1.5	0.024	0.09	40	1.3	80	0.47	16.3	105	0.58	0.17	2.2	2.8	2.2	1.1	2.6	6.5	6.6	5.4	7.7	6.3
46P	44	18	43	~1.4	0.022	0.08	41	1.3	82	0.45	16.6	100	0.45	0.13	2.2	2.8	2.0	1.4	2.9	6.2	6.3	5.0	7.2	6.4
47P	46	16	42	~1.4	0.021	0.08	41	1.3	82	0.45	16.6	99	0.43	0.10	1.9	2.6				6.4	6.5	5.4	7.1	6.7
48P	48	16	42	~1.5	0.02	0.09	39	1.3	79	0.49	15.8	101	0.62	0.06	2.0	2.7	2.9	0.9	2.1	6.4	6.8	6.2	7.9	6.3
49P	49	16	42	~1.5	0.019	0.17	38.5	1.3	80	0.49	16.5	101	0.86	0.16	1.95	2.65	2.7	1.2	2.4	6.4	6.6	5.9	7.5	6.3
50P	50	16	42.5	~1.5	0.022	0.22	40.3	1.3	80	0.45	15.3	99	2.4	0.19	2.15	2.8	2.6	1.5	2.6	6.6	6.7	5.9	8.0	6.4
51P	51	16	42.4	~1.5	0.019	0.19	40.5	1.3	82	0.45	16.0	97	0.4	0.24	2.0	2.6	2.4	0.9	2.6	6.4	6.5	5.7	7.7	6.6

(A) Lower nitric acid concentration than specified on flowsheet used in run feeds to prevent buildup of nitric in stripping column and resultant high plutonium stripping losses.

(B) Second cycle feed made 0.02 M in sodium dichromate, and let stand for 2 hours, a crossover oxidation step.

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Table III

Summary of Second Uranium Cycle Redox Operations

Columns (ID and IE): 1-inch Pyrex pipe packed with 1/4-inch Raschig rings.

Operating Conditions for Second Uranium Cycle Run No. 31*

<u>Solution Compositions</u>	<u>Solution Rates (ml/min)</u>
Feed:	
1.94 M uranyl nitrate	
0.2 M acid-deficient	30.7
Scrub Solution:	
2.0 M aluminum nitrate	
0.2 M acid-deficient	32.0
0.05 M ferrous sulfamate	
Recovered Hexone Extractant:	
0.11 M nitric acid	122
Aqueous Strip Solution:	
Water, 0.1 M in nitric acid	60

Product Quality and Distribution for Run No. 31

Uranium Recovery - - 103 per cent
 Uranium Loss with Fission Products (IDW) - - 0.02 per cent
 Uranium Loss in Solvent - - 0.01 per cent

Average Uranium Decontamination:

Beta Decontamination Factor - - 20
 Gamma Decontamination Factor - - 20**
 Decontamination from Specific Fission Products:
 Ruthenium - - 15
 Zirconium - - 400
 Cerium - - 8***

Uranium accompanied with 0.06 per cent of plutonium in first cycle feed.

* Duration of run was 26 hours.

** Determined with high pressure ionization chamber.

*** Cerium concentration was too low for accurate analysis.

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TABLE IV

EQUILIBRIUM DATA FOR URANIUM EXTRACTION BY HEXONE --
REDOX ACID-DEFICIENT CONDITIONS OF ORNL NO. 1 FLOWSHEET

(Mixer-Settler Run 17-Y)

Results obtained by simultaneous sampling of stage compartments in multi-stage box extractor. Samples removed after 6 or 7 aqueous throughputs (after about 7 hours of operation), and analyzed by Hanford Engineer Works.

Composition and Rate of Flow of Feed Streams

Stream Compositions		Density (25°C)	Flow Rate (cc./min.)
Feed (IAF)	2.1 M uranyl nitrate	1.673	15.8
	0.2 M acid-deficient*		
Scrub (IAS)	2 M aluminum nitrate	1.2908	15
	0.15 M acid-deficient*		
Solvent (IAX)	Recovered hexone	0.7994	60
	0.01 M in nitric acid		

Overall Uranium Extraction Loss (10 extraction stages) -- 0.85 per cent

Stage Equilibrium Data -- Aqueous Phase

Stage No.	Density (25°C)	Aluminum Nitrate (M)	Uranyl Nitrate (M)	Nitric Acid (M)	Grams of UNT** Gram of non UNT
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	1.69	0.10	-	-
5	(Feed Point) ←				
6	1.3526	0.86	0.69	-0.139	0.297
7	1.2698	0.93	0.39	-0.137	0.161
8	1.2359	0.99	0.25	-0.159	0.10
9	1.2054	1.04	0.14	-0.168	0.056
10	1.1934	1.06	0.095	-0.162	0.037
11	1.1847	1.06	0.067	-0.160	0.026
12	1.1780	1.07	0.049	-0.160	0.019
13	1.1742	1.07	0.034	-0.171	0.013
14	1.1707	1.08	0.017	-0.166	0.0037
15	1.1677	1.09	0.011	-0.167	0.0044

Organic Phase

1	0.9811	-	0.524	0.05	0.314
2	-	-	-	-	-
3	0.9904	-	0.55	0.27	0.331
4	0.9924	-	0.56	-	0.340
5	(Feed Point) ←				
6	0.9851	-	0.53	0.05	0.319
7	0.9061	-	0.30	-	0.177
8	0.8762	-	0.21	0.3	0.123
9	0.8362	-	0.10	-	0.056
10	0.8271	-	0.070	-	0.039
11	0.8135	-	0.035	-	0.020
12	0.8105	-	0.032	-	0.018
13	0.8057	-	0.016	-	0.0088
14	0.8044	-	0.011	0.09	0.0060
15	0.8013	-	0.0044	-	0.0023

* Acid-deficient conditions produced by neutralization with ammonium hydroxide.

** UNT represents uranyl nitrate trihydrate.

TABLE V

EQUILIBRIUM DATA FOR URANIUM EXTRACTION BY HEXONE --
ACIDIC HEXONE EXTRACTANT USED WITH ACID-DEFICIENT AQUEOUS FEEDS

(Mixer-Settler Run 18-Y)

Results obtained by simultaneous sampling of stage compartments in multi-stage box extractor. Samples removed after 6 or 7 aqueous throughputs (after about 7 hours of operation), and analyzed by Hanford Engineer Works.

Composition and Rate of Flow of Feed Streams

	<u>Stream Compositions</u>	<u>Density (25°C)</u>	<u>Flow Rate (cc./min.)</u>
Feed (IAF)	2.4 M uranyl nitrate 0.255 M acid-deficient*	1.6779	14.7
Scrub (IAS)	1.9 M aluminum nitrate 0.18 M acid-deficient*	1.2927	15.0
Solvent (IAX)	Recovered hexone 0.2 M in nitric acid	0.8082	59

Overall Uranium Extraction Loss (10 extraction stages) -- 0.04 per cent.

Stage Equilibrium Data -- Aqueous Phase

<u>Stage No.</u>	<u>Density (25°C)</u>	<u>Aluminum Nitrate (M)</u>	<u>Uranyl Nitrate (M)</u>	<u>Nitric Acid (M)</u>	<u>Grams of UNT** Gram of non UNT</u>
1	-	1.74	0.048	-0.196	-
2	1.3034	1.77	0.053	-0.177	0.018
3	-	1.80	0.072	-0.207	-
4	-	1.74	0.075	-0.210	-
5			(Feed Point) ←		
6	1.3565	0.825	0.67	-0.210	0.285
7	1.2460	1.01	0.27	-0.068	0.107
8	1.2048	1.02	0.10	+0.049	0.038
9	1.1858	1.04	0.031	+0.051	0.019
10	1.1783	1.04	0.012		0.0046
11	1.1774	1.11	0.0039	+0.161	0.0015
12	1.1768	1.09	0.0015	+0.207	0.00051
13	1.1767	0.96	0.00040	+0.208	0.00015
14	1.1763	0.99	0.00054	+0.208	0.00020
15	1.1765	1.11	0.00068	+0.208	0.00026

Organic Phase

1	0.9863	-	0.536	-0.0196	0.322
2	-	-	-	-	-
3	0.9905	-	0.55	-0.041	0.332
4	0.9909	-	0.55	-0.019	0.328
5			(Feed Point) ←		
6	0.9790	-	0.51	-0.017	0.304
7	0.9040	-	0.30	-0.033	0.173
8	0.8707	-	0.20	+0.032	0.112
9	0.8417	-	0.11	+0.090	0.061
10	0.8193	-	0.035	+0.157	0.020
11	0.8094	-	0.0036	+0.186	0.0020
12	0.8087	-	0.0014	+0.187	0.00076
13	0.8088	-	0.00078	+0.191	0.00043
14	0.8088	-	0.00024	+0.191	0.00014
15	0.8078	-	0.00015	+0.205	0.000080

* Acid-deficient conditions produced by neutralization with ammonium hydroxide.

** UNT represents uranyl nitrate trihydrate.

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TABLE VI

EQUILIBRIUM DATA FOR URANIUM EXTRACTION BY HEXONE --
MODIFIED ACID-DEFICIENT FLOWSHEET CONDITIONS (2.1 M ALUMINUM NITRATE SCRUB)

(Mixer-Settler Run 20-Y)

Results obtained by simultaneous sampling of stage compartments in multi-stage box extractor. Samples removed after 6 or 7 aqueous throughputs (after about 7 hours of operation), and analyzed by Hanford Engineer Works. Samples of this run only were re-equilibrated. This was done in ratio of volumes instead of in ratio of flow rates.

Composition and Rate of Flow of Feed Streams

Stream Compositions		Density (25°C)	Flow Rate (cc./min.)
Feed (IAF)	2.1 M uranyl nitrate 0.21 M acid-deficient*	1.6887	14.8
Scrub (IAS)	2.1 M aluminum nitrate 0.07 M acid-deficient*	1.3123	15.3
Solvent (IAX)	Neutral Recovered Hexone	0.8006	59.7
Overall Uranium Extraction Loss (10 extraction stages) -- 0.15 per cent			

Stage Equilibrium Data -- Aqueous Phase

Stage No.	Density (25°C)	Aluminum Nitrate (M)	Uranyl Nitrate (M)	Nitric Acid (M)	Grams of UNT** Grams of non UNT
1	-	1.98	0.040	-	-
2	-	1.98	0.027(?)	-	-
3	-	1.98	0.043	-	-
4	-	1.89	0.048	-	-
5	(Feed Point)				
6	1.3113	1.09	0.441	0.179	0.178
7	1.2461	1.09	0.249	0.184	0.098
8	1.2268	1.11	0.184	-	0.072
9	1.1951	1.11	0.081	0.194	0.031
10	1.1893	1.12	0.067	0.192	0.026
11	1.1786	1.13	0.029	0.195	0.011
12	1.1755	1.13	0.017	0.195	0.0066
13	1.1717	1.12	0.0069	0.206	0.0027
14	1.1716	1.13	0.0039	0.178	0.0015
15	1.1694	1.12	0.0016	0.179	0.00061

Organic Phase

1	0.9792	-	0.524	+0.024	0.315
2	-	-	-	-	-
3	0.9816	-	0.525	+0.041	0.316
4	-	-	0.492	-	-
5	(Feed Point)				
6	-	-	0.556	-	-
7	0.8966	-	0.278	+0.017	0.162
8	0.8646	-	0.191	-	0.110
9	-	-	-	-	-
10	0.8173	-	0.049	+0.024	0.027
11	-	-	-	-	-
12	0.8038	-	0.011	+0.025	0.0064
13	0.8015	-	0.0045	+0.024	0.0025
14	0.8008	-	0.0025	+0.024	0.0014
15	0.7993	-	0.0013	+0.024	0.00070

* Acid-deficient conditions produced by neutralization with ammonium hydroxide.

** UNT represents uranyl nitrate trihydrate.

TABLE VII

EQUILIBRIUM DATA FOR URANIUM EXTRACTION BY HEXONE --
MODIFIED ACID-DEFICIENT CONDITIONS (1.65 M ALUMINUM NITRATE SCRUB)

(Mixer-Settler Run 19-Y)

Results obtained by simultaneous sampling of stage compartments in multi-stage box extractor. Samples removed after 6 or 7 aqueous throughputs (after about 7 hours of operation), and analyzed by Hanford Engineer Works.

Composition and Rate of Flow of Feed Streams

Stream Compositions		Density (25°C)	Flow Rate (cc./min.)
Feed (IAF)	2.08 M uranyl nitrate	1.6878	14.7
	0.165 M acid-deficient*		
Scrub (IAS)	1.63 M aluminum nitrate	1.2385	15.0
	0.13 M acid-deficient*		
Solvent (IAX)	Recovered hexone	0.8072	59
	0.19 M in nitric acid		

Overall Uranium Extraction Loss (10 extraction stages) -- 0.3 per cent

Stage Equilibrium Data -- Aqueous Phase

Stage No.	Density (25°C)	Aluminum Nitrate (M)	Uranyl Nitrate (M)	Nitric Acid (M)	Grams of UNT** Gram of non UNT
1	1.2750	1.51	0.134	-0.110	0.049
2	1.2778	1.50	0.162	-0.044	0.060
3	-	-	0.160	-	-
4	-	-	-	-	-
5	-	-	-	-	-
6	-	0.96	0.564	-0.060	-
7	1.2694	1.09	0.332	-0.089	0.133
8	-	-	0.343	-	-
9	1.2121	0.93	0.205	+0.191	0.082
10	1.2159	0.88	0.240	+0.151	0.097
11	1.1676	0.87	0.070	+0.214	0.028
12	1.1591	0.87	0.043	+0.296	0.017
13	1.1543	0.89	0.018	+0.311	0.0070
14	1.1496	0.88	0.0061	+0.318	0.0024
15	1.1518	0.91	0.0030	+0.273	0.0012

Organic Phase

1	0.9705	-	0.483	+0.015	0.285
2	-	-	-	-	-
3	0.9861	-	0.53	+0.016	0.313
4	-	-	0.50	-	-
5	-	-	-	-	-
6	1.0034	-	0.576	+0.019	0.346
7	0.9408	-	0.408	+0.113	0.241
8	0.8834	-	0.239	+0.060	0.132
9	0.8710	-	0.195	+0.116	0.112
10	0.8361	-	0.088	+0.165	0.049
11	-	-	-	-	-
12	0.8158	-	0.017	+0.208	0.0093
13	0.8107	-	0.0065	+0.195	0.0036
14	0.8104	-	0.0065	+0.192	0.0036
15	0.8091	-	0.0015	+0.206	0.00083

* Acid-deficient conditions produced by neutralization with ammonium hydroxide.

** UNT represents uranyl nitrate trihydrate.

Table VIII

Effect of Nitric Acid Concentration on Complexing of Plutonium-VI

Conc. of HNO ₃ (M)	Ext. Coeff. at 813 m	HPuO ₂ (NO ₃) ₃ (M)	PuO ₂ (NO ₃) ₂ (M)	Pu-VI Complexed (%)	K*
0.01	56.6	0.00017	0.0021	7.4	11.5
0.026	50	0.0005	0.0018	21.3	10.7
0.041	46	0.0007	0.0016	30	10.7
0.057	42.5	0.0008 ₅	0.0014 ₅	37	10.3
0.072	40.5	0.0009 ₆	0.0013 ₄	41.5	10.3
0.103	37	0.0011 ₃	0.0011 ₇	49	9.7
0.18	30	0.0015	0.0008	64	10.4
0.25	23	0.0018	0.0005	78.5	14.5
0.41 ₅	20.5	0.0019 ₃	0.0004	84	11.5
0.64	19	0.0023 ₈	0.0003 ₂	88	11.6
0**	60			0	
	13***			100	

$$* K = \frac{[\text{HPuO}_2(\text{NO}_3)_3]}{[\text{HNO}_3][\text{PuO}_2(\text{NO}_3)_2]}$$

** Extrapolated value

*** Obtained with excess tetrabutyl ammonium nitrate.

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Table IX

Relative Association Constants of Uranyl and Plutonyl-Nitrate Complexes

Concentrations Calculated from Absorption at Given Wavelength*

Pu(Tot.) (M)	Pu-VI (M)	Bu ₄ NNO ₃ (M)	U-VI (M)	Volume (ml.)	UO ₂ (NO ₃) ₂ (M)		Bu ₄ N UO ₂ (NO ₃) ₃ (M)		PuO ₂ (NO ₃) ₂ (M)		Bu ₄ N PuO ₂ (NO ₃) ₃ (M)		K Pu U
					454 mμ	469 mμ	454 mμ	469 mμ	813 mμ	813 mμ	813 mμ	813 mμ	
0.0054 ₃	0.0051	0.0026 ₃	0.0029 ₈	5.0	0.0022 ₅	0.0022 ₆	0.000 ₇	0.0007 ₂	0.0031 ₅	0.0019 ₅			2.0 ₂
0.0055	0.0051 ₇	0.0026 ₈	0.0061	4.9	0.0051	0.0050 ₅	0.0010	0.0010 ₅	0.0036 ₅	0.0015 ₂			2.0 ₅
0.0056 ₅	0.0053	0.0027 ₄	0.0095	4.7	0.0080 ₁	0.0080	0.0014 ₉	0.0015	0.0040 ₄	0.0012 ₆			1.7 ₅
0.0057	0.0053 ₆	0.0027 ₆	0.0130	4.6	0.0113 ₇	0.0113 ₇	0.0016 ₃	0.0016 ₃	0.0041 ₂	0.0012 ₄			2.0 ₅
0.0058	0.0054 ₅	0.0028 ₂	0.0166	4.5	0.0147	0.0148 ₅	0.0019	0.0017 ₅	0.0044 ₅	0.0010			1.7 ₅
0.0059	0.0056	0.0028 ₆	0.0207	4.2	0.0183	0.0183	0.0019	0.0019	0.0047	0.0009			1.8 ₅

* Extinction Coefficients:

UO₂(NO₃)₂ at 454 mμ = 8.5

UO₂(NO₃)₂ at 469 mμ = 5.5

PuO₂(NO₃)₂ at 813 mμ = 57

Bu₄N UO₂(NO₃)₃ at 454 mμ = 30

Bu₄N UO₂(NO₃)₃ at 469 mμ = 19.3

Bu₄N PuO₂(NO₃)₃ at 813 mμ = 57

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Table X

Summary of Americium Isolation Runs

<u>C o n d i t i o n s</u>	<u>Run 12</u>	<u>Run 13</u>	<u>R e m a r k s</u>
Feed:			
Total plutonium (grams)	97.6 ^(a)	55.6 ^(a)	Specific activity of Pu: Run No. 12 — 7.65×10^{10} c/m/mg. Specific activity of americium — 3.3×10^9 c/m/mg.
Total Pu + americium (cpm)	7.72×10^{12}	4.10×10^{12}	
Pu-IV in total Pu (%)	3.6	2.0	
Ammonium nitrate (<u>M</u>)	8.3	8.4	
Sodium dichromate (<u>M</u>)	0.1	0.1	
Nitric Acid (<u>M</u>)	0.23	0.30	
Flow rate (ml/min)	44.1	43.9	
Volume (liters)	9.65	9.95	
Hexone Solvent:			
Nitric acid (<u>M</u>)	0.22	0.22	
Flow rate (ml/min)	44.1	46.2	
Plutonium Stripping Solution (water, 0.1 <u>M</u> in nitric acid):			
Flow rate (ml/min)	27.0	27.2	

<u>R e s u l t s</u>			
Americium recovered (mg)	11.4	4.8	Based on lanthanum fluoride counting techniques.
Americium lost in iron hydroxide carrying step (%)	0.2	0.7	
Plutonium recovered (grams)	99.7 ^(b) 105.7 ^(c) 102.0 ^(d)	56.0 ^(b) 59.4 ^(c) 58.1 ^(d)	Run 12: ferric ion conc. - 2 g/l; Run 13- 0.5 g/l.
Plutonium extraction loss (%)	0.016	0.010	
Plutonium column stripping loss (%)	0.2	0.6	
Stripping loss after batch stripping operations (%)	0.0002	0.00035	

- (a) Counted on stainless steel; volume by telegauge.
 (b) Counted on stainless steel; volume by weight.
 (c) Counted on platinum plates.
 (d) Chemical assay at Hanford Works.

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