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JANUARY, FEBRUARY, MARCH, 1953

AUTHOR

A. H. Bushey

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AEC RESEARCH AND DEVELOPMENT REPORT

QUARTERLY PROGRESS REPORT

CHEMISTRY UNIT

JAN., FEB., MAR., 1953

By

A. H. Bushey

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PUREX FIRST CYCLE EXTRACTION-SCRUB STUDIES -- E.E. Voiland

This study is part of a series of investigations aimed at improving the overall decontamination in the Purex Process. Reported here is the effect of phosphate and sulfate (possible complexing agents for fission products) under extraction conditions of high acidity, which are already known to improve decontamination.

The combined effect of increased acidity (ca. 5 M HNO_3) and the presence of H_3PO_4 in the HA feed-scrub system of the Purex Process is a suppression of rare earth, ruthenium, zirconium, and niobium extraction into 30% TBP-Amsco (1). Because of the beneficial results noted in the extraction step, these studies were extended to include the effect of extensive scrubbing on the extracted fission products. The effect of H_2SO_4 as a complexing agent in the extraction step was also investigated. The results are listed in Table I.

Some points to be noted and their implications with respect to a plant process are:

1. Gross Gamma Decontamination. The effect of both sulfate and phosphate is small on the overall D.F. (ca. 10^5) through an extraction and three scrubs. However, the presence of H_3PO_4 in the feed results in essentially all the decontamination taking place in the extraction step. Thus, in the scrubbing section the D.F. decreases about a hundredfold with the addition of phosphate, and the second and third scrubs contribute practically nothing towards decontamination.

For a given column height, this means that a greater percentage can be devoted to extraction, thus providing lower waste losses and a possibility of increased throughput.

2. Gross Beta Decontamination. Although not as marked as with the gamma, the improved extraction D.F. results in a lessening of the required scrubbing facilities. In all cases a beta D.F. of 5×10^5 was obtained.

3. Activity In The Final Organic Solution. The beta activity is within a factor of five of beta (30%) specifications in all cases. The gamma activity is within a factor of 20 of the gamma (300%) specifications, assuming a final organic concentration of 90 g/l uranium. Even though these results were obtained on five-month old dissolver solution, it means that a second cycle would probably result in a decontaminated uranium and plutonium product and that a one-cycle uranium process is not out of the question. The use of a still more acidic feed may prove desirable if ruthenium is limiting. A silica gel column could supply added decontamination if zirconium and/or niobium prove to be limiting.

4. Ruthenium In The Final Organic. The organic ruthenium activity from runs E and F is probably not due to the effect of phosphate but rather to an aging effect which results in formation of a non-scrubbable ruthenium species when feeds containing high acid concentrations are allowed to stand for a week or longer. This phenomenon can be circumvented by acidifying at the feed plate rather than in feed make-up.

5. Nature Of The Limiting Species. Although final organic gross activities were similar in the presence or absence of phosphate, a comparison of the gross gamma to gross beta ratios is illuminating. In runs A and B this ratio is about six, most of the beta being ruthenium. In C and D, the ratio is about four, and the beta activity is approximately that of A and B. In runs E and F, the gamma to beta ratio

TABLE I

DECONTAMINATION FACTORS IN THE EXTRACTION AND SCRUB STEPS OF A MODIFIED
PUREX PROCESS - EFFECT OF H_3PO_4 AND H_2SO_4 IN A 5 M H^+ FEED-SCRUB SYSTEM

HAFS: 5.1 M HNO_3 , 300 g/l U	Rel. Flows
HAS (Scrubs 1 and 2): 3 M HNO_3	0.6
HAS (Scrub 3): 30 g/l U	0.22
HAX: 30% TBP-Amsco	0.2
Organic saturation: ca. 80%	1.
Additives: As specified	
Feed source: 5-month old dissolver solution	

Exp't. Designation	A	B	C	D	E	F
Additive	None		0.12 M H_2SO_4		0.18 M H_3PO_4	
Gross γ D.F. - Ext.	190	110	160	165	7×10^4	5×10^4
1st scrub	13	20	16	16	3.4	4
2nd scrub	10	9	9	10	1.4	1.6
3rd scrub	3	5	8	12	1.3	1.1
c/m/ml in final org.	2.1×10^4	$1. \times 10^4$	7.1×10^3	4.2×10^3	5.4×10^3	6.8×10^3
Gross β D.F. - Ext.	2.5×10^3	2.3×10^3	3.8×10^3	3.2×10^3	1.2×10^4	$.8 \times 10^4$
1st scrub	19	23	14	16	15	22
2nd scrub	7.5	7	7	9	2.5	1.5
3rd scrub	2	2	2	2	1	1
c/m/ml in final org.	1.8×10^3	1.7×10^3	1.7×10^3	1.3×10^3	4.2×10^3	6.1×10^3
Ru D.F. - Ext.	6×10^3	1.4×10^4	3×10^4	1.6×10^4	2.8×10^4	1×10^4
1st scrub	3	5	2	5	2	2
2nd scrub	6.5	1.3	2	2	1	2
3rd scrub		1.3	1	1	1	1
c/m/ml in final org.	1.13×10^3	1.2×10^3	$1. \times 10^3$	800	2.9×10^3	3.6×10^3
Zr D.F. - Ext.	50	43	80	72	$> 10^4$	$> 10^4$
1st scrub	17	21	16	15		
2nd scrub	12	9	9	13		
3rd scrub	5	7	8	17		
c/m/ml in final org.	1×10^4	$.8 \times 10^4$	$5. \times 10^3$	$2. \times 10^3$		
RE D.F. - after Ext. and						
1st scrub	$> 10^6$	$> 10^6$	$> 10^6$	$> 10^6$	$> 10^6$	$> 10^6$

is slightly greater than unity which is expected for ruthenium counted under these conditions. Thus, it can be inferred that less zirconium and/or niobium is found in the system containing phosphate, and ruthenium alone is probably limiting. Direct analyses for zirconium and niobium gave uninterpretable results. This is probably due to the stability of the phosphate complex interfering with exchange in the carrier method used.

Reference

- (1) HW-26104, Quarterly Report, July through Sept., 1952, Chemical Research, p. 20.

PUREX SECOND URANIUM CYCLE MINI RUNS -- H.H. Hopkins, Jr.

This work is part of a program aimed at finding ways of improving decontamination in the Purex Process. Earlier batch work (1) showed the improvements possible by varying acidity in first cycle studies. The present work extends the method to a second uranium cycle. Countercurrent Mini runs tested the decontamination obtainable in a second uranium cycle when employing a high acid feed containing phosphate. Feed was prepared from Purex 1CU (one cycle) produced in the ORNL Pilot Plant.

Preliminary runs (#210) compared the normal HW #1 flowsheet with a run in which the feed was adjusted to 6 M HNO_3 , 0.94 M U, and 0.1 M H_3PO_4 . The feed flow rate was increased to maintain the same uranium flow. Whereas the normal run produced a 2EU of activity 47% of natural uranium beta and 790% of natural uranium gamma, the high acid run produced a 2EU product of 27% and 180% of beta and gamma activity of natural uranium. Individual analysis bore out these results, showing improvement factors of five for ruthenium, two for thorium, and two for zirconium-niobium decontaminations.

Analysis of scrub section data substantiated previous evidence that the improvement under high acid extraction conditions is largely due to the suppression of ruthenium extraction at the feed plate.

A second set of runs (#213) was performed under conditions of improved scrub stage efficiency. Stream compositions were the same as in the first runs. However, in these runs the improved scrubbing conditions resulted in a uranium product 2EU which easily met specifications in both cases. For the normal conditions (HW #1) the product activity was 5% and 100%, respectively of the beta and gamma activity of natural uranium, whereas the high acid conditions resulted in product 3% and 60%, respectively.

A comparison of the results of both sets of runs reveals that the high acid extraction conditions reduce the scrubbing requirements to meet a given decontamination, and consequently permit shorter columns or less efficient scrub sections.

Table I is presented to show the slow approach to steady state exhibited in Mini operation. The steady state is approached more rapidly under the high acid conditions (transfer of less fission product activity).

TABLE I

PUREX 2nd U CYCLE MINI RUN 213 - APPROACH TO STEADY STATE

Flowsheet: HW #1: 1.3 M U, 2 M HNO₃
 High Acid: 0.94 M U, 6 M HNO₃

Feed Source: ORNL 1CU,
 6000 c/m/mg U, 29,000 c/m/mg U

Mini Stages: 10 scrub, 8 extraction

Activity of Product 2EU in c/m/mg at Fifteen-Minute Intervals

Sample	HW #1 Conditions		High Acid Conditions	
	<u>P</u>	<u>Y</u>	<u>P</u>	<u>Y</u>
1	16.	10	3	7
2	7.	11	2	5
3	6.	13	1	4
4	5.	12	1	-
5	5.	12		3
6	4.	10	1	3
7	1.7	4	1	4
8	1.6	4	1	3
9	2.5	4	1	3
10	1.5	5	1	3
11	1.9	6	1	4

Reference

- (1) HW-26104, Quarterly Report, July through Sept., 1952, Chemical Research, p. 20.

PLUTONIUM, URANIUM, AND NITRIC ACID DISTRIBUTIONS UNDER MODIFIED PUREX EXTRACTION CONDITIONS -- E.E. Voiland

Although the extraction of fission products from a Purex type HAFS is greatly suppressed by 0.18 M H₃PO₄ and 5 M HNO₃, the applicability of phosphoric acid as a complexing agent for zirconium and niobium in the Purex system depends upon its effect on the plutonium(IV) distribution coefficient. Since the existence of a complicated system of plutonium-phosphate complexes is known (1), it is to be expected that the plutonium distribution coefficient, like that of uranium, will be adversely affected by the presence of phosphates. The purpose of this investigation was to study the effect of varying phosphoric acid concentration (0 - 0.125 M) on the distribution of Pu(IV) between 30% TBP-Amsco and a simulated Purex type HAFS containing nitric acid and UNH.

Solutions of Pu(IV) were prepared from nitrite treated AT solution (plutonium product from the BiPO₄ Process) by the addition of C.P. chemicals to give a range of from 2.4 to 7 M in nitric acid. Uranium was added such that after equilibration the saturation of the organic would range 0 - 65%. Each aqueous solution was contacted with 30% TBP-Amsco in approximately the organic to aqueous ratios (ca. 2) specified for the HA

column in the Purex Chemical Flowsheet #1. Contactings for each set of conditions were run in duplicate and were accomplished by agitating for five minutes on the Burrell wrist-action shaker.

Distribution coefficients for plutonium, uranium, and nitric acid were calculated and are listed in Table I. The plutonium distribution data are graphed in Figures 1, 2, and 3.

Reference

- (1) Seaborg, Katz, and Manning, "The Transuranium Elements," pp. 638-665, McGraw Hill Book Co., Inc., 1949.

TABLE I

PLUTONIUM, URANIUM, AND NITRIC ACID DISTRIBUTION COEFFICIENTS
IN A PUREX TYPE SYSTEM CONTAINING PHOSPHORIC ACID

Volume ratios: Org/aq 1.7 - 2
Extractant: 30% TBP-Amsco
Pu(IV): 0.02 - 0.05 g/l in uncontacted FS

<u>H⁺ (aq)</u>	<u>U Sat. Org.</u>	<u>E_a (Pu)</u>	<u>E_a (U)</u>	<u>E_a (H⁺)</u>
<u>M</u>	<u>%</u>			
2.2	0	8.2, 8.7	--	.23
2.6	32	5.3, 4.6	10.8	.21
3.0	65	2, 2.1	6.	.18
4.6	0	21, 20	--	.18
4.6 (a)	0	23, 20	--	--
4.9 (b)	0	27, 26.7	--	--
4.6	33	14, 13.7	24	.16 est.
5.2	66	4.3, 4.3	6.8	.12
7 est.	0	23, 24	--	--
6.9 (a)	0	31.4, 30	--	--
7.3 (b)	0	35, 33.3	--	--
7.0	25	19.6, 20.8	22	.12
6.7	44	13.3, 12.3	16.5	.12
8.2	60	4.8, 4.8	4.4	.09

(a) Org/aq = 1, Pu = 0.15 g/l in uncontacted FS.

(b) Org/aq = .5, Pu = 0.15 g/l in uncontacted FS.

TABLE I (CONT)

H₃PO₄ = .025 M (aq)

<u>H⁺ (aq)</u> <u>M</u>	<u>U Sat. Org.</u> <u>%</u>	<u>E_a^o (Pu)</u>	<u>E_a^o (U)</u>	<u>E_a^o (H⁺)</u>
2.2	0	4.3, 4.2	--	.22 est.
2.6	33	2.2, 2.5	12.5	.20
3.0	62	1.2, 1.0	5	.17
4.6	0	14, 13	--	.18
4.6	33	8.2, 7.8	20.5	.17 est.
5.2	67	2.8, 2.9	6.3	.12
7.0	0	19, 19	--	.14 est.
6.9	25	12, 14	19	.13
6.7	43	9.5, 9.5	14.5	.12
8.2	58	4.1, 3.7	4.2	.09

H₃PO₄ = 0.061 M (aq)

2.2	0	1.1, 1.1	--	.22 est.
2.6	32	0.8, 0.8	8.5	.19
3.0	63	.37, .35	4.2	.17
4.6	0	8.3, 8.3	--	.18
4.6	32	4.4, 3.9	17.2	.15 est.
5.2	65	1.5, 1.5	5.2	.12
7.0 est.	0	13, 13	--	.14 est.
6.9	25	8.6, 9.1	16	.13
6.7	44	6.4, 5.8	13.5	.12
8.3	58	3.0, 2.9	3.8	.08

H₃PO₄ = 0.125 M (aq)

2.2	0	.36, .32	--	.22 est.
2.6	35	.23, .23	6.2	.21
3.0	61	.14, .13	3.3	.17
4.6	0	3.8, 3.8	--	.17
4.6	34	1.8, 2.1	13.1	.13 est.
5.2	64	.7, .7	4.4	.12
7	0	7, 7	--	
7	24	4.4, 4.2	12	.13
6.8	42	3.0, 3.0	10	.12
8.2	58	1.4, 1.5	3.3	.09

PHOSPHONIUM DISTRIBUTION COEFFICIENTS

Uranium, HNO_3 , and H_3PO_4 parameters

1. 0. moles/l H_3PO_4 in aq. phase
2. 0.025 " " " "
3. 0.061 " " " "
4. 0.125 " " " "

FIGURE 1

PLUTONIUM DISTRIBUTION COEFFICIENTS

Uranium, HNO_3 , and H_3PO_4 parameters

1. 0. moles/l H_3PO_4 in aq. phase
2. 0.025 " " " " "
3. 0.061 " " " " "
4. 0.125 " " " " "

Uranium sat. of org. 35%

Extractant 30% TBP-Amsco

FIGURE 2

0142 017

PLUTONIUM DISTRIBUTION COEFFICIENTS

Uranium, HNO_3 , and H_3PO_4 parameters

1. 0. moles/l H_3PO_4 in aq. phase
2. 0.025 " " " " "
3. 0.061 " " " " "
4. 0.125 " " " " "

Uranium sat. of org. 65%
Extractant 30% TBP-Amsco

FIGURE 3

0142 018

EQUILIBRIUM CONSTANTS FOR PLUTONIUM-PHOSPHATE COMPLEXING -- E.E. Voiland

An analysis of the plutonium distribution data (see above) can be made assuming a competition between TBP and phosphate (here used in the generic sense) for plutonium(IV). The net result, if the phosphate complex is not readily extracted, is a reduction of available plutonium for TBP complexing and a reduction in the distribution coefficient for plutonium.

For the general reactions,

Equilibrium constants can be written

$$\begin{aligned} 3) \quad K_1 &= \frac{[\text{Pu} \cdot x \text{ Phos}]}{[\text{Pu}] [\text{Phos}]^x}, \\ 4) \quad K_2 &= \frac{[\text{Pu} \cdot x \text{ TBP}]}{[\text{Pu}] [\text{TBP}]^y}, \end{aligned}$$

where [Phos] represents a species linearly related to H_3PO_4 .

The distribution coefficient, considering the phosphate complex not to be extracted is

$$5) \quad E_a^\circ(\text{Pu}) = \frac{[\text{Pu} \cdot y \text{ TBP}]}{[\text{Pu}] + [\text{Pu} \cdot x \text{ Phos}]},$$

which by substitution and rearrangement transforms to

$$6) \quad E_a^\circ(\text{Pu}) = \frac{K_2 [\text{TBP}]^y}{1 + K_1 [\text{Phos}]^x},$$

and eventually to

$$7) \quad \log \left[\frac{1}{E_a^\circ(\text{Pu})} - \frac{1}{E_a^\circ(\text{Pu})_0} \right] = x \log [\text{Phos}] + \log \frac{K_1}{E_a^\circ(\text{Pu})_0},$$

where $E_a^\circ(\text{Pu})_0$ refers to the distribution coefficient in the absence of H_3PO_4 and UNH. The value of x is determined graphically. The value of K_1 is also obtained graphically, from the relation

$$8) \quad \frac{E_a^\circ(\text{Pu})_0}{E_a^\circ(\text{Pu})} \times K = \frac{E_a^\circ(\text{Pu})_0}{E_a^\circ(\text{Pu})} = K_1$$

At acidities of 4.5 and 7 M, x was determined as 1.1 and 1.2, respectively. Graphical evaluation of K_1 with x equal to unity gave satisfactory linear plots of $E_a^\circ(\text{Pu})_0/E_a^\circ(\text{Pu})$ against $[\text{H}_3\text{PO}_4]$, and values of 47 and 32 for the equilibrium constant at these same acidities. For the 3 M acid system, x could not be determined as the slope of $\log \left[\frac{1}{E_a^\circ} - \frac{1}{E_a^\circ} \right]$ vs. $\log [\text{H}_3\text{PO}_4]$ increased rapidly with H_3PO_4 concentration. However,

if a value of 2 for x was used, an approximately linear plot of $\frac{E_a(\text{Pu})_0}{E_a(\text{Pu})}$ against $[\text{H}_3\text{PO}_4]^2$ was obtained. This may be interpreted as evidence for a 1:1 plutonium-phosphate complex at the higher acidities with transition to another species of greater phosphate to plutonium content at an acidity between 4.5 and 3 M.

The values of y and K_2 can be determined in the same way. The plutonium distribution coefficient has been observed to vary approximately with the square of the TBP concentration. This may also be true for TBP uncomplexed by uranium, which is equal to the total TBP concentration less twice the dissolved uranium concentration, since the ratio of TBP to uranium in the complex is two (1).

In the absence of phosphoric acid $E_a(\text{Pu})$ should equal $K_2(\text{TBP}-2\text{U})^2$. However, when this relation was tested at 3, 4.5, and 7 M HNO_3 concentrations, a consistent trend was found. With increasing (TBP-2U) concentration, $E_a(\text{Pu})$ dropped below the expected values. Graphical evaluation of the exponent gave 1.7, which satisfied the equation for uranium saturation (30% TBP) of from 0 to 65%. The values of K_2 were 12, 22, and 32* for the acidities 3, 4.5, and 7 M, respectively. The wide range of applicability of 1.7 as the value for y is surprising and merits further investigation for possible theoretical significance.

The expressions derived from this analysis are summarized:

$$9) \quad 7.0 \text{ M } \text{H}^+, \quad E_a(\text{Pu}) = \frac{32*(1.1-2\text{U})^{1.7}}{1 + (32)(\text{H}_3\text{PO}_4)} ,$$

$$10) \quad 4.5 \text{ M } \text{H}^+, \quad E_a(\text{Pu}) = \frac{22 (1.1-2\text{U})^{1.7}}{1 + 47 (\text{H}_3\text{PO}_4)} ,$$

$$11) \quad 3.0 \text{ M } \text{H}^+, \quad E_a(\text{Pu}) = \frac{12 (1.1-2\text{U})^{1.7}}{1 + 600 (\text{H}_3\text{PO}_4)} .$$

The results of this investigation indicate that in the Purex extraction systems 0.06 M H_3PO_4 at an HAFS acidity of 5 M and 0.11 M H_3PO_4 at an acidity of 7.0 M can be tolerated without increasing waste losses. The value of the plutonium distribution coefficients at these conditions is about 9.

Since the effect of H_3PO_4 on the uranium and plutonium distribution coefficients need not be prohibitive and since its effect on fission product decontamination appears to be beneficial, a high acid-phosphate feed in the Purex Process Flowsheet seems potentially desirable. Further investigation will determine where in the Purex system advantage of these effects can best be taken.

Reference

- (1) Moore, R.L., "The Extraction of Uranium in the Tributylphosphate Metal Recovery Process," HW-15230, Sept. 1, 1949.

*When $E_a(\text{Pu})$ was determined at an acidity of 7 M and in the absence of uranium, an increase was noted with the decreasing org/aq volume ratios 2, 1, and 0.5. Extrapolation to 0 resulted in a limiting value of 35-36, with a corresponding value for K_2 of ca. 32.

EFFECT OF SOLVENT-FIXED FISSION PRODUCT ACTIVITY ON PUREX DECONTAMINATION -- C. Groot

The object of these experiments was to determine whether the increased fission product activity fixed in recirculated Purex solvent as a function of time affects first cycle decontamination. The problem was studied by synthesizing "hot" solvent and measuring the decontamination obtainable in a batch extraction cycle.

The Purex solvent retains activity because of the accumulation of chemical species capable of complexing fission products. These species originate in chemical reactions of the solvent, such as hydrolysis, or in radiation induced decomposition. If the chief reaction is only chemical, then used solvent from the "cold" test facility (321 Building) should contain the active agent, and contact of this solvent with dissolver solution should fix some fission products in the solvent. If the reaction is radiation induced, prolonged contact of the solvent with dissolver solution should produce a hot solvent.

Tests were made with new distilled and carbonate-washed solvent, used solvent from the 321 Building (RCW from 3" - 37-R7, 11-12-52), and some of this same used solvent after carbonate and water washing.

The testing procedure adopted was to duplicate, as well as could be done in test tubes, Purex Chemical Flowsheet #1 (1). The procedure consisted of a batch contacting of dissolver solution with solvent for a specified time, followed by three scrubbing and three stripping stages. This procedure resulted in recovery of about 70% of the uranium and 40% of the plutonium. The activity of the resulting WCP was measured.

Results are given in Table I. With a long contact time, 30 times as much γ activity carried over in the solvent, did not scrub out, but was stripped out. This change in solvent behavior was due to radiation damage, since new and used solvent behaved normally with a short contact. However, used solvent from the 321 Building, even after washing, complexed an unusually large amount of beta and gamma activity irreversibly, although decontamination was not hurt. The above interpretation is complicated by the improvement shown when extracting from a solution of lower acidity and when using longer scrubbing time.

TABLE IACTIVITY OF WCP AND RCW AS FUNCTION OF SOLVENT AND CONTACT TIME

Solvent	Stirring Time/ 4 ml D.S.	HNO ₃ in HAFS M	Scrubbing Time, min.	WCP		RCW	
				c/m/mg U		c/m/ml	
				β	γ	β	γ
Used(321 Bldg.)	5 min.	5	5	75	710	10,000	68,000
Used, washed	5 "	5	5	69	580	13,000	62,000
New	5	5	5	180	560	2,200	6,700
New	5	3	10*	50	130	5,500	10,000
New	69 hrs.	3	10*	210	3800	3,700	14,000

*More effective, as well as longer agitation.

On the basis of the meager data, when fission products are fixed in the organic due to chemically produced active agents, the decontamination was not adversely affected. Extensive solvent irradiation, however, was shown to lower decontamination.

Reference

- (1) Tomlinson, R.E. and Woodfield, F.W., "Purex Chemical Flowsheet #1," HW-24763, 6/30/52.

FISSION PRODUCT BEHAVIOR AS A FUNCTION OF DISSOLVING CONDITIONS -- R.L. Moore, W.W. Schulz, and R.A. Watts, Jr.

A program to determine the effect of changes in the conventional nitric acid dissolving conditions on subsequent solvent extraction was continued. The apparatus and experimental techniques used in this study were discussed in detail in a previous quarterly report (1). Emphasis this quarter was directed toward determining the effects produced by additives during dissolution.

Work reported by E.E. Voiland (2) indicates that the addition of phosphate ion to high-acid Purex LAFS solutions results in improved zirconium and niobium decontamination. It was thought that this beneficial effect might also occur under normal Purex conditions if the phosphate were present during dissolution of the metal.

Consequently, a dissolving (N-7) of irradiated uranium pellets was carried out to test this supposition. Standard Redox dissolving conditions were simulated, and sufficient H_3PO_4 was added to make the final solution 0.01 M in H_3PO_4 . The presence of phosphate was observed to increase the initial rate of dissolution, resulting in a reduction of dissolving time and a lower final acidity (-0.6 M) than is usually obtained in the laboratory dissolvings. A phosphate concentration of 0.01 M was used since several dissolvings of unirradiated uranium pellets showed this concentration to be the maximum one permissible under acid deficient conditions. At low acidities, phosphate concentrations greater than 0.01 M produced insoluble uranium phosphates.

Duplicate Purex extraction-scrub studies were carried out with solution N-7. A comparison of the results with individual fission product decontamination factors obtained for plant dissolver solution containing no phosphate indicated no significant differences. Apparently under normal Purex flowsheet conditions, 0.01 M H_3PO_4 is too small a concentration to cause any change in niobium or zirconium behavior.

Table I lists the results of several extraction-scrub studies carried out under Redox conditions to test the effects of phosphate addition. For solution N-7, produced by dissolution in the presence of H_3PO_4 , ruthenium, cerium, and zirconium decontamination was adversely affected. Niobium behavior, on the other hand, was improved by a factor of six. It is difficult to reconcile the adverse effects of the presence of phosphate during dissolution with the results obtained when phosphate was added to plant dissolver solution. In the latter experiments, normal ruthenium and cerium behavior was noted. In the case in which a Redox LAFS, 0.005 M in H_3PO_4 , was allowed to stand 15 days before extraction, an improvement in niobium decontamination was again noted. Zirconium behavior was also improved.

References

- (1) HW-26937, Quarterly Report, Oct. through Dec., 1952, Chemical Research, pp. 39-56.
- (2) HW-27727, Quarterly Progress Report, Chemistry Unit, Jan., Feb., Mar., 1953, pp. 12-14.

TABLE I

THE EFFECTS OF THE PRESENCE OF PHOSPHATE UPON FIRST-CYCLE REDOX DECONTAMINATION FACTORS

One extraction, three scrubs under conditions of HW #4 Redox Flowsheet

<u>Dissolver Solutions Number and Type</u>	<u>Time since Dissolved (days)</u>	<u>Relative Improvement in Decontamination</u>					
		<u>Gross beta</u>	<u>Gross gamma</u>	<u>Ruthenium</u>	<u>Cerium</u>	<u>Zirconium</u>	<u>Niobium</u>
N-7 H ₃ PO ₄ present during dis- solution	10	0.07	0.3	0.05	0.08	0.09	6.3
Plant dissolver solution*	55	0.8	1.0	0.9	1.9	0.9	0.9
Plant dissolver solution**	76	2.2	14.	2.2	--	5.9	35.

*LAFS made 0.005 M H₃PO₄ and extracted immediately.**LAFS made 0.005 M H₃PO₄ and allowed to stand 15 days before extracted.

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TAIL-END TREATMENT OF PUREX LEU -- R.L. Moore and W.W. Schulz

This investigation is another of a series designed to find ways of improving decontamination of Purex Process product streams by the use of simple adsorption or scavenging techniques.

Previous investigations have shown the CuS-precipitation, silica gel adsorption, Tail-End treatment to be effective in decontaminating Redox 2DF and/or 3DF streams from ruthenium, zirconium, and niobium. Further testing of this Tail-End treatment has now been carried out with portions of off-standard Purex LEU produced in Oak Ridge Pilot Plant Run HCP-20. Flowsheet conditions employed in Run HCP-20 resulted in only 50% uranium saturation of the TBP extractant as compared to a normal uranium saturation of 75%. The lower uranium saturation of the organic phase probably accounts for the abnormally high level of ruthenium, zirconium, and niobium activity in the concentrated LEU solution.

To carry out the copper sulfide precipitation, the HNO_3 concentration of the LEU solution was adjusted from 0.82 M to 0.0 M by addition of NH_4OH . The solution was then made 0.003 M $\text{Cu}(\text{NO}_3)_2$, saturated with H_2S for two hours at room temperature, and finally air sparged until the exit air did not darken filter paper moistened with lead nitrate solution. The copper sulfide precipitate was then filtered off and the filtrate analyzed for ruthenium activity. This analysis showed <20 c/m/ml of ruthenium; in comparison, the LEU solution before CuS precipitation contained 13,000 c/m/ml of ruthenium (counts made through 25 mg/cm² Au Abs.). Thus, precipitation of CuS to remove ruthenium was again demonstrated to be a highly effective procedure, providing in this case a ruthenium D.F. of 500.

The filtrate from the CuS precipitation step was then utilized as feed for a three milliliter silica gel bed in order to test zirconium and niobium adsorption. Before passage through the bed, the filtrate was acidified to 0.3 M HNO_3 . Acidification to this concentration permits more effective niobium and zirconium adsorption and also serves to reoxidize small amounts of uranium(IV) produced when the solution is saturated with H_2S . Adsorption conditions and results are shown in detail in Table I.

Zirconium and niobium decontamination factors for the first portions of effluent are comparable to those obtained in earlier work with solutions containing smaller amounts of zirconium and niobium activity. However, even though the silica gel bed operated as efficiently as in previous experiments, the per cent zirconium and niobium not adsorbed was sufficient to exceed gamma specifications in even the first portions of effluent. Thus, these results indicate that for a given size bed there is an upper limit to the feed concentration of zirconium and niobium which may be effectively adsorbed. This LEU solution, being off-standard, contained far more zirconium and niobium activity than is usually found in either Purex LEU or Redox 3DF streams. The zirconium and niobium activity normally present in these solutions would be easily removed by this Tail-End treatment.

TABLE I

SILICA GEL ADSORPTION OF ZIRCONIUM AND NIOBIUM ACTIVITY
FROM PUREX LEU SOLUTION

<u>Bed Dimensions</u>	<u>Feed Composition</u>
Volume = 3.0 cm ³	Acidified filtrate from CuS precipitation
Height = 15.0 cm	21 g/l HNO ₃ , 407 g/l U
<u>Silica gel Specs.</u>	Gross gamma = 1.90x10 ⁵ c/m/ml
Davison Grade A, Type 3	Gross beta = 3.0x10 ⁴ c/m/ml
40-50 mesh	U _x beta = 1.7x10 ⁴ c/m/ml
<u>Flow Rate</u>	Ruthenium β = < 20 c/m/ml
2.1 m/min/cm ²	Cerium β = 160 c/m/ml
	Zirconium γ = 1.0x10 ⁵ c/m/ml
	Niobium γ = 1.1x10 ⁵ c/m/ml
	Gross beta, U _x beta, ruthenium beta, and cerium beta counted on 2nd shelf BGO, 7.5% geometry, through 25 mg/cm ² Au absorber.
	Gross gamma, zirconium gamma, and niobium gamma counted on 1st shelf GSC, 10% geometry, through 1.7 g/cm ² Pb absorber.

<u>Sample No.</u>	<u>Total Bed Volumes Passed</u>	<u>Effluent Composition</u>			
		<u>% γ * of ANU</u>	<u>% β * of ANU</u>	<u>Zr c/m/ml</u>	<u>Nb c/m/ml</u>
1	9.3	630	39	9,700	3,400
2	32.3	930	48	13,000	8,400
3	48.6	1300	50	15,000	13,400
4	102	2000	53	20,000	22,000
5	177	4500	72	38,000	61,000
6	200	2100	52	25,000	25,000
7	265	2300	54	27,000	29,000

*Percentages of beta and gamma activity of aged natural uranium calculated after correction for U_x activity.

DECONTAMINATION OF RCU BY PASSAGE THROUGH DOWEX 50 RESIN -- R.L. Moore, W.W. Schulz, and R.A. Watts, Jr.

For the start-up of the Metal Recovery Plant on six-year old metal waste, the beta specification for the RCU stream was tentatively set at 30% of the beta activity of aged natural uranium. Although this goal was realized during start-up, the beta activity of the major portion of RCU produced in December, 1952, exceeded the tentative specification. Radiochemical analyses showed yttrium and rare earth contamination to be largely responsible for the excessive beta activity.

The possibility that the RCU stream might be contaminated with rare earth activity had been considered earlier during an investigation of a Tail-End Process for the removal of zirconium, niobium, and ruthenium contamination from process uranium streams (1). In these earlier experiments the ion exchange resin Dowex-50 was found to have a high capacity for adsorbing rare earth activity from RCU solutions produced by a 3/8 inch MINI unit. As a result of the recent plant difficulties, these previous experiments with Dowex-50 were repeated and extended using plant RCU solutions.

A six-milliliter bed of 50-100 mesh Dowex-50 was prepared for downflow adsorption of rare earth activity. Column dimensions and resin specifications are given in Table I. The particular portion of Dowex-50 used in this work had been converted to the hydrogen form by washing with 6 M HCl.

The feed for the column was a composite sample of eight off-standard RCU solutions produced in the Metal Recovery Plant. These RCU solutions had been stored approximately five days before adsorption work was commenced. Results of a radiochemical analysis of this feed are listed in Table I. Approximately 600 bed volumes of RCU solution were passed through the resin bed at an average flow of 1.0 ml/min/cm². Table I lists the results of analyses of the effluent. At the conclusion of the adsorption step, the bed was eluted with 6 M HNO₃.

The results in Table I demonstrate the feasibility of Dowex-50 for decontaminating RCU solutions from rare earth activity. After passage of approximately 600 bed volumes of feed, the effluent beta activity was still less than 30% of the beta activity of aged natural uranium. The absence of a breakthrough point indicates the high capacity of Dowex-50 for adsorbing rare earth activity.

It should also be noted that the effluent beta percentages given in Table I were calculated on the assumption that yttrium and rare earths were the only fission products adsorbed. This assumption results in high values for the beta percentages since zirconium, and possibly strontium, are also partially adsorbed. This method of calculation was adopted because of the uncertainties resulting from growth of UX activity and unknown amount of adsorption of UX activity. The capacity of the Dowex-50 bed is thus somewhat higher than indicated by the data in Table I.

After passage of eleven bed volumes of RCU solution, the effluent and feed uranium concentrations were equal. Approximately 1.60 grams of uranium were adsorbed in converting the bed from the hydrogen to the uranyl form. For passage of 600 bed volumes of RCU, the uranium adsorbed represents a 1.5% hold-up. Further operation of the column to breakthrough would, of course, have decreased the percentage uranium hold-up.

TABLE I
DOWEX-50 ADSORPTION OF RARE EARTH ACTIVITY
FROM PLANT RCU SOLUTION

Bed Dimensions
Volume = 6.0 cm³
Height = 6.2 cm

Resin Specifications
Dowex-50W, 50-100 mesh
12% cross linkage

Flow Rate
1.0 ml/min/cm²

Feed Composition
Plant RCU, 9.7 g/l HNO₃, 26.8 g/l Uranium

Gross gamma = 420 c/m/ml -- 12/19/52
Gross beta = 1500 c/m/ml -- 12/19/52
Ruthenium β = 170 c/m/ml -- 12/19/52
Strontium β = 67 c/m/ml -- 12/19/52
Zirconium β = 10 c/m/ml -- 12/19/52
Yttrium plus
rare earths β = 1000 c/m/ml -- 12/19/52
 = 720 c/m/ml -- 12/23/52
 = 610 c/m/ml -- 12/29/52

Gross beta, strontium beta, ruthenium beta,
zirconium beta, and yttrium plus rare earth
beta counted on 2nd shelf BGO, 7.5% geometry,
with no absorber.

Gross gamma counted on 1st shelf GSC, 10%
geometry, through 1.7 g/cm² Pb absorber

Sample No.	Total Bed Volumes Passed	Y plus RE Activity* (c/m/ml)	% beta of ANU** Due to Fission Products
1	52	42	15
2	104	95	18
3	149	67	17
4	199	52	16
5	256	130	20
6	303	76	17
7	352	210	24
8	395	160	23
9	449	220	25
10	502	200	24
11	553	180	23
12	597	230	25

*Yttrium plus rare earth activity counted 12/30/52.

**Per cent beta of aged natural uranium calculated on assumption
that no zirconium, strontium, or ruthenium were adsorbed. On
this basis the feed on 12/30/52 was 46% ANU.

In the absence of a material balance across the elution cycle, elution with 6 M HNO_3 did not appear to be successful. Only 64% of the activity associated with the bed was removed by passage of forty bed volumes of eluting agent. Essentially all the uranium was removed. Thereafter, additional eluting agent removed negligible amounts of activity.

Considerable column gassing was noted during elution with 6 M HNO_3 . Reas and co-workers (2) in their studies of the application of Dowex-50 for concentrating plutonium streams, have also experienced difficulties from column gassing during elution with 6 M HNO_3 , 0.4 M $\text{NH}_2\text{SO}_3\text{H}$. These investigators have shown that gassing during elution can be eliminated by using 20-50 mesh Dowex-50 with a smaller percentage (8%) of cross linkage. Elution of 12% cross linkage Dowex-50 with 3 M H_2SO_4 was also shown to eliminate gassing. This latter reagent appears feasible for eluting Dowex-50 beds used with RCU solutions. Better rare earth removal might be obtained, and, in view of the fact that the RAF streams contain 0.26 M sulfate ion, the first portions of the sulfuric acid effluent could be recycled for uranium recovery if desirable. Citric and oxalic acids have also been suggested as possible eluting agents.

References

- (1) HW-26104, Quarterly Report - July through Sept., 1952, Chemical Research, p. 63, Nov. 3, 1952.
- (2) HW-26104, Quarterly Report - July through Sept., 1952, Chemical Research, p. 88-93, Nov., 3, 1952.

PEROXIDE PRE-TREATMENT OF THE REDOX 2nd URANIUM CYCLE FEED -- R.L. Moore and R.A. Watts, Jr.

Previously reported results (1) indicated that improved decontamination from beta and gamma activity resulted from a drastic hydrogen peroxide pre-treatment of a simulated Metal Recovery feed solution. Consequently, a similar treatment was carried out on a Redox 2DFS solution in order to test its effects upon decontamination in the Redox second uranium cycle.

The treatment used consisted of making the 2DFS solution 5.0 M in hydrogen peroxide, digesting the uranyl peroxide thus produced for one hour at 50°C , and destroying the excess peroxide by boiling the solution back to its original volume. Duplicate extraction-scrub studies were run on the solution thus treated.

The treatment described above resulted in a lowering of the beta, gamma, and ruthenium decontamination factors by factors of 16, 18, and 15, respectively. Formation of emulsions and inter-face crud, occurring in the extraction stage, may have been an indication of the presence of incompletely destroyed peroxide. If this were the case, the poor decontamination probably resulted from the presence of hexone decomposition products produced from the oxidation of hexone by the undestroyed peroxide.

At this time, due to the poor results found in this scouting experiment, no further work is planned on the peroxide treatment for Redox uranium streams.

Reference

- (1) HW-26104, Quarterly Report - July Through Sept., 1952, Chemical Research, p. 63, Nov. 3, 1952.

EFFECTS OF MERCAPTAN PRE-TREATMENT UPON REDOX AND PUREX DECONTAMINATION -- R.L. Moore and R.A. Watts, Jr.

Work was continued this quarter upon improving decontamination in both the Redox and Purex Processes by the use of BAL (2,3 dimercaptopropanol-1) and β -mercaptopropionic acid. However, emphasis was placed upon a digestion type of treatment rather than the mercaptan-metal ion scavenging techniques previously demonstrated.

1. Redox 2nd Uranium Cycle Studies: A series of experiments were performed employing Redox plant 2DF solution. The mercaptans were added either to the feed or scrub solution and extraction-scrub studies (one extraction, two scrubs) were carried out under the standard HW#4 flowsheet. The beta, gamma, and ruthenium decontamination factors across this cycle were compared with those of a control experiment containing no mercaptan. The addition of BAL to the feed (to 0.05 M) was found to have a decidedly detrimental effect, the decontamination from ruthenium being reduced by a factor of about 13 when the feed was digested at room temperature and by a factor of almost 140 when digested for one hour at 50°C. Beta and gamma decontamination was similarly affected. Decomposition of the BAL and a tendency to promote emulsion formation was also noted.

These difficulties were not observed with β -mercaptopropionic acid, and some improvement in decontamination was apparently obtained. However, this amounted to a factor of only 2.5 for 50°C digestion of a feed 0.05 M in the mercaptan and to a factor of 1.7 for room temperature digestion. Addition of either mercaptan to the scrub was apparently less effective than digestion with the feed.

2. Purex 2nd Uranium Cycle Studies: Purex 2nd cycle feed solutions prepared from Redox 2DF and ORNL pilot plant first cycle LCU were given digestion treatments similar to those described for the Redox stream. The ruthenium decontamination factor was 0.05 M β -mercaptopropionic acid, and scrubs were made 0.02 M. When the mercaptan concentrations in the feed and scrubs were raised to 0.1 M and 0.05 M, respectively, and the treatment applied to the Oak Ridge material previously mentioned, the ruthenium improvement factor jumped to 16. MINI runs have been recommended to test the effectiveness of this treatment under dynamic flow conditions.

3. Purex 1st Cycle Studies: In view of the large improvements noted in second cycle Purex, β -mercaptopropionic acid digestion was applied to first cycle Purex solutions. This was done with the hope that the improvement would then apply to both the uranium and the plutonium cycles. Cold experiments had indicated previously the necessity of having a nitrite suppressor present with dissolver solutions containing β -mercaptopropionic acid. Ferrous sulfamate proved satisfactory to prevent nitrite attack on the mercaptan. With this one addition, plus the lowering of mercaptan concentration in the feed to 0.024 M, the treatment used in second cycle work was applied to a Purex HAFS prepared from plant dissolver solution. The results indicate a two-fold improvement in ruthenium decontamination plus an unexpected and unexplained six-fold improvement in niobium behavior. It is planned to repeat and extend these experiments.

PULSE COLUMN LIMITING FLOW RESEARCH -- W.H. Swift and L.L. Burger

One of the greatest uncertainties in pulse column operation is the prediction of the flooding point. Experience has indicated that a program for the fundamental study of the limiting flow or "flooding" phenomena in pulse columns would be desirable. The possibility of interaction between operational, column design, and physical property variables indicated that the program should include as many of the pulse column variables as can conveniently be studied, in addition to the effect of physical properties.

In order to firm the design of a column to give the best representation of flooding capacity, and to demonstrate the reproducibility of the flooding point, seventeen runs were made in a 1.00" I.D. by 27.5" packed height column using the system water (continuous) - Amsco 125-90W (dispersed). The plate cartridge consisted of 27 stainless steel plates of 0.040" diameter holes, 22.7% open area and at 1.00" face to face spacing. Nominal frequency and amplitude used in these runs were 58 cyc/min and 0.75" respectively. The results of these runs are tabulated below, and the B series runs plotted in Figures 4 and 5.

As can be seen from Figure 5, total flooding volume velocity (sum of both phases) shows greater dependency on the dispersed phase flow rate than on that of the continuous phase. It was also evident from observation of the column that the mechanism of flooding changes in going from low to high values of the flow ratio. At low (< 1) ratios of continuous to dispersed phase flow, flooding occurs almost simultaneously over the entire column length, though there is some tendency for the flood to start at the end where the dispersed phase leaves the "packed" section. At high (> 1) ratios of continuous to dispersed phase flow, flooding is initiated at the point where the dispersed phase enters the "packed" section. The latter phenomenon is related to the apparent formations of drops in two distinct size ranges, with random distribution in each. Due to the high continuous phase rate, elution of the smaller drops to the dispersed phase inlet end of the packing occurs, the apparent specific gravity of the continuous phase is lowered, and the driving force for flow of the dispersed (lighter) phase is reduced. Hold-up of the dispersed phase at this end of the column is also increased, and the average dispersed phase velocity changes according to the relation $v_d = U_o/H$ where v_d is the average dispersed phase drop velocity, U_o linear velocity of the dispersed phase based on the overall column cross section, and H is the fractional hold-up of the dispersed phase.

A 2.00" I.D. pulse column operating with a sinusoidal pulse was chosen as the apparatus in which the majority of the future runs will be made. A 2.00" I.D. will make it possible to study the effect of large perforated plate hole size and still maintain a reasonable ratio of hole diameter to column diameter. Wall effect and leakage around the plate circumference will also be reduced relative to a 1.00" I.D. column. The sine wave pulse shape was chosen since it can be completely specified by its amplitude and frequency. A pulse generator utilizing a Scotch-Yoke driving a Teflon bellows was obtained, installed, and preliminary runs started at the end of the quarter.

On the completion of the 2.00" I.D. installation, orifice coefficients for a perforated plate cartridge (0.040" dia. holes, 22.7% open area, approximately 0.020" thick, and at 1.00" plate spacing) were measured for single phase (water) flow without application of a pulse to the column. The pressure drop was measured with a nitrobenzene/water manometer. The results of these runs are tabulated below (Table II) and plotted in Figure 6. It is hoped that the orifice coefficient (a measure of the irreversibility of the process of flow through an orifice) will be of use in correlating flooding data.

FLOODING CAPACITY OF A 1.00" DIAMETER PULSE COLUMN AS A FUNCTION OF FLOW RATIO

CARTRIDGE
.040" Dia. Holes
22.7% Open Area
1.00" Plate Spacing, 26 Plates

SYSTEM
Continuous Phase: DISTILLED WATER
Dispersed Phase: AMSCO 125-90W
Pulse Freq. = 58 cyc./min. (nom), Amplit. = 0.75" (nom)

FIGURE 4

FLOODING CAPACITY OF A 1.00" DIAMETER PULSE COLUMN

CARTRIDGE:

.040" Dia. Holes
22.7% Open Area
1.00" Plate Spacing
26 Plates

SYSTEM:

Continuous Phase: DIST. WATER
Dispersed Phase, AMSCO 125-90W
Pulse Freq. = 58 cyc./min. (nom.)
Amplitude = 0.75" (nom.)

FIGURE 2

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TABLE I

FLOODING CAPACITY OF A 1.00" DIAMETER PULSE COLUMN

Cartridge				System			Remarks
0.040" Dia. Holes 22.7% Open Area 1.00" Plate Spacing, 27 Plates				Continuous Phase: Distilled Water Dispersed Phase: Amsco 125-90W			
Run No.	Frequency cyc/min	Amplitude In.	U _c - Continuous gal/hr sq.ft.	U _d - Dispersed gal/hr sq.ft.	Flow Ratio U _c /U _d	Vol. Velocity U _c +U _d Sum of Both Phases gal/hr sq.ft.	Column Wall Partially Organic Wet
A-1	58.5	0.75	260	400	0.649	660	
A-2	"	"	357	295	1.208	652	
A-3	"	"	108	390	0.277	498	
A-4	"	"	108	390	0.277	498	
A-5	56	"	200	357	0.560	557	
A-6	"	"	483	261	1.855	744	
A-7	57	"	0	435	0	435	
A-8	57	"	58.5	402	0.145	460	
B-1	58.5	0.72	526	408	0.628	664	
B-2	58.0	"	408	390	1.047	798	
B-3	"	"	492	378	1.302	870	
B-4	"	"	582	348	1.673	930	
B-5	"	"	170	456	0.372	626	
B-6	"	"	844	270	3.120	1114	
B-7	59.0	"	87	483	0.180	570	
B-8	"	"	309	432	0.715	741	
B-9	58.0	"	1140	210	5.31	1350	

TABLE II

PRESSURE DROP AND ORIFICE COEFFICIENT FOR CONTINUOUS WATER FLOW
THROUGH A 2.00" PULSE COLUMN CARTRIDGE

Cartridge

0.040" Dia. Holes

22.7% Open Area

1.00" Plate Spacing

Plate Thickness = ~0.020"

Staggered Hole Spacing

Conditions

Water at 20°C

ΔP Across 18 Plates

in a 25 Plate Cartridge

Run No.	Volume Velocity gal/hr sq.ft.	Pressure Drop/Plate Δ H- Ft. of Water	Orifice Veloc. V _o ft/sec.	Reynold's No. $NR_e = \frac{D_o V_o \rho}{\mu}$	Orifice Coef. C _o $\frac{V_o}{\sqrt{2g\Delta H}}$
1	144	1.28 x 10 ⁻⁴	0.0237	7.26	0.261
2	228	1.78 x 10 ⁻⁴	0.0375	11.49	0.351
3	299	2.11 x 10 ⁻⁴	0.0490	15.01	0.417
4	435	3.61 x 10 ⁻⁴	0.0714	21.88	0.463
5	605	5.22 x 10 ⁻⁴	0.0992	30.39	0.540
6	737	7.06 x 10 ⁻⁴	0.121	37.07	0.566
7	862	8.89 x 10 ⁻⁴	0.142	43.50	0.588
8	1005	11.11 x 10 ⁻⁴	0.165	50.56	0.612
9	1315	16.67 x 10 ⁻⁴	0.216	66.18	0.655

ORIFICE COEFFICIENT VS REYNOLD'S NUMBER

CONTINUOUS FLOW OF WATER THROUGH A 2.00" I.D. PULSE COLUMN CARTRIDGE

CARTRIDGE: 25 PLATES, .040" HOLES, 22.7% OPEN AREA, 1.0" BRACING, .020" THICK, STAGGERED

CONDITIONS: 20°C, H ACROSS 18 PLATES BY NITROBENZENE / WATER MANOMETER

HOLES.

FIGURE 6

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INTERACTION OF TRIBUTYLPHOSPHATE WITH DILUENTS -- R.L. Dillon, W.F. Johnson, and L.L. Burger

Consideration of diluents for TBP from a process point of view has been based largely on availability, flash point, viscosity, density, and stability. However, when one considers either the equilibria of a two-phase system or the kinetics of transfer between the phases, it is readily apparent that interactions between the solvent TBP and the various diluents are in many cases large, and a study of extraction mechanism necessitates some investigation of these interactions. It has been previously noted, for example, that the use of pentachlorethane as a diluent suppressed the extraction of uranyl nitrate (1) and that water solubilities of TBP from different diluents show wide variations (2).

The data presented here is a continuation of the work discussed in the last quarterly report (2).

Solubility of TBP in Water

The determination of the solubility of TBP in water as a function of the TBP concentration in various diluents has been completed. The data for the diluents dodecane, mineral oil (average molecular weight corresponding to C_{18}), chloroform, pentachlorethane, and n-octyl bromide are presented as Table I.

TABLE I

SOLUBILITY OF TBP IN WATER FROM TBP-DILUENT SOLUTIONS AT 25° C

<u>Diluent/Vol.% TBP</u>	<u>Conc. TBP (g/l) in Aqueous Phase</u>					
	<u>100</u>	<u>70</u>	<u>50</u>	<u>25</u>	<u>10</u>	<u>5</u>
Dodecane	0.44	0.33	0.28	0.24	0.18	0.11
Mineral Oil	--	0.37	0.33	0.30	0.24	0.17
Chloroform	--	0.09	0.04	0.01	0.005	--
Pentachlorethane	--	0.19	0.08	0.02	0.01	0.005
n-octyl bromide	--	0.31	0.22	0.11	0.04	0.02

Comparing these data with those reported in HW-26937, it is noted that for the paraffin hydrocarbon diluents the solubility of TBP in water increases regularly with increasing molecular weight.

Solubility of Water in TBP

The solubility of water in TBP-diluent solutions has been determined for the diluents used on the study of TBP solubility in water. The solutions were equilibrated with water at room temperature which varied between 24 and 27°C. Water analysis was made with Karl Fischer reagent. The data are presented in Table II.

TABLE IIWATER SOLUBILITY IN TBP-DILUENT SOLUTIONS

<u>Diluent/Vol.% TBP*</u>	<u>100</u>	<u>70</u>	<u>50</u>	<u>25</u>	<u>10</u>	<u>5</u>
Dodecane	3.54	1.82	0.98	0.32	0.08	0.03
Hexane	--	1.77	0.98	0.32	0.07	0.03
Cyclohexane	--	1.74	0.93	0.29	0.07	0.03
Benzene	--	1.84	1.00	0.36	0.15	0.09
n-Octylbromide	--	1.60	0.85	0.20	0.08	0.04
Carbon Tetrachloride	--	1.40	0.66	0.40	0.06	0.03
Chloroform	--	0.81	0.35	0.40	0.13	0.10
Pentachlorethane	--	0.94	0.30	0.09	0.08	0.08

*TBP conc. prior to saturating with H₂O.

The above data were obtained from smooth curves drawn through the experimental points. The results for dodecane are in good agreement with those reported by Burger using Amsco-125-90W as a diluent (3).

Water solubility in TBP-hydrocarbon systems is essentially independent of the molecular weight of the hydrocarbon, whereas the solubility of TBP in water from these solutions is markedly dependent on the molecular weight of the diluent. The data suggest that the solution of water in TBP or TBP-diluent mixtures does not result in TBP-water complexes of a definite simple mole ratio.

Partial Molal Volume of TBP

In the course of the above studies the densities of all the solutions prepared were measured. This allowed the calculation of the partial molal volume of the TBP in these various diluents. In all cases the partial molal volume of TBP was found to be constant from 0 to 75% by volume and only slightly different from the molal volume of TBP. Within experimental error the partial molal volumes of the diluents were found to be equal to their molal volumes over the same concentration range. The partial molal volumes of TBP obtained are given in Table III.

TABLE IIIPARTIAL MOLAL VOLUME OF TBP IN VARIOUS DILUENTS AT 25.0°C

Concentration of TBP = 0 to 75% by Volume

<u>Diluent</u>	<u>Partial Molal Volume TBP</u>	<u>Diluent</u>	<u>Partial Molal Volume TBP</u>
Dodecane	275.2	n-Octylbromide	275.3
Hexane	272.6	Carbon tetrachloride	273.6
Cyclohexane	274.5	Chloroform	275.3
Benzene	273.3	Pentachlorethane	273.0

In view of the differences shown by these diluents in deviations from ideality, e.g., solubility, viscosity, and freezing point depression, it is surprising that the partial molal volumes appear to be independent of the diluent.

Diffusion Coefficient of TBP

The diffusion coefficient of TBP in cyclohexane, dodecane, and pentachlorethane has been determined. The method of Anderson and Saddington was used, which gives a self-diffusion coefficient. Tributylphosphate labeled with P-32 was used as a tracer. The temperature was maintained at $25.000 \pm 0.004^\circ\text{C}$, and the cell was supported on a vibration-free mount. In all cases the diffusion was allowed to proceed until 50 to 70% of the initial labeled TBP had diffused from the cell. The results reported are the average of six determinations at each concentration. The diffusion coefficients and the product of the diffusion coefficient and the solution viscosity are given in Table IV.

TABLE IV
DIFFUSION COEFFICIENT OF TBP AT 25°C

<u>Diluent</u>	<u>Conc. TBP (vol. %)</u>	<u>$D \times 10^6$ (cm^2/sec)</u>	<u>$D\eta \times 10^6$</u>
Cyclohexane	10.3	5.56 ± 0.17	51.7
	10.0	4.88 ± 0.05	69.5
	32.5	4.27 ± 0.11	71.7
	58.0	3.24 ± 0.05	68.2
Pentachlorethane	10.4	2.73 ± 0.05	66.8
	29.7	2.08 ± 0.03	67.4
None	100	2.29 ± 0.01	76.0

The Nernst-Einstein relation for the diffusion coefficient of diffusion when combined with Stoke's law for the mobility of spherical particles in a viscous liquid gives the relation between viscosity and coefficient of diffusion

$$D\eta = \frac{kT}{6\pi r}$$

where r is the radius of the diffusing particles, considered as spheres. A similar relation is obtained from the theory of absolute reaction rates

$$D\eta = f(r).$$

For the derivation of the latter equation it is not necessary to assume that the diffusing particles are of large dimensions compared to the molecules of the solvent. The right-hand side of the latter equation may show some variation with concentration in binary mixtures. This variation is inversely proportional to some effective average linear dimension of the two types of molecules involved. The product of $D\eta$ may be expected to vary not more than the reciprocal of the average linear dimension of the molecules. This can be true, however, for ideal mixtures only.

The constancy of the product D_m for the systems shown in Table IV fits well with the observed constancy of the partial molal volumes (see Table III). It is somewhat unexpected, however, when one considers that these are not ideal solutions.

References

- (1) HW-24139, Quarterly Report, Jan. through March, 1952, p. 65.
- (2) HW-26937, Quarterly Report, Oct. through Dec., 1952, p. 70.
- (3) HW-20936.

THE EFFECT OF NONEXTRACTABLE SALTING AGENTS ON URANYL NITRATE DISTRIBUTION -- R.L. Dillon

The general study of the effect of salting agents on the distribution of uranyl nitrate between an aqueous phase and 30% TBP-hydrocarbon organic phases has been continued (1). Although considerable data is available for uranyl nitrate-nitric acid systems, it was felt that the use of nitric acid, which is itself distributed, was an unnecessary complication. Therefore, a series of uranium distribution studies employing a variety of nonextractable inorganic nitrate salts as salting agents has been undertaken.

The general method consists of determining a uranyl nitrate distribution curve at constant salting strength. These distribution curves are plotted with the log of the organic uranium concentration as the ordinate and the log of the aqueous uranium concentration (UNH) as the abscissa. A line corresponding to constant uranium concentration in the organic phase intercepts the distribution curves at constant uranium activity. Figures 7, 8, and 9 are graphs of the various isoactive UNH concentrations in the aqueous phase in g/l plotted against the concentration of the salting agents NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$.

As was shown in an earlier report (1), the parameters which describe the slope of the $\log (\text{UNH})_{\text{aq}}$ vs. salting agent concentration curve are found to be an inverse function of the aqueous uranium concentration at zero salting agent concentration, $(\text{UNH}^\circ)_{\text{aq}}$, with only a minor dependence on the nature of the salting agent. The function for isoactive solutions is

$$1) \log (\text{UNH})_{\text{aq}} = \log (\text{UNH}^\circ)_{\text{aq}} - \frac{C}{(\text{UNH}^\circ)_{\text{aq}}^n} (\text{NO}_3^-)_{\text{S.A.}}$$

where $(\text{UNH})_{\text{aq}}$ is the concentration in g/l, $(\text{UNH}^\circ)_{\text{aq}}$ is the concentration in g/l with no other salting agent present, and $(\text{NO}_3^-)_{\text{S.A.}}$ is the concentration in moles per liter of nitrate provided by the salting agent. The values of the parameters n and C are shown in Table I.

COMPOSITION OF UNH- NaNO_3 SOLUTIONS
IN EQUILIBRIUM WITH THE SAME ORGANIC PHASE

FIGURE 7

COMPOSITION OF UNH-CO(NO₃)₂ SOLUTIONS
IN EQUILIBRIUM WITH THE SAME ORGANIC PHASE

EIGHTY-8

COMPOSITION OF UNH-AMH SOLUTIONS IN
EQUILIBRIUM WITH THE SAME ORGANIC PHASE

FIGURE 2

TABLE I
PARAMETERS FOR SALTING EQUATION

<u>Salting Agent</u>	<u>n</u>	<u>C</u>
LiNO ₃	0.92	0.22
NaNO ₃	0.90	0.19
Mg(NO ₃) ₂	0.87	0.20
Ca(NO ₃) ₂	0.92	0.16
Zn(NO ₃) ₂	0.91	0.18
ANN	0.85	0.20
La(NO ₃) ₃	0.91	0.14

The salting agent concentration range to which the above relation applies is strongly dependent on the (UNH^o)_{aq}. To illustrate, we may make use of the data for NaNO₃, which is a typical salting agent; for (UNH^o)_{aq} = 381, log (UNH)_{aq} vs. [NO₃⁻]_{S.A.} is linear only to 0.3 M NaNO₃ salting agent; for (UNH^o)_{aq} = 215 g/l, (UNH)_{aq} vs. (NO₃⁻)_{S.A.} is still linear at [NaNO₃] = 5 M.

For the second linear portion of the curves the effect of salting agent is somewhat different. The slope is no longer dependent on (UNH^o)_{aq}; for small values of (UNH^o)_{aq} there is marked decrease in slope in going from the first linear portion of the curve to the second. Furthermore, a comparison of Figures 7, 8, and 9 shows a decided specific salt effect.

The data might be qualitatively explained by the change in the predominant uranium species existing at low and high nitrate ion concentration. From the expression given by Ahrlund (2)

$$2) \frac{(UO_2NO_3^+)}{(UO_2^{++})(NO_3^-)} = 0.5$$

it might be concluded $\frac{UO_2^{++}}{UO_2NO_3^+}$ is large in the first linear portion of the curve and

small in the second. Therefore, the initial slope might be interpreted as related to the equilibrium between uranyl mononitrate ion and uranyl ion; the second linear portion of the curve as the characteristic salting behavior of uranyl mononitrate. It is interesting to note that Ahrlund observed no evidence for a higher complex than UO₂NO₃⁺ in aqueous solution.

References

- (1) HW-23160, Quarterly Report, Oct. through Dec., 1951, Chemical Research, p. 36.
- (2) Ahrlund, Acta chem Scand., 5, 1271 (1951).

LIQUID-LIQUID DISPERSIONS -- L.H. Clark, E.D. McClanahan, and L.L. Burger

In the previous quarterly report (1), the dispersion times and disengaging times for systems showing a delayed or slow initial rate of dispersion, e.g., Purex IAF-IAX or Metal Recovery RAF-RAX, were discussed as a function of TBP concentration, temperature, rate of stirring, and the degree of approach to equilibrium. This work has now been extended to include rate of extraction during dispersion, interfacial tension, and degree of saturation of the organic phase.

Rate of Interphase Transfer

Use of the carefully standardized stirring apparatus described previously enabled sampling of organic and aqueous phases after measured stirring times. Ten identical two-phase non-equilibrated samples were made up, and at once stirred at 48 cycles per minute for varying lengths of time. Three different aqueous phases have been employed in these studies: 1) 150 g/l HNO_3 , 2) 450 g/l UNH, and 3) 150 g/l HNO_3 , 450 g/l UNH. These were contacted with 12 1/2% TBP, 30% TBP, or 50% TBP. The data are shown in Figures 10 and 11. In each case about 60-80 strokes or 1.25 - 1.66 minutes were required to reach equilibrium. The more rapid transfer of nitric acid as compared to uranyl nitrate was demonstrated by the experiments with the aqueous solution containing both nitric acid and uranyl nitrate. While equilibrium with respect to either component was not reached until the solutions were stirred for about 80 strokes, the nitric acid concentration in the organic went through a maximum in from 4 to 10 strokes (5 - 12 seconds), and this maximum was from two to three times the final concentration. The data are best compared by reference to Figure 11. It will be noted that both the position of the maximum and the degree of "overshoot" is dependent upon the concentration of TBP. Further comparisons are under way using sodium nitrate and aluminum nitrate as salting agents.

Interfacial Tension

It would be expected that interfacial tension should be an important factor in dispersion and emulsion behavior in liquid-liquid systems, but past periodic examination of such data has not led to significant correlations. The delayed dispersion or "induction" phenomena described previously is, however, apparently dependent on interfacial tension since the addition of surface active agents permits rapid dispersion.

Thus, since the dispersion time is a function of uranium (or nitric acid) transfer to the organic phase and is also dependent on surface active agents, it was of interest to examine the interfacial tension in these systems.

The interfacial tensions of the system TBP-Amsco 125-90W against 1) pure water, 2) 5 M HNO_3 , and 3) 0.8 M UNH have been measured for different TBP concentrations. The Harkins drop-volume method was used for the measurements. Data for the three systems are listed in Table I and shown graphically in Figure 12.

It will be noted that the presence of either nitric acid or uranyl nitrate raises the interfacial tension. Such is not the usual case with a mutually soluble component. An explanation for this may be that these molecules are replacing the more surface active TBP at the interface. That TBP is a moderately surface active agent may be seen from the rapid drop in interfacial tension as TBP is added to Amsco. It is interesting to note that the curves for the nitric acid and uranium solutions approximate the pure water curve if one plots interfacial tension against the "free" or uncomplexed TBP.

FIGURE 10
URANIUM EXTRACTION AND NITRIC ACID EXTRACTION (SEPARATE)

FIGURE 11
URANIUM AND NITRIC ACID EXTRACTION WHEN TOGETHER

INTERFACIAL TENSION OF
TDP-AMSCO 125-90W AGAINST
AQUEOUS SOLUTIONS

In view of these observations, one is tempted to postulate that the difficulty of dispersing while transfer is taking place is related to the rate at which TBP molecules can be brought up to the interface. Further study of this system must be made before a definite conclusion can be drawn.

These interfacial tension data are, of course, equilibrium data, and surface tension or interfacial tension are normally considered only for equilibrium cases. It is apparent that the region of interest in this problem is not the equilibrium case, but the steady state process where material is being transported across the interface. The problem of obtaining a reproducible and meaningful measurement for this situation is difficult.

TABLE I

INTERFACIAL TENSION OF TBP-AMSCO AGAINST AQUEOUS SOLUTIONS AT 25°C

Equilibrium Conditions

<u>% TBP by volume</u>	<u>Org. - H₂O dynes/cm</u>	<u>Org. - HNO₃(5 M) dynes/cm</u>	<u>Org. - UNH (.8 M) dynes/cm</u>
0	44.0 ± .1	39.2 ± .2	42.0 ± .3
10	13.60 ± .05	14.23 ± .09	20.4 ± .1
20	11.78 ± .06	12.46 ± .05	
30	10.64 ± .06	12.07 ± .09	17.13 ± .04
50	9.83 ± .05	10.74 ± .05	14.60 ± .19
75	9.06 ± .03	9.95 ± .02	
100	7.35	8.69 ± .02	

Reference

- (1) HW-26937, Quarterly Report, Oct. through Dec., 1952, Chemical Research, p. 71.

URANYL NITRATE - ORGANO PHOSPHORUS ESTER COMPLEXES -- L.L. Burger and B.R. Jones

In previous reports the properties of various organo-phosphates, phosphonates, phosphinates, and phosphine oxides have been described and their solvent strengths compared. The primary effect of increasing the electronegativity of the phosphoryl oxygen in these compounds is one of increasing the extraction ability for acidic compounds. A secondary effect appears to be that this increased bonding strength results in co-valent complexes of sufficient stability that they exist as definite chemical species, and in many cases may be easily crystallized from solution. Thus, with phosphine oxides, phosphinates, and with some phosphonates, stable complexes are formed with a number of acids and with many divalent and tetravalent salts. Pickard and Kenyon (1) prepared phosphine oxide complexes with zinc, copper, cobalt, and mercury halides, and with complex acids, such as chloroplatinic acid. Solid complexes with phosphinates and phosphonates apparently have not been previously reported.

In this work, the uranyl salts have been studied. The complexes were prepared by adding a solution of uranyl nitrate in alcohol to a solution of the ester in alcohol. The mixture was then cooled, when necessary, to hasten crystallization. The complexes isolated are listed in Table I. The chemical analyses correspond closely to the assumed composition of $\text{UO}_2(\text{NO}_3)_2 (\text{ester})_2$. A typical analysis is that for the triphenyl phosphine oxide complex: C, calc. 45.5, found 45.9; H, calc. 3.18, found 3.18; U, calc. 25.04, found 26.4; N, calc. 2.94, found 3.06.

It is to be noted that water has been completely eliminated from the coordination sphere of uranyl nitrate, and the compounds show no tendency to form hydrates. The compounds in general show low melting points and are quite soluble in organic liquids. The triphenyl phosphine oxide complex is different in these respects. It shows a very high melting point and is insoluble in all common solvents.

TABLE I

COMPLEXES OF ORGANO PHOSPHORUS ESTERS WITH URANYL SALTS

<u>Compound</u>		<u>Melting Point °C</u>
$\text{UO}_2(\text{NO}_3)_2$	.2 $[(\text{BuO})_2\text{PO}]$	42-43
"	.2 $[\text{BuO}(\text{Bu})_2\text{PO}]$	56-57
"	.2 $[(\text{Oct})_2\text{HPO}]$	67-78
"	.2 $[(\text{Bu})_3\text{PO}]$	51-53
"	.2 $[\text{P}_3\text{PO}]$	289-293
UO_2Cl_2	.2 $[\text{P}_3\text{PO}]$	283-285
$\text{UO}_2(\text{NO}_3)_2$	.2 $[(\text{BuO})_2\text{BuPO}]$	1-2
"	.2 $\text{EtO}(\text{Hex})_2\text{PO}$	ca. 27

The latter compound also exhibits strong fluorescence in contrast to the other uranyl complexes.

The high thermal stability of these complexes is interesting. In particular, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{P}_3\text{PO}$ can be heated to 300-310°C before any evidence of decomposition is obtained. The organic molecule P_3PO itself is, of course, an exceptionally stable one.

Reference

- (1) Pickard and Kenyon, J. Chem. Soc., 89, 262 (1906).

EXPLOSIVE REACTIONS IN THE PUREX PROCESS -- R.M. Wagner

Experiments simulating the Purex uranium concentration process using an excess of organic phase have resulted in a slow evolution of NO_2 and organic decomposition. Only when the organic phase ("red oil") was present under conditions of incipient calcination, 150-160°C, did an explosive reaction occur. The violence of the reaction appeared to be largely a function of the amount of "red oil" present.

A report, HW-27492, R.M. Wagner, "Investigation of Explosive Characteristics of Purex Solvent Decomposition Products (Red Oil)," Mar. 17, 1953, covers the details of this work.

SOLUBILITY OF PLUTONIUM TRIFLUORIDE IN HYDROGEN FLUORIDE -- C. Groot

The chief difficulty with the fluoride volatility process is that of removing the plutonium trifluoride and the fission product fluorides from the reactor (1). Most of the fluorides can be dissolved and removed in aqueous solutions of aluminum nitrate. However, engineering difficulties are imposed, and water reacts explosively with fluorinating agents and is corrosive toward Monel metal. Also, the rates of dissolution are low, and some of the fission product fluorides are quite insoluble. Hence, it was desired to find another solvent which was fluid at room temperature, which would not react violently with either fluorine or water, and which would dissolve plutonium fluoride rapidly. Liquid hydrogen fluoride or HF-KF mixtures seemed the only solvents that might meet these specifications. Therefore, the solubility of plutonium fluoride in these solvents was measured.

Tank hydrogen fluoride was distilled by way of a copper condenser into a polythene bottle. About 100 mg. of plutonium(III) fluoride prepared by R.C. Smith (Metallurgy Unit) was added, and the cap screwed on. The mixture was shaken intermittently for three hours, dispersing the plutonium as a very fine powder, and was allowed to stand overnight. The next morning a clear, colorless supernate was poured off into another polythene bottle, the level marked, and the hydrogen fluoride largely evaporated in an air stream. The bottle was filled to the mark with aluminum nitrate solution, which dissolved up a few dark specks on the bottom of the bottle. This solution analyzed 0.011 g/l plutonium, and hence, the saturated hydrogen fluoride solution contained 0.011 g/l plutonium.

A solution of potassium fluoride in hydrogen fluoride was made by dissolving anhydrous potassium chloride in liquid hydrogen fluoride with copious evolution of hydrogen chloride. This was added to the plutonium fluoride-hydrogen fluoride mixture left over from the previous experiment. There was no visible evidence of a dissolution reaction. An attempt was made to measure the solubility by the technique above, but a white precipitate (K_3AlF_6 ?) was obtained which would not settle. The experiment was repeated, and analysis was attempted by boiling off most of the hydrogen fluoride, adding sodium hydroxide, and washing out the soluble sodium fluoride. The transfers were not quantitative, but the residues from this treatment were dissolved in nitric acid and analyzed. The analysis showed a solubility of 0.006 g/l plutonium.

This experiment does not prove that potassium fluoride depresses the solubility of plutonium fluoride in hydrogen fluoride, but it certainly indicates that potassium fluoride does not increase the solubility enough to form the basis of a process.

Further possibilities of increasing solubility are to dissolve plutonium fluoride in fused potassium hydrogen fluoride, or in liquid hydrogen fluoride at higher temperatures. These treatments pose further problems.

Reference

- (1) HW-25757, Groot, C., "Status of the Fluoride Volatility Process," 10/17/52.

ION EXCHANGE STUDIES -- R.E. Burns and H.S. Gile

A. Decontamination of Purex HCP Distillate; Removal of Plutonium. About 100,000 column volumes of a synthetic Purex HCP distillate (15 mg/l UNH, 5 ug/l Pu, pH 2) were passed through a column of hydrogen-form Dowex 50 resin (16 cm x 0.5 cm², 20-50 mesh) at a flow rate of 12 ml/m/cm². The plutonium content in the effluent never exceeded background (2-3 c/m/ml). The column was regenerated with 4 M HNO₃ at a flow rate of 2 ml/m/cm², the flow being upward or reverse to the flow during exhaustion. Removal of plutonium was rapid at first, about 80% being removed in the first nine column volumes of regenerant. Further removal of plutonium was slow; twenty column volumes of regenerant were required to remove an additional 10% of the plutonium. This study has been discontinued because changes in Purex design have eliminated ion exchange treatment of this stream.

B. Decontamination of Condensate from Purex Stored Wastes. A solution meant to simulate the condensate which will be obtained from in-tank evaporation of stored Purex Process waste was prepared as follows. Dissolver solution (about one year old) was acidified and extracted three times with 30% TBP-Amsco 125. The aqueous raffinate was brought to Purex IWW composition by addition of the proper chemicals and then neutralized to pH 11 with 10 M NaOH. Simulated coating removal waste was added in flow sheet volume ratio, and the resulting slurry was allowed to stand until solid materials had settled out. The clear supernatant was then diluted by a factor of 10⁴ with distilled water. Beta and gamma activity of the dilute solution were about 4400 and 4700 c/m/ml, respectively, both measured at 8% counter efficiency.

The simulated condensate was passed through a column of hydroxyl-form IRA-400 resin (anion exchanger) and then through a column of sodium-form Dowex-50 resin (20-50 mesh). In each column the resin bed was 23 cm x 1 cm². About 1500 single column volumes were passed through both columns at a flow rate of 1 ml/m/cm². Beta decontamination over the anion column remained at about 2.5-3, while the beta activity in the effluent from the cation exchanger remained at background (10 c/m/ml). The two columns were regenerated, reverse flow, at a flow rate of 0.1 ml/m/cm². Two M NaNO₃ was used for the Dowex-50 column and 2 M NaOH for the IRA-400 column. Activity removal was rapid in the Dowex-50 column, being essentially complete in seven column volumes of regenerant. About 20 column volumes of regenerant were required for the IRA-400 column.

During the exhaustion cycle, a white gelatinous mass deposited on top of the anion exchange column, causing the flow rate to drop. It is not known whether this material was an inorganic solid precipitated from the feed or a bacterial growth sometimes encountered in ion exchange resin columns. No further work with this particular condensate is contemplated since design changes have eliminated ion exchange treatment of this stream.

C. Decontamination of Metal Recovery Process RCU Stream. The purpose of these studies is to extend work started by W. Schulz and R. Watts (HW-26815) on decontamination of off-standard Metal Recovery Process RCU by ion exchange. Primarily it is desired to obtain adsorption capacity and regeneration data for the removal of Ce from this stream by Dowex-50 resin. However, it is expected to extend these studies to include the removal of other activities which may be troublesome as shorter cooled metal wastes are processed.

Since the plant has not recently produced off-standard RCU, it was necessary to simulate a feed for ion exchange studies. This was done by spiking dissolver solution (one year old) into a solution of RCU composition prepared from UO_3 . Cerium content of this solution was 6600 c/m/ml (7.5% Geom.). The simulated RCU was passed through a bed of hydrogen-form Dowex-50 resin (20-50 mesh, 22 cm x 1 cm²) at a flow rate of four ml/m/cm². Concentration of cerium in the effluent was 3% of feed concentration at 60 bed volumes, 21% at 260 bed volumes, and 50% at 510 bed volumes. The low capacity observed in this run, as compared to that given in the work cited above, was due to a higher flow rate and larger resin size (considered desirable from a practical standpoint). Runs involving longer columns will be made to determine to what extent a longer residence time will overcome the adverse kinetic effects of faster flow rate and larger particle size.

DECONTAMINATION OF URANIUM RECOVERY PROCESS WASTES -- R.E. Burns, R.L. Brandt, and W.E. Clifford

Since cesium is perhaps the most difficult of the radioisotopes present in Uranium Recovery Process waste to remove and since it also is poorly adsorbed by soil from cribbed solutions, efforts have been directed primarily to the removal of cesium. Distribution ratios (based on batch contactings) for cesium between various cation exchangers tried and synthetic RAW (acid and neutralized) were so low that column runs were discouraged.

Several precipitants or carriers for cesium were investigated for their application to these wastes. Dipicrylamine (an analytical reagent for potassium), KClO_4 , $\text{Ca}_3(\text{PO}_4)_2$, and NH_4CaPO_4 were tried under conditions considered optimum for cesium carrying. Negligible to poor cesium removal was obtained. Ammonium iodate precipitated from 0.6 M HIO_3 -0.4 M NH_4NO_3 carried 87% of the active cesium spiked into the solution. This carrier has not been studied in a RAW system because of its inherent expense. $(\text{NH}_4)_3\text{Co}(\text{NO}_2)_6$ was found to carry cesium virtually completely from 0.1 M NH_4NO_3 when the solution was made 0.01 M in $\text{Na}_2\text{Co}(\text{NO}_2)_6$. Preliminary experiments indicate that large concentrations of sodium ion, as are present in Uranium Recovery wastes, interfere to some extent with cesium carrying. $\text{K}_3\text{Co}(\text{NO}_2)_6$ was very effective in carrying cesium from 1 M KCl solution but has not been tried on an RAW system.

Precipitates formed by the addition of potassium hexacyanoferrate(II) to synthetic RAW were found to carry cesium very well. Whether the iron present was ferrous or as ferric made little difference in the carrying. Cesium decontamination factors of 500 or greater were obtained in many of these experiments. The carrying must be done from an acidic solution since at high pH the precipitate is metathesized to ferric hydroxide and cesium carrying is poor. Room temperature digestion of the precipitate for an hour appears adequate to give maximum carrying. Digestion at elevated temperature (80°C) appears beneficial when the iron is bivalent but for some as yet unexplained reason decreases carrying very markedly when the iron is trivalent.

Because head-end equipment is available in the Uranium Recovery plant, some investigation has been made of precipitation of uranyl, Fe(II) or Fe(III), hexacyanoferrate(II) or (III) from synthetic RAF as a carrier for cesium. Precipitates formed between uranyl and either cyano complex do not carry cesium. When Fe(III)

is added to RAF immediately after addition of $K_4Fe(CN)_6$, no precipitate is obtained (observed for one hour). This is an unexpected and as yet unexplained result. When $Fe(II)$ is added as above, a green precipitate is obtained which carries cesium moderately well (DF 10+).

Further work on the application of this and other techniques to the decontamination of RAF, RAW, and supernatant from the waste storage tanks is planned.

SOLVENT EXTRACTION OF FISSION PRODUCTS -- R.E. Burns and C.R. McMullen

A preliminary survey of the extraction of fission products from partially neutralized Purex Process IWW waste stream by various solvents was made. Feed solution for these experiments was synthetic IWW spiked to 0.1% Purex Process fission product level with dissolver solution (about one year old) previously extracted with 30% TBP-Amsco 125. A calculated amount of 50% caustic was added to the spiked IWW (7.5 M HNO_3) to produce a solution 2 M in HNO_3 . Equal volumes of this aqueous phase and the organic extractant were contacted for 30 minutes. Distribution ratios for various fission products are shown in Table I.

One of the immediate objectives of these studies is to find means for separating zirconium and niobium from other fission products and long-lived emitters in process waste streams. The data in Table I indicate that reasonably good separation of these elements from other fission products studied may be achieved by monobutylphosphate, dibutylphosphate, and tributylphosphine oxide.

Previously reported data on the stripping of Zr and Nb from tributylphosphine oxide in carbon tetrachloride showed that, of several stripping agents tried, 0.01 M HF was the most effective. Each of the organic phases obtained in the experiments reported in Table I was contacted for 30 minutes with an equal volume of 0.01 M HF and E_a^0 's determined. For those extractants showing high distribution ratios for Zr and Nb, see Table II, stripping of these elements by 0.01 M HF was most effective in the case of monobutylphosphate in carbon tetrachloride.

Further studies of the most promising of these systems will include behavior of plutonium, behavior of fission products at higher concentrations, and the acquisition of sufficient equilibrium and extraction rate data to permit testing of the systems in a Mini.

TABLE I

EXTRACTION OF FISSION PRODUCTS FROM PARTIALLY
NEUTRALIZED PUREX IW

Solvent	Distribution Ratios E_d						
	Zr	Nb	Ru	Ce	R.E.	β	γ
0.1 M MBP* in CCl_4	42.6	62.8	-	0.156	0.182	0.5	5.3
0.1 M DBP in CCl_4	105.0	29.2	0.101	0.225	0.268	0.24	32.0
0.01 M DBP in CCl_4	72.3	19.0	0.091	0.0056	0.047	0.33	5.3
Commercial Mixture of MBP and DBP	75.0	150.0	0.035	0.23	0.202	0.52	6.0
0.1 M TTA in benzene	0.75	0.11	0.26	0.36	0.15	0.41	0.36
12 1/2% TBP in Amsco	low	low	low	0.95	0.182	0.091	0.215
12 1/2% TBP in CCl_4	0.81	0.70	1.24	0.77	1.14	0.008	0.05
CCl_4 alone	low	0.060	0.062	0.21	0.137	0.016	0.011
0.1 M TBPO in CCl_4	6.2	2.2	0.10	0.024	low	0.33	1.8
0.1 M TPPO in CCl_4	1.12	0.20	0.12	0.20	0.069	0.2	0.32
Sat. phenylarsonic acid in benzene	0.11	0.30	0.19	0.22	0.22	0.21	0.30

*MBP = monobutylphosphate

DBP = dibutylphosphate

TBP = tributyl phosphate

TTA = thenoyl trifluoroacetic acid

TBPO = tributylphosphine oxide

TABLE II

REMOVAL OF FISSION PRODUCTS FROM ORGANIC SOLVENTS BY 0.01 M HF

Solvent	Distribution Ratios E_d						
	Zr	Nb	Ru	Ce	R.E.	β	γ
0.1 M MBP* in CCl_4	0.0099	0.006	0.97	0.014	0.03	0.0038	0.0063
0.1 M DBP in CCl_4	3.8	1.05	1.2	4.3	290	4.76	1.46
0.01 M DBP in CCl_4	0.56	1.41	0.18	2.88	0.82	0.11	0.14
2% n-butyl acid phosphate in CCl_4	7.6	0.12	1.83	27.2	88.7	4.0	1.1
0.1 M TTA in C_6H_6	0.26	0.033	0.029	0.039	0.156	0.012	0.045
12 1/2% TBP in Amsco	0.019	0.0065	0.51	0.005	0.00091	0.06	0.13
12 1/2% TBP in CCl_4	0.00088	0.0026	0.0037	0.0016	0.0007	0.008	0.04
CCl_4 alone	0.006	0.014	0.004	0.0056	low	low	low
0.1 M TBPO in CCl_4	0.28	0.88	30.5	0.08	0.04	0.18	0.62
0.1 M TPPO in CCl_4	0.016	0.012	0.033	0.015	0.034	0.018	0.019
Sat. phenylarsonic acid in benzene	0.00046	0.014	0.166	0.094	0.079	0.0035	0.76

*For names of organic compounds see Table I.

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY RUTHENIUM(IV) SOLUTIONS --
A.S. Wilson

Information derived from kinetic investigations (1, 2) has been useful in reaching conclusions about the nature of metallic ion species which exist in solution. A kinetic method which offers possibilities for understanding the nature of ruthenium(IV) species in various aqueous media is the ruthenium(IV)-induced catalytic decomposition of hydrogen peroxide. Initial experiments (3) have been conducted in perchloric acid media because perchlorate ion has the least tendency of all the common inorganic anions to form metallic complexes. Under certain conditions ruthenium(IV) perchlorate causes hydrogen peroxide to decompose according to the following rate law:

$$-d(H_2O_2)/dt = k(H_2O_2)(Ru_T^{IV})(H^+)^0.$$

This rate law is valid only when the initial hydrogen peroxide concentration is of the order of tenth molar or less and when the acid concentration is greater than tenth molar. In a series of experiments in which (Ru_T^{IV}) varied from $0.80 \times 10^{-5} M$ to $6.4 \times 10^{-5} M$ and (H^+) from $0.1 M$ to $1 M$ at constant ionic strength of unity ($LiClO_4 + HClO_4$) at a temperature of $25.1 \pm 0.1^\circ C$, $k(4)$ was fixed at $437 \pm 17 \text{ l mole}^{-1} \text{ min}^{-1}$. The reaction has an energy of activation of 13.3 K cal and an Arrhenius frequency factor of 2×10^{12} . Experiments in one molar acid indicate that neither $10^{-3} M$ quinhydrone, $0.1 M$ glycerine nor strong light affect appreciably the value of k . These experiments imply that any path which involves chains or free radicals is of negligible importance under these conditions. On the basis of the experiments to date, the proposed mechanism is as follows:

Some experiments in media other than perchloric acid have been carried out. These experiments were conducted by adding a solution of ruthenium(IV)-perchlorate to the reaction solution and following the concentration of hydrogen peroxide with time. At $25^\circ C$ with an initial hydrogen peroxide concentration of about tenth molar in solutions whose principal constituents were $1.0 M NaCl + 1.0 M HClO_4$, $1.1 M H_3PO_4$, $1.0 M H_2SO_4$ and $1.0 M HNO_3$, the observed k values were respectively 13, 27, 313, and 515. The low k values imply that complexes are formed which are not catalytically active. The high k value in the nitric acid case is unexplained and may be due to an experimental error. The values for the chloride, phosphoric acid, and sulfuric acid cases were determined after an initial period (ca. 30 min.) in which the ruthenium rapidly changed its species as indicated by visual color changes. The rapidity of the changes implied that hydrogen peroxide catalyzed the formation of these complexes. Additional experiments in which the concentration of the anion is varied should yield information concerning the affinity of ruthenium(IV) for that particular anion.

References

- (1) Taube, H., J. Am. Chem. Soc. 70, 1216 (1948).
- (2) Fudge, A.J. and Sykes, K.W., J. Chem. Soc. 1953, 124.
- (3) See HW-26104, p. 97, for the experimental procedure.
- (4) The value, $193 \text{ l mole}^{-1} \text{ min}^{-1}$, reported in HW-26104, p. 98 corresponds to $k/2.303$.

RUTHENIUM(IV)-CHLORIDE COMPLEXES -- A.S. Wilson and J.L. Swanson

The colored chloride complexes of ruthenium(IV) can be used as indicators for determining the affinity of nitrate ion for ruthenium(IV) if the chloride complexity constants are known. An initial spectrophotometric investigation of the ruthenium(IV)-chloride system has yielded estimates of several complexity constants. These complexity constants were obtained by conducting a "corresponding solution" (1) analysis of the data. The estimated values of the constants are: $k_1 = 3 \times 10^2$; $k_2 = 1 \times 10$; $k_3 = 7$; $k_4 = 4_3$; and $k_5 = 3 \times 10^4$, where $k_1 = (\text{RuCl}_4^{4-})/(\text{RuCl}_3^{3-})(\text{Cl}^-)$. The data were not precise enough to fix the existence in these solutions of a complex containing six chloride ions. The estimated k values do imply, however, that the intermediate chloride complexes are unstable with respect to the formation of the high chloride complex and the complex which contains only one chloride ion per ruthenium. These constants apply to solutions at 64°C , 1 M HClO_4 , 5 M NaClO_4 , 1.3×10^{-4} to $2.6 \times 10^{-3} \text{ M Ru(IV) - ClO}_4$ and 3×10^{-3} to $5 \times 10^{-2} \text{ M NaCl}$.

Reference

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

RUTHENIUM(III) STUDIES -- A.S. Wilson and I.M. Rehn

The behavior of ruthenium(III) in acid solutions is complicated by the formation of complex ions and the slowness at which various ruthenium(III) species reach equilibrium with their environment. In order to understand the nature of ruthenium(III) in strong mineral acids, an investigation of the ruthenium(III) chloride system was initiated. The chloride system offers the best starting point since the chloride salts are easily made and the colored chloride complexes are easily detected spectrophotometrically. A knowledge of the affinity of chloride ion for ruthenium(III) will serve as a reference point for the investigation of other systems.

A. The Behavior of $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ in Solution. The salt $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ was prepared according to a modification of the method of R. Charonnat (1). In the modification mercury instead of alcohol was used as the reductant. An analysis of the salt gave these results: $\text{KCl} - 39.74 \pm 0.19\%$, $\text{Ru} - 26.85 \pm 0.02\%$, $\text{Cl}(\text{volatile in H}_2 \text{ reduction}) - 28.21 \pm 0.09\%$, $\text{H}_2\text{O} - 5.48 \pm 0.14\%$. The corresponding calculated values for the salt are: $\text{KCl} - 39.76\%$, $\text{Ru} - 27.11\%$, $\text{Cl}(\text{volatile in H}_2 \text{ reduction}) - 28.33\%$, $\text{H}_2\text{O} - 4.80\%$. The potassium chloride content was determined by analyzing the washings from the residue of the hydrogen reduction; the leached residue was weighed as ruthenium metal. The volatile chloride in the hydrogen reduction was collected and determined. The water content was determined by the difference between the total weight loss and the chloride lost during the hydrogen reduction.

An x-ray diffraction powder pattern of this salt showed that it had a cubic structure, $a^\circ = 9.74 \text{ \AA}$ and $\rho = 2.69 \text{ g/cm}^3$, and was isomorphous with K_2RuCl_6 . By analogy to the hexachlororuthenate salt, these data indicate that in the crystal ruthenium is coordinated to five chloride ions and one water. When this salt is dissolved in water at 25°C and the conductance of the solution immediately measured, the molar conductance at a dilution of 1024 liters is 273 ohm^{-1} . This value would be given by any one of the following ionic solutions: a) $2\text{K}^+ + \text{RuCl}_5\text{H}_2\text{O}^{-2}$, b) $2\text{K}^+ + \text{Cl}^- + \text{RuCl}_4\text{H}_2\text{O}$, and c) $2\text{K}^+ + 2\text{Cl}^- + \text{RuCl}_3\text{H}_2\text{O}$. However, an experiment in which the free

chloride available for titration by a mercurimetric method (2) was determined within two minutes after dissolving the salt in 1.0 M trifluoroacetic acid at 5 to 10°C indicated that two chlorides per ruthenium were available for titration. This result may indicate that the salt yields $2K^+$, $2Cl^-$, and $RuCl_3H_2O$ when dissolved in water. This conclusion is only valid if Hg^{++} does not catalyze the aquation of $RuH_2OCl_5^-$ or $Ru(H_2O)_2Cl_4^-$. Additional experiments are planned to test the validity of the above conclusion.

B. $K_2RuCl_5H_2O$ in Trifluoroacetic Acid (HTFA). A 5.00×10^{-4} M $K_2RuCl_5H_2O$ solution in 1.00 M HTFA equilibrated at 64°C showed no bound chloride (3) after fourteen days. After this time, these molar extinction coefficients were recorded: $E_{400} = 40$, $E_{300} = 270$. The character of the absorption was entirely different from the ruthenium(III)-perchlorate spectrum obtained by Wehner and Hindman (4). No peak at 390 mμ was observed in our experiment, and the molar extinction coefficients were much lower for our solution. It is believed that this HTFA solution contained principally aquo ruthenium(III) ion, and experiments are continuing in order to substantiate this hypothesis.

References

- (1) Charonnat, P., *Annals de Chimie*, Series 10, Vol. 16, p. 40 (1931).
- (2) Kolthoff, I.M. and Stenger, V.A., "Volumetric Analysis," Vol. 2, Interscience Publishers, New York, p. 331.
- (3) Measured by the Votocek method.
- (4) Wehner, P. and Hindman, J.C., *J. Am. Chem. Soc.* 72, 3911 (1950).

OBSERVATIONS ON THE BEHAVIOR OF AN ORGANIC SOLUBLE RUTHENIUM SPECIES -- G.B. Barton

An organic soluble species of ruthenium was prepared by oxidizing a solution of ruthenium(III)(IV) chloride with NaOCl and extracting the solution with TBP. When insufficient NaOCl was added for oxidation to RuO₄, the organic phase extracted a green substance from the aqueous solution. Sufficient NaOCl to oxidize the Ru to RuO₄ (color change from brown to yellow) resulted in a yellow organic solution which turned dark and deposited a dark solid on standing. The green organic solution was subjected to a variety of qualitative reactions. From these, it appeared that the Ru was present as an oxidized species that could be back-extracted with water or basic solutions, or concentrated HNO₃, but not by dilute acids or concentrated HCl or H₂SO₄. Dilution of the TBP solution with spray base or Amsco solvents resulted in the formation of a dark-colored substance which gradually separated out.

Observation of the potential of a Pt, sat'd. calomel electrode system during the titration of Ru with NaOCl did not indicate any clearly defined breaks. Measurement of the potential of an aqueous phase in contact with the green TBP solution gave a value of 0.97 v (Pt vs. sat'd. calomel). This indicates a fairly strong oxidizing agent (equivalent to bromine). It was observed that the potential varied somewhat with pH. Titration of a sample indicated an inverse dependence of potential on pH, i.e., potential decreased as pH increased. At pH 1E = .97 v., at pH 12E = .005 v.

The absorption spectrum indicated a single, broad band in the visible range. No measurements were made in the ultraviolet.

A qualitative check appeared to indicate the presence of chloride in the organic phase. This may indicate a chloro complex.

It is possible that the ruthenium in the TBP solution is a Ru(VI) species which undergoes comparatively rapid reactions.

DETERMINATION OF YTTRIUM IN URANIUM -- A. Chetham-Strode, Jr., B.T. Stark, and E.M. Kinderman

The uranium recovered by the TBP process has as principal beta active contaminants yttrium, thorium, and cerium. If beta tolerance limits as measured by gross beta activity measurements are exceeded, it is necessary to decide whether the excess activity is attributable to cerium, which will persist, or yttrium, which quickly decays.

The current analytical approach to this problem is based on a radiochemical determination of thorium plus a 24-hour decay measurement on the uranium as a measure of yttrium. These values are then subtracted from the gross beta determination and the remainder taken to be fission product contamination. While the current procedure has given satisfactory answers over the course of several months, the time lag involved in the decay measurement is highly undesirable in that extensive storage of uranium batches over a 24-hour period is required. In an effort to improve this situation, two radiochemical methods for the determination of yttrium in the presence of cerium have been developed.

A. Yttrium by Oxalate Precipitation

An adaptation of the rare earth separation procedure of Noyes and Bray (1) as modified by Ballou (2) and Baldrige and Hume (3) is used to separate uranium, thorium, and cerium from yttrium and the remainder of the rare earths. Figure 13 summarizes the steps taken in the separation, which requires approximately two hours for completion. The scheme was tested by analysis of mixtures containing equal activities of yttrium and cerium. Recovery of yttrium was $95 \pm 5\%$ with less than one percent of the measured activity attributable to cerium.

FIGURE 13

SEPARATION SCHEME FOR YTTRIUM DETERMINATION

B. Yttrium by TTA Extraction

In principle, yttrium, thorium, and uranium are separated from cerium and other F.P.'s by solvent extraction of the thenoytrifluoroacetone (TTA) chelates at carefully controlled pH. The combined ions are first extracted into an organic phase from an acetate buffered system. Cerium is subsequently removed by back-extraction into an aqueous phase of pH 3.15. Yttrium, thorium, and uranium remain in the organic phase and are counted together. Since the chelation of large amounts of material produces appreciable quantities of acid through the reaction

close control of the pH is not possible in the initial extraction. Consequently, the separation is made in a back-extraction in which only micro quantities of cerium undergo reaction, and the resulting change in acid concentration may be easily buffered to a minimum. A biphthalate buffer provides the proper pH for this back-extraction.

The extraction behavior of the ions in question is shown in Figure 14 as a function of pH of the aqueous phase. The data shown were determined with separated tracers of known purity. No differences in behavior were found between extraction in the forward and reverse directions.

The separation of cerium from yttrium is not complete. Ten percent of the cerium is counted with 90% of the yttrium and all of the thorium and uranium at pH 3.15. If present in the sample, zirconium and promethium will follow yttrium in the procedure. The method is rapid, requiring about 45 minutes for a complete determination.

References

- (1) Noyes, A.A. and Bray, W.C., "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927.
- (2) Ballou, N.E., Paper 292. "Radiochemical Studies: The Fission Products," Coryell, C.D. and Sugarman, Eds. New York. McGraw Hill Book Co. 1951.
- (3) Baldrige, W.F. and Hume, D.N. Paper 294. "Radiochemical Studies: The Fission Products," Coryell, C.D. and Sugarman, N., Eds. New York, McGraw Hill Book Co., 1951.

FIGURE 14 - EXTRACTION OF Th, U, Y, AND Ce
BY 0.5 M TTA IN BENZENE.

0142-061

REMOVAL OF IRON AND COPPER INTERFERENCES IN THE OXINE METHOD FOR DETERMINATION OF ALUMINUM -- J.E. Meinhard

Alpha-nitroso- β -naphthol is known to precipitate, in addition to cobalt(II), the following elements from a weakly acidic solution: Cu, Fe(II & III), Pd, Zr, Bi, Cr(III), Ag, Sn(IV), Ti, W(VI), U(VI), V. Elements not precipitated include Al, Sb, As, Be, Cd, Pb, Mn, Hg, Ni, R.E.(III), alkaline earths, alkali metals. It would be expected, then, that traces of elements in the first group will be effectively carried on a precipitate formed from Co(II) and the reagents, while elements in the second group will be retained in solution. This principle is successfully employed in the following procedure for the determination of aluminum in water samples of process origin.

The sample is acidified to pH 1, treated with α -nitroso- β -naphthol reagent, buffered to pH 4.3 to 4.6, and then treated with about half the necessary cobaltous chloride to combine with the reagent. The precipitate is allowed to coagulate (at room temperature) before filtering directly into a separatory funnel. The filtrate is extracted several times with chloroform to remove the remaining traces of reagent. The aqueous residue, which now contains the aluminum uncontaminated by iron, copper, cobalt, or α -nitroso- β -naphthol, is treated with 8-hydroxyquinoline and extracted with two portions of chloroform. These are combined and clarified from suspended water droplets either by filtering through paper or by addition of a small portion of water miscible solvent (e.g., i-propyl alcohol, dioxane, etc.). The aluminum oxinate is then estimated spectrophotometrically by reading the optical density at 390 mu.

A 50 milliliter sample containing 0 to 30 micrograms of aluminum is taken for analysis. Large amounts of salts of the alkali metals, magnesium, the alkaline earths, as well as up to 100 ug. of copper and iron, and 50 ug. of manganous and chromic ions, may be tolerated in the sample. The sample is acidified in order to make all the metallic species available as ions to the complexing agent. Essentially neutral samples of low salt content (i.e., most water samples) are acidified by adding (in 3-5 ml. volume) 5.6 millimoles hydrochloric acid and 5.6 millimoles ammonium chloride. Other samples are brought to pH 1 by the addition of hydrochloric acid. In such cases the procedure must then be monitored with a pH meter to insure that the final extraction of aluminum oxinate takes place at pH 4.3 to 4.6.

A 2% solution of α -nitroso- β -naphthol is prepared by adding the reagent to the appropriate volume of hot dilute (1:1) acetic acid. The solution is filtered after being allowed to stand 24 hours. A volume of 0.5 ml. of this solution is added to the sample. A definite turbidity appears at this point consisting mainly of micro-crystals of precipitated reagent. Macro amounts of iron and copper, if present, also precipitate and contribute to the turbidity. Additional amounts of the impurity ions are "driven" into the complexed form by increasing the pH to 4.5. This is done by adding 5 ml. of a sodium acetate solution (350 g. of trihydrate per liter of solution).

The final precipitate, which sequesters the impurities and serves to gather and coagulate the remaining colloidal species, is formed by adding slowly with stirring 0.5 ml. of a solution of cobaltous chloride (4 g. of the hexahydrate per liter). Filtration may be begun immediately without waiting for the precipitate to coagulate. Filtration is somewhat more rapid, however, if about fifteen minutes is allowed for coagulation. The procedure may be interrupted at this point, either before or after filtration, and resumed several days later without materially affecting the result. The filtrate should be distinctly yellow in color with excess reagent.

EFFECT OF Cu AND Fe ON
Al RECOVERIES

FIGURE 15

The filtrate, which contains the aluminum, is extracted three times (or more, if necessary) with chloroform to remove the residual α -nitroso- β -naphthol. The final extract, as well as the aqueous raffinate, should be completely free of color. The solution is then treated with 2 ml. of 8-hydroxyquinoline solution (20 g. 8-hydroxyquinoline and 60 ml. glacial acetic acid per liter). The solution is re-extracted with chloroform to obtain the aluminum oxinate which is then estimated with a spectrophotometer.

A typical calibration curve is given in Figure 15, which also includes evidence that 20 ug. of copper and iron do not interfere in the analysis of 0-25 ug. of aluminum. Further evidence of the efficiency of impurity scavenging is presented in Table I. All of these values were obtained on distilled water samples which were inoculated with the indicated amounts of specific ions. Optical densities were read on a Cary recording spectrophotometer using a 5 cm. light path. Precision is approximately ± 0.5 ug. Al for most samples. The procedure has been successfully adapted to samples other than process water, i.e., process solutions, tin alloy. It is sometimes necessary, particularly at low levels of aluminum, to remove the bulk of major interferences by special methods before scavenging the remaining interferences on the cobalt precipitate.

TABLE I

EFFICIENCY OF ELIMINATION OF Cu AND Fe INTERFERENCES

Added to Sample, ug:			O.D.	Recovered, ug:
<u>Cu</u>	<u>Fe</u>	<u>Al</u>	<u>390 mu</u>	<u>Al</u>
50	0	20	1.012	21
100	50	20	.985	20
0	250	20	1.007	21
100	250	20	1.098	23
0	0	20	.976	

DETERMINATION OF IMPURITIES IN URANIUM -- H.H. Van Tuyl

At present there is an uncertainty of over 300 in-hours using the available analytical data on trace impurities in uranium to calculate the in-hour loss per pile. In addition to this 300 in-hour uncertainty, there are six elements for which no analytical methods are available and which might cause additional in-hour losses. This indicates that more sensitive analyses of uranium metal could possibly lead to savings of several in-hours per pile (1). A knowledge of the impurities present in uranium is also important to a better understanding of the metallurgical properties of uranium.

The TBP extraction-copper spark spectrographic method (2) for determining impurities in uranium can be readily applied to the analysis of uranium metal. Table I shows the sensitivity of this method for determining many impurities in uranium, based on a 100 mg. sample size. Better sensitivity by this method may be achieved by increasing the sample size.

TABLE ISENSITIVITY OF TBP METHOD

<u>Element</u>	<u>Sensitivity</u>	<u>Element</u>	<u>Sensitivity</u>	<u>Element</u>	<u>Sensitivity</u>	<u>Element</u>	<u>Sensitivity</u>
Al	0.02 ppm	Eu*	0.1 ppm	Na	0.1 ppm	Sm*	0.2 ppm
As	2	Fe	1	Nd*	0.5	Sn	1
B	0.2	Ga	0.05	Ni	0.5	Sr	0.01
Ba	0.01	Gd*	0.5	Os	1	Ta	1
Be	0.001	Ho*	0.5	Pb	0.2	Tb*	0.5
Bi	0.5	In	0.2	Pd	0.1	Te	5
Ca	0.05	Ir	2	Pr*	0.5	Tl	0.2
Cd	0.2	K	1	Pt	0.5	Tm*	0.2
Ce*	0.5	La*	0.1	Rb	2	V	0.2
Co	0.5	Li	0.01	Re	1	W	0.5
Cr	0.01	Lu*	0.2	Rh	0.2	Y*	0.1
Cs	5	Mg	0.2	Ru	0.2	Yb*	0.1
Dy*	0.2	Mn	0.01	Sb	2	Zn	2
Er*	0.1	Mo	0.1	Sc*	0.1		

*These elements are not determinable if the acid concentration exceeds 3 N.

This method is more sensitive than present methods for several important elements but not as good for some other elements. Table II lists the sensitivity limits in ppm and the possible undetected in-hour loss corresponding to this sensitivity limit. The good sensitivity for the platinum metals would help to reduce the in-hour uncertainty markedly.

TABLE IIPOSSIBLE UNDETECTED IN-HOUR LOSSES

<u>Element</u>	<u>Best Present Method</u>		<u>TBP Method</u>	
	<u>Sensitivity</u>	<u>In-Hours</u>	<u>Sensitivity</u>	<u>In-Hours</u>
Ir	100 ppm	263.16	2 ppm	5.26
Rh	20	32.3	0.2	0.32
B	0.1	7.2	0.2	14.4
Hf	10	6.33	No method	
Sm	0.075	5.72	0.2	15.3
Ta	40	5.19	1	0.13
Cl	5	5.05	No method	
W	40	4.26	1	0.11
Cd	0.1	3.2	0.2	6.4
Gd	0.01	2.5	0.5	125
Cs	8	1.90	5	1.19
Hg	1	1.89	No method	
Li	0.1	1.06	0.01	0.11
In	0.5	0.91	0.2	0.36
Re	No method		1	0.50
Se	" "		No method	
Os	" "		1	0.08
Te	" "		5	0.19
S	" "		No method	
Sr	" "		0.01	0.00

References

- (1) Kattner, W.T., "Metal Quality Meeting at Mallinckrodt Chemical Works, February 27 and 28, 1951," Document HW-20640 (Secret).
- (2) Bushey, A.H., "Quarterly Progress Report, Analytical Research Sub-Unit, Oct., Nov., Dec., 1952," HW-27139 (Secret).

ELECTRODEPOSITION OF PLUTONIUM -- Roy Ko and E.M. Kinderman

In the plutonium electrodeposition procedure used in this laboratory, Pu(VI) in KOH solution is reduced at the cathode and precipitated there as Pu(IV) hydroxide. It should be possible to deposit Pu(IV) hydroxide at the cathode by base generation at that electrode in an initially acid Pu(IV) solution. Such deposition was achieved in both compartmented and non-compartmented electrolytic cells, with the latter being the more convenient.

To prevent acid formation because of oxygen evolution at the anode in a single compartment cell, an organic compound was sought whose anodic oxidation efficiency was high enough to prevent appreciable oxygen evolution. Of the compounds tried -- potassium acetate, potassium oxalate, ammonium formate, potassium citrate, hydroxylamine sulfate, and hydrazine sulfate -- potassium oxalate seemed the most promising. Table I shows data of the coulometric titration of HNO_3 by cathodic base generation in the presence of potassium oxalate to prevent anodic acid formation. As long as the molar ratio of oxalate to acid is equal to, or greater than 0.5, the acid present can be neutralized electrolytically. One mol of oxalate is equivalent to 2 mols of hydrogen ion, and the anode reaction is:

TABLE ITITRATION OF HNO_3 WITH VARYING OXALATE TO ACID RATIOS*

200 ma. 2.5 cm² stainless steel cathode. Manual control of current. Timed with stopwatch to phenolphthalein endpoint.

<u>mmols Oxalate</u>	<u>mmols HNO_3</u>	<u>mols Oxalate mols HNO_3</u>	<u>t, Theoretical, minutes</u>	<u>t, observed, minutes</u>
6	3.6	1.7	30	35
3	3.6	0.8	30	35
3	4.0	0.75	33	34
2	4.0	0.50	33	40
1.5	3.6	0.40	30	∞

*Potassium oxalate may be used in a quantitative coulometric titration of acid in a single compartment cell. In a preliminary experiment the titration of 1 ml. of 0.4715 N HNO_3 in saturated potassium oxalate, with 100 ma. current, 2.5 cm² stainless steel cathode, mixed indicator cresol red-thymol blue, manual control of current, and stopwatch timing, the following results were obtained: 0.447, 0.437, 0.490, 0.507, 0.446, 0.497, and 0.479 N, or an average of 0.472 N.

Plutonium electrodepositions with ammonium oxalate* gave low deposition yields if no HNO_3 were present and if the oxalate to HNO_3 ratio were too high or too low. The optimum equivalents ratio of oxalate to HNO_3 was found to be 0.8. The data are summarized in Table II.

TABLE II

EFFECT OF OXALATE TO HNO_3 RATIO ON THE ELECTRODEPOSITION OF PLUTONIUM

2.5 cm^2 stainless steel cathode. 120 ma/cm^2 current density.
68,000 c/m Pu. 1 hour electrolysis.

<u>meq. HNO_3</u>	<u>meq. Oxalate</u>	<u>meq. Oxalate</u> <u>meq. HNO_3</u>	<u>% Deposition</u>
0	5	∞	27
2	6	3	37
0.7	1.5	2.1	62
.75	1.2	1.6	82
1.0	1.0	1.0	90.8
1.1	1.0	0.9	91.5
1.25	1.0	0.8	95.4
1.4	1.0	0.7	93.2
1.0	0.5	0.5	87.4

The effect of time, cathodic current density, and HNO_3 concentration on the electrodeposition of plutonium has also been investigated. At least one hour electrolysis and 120 ma/cm^2 current density were required; a HNO_3 concentration of 0.25 M was found to be optimum. 100% deposition of 81,000 c/m Pu in 1.5 ml. of 0.25 M HNO_3 and 0.10 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at a cathodic current density of 120 ma/cm^2 has been obtained.

The effect of anode to cathode distance, the electrodeposition of larger quantities of plutonium, and the electrodeposition of uranium and other transuranium elements will be investigated.

*Ammonium oxalate was substituted for the potassium oxalate previously used to eliminate non-volatile residue on the disc.

RADIAL DISTRIBUTION OF PLUTONIUM IN AN IRRADIATED SLUG -- G.B. Barton, M.W. Gift, and E.M. Kinderman

The analyses of a sectional slug previously reported (1) have been extended to include U-235 determinations; as is mentioned elsewhere in this report, the precision of the determinations is excellent. A re-evaluation of the radial distance for the sectional pieces has been made in some cases. These data plus additions are given in Table I.

Examination of the data reveals a possible asymmetry. A second irradiated slug, chosen because its pile location during irradiation would minimize asymmetrical flux, is to be sectioned and analyzed in the near future.

Reference

- (1) Bushey, A.H., "Quarterly Progress Report, Analytical Research Sub-Unit, July, Aug., Sept., 1952," HW-25969, 10/31/52 (Secret).

TABLE I

RADIAL DISTRIBUTION OF ACTIVITIES ACROSS A SLUG

Distance* from Center, in		Alpha	Beta	Gamma	ug Pu	c/m Am	c/m Am		
<u>Previous</u>	<u>Present</u>	<u>c/m/mg U</u>	<u>c/m/mg U</u>	<u>c/m/mg U</u>	<u>mg U</u>	<u>mg U</u>	<u>10⁶ c/m Pu</u>	<u>% Pu-241</u>	<u>% U-235</u>
0.66	0.62	26895	55800	2543	.363	98740	3700	0.103	0.6705
0.38	0.38	20193	44760	2034	.276	56210	2820	0.0772	0.6797
0.19	0.19	18141	41510	1944	.246	46880	2657	0.0723	0.6818
0.00	0.00	18970	42990	1949	.261	47630	2537	0.0692	0.6863
0.16	0.14	18193	40280	1903	.254	44880	2500	0.0693	xx
0.31	0.27	18434	41340	1836	.256	48120	2617	0.0712	0.6813
0.47	0.42	19732	44250	2042	.273	56250	2859	0.0792	0.6780
0.63	0.53	22406	49230	2243	.306	71320	3215	0.0885	0.6725

*These are listed in order across the diameter of the slug.
 xxFluorination of sample failed. No analysis made.

RADIOAUTOGRAPHIC EXAMINATION OF IRRADIATED SLUGS -- G.B. Barton and M.W. Gift

Analysis of macrosamples is being used in an attempt to discover the radial distribution of plutonium and associated materials, in an irradiated slug (see above). Radioautographic examination has been employed without definite success in an attempt to eliminate the labor involved in the analyses and to examine fine structure differences not revealed by the macro sampling.

Direct radioautographic detection of plutonium alpha particles by exposure of a nuclear film (Type NTC 3, Eastman Kodak Co.) to an irradiated slug was not possible because of the heavy background of soft beta radiation. Utilization of the Herschel effect* to remove this beta background was not successful as too great a removal of the desired alpha tracks was effected by infrared radiation sufficient to remove the background tracks. Figure 1a shows a photomicrograph of film exposed to an irradiated slug and developed; Figure 1b shows a photomicrograph of a similarly exposed film which was treated with infrared radiation. Figures 1c and 1d are photomicrographs of film exposed to a plutonium source; d being the infrared treated film.

The technique of alpha radiography for location of plutonium, while not successful when applied to an irradiated slug, has proven useful in finding the distribution of plutonium on counting discs, etc.

Radioautography of the fission products in the irradiated slug section was also attempted. Variations in activity within the slug section can be detected by densitometric techniques and indicate the asymmetry mentioned in the previous section. The photograph of Figure 2A shows the appearance of the developed film. The band through the middle of the figure and the grainy appearance in various locations are apparently caused by surface irregularities in the section which cannot be removed without smearing the activity distribution picture. Because of the surface effects, this technique is not completely successful.

*This effect is the reversal of the latent image formation in an exposed but undeveloped emulsion by irradiating the exposed emulsion with a red or infrared source.

Fig. 1a
5 min. exposure to slug

Fig. 1b
5 min. exposure to slug
150 min. exposure to infrared

Fig. 1c
5 min. exposure to 200 ug Pu

Fig. 1d
5 min. exposure to 200 ug Pu
150 min. exposure to infrared

Figure 2 A

X-RAY DIFFRACTION RESULTS ON SOME PLUTONIUM SULFATE SAMPLES -- G.B. Barton

Some plutonium sulfate samples were prepared by evaporating a nitrate stock solution with an excess of sulfuric acid. As the evaporation proceeds, a red crystalline solid precipitates out. On further heating to fumes of SO_3 , the crystals break down to a pink solid which appears to be a plate form. Samples of the first solid, the second solid in a slurry with the mother liquor, and the second solid after removing the excess acid with methanol were mounted in capillary tubes for x-ray diffraction measurements.

Spectrophotometric measurements showed the plutonium to be in the IV valence state in the starting nitrate solution and in the finished solids.

The x-ray diffraction patterns were obtained by I.D. Thomas of the Metallurgy group in 234-5. He reported, "X-ray diffraction photographs indicate that the crushed crystals and the fuming sulfuric acid dried material are similar and probably isomorphous with $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The pattern obtained from the methyl alcohol dried sample was definitely different from those obtained from the other two samples."

These results were surprising in view of the observed transformation in crystal form and color that occurred as the first crystals were further heated in the sulfuric acid.

THE SPONTANEOUS FISSION OF PLUTONIUM-240 -- E.M. Kinderman

A value of 1.51×10^6 f/g/hr for the fission rate, which corresponds to a half-life of 1.31×10^{11} yr., has been determined and is reported in the captioned document HW-27660.

RECUPLEX IN-LINE PLUTONIUM MONITORING INSTRUMENTS -- R.E. Connally, U.L. Upson, and M.B. Leboeuf

The counting instruments group of the Radiochemistry Sub-Unit has been requested to develop in-line instrumentation for the continuous monitoring of the plutonium content of the waste (CAW and CCW) and product (CCP) streams in the Recuplex Process. The waste streams monitors are required to reliably detect 1 g/l of plutonium in the presence of a variable proportion of fission products and americium, and the product stream monitor is to accurately evaluate the Pu present in nominally 80 g/l concentrations. Since different approaches seem advisable for these two quite diverse cases, the requirements are being considered as two separate problems.

Plutonium Monitoring of Recuplex CCP Stream Using a Gamma-Ray Photometer

In the Recuplex Process CCP stream, it is desired to continuously monitor the plutonium concentration. The nominal concentration level is 80 g/l.

A prototype gamma-ray photometer employing a 0.5 ug. Am-241 source has been assembled and tested. From preliminary test data it is estimated that the photometer with a 10 mg. Am-241 source could monitor plutonium concentrations from 10 to 200 g/l with an accuracy of ± 2 g/l (standard deviation).

The gamma-ray photometer consists of the following components as compared to the x-ray photometer:

1. The x-ray tube is replaced with a long-lived (490 y) gamma-ray source (60 kev Am-241).
2. The single absorption cell of the gamma-ray photometer is similar to that of the x-ray photometer. There is no provision for the multiple cells and comparison type detectors in the present gamma-ray instrument.
3. The gamma detector is composed of a 2 mm. thick NaI(Tl) crystal optically coupled to a photomultiplier tube, instead of a fluorescent screen and phototubes used in the x-ray photometer.
4. The remaining components of the gamma-ray photometer are a negative high voltage supply, micromicrammeter, and a recorder. The x-ray photometer employs an x-ray tube power supply, an amplifier with synchronous detection at the beam chopping frequency, and a balance meter.

As the concentration of the plutonium solution in the absorption cell is increased, the number of gamma photons reaching the detector is decreased exponentially, thus indicating the plutonium concentration.

The presence of any gamma emitting isotope in the plutonium solution would increase the detector reading with increase in plutonium concentration, and thus introduce an error in the photometer reading. The effect of solution gamma activity and phototube noise has been investigated with the prototype gamma-ray photometer.

The following interference values are obtained by extrapolating the data taken with a 0.5 ug. Am-241 source to that expected for a 10 mg. Am-241 source:

1. The gamma sensing element background current due to 0.4 uC/ml of fission product gamma is 1/1,000 of the current due to a 10 mg. Am-241 source.

2. The current background due to noise in an average phototube is 1/7,000 of the current due to a 10 mg. Am-241 source.
3. The gamma sensing element current due to Am-241, which has grown into an 80 g/l solution of plutonium (600 MWD) over a period of one month, will be 1/500 of the current due to the 10 mg. Am-241 source.

In the above signal to noise ratios the source geometry was 1%, and the solution geometry was 10% with respect to the detector.

From the preliminary test data it is concluded that a 10 mg. Am-241 source will have sufficient gamma activity to give very good signal to noise ratios for the CCP stream. The ultimate precision and accuracy of the method will be determined when the 10 mg. Am-241 source is available for use with the gamma-ray photometer.

Plutonium Monitoring of Recuplex CAW and CCW Streams Using a Gamma Spectrometer

The CAW and CCW Recuplex waste streams may be expected to contain, in addition to the Pu losses, the entire F.P. and americium content of the Recuplex feed. This can be expected to be very similar to the present Redox product of 10 g. plutonium and about 50 uC fission products per liter, or about 5 uC F.P./g plutonium. Assuming at least 99.9% recovery of plutonium in the process, and assuming that possibly all the F.P. may go into either waste stream, these streams might be expected to contain up to 50 uC F.P. and about 1 mg. plutonium/l.

The present approach to the solution of this problem is through the selective counting of gamma events lying within a restricted energy range and most nearly characteristic of the desired emitter. In this manner some degree of discrimination against the fission product contaminants is effected. A scintillation gamma spectrometer is used for this purpose. The plutonium gamma peak occurring at about 95 kev (relative to 60 kev for Am-241) appears to be most promising in this respect. It occurs most nearly above the noise and the Compton scattering of the more energetic gammas, and its amplitude is most nearly dependent upon the Pu-239 content, and thus least sensitive to product variations. For 600 MWD/t material, the counting rate of 2000 c/m/mg plutonium obtained for the band from 85 to 115 kev, appears to result 65% from the Pu-239 content and 35% from some other Pu isotope, possibly 241.

Several sources of interfering activity were evaluated, using a 2 mm. thick NaI(Tl) scintillation crystal, in terms of the counts falling within the above energy range. Using the minimum absorption path, the high energy gamma emitters were found to be equivalent to 1.2 mg. plutonium per uC, but because of a Bremsstrahlung peak from the 3.5 Mev beta, 1 uC Ru-106 was found equivalent to 26 mg. plutonium. By inserting 1.7 g/cm² of Al between the sources and the crystal, only slight reduction in the plutonium count was obtained; the F.P. gamma emitters were found now equivalent to 1.8 mg. plutonium/uC, because of scattering from the absorber, and the Ru-106 equivalence was reduced to 6.2 mg. plutonium/uC. The use of beryllium absorbers will further reduce this interference.

On the basis of the above data, for a waste stream containing 50 uC/l of Ru-106 the F.P. equivalence amounts to about 300 mg. Pu/l. Thus, the limit of reliable detection would be about this value, or 1/3 of the maximum tolerance for this very unfavorable case. Should the F.P. concentration be subject to large variations, the instrument could not reliably detect the plutonium below the 1 g/l level.

It thus appears necessary to compensate for the interference due to fission products in the sensitive range. If, in addition to the count within the prescribed energy limits, the total counting rate above the upper limit is separately obtained, this latter count is a measure of the F.P. activity of the sample. For the arrangement stated, the F.P. count in the 80-115 kev band was found to be from 22% (Cs-137) to 36% (Ru-106) of that above 115 kev. Thus, if the upper level F.P. count is known, a correction can be applied to the "plutonium" count, and a value for the "net Pu" activity obtained. This correction can be made automatically and electronically for a moderate additional cost.

Such a correction is subject to error if the composition of the F.P. contaminants is not known. For the case of an upper level total count equivalent to 50 uC/l of Ru-106, the Ru-106 correction is 300 mg/l Pu equivalence. If, in the extreme case, the correction is applied as if for 100% Ru-106 when no Ru-106 is present, the reported Pu content would be low by 140 mg/l. For extremely high upper-level counts, resulting in high correction uncertainty, a determination could be made to identify the F.P. and the corresponding correction factor electronically applied. In normal usage, by using an intermediate factor, as dictated by experience, the maximum compensation error can be brought below 100 mg/l, and thus the Pu detection level brought down to this value.

With the use of a beryllium absorber and other lesser refinements, the detection limit may possibly be reduced to 50 mg. Pu/l.

REDOX AND METAL RECOVERY FISSION PRODUCT DISTRIBUTION STUDIES BY GAMMA SPECTROMETRY --
M.B. Leboeuf and F.P. Brauer

To demonstrate the application of the gamma spectrometer as a useful tool to obtain rapid and accurate knowledge of the distribution of fission products in various plant streams under known operation conditions, scans were made of the product and feed streams of the five Redox cycles. These measurements were made under standard conditions in order to give data from which decontamination factors could be calculated. In establishing these standard conditions, tests showed that the absorption of ≥ 0.5 Mev gamma rays by the uranium in the samples was sufficiently small to neglect.

The major gamma active fission products found in the Redox streams were cerium, ruthenium, zirconium, and niobium. Decontamination factors across the five Redox cycles have been calculated from the gamma scans for the principal fission product gamma activities present (1). The gamma spectrometer has proven to be a useful tool for determination of gamma active fission product decontamination factors in the Redox streams in addition to giving distribution data.

Various samples from the Metal Recovery plant were obtained. Only the RAF and the RAW were sufficiently gamma active to give meaningful scans. Cs-137 was the principal gamma active fission product present. A liter of RCU was found to contain insufficient gamma activity for a good scan. Because no values could be obtained by the gamma spectrometer for the RCU gamma activity, it was impossible to calculate decontamination factors for the Metal Recovery plant. The gamma spectrometer may prove more useful for Metal Recovery stream fission product analysis when younger waste is used for feed.

Reference

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GAMMA SPECTROMETER MEASUREMENTS ON Ce-144-Pr-144 -- F.P. Brauer and M.B. Leboeuf

Gamma spectrometer scans have shown a 0.14 Mev gamma associated with cerium. In order to facilitate the interpretation of gamma spectrometer scans of plant streams, it is necessary to know if this gamma originates from Ce-141 or from Ce-144-Pr-144. Greater than three-year old dissolver solution was obtained. Ce-141 with a 33-day half-life would no longer be present in significant quantities, and thus, (by usual radio-chemical methods) Ce-144 was separated from this dissolver solution. A gamma spectrometer scan of the Ce-144-Pr-144 activity was measured after the 17.5-minute Pr-144 daughter activity reached equilibrium. The following gamma energies were observed:

2.08 Mev	(0.2%)
1.40 Mev	(0.3%)
0.68 Mev	(2.5%)
0.14 Mev	(100%)
0.09 Mev	(43%)
0.04 Mev	(30%)

The percentages are relative photopeak heights and not per cent of total disintegrations. By absolute beta counting of an aliquot of the Ce-144-Pr-144 sample, a d/m/ml value was obtained for the Ce-144 (1). It was found that approximately 25% of Ce-144 d/m led to a 0.14 Mev gamma.

These results agree with the latest literature within experimental errors (2). The principal gamma ray (0.14 Mev) together with the 0.09 and the 0.04 Mev gamma rays have proven to be an excellent indication of the presence of Ce-144-Pr-144 in several plant streams for which gamma scans have been made (1).

References

- (1) Upson, U.L., Unpublished work.
- (2) Hollander, J.M., Perlman, I., and Seaborg, G.T., Table of Isotopes, UCRL-1928, Dec., 1952.

ALPHA IN-LINE MONITOR FOR PLUTONIUM WASTE LOSSES -- M.B. Leboeuf

An instrument is being developed to monitor for plutonium waste losses in Redox and Purex streams, by in-line measurement of the alpha counting rate of small aliquots taken automatically. The Redox streams of particular interest are the 10W, 2BW, 3BW, 2AW, 3AW, and 2DW. A direct and essentially continuous indication of the plutonium losses in these streams is potentially capable of effecting substantial savings in Redox plant operation.

A prototype automatic sampler for this instrument was tested using Redox 3BW hexone solution and dilutions thereof. This sampler is an air-actuated, stopcock type device which deposits 150 u liter samples of solution, at 15-minute intervals, on a polyethylene coated paper tape. A sample area of the moving tape is counted by an alpha scintillation detector to determine the plutonium concentration of the solution. Tests were performed which revealed the following:

Performance Test

Results

1. Sample counting rate reproducibility at a fixed plutonium concentration.
2. Sample counting rate as a function of changes in plutonium concentration.
3. Effectiveness of sampler operations.
4. Probability of long term reliability.

Std.Dev. of 10 measurements = $\pm 10\%$, when precaution is taken to avoid air entrapment in the stopcock bore. Air entrapment can cause variations as large as a factor of 3.

Directly proportional in the range 6,000 to 120,000 alpha d/m/ml. Does not exhibit appreciable memory of high activity samples.

Choice of "wash only" cycle at will permits check on satisfactory operation of sampler and counter.

Sampler was operated satisfactorily over 20-hr. period. Since stopcock has very short duty cycle, long term reliability can be expected.

Results similar to the above may be expected for aqueous plutonium solutions of low salt concentration. This will be tested for a synthetic low solution, since a monitor on this stream would effectively detect plutonium losses in both the 2BW and 3BW streams.

The problem of air entrapment in the stopcock bore is not yet satisfactorily solved. Design work has been initiated on a complete prototype alpha in-line monitor primarily intended for the LOW stream. The three principal design problems to be solved are: 1) providing a continuous, gas-free sample to the sampler; 2) providing means for sample replacement of the whole sampler-detector assembly for servicing; and 3) providing a satisfactory enclosed design to prevent spread of plutonium and fission product contamination.

COULOMETRIC TITRATION OF PLUTONIUM -- W.N. Carson, Jr., and J.W. Vanderwater

The investigation of the coulometric titration of plutonium by the reductimetric method reported previously (1) was continued. The design of the titration equipment has advanced to the point where it is complete in all but minor details; therefore, it will be described in detail at this time. In the discussion, a high level titration refers to the titration of over 50 ug. of plutonium; a low level titration refers to the titration of less than 50 ug.

Titration Cell Assemblies. Figure 16 gives the basic titration cell assembly. The sample is pretreated (see below) in the fuming unit and then transferred to the titration cell. The titration cell and the fuming cell are each fitted with an entry port placed at right angles to the plane of the section shown in the figure; this is not shown in the drawings. The entry ports are used to introduce sample and reagents, and for cleaning.

The titration cell is fitted with the generator and indicator electrode sub-assemblies. The generator sub-assembly consists of a 90% platinum-10% iridium cathode and a platinum anode placed in 1:1 H_2SO_4 solution separated from the titration zone by a silica gel salt bridge. The indicator assembly consists of two small 90% platinum-10% iridium electrodes. The titration solution is stirred by a magnetic stirrer and blanketed by oxygen-free carbon dioxide. The entry port is normally closed with a glass stopper.

The fuming unit is heated by a small ring heater. The solution is stirred by a stream of carbon dioxide; this must be done to prevent bumping. The entry port is closed during heating with a safety cap which is a small, inverted, U-tube whose outer leg is inserted into a venturi fitted with glass wool. This permits a rapid flow of air through the upper part of the fuming unit to remove the fumes without reducing the pressure in the unit, and at the same time prevents any spattering that may accidentally occur from blowing into the operator's face.

Since the fuming is carried out in a perchloric acid solution, the scrubber is used to prevent accumulation of perchloric acid in the off-gas train. The apparatus is all glass to this point as an additional safety precaution; no grease is used on the ball joint. Marble chips neutralize the acid; the water covering them is replaced from time to time. The carbon dioxide used to blanket the cell and stir the solution is passed through hot copper oxide and hot copper. This removes traces of organic vapors and oxygen.

The semiautomatic and automatic low level titration and the manual high level titration are carried out in the assembly as shown. For the high level automatic titration, the titration cell has a side arm and solenoid assembly similar to that on the titration cell used in the automatic titration of oxidizing agents (2).

Titration Set-Ups. The manual titration set-up is similar to the manual titration apparatus used in the coulometric titration of uranium (3). It consists of a constant current source and associated measuring equipment (precision resistor, potentiometer, and electric stopwatch), the titration cell assembly, and the indicator system (polarization current source and pH meter).

Figure 17 gives the block diagram of the semiautomatic low level titration assembly reported previously (2). This titrator adds titration current in small increments at relatively large intervals. This type of addition is necessary because the indicator system is very sluggish, and continuous titration is not feasible at this low level. The constant current source for the titration current consists of several 45 v "B" batteries in parallel, with a high value resistor in series. A switch permits selection of several ranges. Measurement of the IR drop across the 10,000 ohm series resistor with the potentiometer measures the value of the current. The constant current source for the indicator system is a 3 v battery with a 30 megohm series resistor. The indicator current is 0.1 microamperes and is critical. The voltage across the indicator electrodes is amplified by the pH meter, and the amplified signal is fed by way of the controller to the recorder. The pH meter is a modified Beckman H-2; the modification has been described previously (4). The clock is an electric stopwatch (Standard Time Co. SM 60); the recorder is a standard strip chart 10 mv. potentiometer (Bristol Dynamaster).

Figure 18 gives the controller circuit. The function of the controller is to add titration current in small equal increments at fixed intervals. Whenever titration current is added, the controller also turns on the stopwatch. At the same time, the indicator signal is disconnected from the recorder and a marker signal substituted. This action makes a blip on the chart for each increment added. A zero offset circuit is used to suppress the unvarying portion of the pH meter output. Figure 19 gives a typical recording, which will be discussed later.

The automatic low level assembly uses a trigger circuit (4) in place of the recorder. This has not been used to date and may not be satisfactory.

The high level automatic titration assembly is the same as the oxidant titration described previously (2), except, of course, for the titration cell assembly.

Both the high and low level titrators have been operating satisfactorily for 2 to 3 months; checks on their operation using standard dichromate solutions as stand-in for plutonium have given precise and accurate results. The low level titration is very tedious and slow if performed manually; the semiautomatic titrator materially increases the precision and accuracy, and allows more determinations to be made per day with much less operator effort. It is recommended that the low level titrations always be semiautomatic or automatic.

Procedure for High Level Titration

<u>Step</u>	<u>Explanation</u>	<u>Remarks</u>
1. Take sample and add to 1 ml. 1:3 HClO ₄ in fuming unit.		
2. Add a small excess of Fe(ClO ₄) ₂ soln. and heat to appearance of dark brown color. Cool slightly.	To destroy nitrates which interfere with indicator system.	Not needed if NO ₃ ⁻ absent. Stir while heating. Evolution of NO ₂ is sudden and rapid. Addition of small amt. of Ag ⁺ catalyzes reaction.

3. Add 200 ul. conc. HClO_4
10 ul. conc. H_3PO_4	To increase acidity
PO_4^{3-} aids oxidation.	Do not allow plutonium
to precipitate; high
acid prevents this.
4. Add excess, freshly pre-
pared KMnO_4 soln. ($\sim 0.1 \text{ M}$)
Heat until violet color
disappears.	To oxidize plutonium
to VI valence state.	KMnO_4 soln. must be fresh;
old solns. (8 hrs. or more)
contain unreactive MnO_2
which interferes with next
step. Violet color should
persist for at least 2 min.
5. Add 10 ul. conc. HCl and
boil gently until brown
color disappears.	To destroy MnO_2
formed in oxidation
step.	Do not boil to HClO_4 fumes.
Add extra HCl if brown
color persists.
6. Add 50-100 ul. $0.1 \text{ N K}_2\text{Cr}_2\text{O}_7$
to electrolyte in titration
vessel. Titrate to endpoint.	To destroy traces of
oxidizing or reducing
agents present in
solns.	Electrolyte is 5 ul. 0.6 N
$\text{Fe}_2(\text{SO}_4)_3$ in $4 \text{ N H}_2\text{SO}_4$
plus 500 ul. H_3PO_4 . This
treatment should be made
during the MnO_2 destruction.
7. Remove 2-3 ml. treated
electrolyte in a transfer
pipet; close cell.	To serve as rinse for
fuming unit.	
8. Pull sample from fuming unit
to titration cell. Rinse
fuming unit with treated
electrolyte.		
9. Titrate to endpoint.		For manual titrations use
small increments across
endpoint. Indicator system
is very sluggish, and care
should be exercised not to
overshoot the endpoint.

The titration requires two equivalents of ferrous ion for each plutonium, since the titration is from the VI to the IV valence state.

A few results on the high level were obtained. In one series, thirteen 25 ul. samples of 11.13 g/l Pu standard were titrated. The average value obtained was 11.09 g/l, with a standard deviation* of $\pm 0.097 \text{ g/l}$. Nitrates were not destroyed in this series for reasons explained later. Results of the titration of standards in which nitrates were destroyed using $\text{Fe}(\text{ClO}_4)_2$ are: 1) taken: 24.09 g/l (25 ul. samples), found: 24.09, 24.13, 24.00 g/l; 2) taken: 4.50 g/l (100 ul. samples), found: 4.50, 4.53 g/l; 3) taken: value not independently known (100 ul. samples) 3.66, 3.62, 3.56 g/l; 4) taken: value not independently known (100 ul. samples) 1.81, 1.80 g/l.

Low Level Titration Procedure (Semiautomatic)

The pretreatment is the same as for the high level. A titration record is given in Figure 19. The first part of the curve (A) is the titration of dichromate, the second is the titration of the plutonium. The total time is measured on the stopwatch;

*Precision of a single determination.

this divided by the total number of increments added gives the time per increment. The endpoint is taken in the middle portion of the curves, and the number of increments between them gives the increments required to titrate the sample. In the figure, the endpoints are taken at the 30 line, which is merely a reference line.

Work on the low level has been concentrated on the study of removal of nitrate interference and solving unexpected difficulties. No precision runs have been made; Table I gives results from some miscellaneous titrations.

TABLE I
LOW LEVEL TITRATION RESULTS

<u>Sample</u>	<u>Taken</u>	<u>Obtained</u>	<u>Remarks</u>
0.1120 g/l	50 ul (5.6 ug)	0.1040 g/l	Plutonium nitrate in dil. HClO ₄ solution
		0.1118	
		0.1164	
	25 ul (3.2 ug)	0.1144	
		0.1118	
		0.1195	
0.1213 g/l	25 ul (3.3 ug)	0.1125	Plutonium nitrate in dil. HClO ₄ solution
		0.1240	
		0.1229	
		0.1191	
		0.1127	
0.1199 g/l	100 ul (11.99 ug)	0.1215	Plutonium nitrate in 2 M HNO ₃
		0.1218	
0.1199 g/l	100 ul (11.99 ug)	0.1158	Plutonium nitrate in 2 M HClO ₄ , 0.5 M UNH
		0.1234	
0.2409 g/l	25 ul (6.0 ug)	0.2478	Synthetic dissolver solution 2 M UNH, 0.2 M HNO ₃ (500 g. Pu per ton uranium)
		0.2381	
		0.2468	

Difficulties Encountered. A series of low results led to the discovery that the pure platinum electrodes employed at first for the generator and indicator electrodes were being attacked by the sample solution. The presence of nitrate aggravates this attack, although at the high level titration with new electrodes, the results are not apparently affected. In a short time the electrodes become etched, and poor results are obtained. The high level results obtained without destruction of nitrate were obtained with new electrodes; later attempts to titrate with these electrodes were failures. The use of the Pt-Ir alloy for these electrodes has apparently eliminated this problem.

A series of high runs disclosed the presence of a refractory form of MnO₂ in the KMnO₄ solution which resists reduction by HCl. Freshly precipitated MnO₂ does not offer this difficulty, but aged MnO₂ does. Thus, it is important to use only freshly prepared KMnO₄ solution.

The nitrate destruction with $\text{Fe}(\text{ClO}_4)_2$ is not completely satisfactory, since occasionally this treatment does not destroy nitrates. This was noticed particularly for solutions in which the acid strength was very high. Silver ion is a good catalyst and should be added as a saturated solution of AgCl in the 1:3 perchloric acid. This prevents an excess of silver which precipitates in the MnO_2 destruction step.

References

- (1) Bushey, A.H., Quarterly Progress Report, July, Aug., Sept., 1952, HW-25969 (Secret).
- (2) Bushey, A.H., Quarterly Progress Report, Oct., Nov., Dec., 1952, HW-27139 (Secret).
- (3) Carson, W.N., Jr., Anal.Chem. 25, 466 (1953).
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BASIC TITRATION
CELL ASSEMBLY

FIGURE 16

0142-000-083

BLOCK DIAGRAM
LOW LEVEL PLUTONIUM TITRATOR

FIGURE 17

0142-086

FIGURE 18

0142-087

**INCREMENT
MARKERS**

**INCREMENTS
USED IN TITRATION
OF $Pu(VI)$**

**INCREMENTS
USED IN TITRATION
OF $Cr_2O_7^{2-}$**

FIGURE 19

0142-088

AUTOMATIC COULOMETRIC TITRATION OF OXIDIZING AND REDUCING AGENTS -- W.N. Carson, Jr.

The titration study reported previously (1) has been continued and extended to reducing agents. The apparatus used is the same as previously reported. For oxidizing agents the electrolyte is 0.6 N $\text{Fe}_2(\text{SO}_4)_3$ and 4 N H_2SO_4 ; phosphate is added for KMnO_4 titrations. Table I gives a summary of additional runs made in this study.

The titration for reducing agents is based on the use of electrolytically generated ceric ion according to the method of Cooke (2). Table II shows the results. Precisions are given as the 95% limits (2 x standard deviation). In addition to the agents shown in the table, stibnite, hypophosphite, nitrite, and hydroxylamine were tried, but the direct titration is unsuccessful. In the table the effect of air oxidation on the chromous titration and SO_2 evolution for sulfite is apparent. Further work on these titrations is being conducted.

TABLE IAUTOMATIC TITRATION OF OXIDIZING AGENTS*

<u>Solution</u>	<u>N Taken</u>	<u>N Found</u>	<u>No. Samples</u>	<u>Precision</u>
KMnO_4	0.1019	0.1019	16	$\pm 1.6\%$
	0.05	0.04869	11	1.1
	0.01	0.009842	8	2.4
	0.005	0.004970	9	4.4
	0.0013	0.00125	8	22.4
$\text{K}_2\text{Cr}_2\text{O}_7$	0.1027	0.1033	7	1.48

*100 ul. samples

TABLE IIAUTOMATIC TITRATION OF REDUCING AGENTS

<u>Solution</u>	<u>Taken, ul</u>	<u>N Found</u>	<u>No. Samples</u>	<u>Precision</u>
$\text{Fe(II)} \ 0.1 \ \text{M}$	100	0.1027	9	$\pm 1.38\%$
	50	0.1018	9	1.66
	25	0.1029	9	0.88
	10	0.1066	9	1.42
$\text{As(III)} \ 0.1 \ \text{M}$	100	0.1033	10	1.54
	75	0.0993	9	1.2
	50	0.0998	9	2.2
$\text{Cr(II)} \ 0.1 \ \text{M}$	100	0.0920	9	1.0
	75	0.0896	9	3.12
	50	0.0868	9	5.6
$\text{Na}_2\text{SO}_3 \ 0.1 \ \text{M}$	100	0.120	9	9.8

References

- (1) Bushey, A.H., Quarterly Progress Report, Oct., Nov., Dec., 1952, HW-27139 (Secret).
- (2) Furman, N.H., Cooke, W.D., and Reilley, C.N., Anal.Chem. 23, 945 (1951).

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089

PUREX FEED STUDY -- W.N. Carson, Jr.

A study of methods of in-line analysis of Purex feed streams for the determination of UNH and HNO_3 concentration has shown that the use of refractive index and density possesses many advantages. No precise sampling would be required, automatic instruments are commercially available, no chemical operations on the streams would need to be made, and the bulk of the equipment used can be isolated from contamination. The commercial instruments will require some revamping to be usable, however.

To check the feasibility of this system for in-line analysis, a series of standard solutions were analyzed for density and refractive index. These covered the range 1.1 M - 1.6 M UNH, and 1.5 - 2.5 M HNO_3 . Statistical analysis of the data gave the following equations:

$$\text{M UNH} = 32.9440 + 6.0995 \text{ Sp.G.} - 29.2394 \text{ R.I.}$$

$$\text{M HNO}_3 = -350.8597 - 27.9528 + 283.5247 \text{ R.I.}$$

The 99% (2.58 σ) limits of the variance between calculated and observed values are $\text{M UNH} = \pm 0.023$, $\text{M HNO}_3 = \pm 0.139$. A variation of ± 0.001 Sp.G. and ± 0.0001 R.I. would give $\Delta \text{M UNH} = \pm 0.003$, $\Delta \text{M HNO}_3 = \pm 0.001$. Since a measurement of ± 0.001 Sp.G. and ± 0.0001 R.I. can be made by the commercial instrument (for Sp.G., the Densitrol Precision Thermometer and Instrument Co.; for R.I., the Robomatic Refractometer, Precision Scientific Co.), the proposed system is basically sound. The cost of such an installation is quite high, and the Densitrol requires a very large (for highly radioactive streams) sample. Therefore, other means for making this in-line analysis are being investigated that may overcome these difficulties.

ACID DETERMINATION -- C.E. Michelson and W.N. Carson, Jr.

Conductometric Titration. A satisfactory determination of the free acid in Purex type streams (nominal 2.0 M HNO_3 , 1.3 M UNH) by use of the conductometric titration of Pepkowitz (1) has been made. The original procedure used an A.C. bridge with platinized-platinum electrodes. This is satisfactory, but the simpler bridge of Taylor and Furman (2) is easier to obtain and use. This bridge is a D.C. bridge, and consists of two bright platinum electrodes through which is passed a small constant current and a pair of tungsten electrode acting as probes in the field between the platinum electrodes. The voltage between the probes is measured by a high impedance voltmeter (a pH meter is ideal). Since constant current is used, the voltage drop across the platinum electrodes (which determines the field strength) is proportional to the resistance of the solution. Hence, the voltage across the probes varies inversely with changes in the resistance of the solution. The curves obtained with this bridge are similar to those obtained by use of the A.C. bridge.

An automatic conductivity apparatus was set up, using a motor-driven, E. Greiner buret to deliver the sodium hydroxide titrant, and a Leeds and Northrup pH Speedomax recorder. All D.C. bridge results reported were obtained using this set-up. A Rubicon, 60 cycle, A.C. bridge was used for the A.C. results. The procedure was: take 10 ul. samples, dilute to 50 ml. with distilled water, add a small excess ($> 25\%$) NaF to

complex the uranium, and titrate with 0.1 N NaOH. The results of several series of determinations are given in Table I. Ten samples of 10 ul. each were used for each series except for the pure acid. Precision is given as the 95% limits (2 x standard deviation). These results are comparable to those obtained by using the modified oxalate method given below.

TABLE I
CONDUCTOMETRIC TITRATION OF FREE ACID

<u>Sample Make-up</u>	<u>Found(Avg.)</u>	<u>Precision</u>	<u>Remarks</u>
0.09981 M HNO ₃	0.09610 M	± 0.54%	250 ul. sample D.C. Bridge
2.471 M HNO ₃	2.445	1.98	35 ul. NaF soln.(40 g/l) added D.C. Bridge
	2.498	2.08	50 ul. NaF soln. added D.C. Bridge
	2.45	3.2	50 ul. NaF soln. added A.C. Bridge
2.088 M HNO ₃ 1.117 M UNH	2.015	3.86	35 ul. NaF soln. added D.C. Bridge
	2.088	3.54	50 ul. NaF soln. added D.C. Bridge
	2.04	2.2	50 ul. NaF soln. added A.C. Bridge

Coulometric Titration. The modified oxalate method reported previously (3) has been examined for use with Purex feed samples and found satisfactory. The procedure has been changed to the following:

<u>Step</u>	<u>Explanation</u>	<u>Remarks</u>
1. Add 35 ul. 25% K ₂ C ₂ O ₄ to sample vial. Add 5-10 ul. of UO ₂ C ₂ O ₄ slurry in water.	To seed mixture so that proper form of UO ₂ C ₂ O ₄ is formed from UNH in sample.	Must be done to prevent hydrolysis of UNH.
2. Add 1500 ul. 90% isopropanol, 500 ul. 5% KBr, and 1 drop 0.05% bromethymol blue indicator.	Electrolyte make-up.	Do not seed until just before adding sample. More bromthymol blue indicator soln. may be used if preferred.
3. Add 5 or 10 ul. sample. Stir vigorously.		Precipitate of UO ₂ C ₂ O ₄ (yellow) must form or detn. is ruined.

4. Titrate, using a silver anode and platinum cathode. Generator system is explained in ref.(4) Colorimetric endpoint should be taken to bright blue. Potentiometric endpoint using glass vs. Ag-AgCl can be used.

The above titration procedure may be used for uranium solutions up to 2.0 M and from 0.1 M HNO_3 . For solutions containing less than 1.0 M HNO_3 , the potentiometric indicator system should be used. The minimum current employed should be 2 ma, maximum about 10 ma. The glass electrode should be soaked briefly in water between determinations.

Results on Purex type samples are given in Table II. Ten titrations were made for each sample, using 10 ul. aliquots.

TABLE II
COULOMETRIC TITRATION OF FREE ACID

<u>Sample</u>	<u>Found</u>	<u>Precision</u> (95% C.I.)
1.117 M UNH 2.088 M HNO_3	2.110 M	$\pm 5.4\%$
1.543 M UNH 2.471 M HNO_3	2.460	± 2.68
1.120 M UNH 1.555 M HNO_3	1.610	± 5.46

References

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- (2) Taylor, R.P. and Furman, N.H., Anal.Chem. 24, 1931 (1952).
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PILE ATMOSPHERE STUDIES AND ESTIMATED GRAPHITE BURNOUT -- G.J. Alkire and R.D. Tillson

The pile gas studies initiated at the start-up of C Pile in November of 1952 and reported previously (1, 2) are continuing. A summary of the data obtained since 12/16/52 until 3/2/53, together with an estimate of the graphite burnout in the unit are presented herein. The pile gas composition in mole %, power level in megawatts and per cent of total volume of gas added per day are tabulated in Table I.

An examination of these data show a relatively steady state during the periods 12/29/52 to 1/23/53, and 2/13/53 to 2/27/53. In this first period the nitrogen content decreased to a few tenths per cent and the carbon monoxide leveled off between 2.3 and 3.5%. This approach towards a steady state stopped abruptly on 1/30/53, with the nitrogen rising to approximately 8% and the carbon monoxide falling off to less than 1%. This sudden change in composition was due to 61% of the volume of the unit being replaced that day, due to venting for the Ball 3X and subsequent purge. A second approach towards a steady state was not observed again until 2/13/53. The next six samples analyzed showed a rather constant carbon monoxide content although the nitrogen values during this period fluctuated widely.

These data obtained during a steady state condition in the unit coupled with the measured leakage rate of the unit allows one to estimate the graphite burnout due to the reaction of the atmosphere (93-96% CO₂) with the graphite at the elevated temperature in the high neutron flux. Consider for example the period 12/29/52 to 1/23/53. The average CO content during this time was 2.85% with individual values ranging from 2.3 to 3.5%. During this period the amount of make-up gas (CO₂) added each day ranged from 6 to 17% of the volume of the unit, with an average value for the period of 10.8% per day. This percentage of the volume of the unit added per day is likewise a measure of the leakage from the unit per day if a constant pressure is maintained. If we further assume that all gases are lost at the same rate, then in order to maintain a carbon monoxide content of 2.85%, 2724 grams carbon monoxide must be formed per day at the average power level of 709 megawatts. The carbon monoxide detected may be formed by either or all of the reactions represented by the following equations:

K, 327°C

If the carbon monoxide arises from either equations (1) or (2), graphite is consumed at a rate of 584 and 1167 grams per day by equations (1) and (2), respectively. This represents a loss of graphite of 0.014 and 0.03% per year. Carbon monoxide formed by equations (3) or (4) would represent no direct loss of graphite. The thermodynamic equilibrium constants favor equation (3), but these constants do not take into account the rate of reaction or the influence of radiation on the reactants themselves. With the data to date and the small amount of hydrogen being formed, it is felt that most of the carbon monoxide is formed by reaction (1) with much smaller amounts from the other indicated reactions, so that these data indicate a graphite loss of 0.014% per year. The amount of carbon monoxide found is, however, in excess of the amount predicted from the equilibrium constant of equation (1) at this temperature (250°-300°C),

TABLE I

COMPOSITION OF C PILE ATMOSPHERE IN MOLE PERCENT

Date Sample Taken	MW At Time Taken	CO ₂	CO	N ₂	O ₂	A	He ⁴	H ₂	Make-up Volume Added (% total)
12/16	556	89.19	0.92	7.95	1.54	0.10	0.27	0.04	29.20
17	705	92.42	1.09	5.95	0.28	.07	.16	.02	8.16
18	715	91.62	1.50	6.53	< .01	.08	.23	.04	9.40
19	724	92.93	1.57	5.91	< .01	.09	.16	.04	16.10
24	725	92.35	2.21	5.25	.06	.08	.02	.03	15.76
26	735	92.44	2.64	4.63	< .01	.08	.05	.17	10.24
29	735	92.90	3.00	3.75	< .01	.07	.02	.25	10.24
30	710	93.83	2.29	3.73	< .01	.05	.03	.21	11.02
31	710	93.81	3.48	2.56	< .01	.05	.03	.20	11.12
1/2	710	94.77	2.39	2.71	< .01	.03	.02	.21	12.20
5	714	95.52	3.42	0.75	< .01	.03	< .01	.29	12.00
7	725	96.0	2.55	1.35	< .01	.02	< .01	.22	0.32
12	715	96.49	2.43	0.60	< .01	.11	< .01	.46	11.40
14	714	96.35	2.73	0.70	< .01	< .01	< .01	.21	8.36
16	700	96.16	2.65	.62	< .01	< .01	< .01	.56	11.80
20	693	96.37	2.43	.91	.02	< .01	< .01	.27	13.20
21	690	96.43	3.21	0.11	< .01	.04	< .01	.24	12.58
23	695	*96.00	89.28(3.57)	10.3(.41)	.08(.003)	.33(.0132)	< .01	.01	16.84
30	587	*90.	7.13(.71)	78.57(7.86)	13.10(1.31)	.89(.09)	< .01	.03 .33	60.9
2/3	690	*90.	7.2(.72)	82.5(8.25)	9.13(.91)	.92(.09)	< .01	.02 .24	5.68
4	694	90.69	1.40	7.6	0.21	0.10	< .01	.02	13.48
9	755	94.95	1.16	3.77	< .01	.04	< .01	.07	12.00
11	760	96.04	1.23	2.62	< .01	.03	< .01	.07	14.12
13	760	96.01	2.47	1.50	< .01	.02	< .01	.01	6.72
16	750	95.66	2.42	1.78	< .01	.02	< .01	.12	10.76
18	746	96.63	2.24	1.08	.03	.02	< .01	.01	14.72
24	755	92.97	2.48	4.20	.05	.05	< .01	.30	9.42
25	760	93.73	2.56	3.56	< .01	.05	< .01	.10	4.78
27	770	94.52	2.42	2.90	< .01	.05	< .01	.11	7.60
3/2	777	96.29	1.56	2.00	.02	.02	2.01	.11	10.42

*These three samples were not analyzed for CO₂ content. The CO₂ content listed is estimated and the values in brackets are the calculated amounts based on the estimated CO₂ and the measured constituents in the residual gas.

but the constant is for a static system outside of a radiation influence. The dynamic system within the reactor is very complex and does not attain equilibrium but does approach attainment of a steady state if the leakage rate is not excessive.

The burnout rate, for the second shorter period of steady state (2/13 - 2/27), is 0.013% per year.

More data are being taken and will be correlated with actual operating conditions within the reactor.

References

- (1) Bushey, A.H., Quarterly Progress Report, Oct., Nov., Dec., 1952, HW-27139.
- (2) Alkire, G.J., "Estimation of Graphite Burnout in C Pile," HW-27442.

GASES EVOLVED FROM URANIUM SLUGS AND ALUMINUM CAPS -- K. Koyama

A report with the above title has been issued as document HW-27465.

Abstract. The procedure and apparatus used for collecting gases evolved at elevated temperatures from uranium slugs and aluminum caps are given. Slugs which have been heat treated in a salt bath evolved 7 to 9 cc., or three to four times more gas than standard slugs. Between 85 and 90% by volume of these gases is hydrogen, as determined with the mass spectrometer. Small amounts of oxygen, nitrogen, carbon dioxide, and carbon monoxide are also present.

The gases from aluminum caps contained hydrogen and nitrogen with traces of carbon monoxide, nitric oxide, and carbon dioxide. Approximately 2.5 cc. of gas per 6 caps were found. The mass spectrum of the gas from these caps is extremely complex.

URANIUM ISOTOPIC ANALYSIS -- C.A. Goodall, K. Koyama, G.J. Alkire

The isotopic distribution of uranium in samples from an irradiated slug have been determined with the Consolidated Model 21-221 Isotope Ratio Mass Spectrometer. These results are tabulated elsewhere in this report along with the distribution of plutonium, americium, and gross beta-gamma count. The individual determinations for uranium-235 are tabulated here to show the performance of the 21-221 mass spectrometer. Table I lists the measured ion beam ratios of the standard and the unknown, the weight per cent of uranium-235 and the average weight per cent of the three values for each sample with the indicated precision limits. The precision limits shown are the range of the three individual values.

TABLE I

PERFORMANCE OF CONSOLIDATED 21-221 ISOTOPE RATIO
MASS SPECTROMETER

<u>Sample No.</u>	<u>Standard Ratio</u>	<u>Sample Ratio</u>	<u>Wt. %</u>	<u>Average and Range</u>
1	14643	14641	0.6864	0.6863 ± 0.0005
	14641	14635	0.6860	
	14639	14644	0.6865	
3	14660	14540	0.6807	0.6813 ± 0.0011
	14619	14512	0.6813	
	14627	14531	0.6818	
4	14600	14420	0.6779	0.6780 ± 0.0007
	14569	14399	0.6784	
	14575	14391	0.6777	
5	14659	14365	0.6726	0.6725 ± 0.0007
	14656	14366	0.6728	
	14672	14367	0.6721	
6	14656	14538	0.6808	0.6818 ± 0.0016
	14645	14553	0.6820	
	14650	14566	0.6824	
7	14723	14578	0.6796	0.6797 ± 0.0006
	14662	14512	0.6794	
	14662	14526	0.6800	
8	14673	14329	0.6703	0.6705 ± 0.0009
	14672	14323	0.6701	
	14584	14256	0.6710	
Average range of 21 determinations				± 0.0008

THE DETERMINATION OF DIBUTYLPHOSPHATE -- D.W. Brite

Experimental work was performed directed toward the determination of dibutylphosphate (DBP) in uranyl nitrate solutions saturated with tributylphosphate. Attempts were made to extract the uranyl-DBP complex into carbon tetrachloride and to correlate the uranium concentration of the resulting solution with the amount of DBP present initially. Portions of uranyl nitrate solution were contacted with two portions of carbon tetrachloride. The carbon tetrachloride was then concentrated by a factor of 10, and the uranium content determined fluorimetrically. Table I lists the results obtained for a typical set of experiments. It is evident that agreement is only qualitative and that uranium appears in the carbon tetrachloride phase only to approximately one-fifth the extent expected if DBP were extracted quantitatively as the uranyl complex.

A new approach to the problem has resulted in a satisfactory method for determining DBP concentrations in the range 0 - 20 mg/l. The method consists of measuring the disengaging time of the dispersion produced with carbon tetrachloride and the uranyl nitrate solution, to which has been added a fixed amount of solid zirconyl nitrate. The observation was made that the addition of zirconyl nitrate to a uranyl nitrate solution containing DBP, followed by violent mixing, resulted in a large amount of foam at the surface of the solution. The height of foam appeared to be proportional to the amount of DBP present. Upon contacting the solution with CCl_4 and mixing phases, a dispersion occurred, the stability of which was a function of the amount of DBP present. Since the stability of the dispersions decreased with the age of the solution and with the age of the $\text{ZrO}(\text{NO}_3)_2$ solution stock, it is necessary to use fresh zirconyl solutions. The use of solid $\text{ZrO}(\text{NO}_3)_2$ and the performance of the dispersion test within a fixed, short interval after the addition of the $\text{ZrO}(\text{NO}_3)_2$ was found to be preferable. It was concluded that the complex formed with zirconyl ion and DBP occurred only with freshly prepared zirconyl solutions, due to some phenomenon such as polymerization, dimerization, etc.

A standard method of dispersing phases and measuring phase disengaging times was adopted. Phase volumes of 8 ml. CCl_4 and 11 ml. aqueous were selected, measurements were performed in 25 ml. graduated cylinders matched in inside diameter, and dispersions were created by stirring at about 150 strokes per minute with a stainless steel rod having two circular stainless steel screens attached at one end. Since the moment at which the two phases are completely separated is indistinct, the time for the CCl_4 layer to settle to a certain distance from the eventual interface was observed. By this method, relative disengaging times could be reproduced to within 2 - 3 seconds for disengaging times of about 40 seconds.

A study of the effect of aging on the disengaging times of a uranyl nitrate solution containing zirconyl nitrate, and of a second uranyl nitrate solution containing the zirconyl dibutylphosphate complex was conducted. The solutions contained 20 g/l UNH, 31.6 g/l HNO_3 , and 13 g/l zirconyl nitrate. The effect of aging on disengaging times is shown in Figure 20. It is apparent that a high rate of change of disengaging time occurs initially, but that after a few minutes the disengaging time falls off more slowly. For this reason a standard procedure was adopted in which the solution was allowed to age ten minutes before determining disengaging time.

The concentration of zirconyl nitrate was found to be unimportant so long as an excess was present. Table II shows the variation in disengaging time caused by a large variation in zirconyl nitrate concentration. A concentration of 13 g/l was chosen as

a standard for subsequent measurements. This value corresponded to the addition of a level-filled, size 1, Coors porcelain spatula of solid zirconyl nitrate to 10 ml. of a sample.

The variation of disengaging time with DBP concentration is shown in Figure 21. Standard conditions were as follows: 20 g/l UNH, 31.6 g/l HNO_3 , 13 g/l $\text{ZrO}(\text{NO}_3)_2$, aqueous phase volume of 11 ml., CCl_4 phase volume of 8 ml., 8-minute aging time before dispersing phases, 2 minutes stirring at 140 strokes per minute, and the time for the CCl_4 phase to settle to the 9 ml. mark observed as disengaging time. A sensitivity of 4 - 5 seconds per mg/l DBP is obtained.

It was noted that a uranyl nitrate solution saturated with TBP when freshly prepared gave the same disengaging time as one containing no TBP when identical amounts of DBP were added to portions of each. Both solutions gave identical "blank" disengaging times, also. However, upon aging, the TBP saturated solution gave longer and longer disengaging times, even when no DBP was added. This observation may be attributed to the buildup of DBP in the solution from the hydrolysis of TBP to DBP and butyl alcohol. Comparisons of the disengaging times of a TBP saturated uranyl nitrate solution and uranyl nitrate solutions spiked with known amounts of DBP, for an aging time up to 25 days, are shown in Table III. The disengaging times were converted to DBP concentration by calibration curves prepared from the uranyl nitrate solution containing no TBP. The non-linearity of the DBP buildup is probably due to the changing rate of photochemical decomposition of the TBP, caused by changes in the light intensity to which the solution was exposed over a period of days. Previous work has shown that TBP in the presence of UNH may be decomposed by diffuse artificial light to the extent of 25% in a period of ten days (1). As a result, the effect shown in Table III probably does not represent a true picture of the hydrolysis rate of TBP in UNH solutions.

The effect of changes in nitric acid concentration of the solution on disengaging time was studied. Table IV lists the disengaging times obtained for solutions containing 20 g/l UNH, 5 mg/l DBP, and 13 g/l $\text{ZrO}(\text{NO}_3)_2$, and varying amounts of nitric acid. It is apparent that nitric acid concentration must be controlled to within 5 - 10 g/l if results consistent to 1 mg/l DBP are to be obtained.

The effect of variations in uranium concentration was studied. As may be seen from Table V, no significant differences in disengaging time occurs over the range 0 - 20 g/l UNH.

The interference effects of a number of other materials were investigated. The results are tabulated in Table VI. The comparison value indicated is for a solution containing the same amount of DBP but no interfering materials. Monobutylphosphate (MBP) and phosphoric acid appear to be the only materials tested which interfere seriously. Both may be present individually up to about 5 times the amount of DBP present without causing interference. These interferences serve to limit the applicability of the method, since both MBP and phosphoric acid are hydrolysis products of DBP.

The method has been used to determine DBP concentrations in several process solutions. As might be suspected, DBP concentrations of less than 1 mg/l result when an RCU sample from the TBP process is analyzed immediately after sampling. Two RCU solutions analyzed 17 days after sampling, however, showed results of 15.1 and 16.9 mg/l DBP. Two RCU solutions found to cause light foaming and heavy foaming, respectively, when calcined in the UO_3 plant, were found to contain 50 and 390 mg/l DBP, respectively,

by the above method. DBP determinations are currently being made on a special basis by this method in the 222-S analytical laboratory.

TABLE I

EXTRACTION OF URANYL-DIBUTYLPHOSPHATE COMPLEX BY CCl₄

Aqueous phase - 42.2 g/l UNH, 16 g/l HNO₃

<u>mg/l DBP Added</u>	<u>mg/l U, CCl₄</u>	<u>mg/l U, CCl₄ calculated</u>
0	2.4	--
10	12	57
20	20	113
30	46	170
40	51	226

TABLE II

VARIATION OF DISENGAGING TIME WITH VARIATIONS
IN ZIRCONYL NITRATE CONCENTRATION

10 mg/l DBP, 20 g/l UNH, 31.6 g/l HNO₃

<u>Zirconyl Nitrate Conc., g/l</u>	<u>Disengaging Time, Sec.</u>
6.5	55.3
13	53.0
26	52.4

TABLE III

VARIATION OF DISENGAGING TIME OF TBP
SATURATED UNH SOLUTION WITH AGE

20 g/l UNH, 31.6 g/l HNO₃

<u>Age, Days</u>	<u>Disengaging Time, Sec.</u>	<u>Apparent DBP Conc., mg/l</u>
0	24.5	0
8	40.3	6.9
18	47.0	8.6
21	52.3	13.7
25	52.2	20.4

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EFFECT OF DPB CONCENTRATION
ON DISENGAGING TIME

FIGURE 21

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TABLE IV

VARIATION OF DISENGAGING TIME WITH
VARIATIONS IN NITRIC ACID CONCENTRATION

<u>Conc. DBP</u> <u>mg/l</u>	<u>Conc. HNO₃</u> <u>g/l</u>	<u>Disengaging</u> <u>Time, Sec.</u>
0	31.6	25.5
5	21.6	46.4
5	26.6	44.0
5	31.6	38.5
5	36.6	36.5
5	41.6	33.6
5	51.6	31.3

TABLE V

VARIATION OF DISENGAGING TIME WITH VARIATIONS
IN URANYL NITRATE CONCENTRATION

5 mg/l DBP, 31.6 g/l HNO₃, 13 g/l ZrO(NO₃)₂

<u>g/l UNH</u>	<u>Disengaging</u> <u>Time, Sec.</u>
20	38.3
15	39.7
10	42.5
5	40.0
0	39.8

TABLE VI

VARIATION OF DISENGAGING TIME WITH THE ADDITION
OF VARIOUS EXTRANEEOUS COMPONENTS

20 g/l UNH, 31.6 g/l HNO₃, 10 mg/l DBP

<u>Component</u> <u>Added</u>	<u>Conc., mg/l</u>	<u>Disengaging</u> <u>Time, Sec.</u>	<u>Comparison</u> <u>Value, Sec.</u>
MBP	40	37.3	39.3
"	60	45.6	"
"	80	43.8	"
"	100	55.8	"
"	200	92.6	"
"	1000	30 min.	49.8
H ₃ PO ₄	15	53.7	50.4
"	30	51.0	"
"	40	45.6	42.2
"	100	62.5	"
"	200	77.0	"
"	1000	5 min.	49.8

TABLE VI (CONT)

Component Added	Conc., mg/l	Disengaging Time, Sec.	Comparison Value, Sec.
BuOH	500	48.8	49.8
"	1000	30.0	"
Al ⁺ 3	500	42.5	"
"	1000	30.5	"
Fe ⁺ 3	100	49.8	"
"	200	37.8	"
Na ₂ SiO ₃	50	40.0	40.4
"	100	40.1	"
"	200	41.4	"
"	300	39.4	"

THE DETERMINATION OF CADMIUM IN LEAD -- D.W. Brite

A method for determining cadmium in lead at the 10% and 3% levels has been developed using a Beckman #9200 flame photometer equipped with a photomultiplier attachment. Table VII shows the relative emissions resulting for solutions containing 10 g/l Pb and various amounts of Cd at the 1 g/l level. Both elements were present as the nitrates, with excess nitric acid present to the extent of 5 g/l. A sensitivity of 0.03 g/l Cd per 1% change in relative emission was obtained.

Table VIII shows the relative emissions obtained for Cd-Pb solutions at the 3% level, and includes a list of the Cd concentrations obtained from the calibration curve for five solutions containing 1.50 g/l Cd. The data show that Cd at the 1.50 g/l level may be determined to within ± 0.02 g/l in the presence of 48.5 g/l Pb.

A laboratory procedure based on this method is recommended for routine use.

TABLE VII

FLAME EMISSION OF 10% Cd-Pb SOLUTIONS AT 326.2 mu

0.15 mm. slit width, sensitivity counterclockwise,
H₂ pressure 3.5 psi, O₂ pressure 18 psi

<u>g/l Cd</u>	<u>g/l Pb</u>	<u>Relative Emission</u>	<u>Avg. Relative Emission</u>
0.7	10	60.4, 59.0	59.7
0.8	10	63.3, 62.9	63.1
0.9	10	66.4, 66.4	66.4
1.0	10	69.8, 69.8	69.8
1.1	10	74.0, 73.5	73.8
1.2	10	77.3, 76.3	76.8
1.3	10	80.0, 80.0	80.0
1.0	9	69.7, 69.4	69.6
1.0	10	70.7, 70.2	70.5
1.0	11	70.4, 70.3	70.4
0	10	32.2, 32.0	32.1
1.0	0	63.3, 62.8	63.1
0	0	22.8, 21.9	22.4

TABLE VIIIFLAME EMISSION OF 3% Cd-Pb SOLUTIONS AT 326.2 mμ

0.12 mm. slit width, sensitivity counterclockwise,
 H_2 pressure 3.5 psi, O_2 pressure 18 psi
 12.5 g/l HNO_3 present

<u>g/l Cd</u>	<u>g/l Pb</u>	<u>Relative Emission</u>	<u>Average Relative Emission</u>	<u>g/l Cd from Curve</u>
0	48.5	39.7, 39.7	39.7	--
1.00	"	67.7, 67.2	67.5	--
1.20	"	72.1, 72.2	72.2	--
1.40	"	77.0, 76.3	76.7	--
1.60	"	81.9, 81.8	81.9	--
1.80	"	85.9, 85.9	85.9	--
2.00	"	90.0, 90.0	90.0	--
1.50	"	79.1, 79.0	79.1	1.49
1.50	"	79.7, 79.0	79.4	1.50
1.50	"	79.2, 78.9	79.1	1.49
1.50	"	79.6, 79.3	79.5	1.51
1.50	"	79.1, 79.4	79.3	1.50

THE DETERMINATION OF CALCIUM IN TBP PROCESS STREAMS -- D.W. Brite

A flame photometric method was found for determining calcium in TBP process streams in spite of serious interferences by TBP, sodium, uranium, iron, sulfate, phosphate and sulfamate. The precision attainable varied from sample to sample, depending upon its composition. In general, errors of about 20% occurred, although occasionally they were as great as 50%. The smallest determinable amount of calcium was 5 - 10 mg/l.

The method involves the use of calcium as its own internal standard. Increasing amounts of calcium are added to aliquots of the sample, which is often as high as 6 M in sodium. The flame emission of calcium is measured at the 422.4 mμ emission line, using a Beckman #9200 flame photometer with photomultiplier attachment. The sodium contribution to the measurement is determined by displacing the wavelength setting a few millimicrons and measuring the emission again. The net calcium emission is obtained by difference and plotted against the amount of calcium added to the aliquot. The resulting curve, when extrapolated to zero calcium emission, gives the calcium content of the aliquot to which no additional calcium was added. All suppression and enhancement interferences are thus corrected for inherently. A detailed description of the method, along with all significant data, has been reported previously (2).

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DETERMINATION OF SMALL CONCENTRATIONS OF PERMANGANATE IN SOLUTIONS CONTAINING DICHROMATE -- M.C. Lambert

Following head-end treatment of certain Hot Semi-Works streams, the permanganate concentration (originally 0.05 M) should be zero. Analyses are made occasionally to determine if all the permanganate has been reduced. Since this may become a routine analysis, a method was developed which will separate manganese dioxide and dichromate interferences in one step and allow the rapid spectrophotometric determination of permanganate.

The considerable amount of suspended manganese dioxide must be removed from the solution prior to making an absorption measurement. Dichromate, present to the extent of 0.15 M, has an appreciable absorption at the two principal permanganate absorption bands and must also be separated from the solution when attempting to measure very small concentrations of permanganate. Most methods of separating Mn from Cr involve reduction and oxidation reactions. Such methods are not permissible in this case without first removing the original MnO_2 present, but then the analysis becomes somewhat tedious. Consequently, the proper conditions were determined for the non-reducing precipitation of chromate so that the MnO_2 and Cr can be removed simultaneously by centrifugation.

Lead and barium will both precipitate chromate from alkaline solution or from weakly acid acetate solutions. Lead reduces permanganate if the solution becomes the least bit alkaline, whereas barium precipitates $BaCO_3$ which is removed during the centrifugation. Therefore, it is safer to use barium. Ammonium ions also reduce permanganate and must not be used to neutralize the sample. However, sodium acetate and sodium hydroxide, if necessary, are satisfactory.

Barium chromate precipitates readily from sodium acetate buffered solutions between pH values of 5 and 7, forming an immediate and fairly dense precipitate at a pH of 6 or above. Since intense radioactivity limits the Hot Semi-Works sample to a very small aliquot which must be diluted considerably, it is an easy matter to obtain a satisfactory pH value without resorting to the use of indicator papers or a pH meter, even if the nitric acid content of the sample varies from 0.0 to 4.0 M.

The maximum sample volume permitted for safety is 25 μ l. This must be diluted to 2.0 ml., an 80-fold dilution, in order to fill a cell of 16 mm. outside diameter and 1.0 cm. path length, or a microcell of 5 cm. path length. If a solution containing 10 g. sodium acetate per 100 ml. is used as the diluent, pH values are obtained as follows:

pH vs. Sample Acidity
2.0 ml. diluent (10 g. $NaC_2H_3O_2$ /100 ml.)
added to 0.025 ml. sample

<u>HNO_3 Molarity of Sample</u>	<u>Final pH</u>
0.0	6.80
0.5	6.27
1.0	6.18
4.0	5.82

The procedure is simple and rapid, requiring ca. 30 min. for one analysis or 60 min. for four. A 25 ul. aliquot of the sample is placed in a centrifuge tube and the pipet rinsed with 25 ul. of the buffer solution. Exactly 2.00 ml. of the sodium acetate buffer are added (giving a dilution factor of 82), and about 5 mg. of solid $\text{Ba}(\text{NO}_3)_2$ are added. The solution is shaken, heated 5 min. in a hot water bath, centrifuged, cooled, and the absorbance of a portion of the supernate is measured at 525 and 545 mu.

Some reduction of permanganate will occur if ordinary distilled water is used. However, even very dilute permanganate solutions are stable, unless the glassware is greasy, if the buffer solution is prepared from distilled water that has been boiled with a little potassium periodate.

The range for the determination of permanganate in the sample before dilution is 0.001 to 0.05 M in a 1.0 cm. cell. The estimated precision (95% C.L.), based on the analyses of 17 synthetic samples containing KMnO_4 in the range 0.001 to 0.03 M, is $\pm 10\%$ or $\pm 10^{-4}$ M in the case of the most dilute samples.

X-RAY PHOTOMETRIC ANALYSIS OF HIGHLY RADIOACTIVE SOLUTIONS -- M.C. Lambert

For possible application to analysis of certain dissolver solutions or to direct in-line analysis of radioactive process streams, it has been of interest to find out if a steady source of gamma rays would interfere with the measurement of x-ray absorption in the General Electric X-Ray Photometer.

A 0.5 ml. sample of H-7 Redox dissolver solution held in a pipet gave a reading on a C.P. monitoring meter of 500 mr/hr. at ca. 6 inches (the distance between sample cell and fluorescent screen in the photometer). This corresponds approximately to 10 millicuries of gamma activity and will cause the zinc sulfide fluorescent screen to glow with sufficient brightness to be seen in a dark room. The fluorescence produced by gamma radiation of this magnitude is very weak compared to that produced by the x-ray beams, which have an intensity of the order of a thousand roentgens and are still of very much greater intensity after attenuation by the solutions. Furthermore, the steady light produced by gamma radiation is balanced out before the 30-cycle x-ray beams are turned on, and the instrument does not detect a steady signal. Thus, the only effect to be expected from a strongly radioactive solution would be an increase in background fluorescence which might cause a loss of sensitivity in balancing the light from the two x-ray beams. No change in sensitivity of measurement, i.e., movement of balance meter per unit change of attenuator thickness, was noted for a five-fold dilution (0.5 ml. sample + 2.0 ml. water) of the above dissolver solution. Nor did any noticeable change occur in the absorption reading over a period of one hour.

For the determination of uranium in the dissolver solutions it was necessary to make an 11-fold dilution to reduce the uranium concentration to about 48 g/l, since cells of path lengths shorter than 12 mm. were not available. A 0.5 ml. aliquot of H-7 was added to exactly 5.0 ml. of water in a 10 ml. Erlenmeyer flask and stirred magnetically. Approximately half of the diluted solution was transferred to the absorption cell, which gave a reading of 1.7 R/hr. when placed on top of the C.P. chamber and a reading of about 50 mr/hr. at 6 inches. Single determinations of twelve H-7 samples were made with the x-ray photometer, with an average total exposure to the analyst of 7.1 mr. per sample. The results averaged 0.8% lower than those obtained by the falling drop specific gravity method and the spread between duplicate samples taken from the same streams was 0.2% as compared to 0.7% by the falling drop method.

X-RAY PHOTOMETRIC ASSAY OF PLUTONIUM IN METAL SHAPES -- M.C. Lambert

Current precision for the x-ray photometric assay of plutonium in metal shapes is $\pm 0.33\%$ at the 95% confidence level. This is satisfactory, but because of the stringent specifications for the metal, further improvement would be desirable. It has been noted that very small shifts in the positions of the calibration curves (or of the intercept values in the equations) occur from time to time. This is probably due to minute changes in the optical alignment of the apertures, cell holder, or beam trimmer. Furthermore, the left-hand curve may shift more than the right-hand curve because of the non-uniform response of different areas of the fluorescent screen, so that the error may not be fully compensated by the criss cross technique (1). However, the slopes of the curves never change.

An attempt was made to improve precision by comparing the absorption of a sample to that of a standard solution. Since the slopes of the calibration curves are constant, shifts in the intercepts of the curves should affect measurements of samples and standard alike. The differences between absorption readings of standard and samples remain constant despite changes in the intercept and when divided by the slope, yield a value for the uranium concentration of the sample which is independent of the value of the intercept. This method may provide more accurate analyses and was given a month's trial by the laboratory in Bldg. 234-5. The precision obtained for the analysis of 36 samples, however, was $\pm 0.32\%$ for both the regular criss cross method and for the method of measuring differences between samples and standard; consequently, the latter method was discontinued.

In the criss cross technique, the sum of the left and right-hand measurements should equal twice the thickness of the aluminum block, which is always used as a tare in the right-hand beam. If it does not, it is an indication that one or both measurements may be inaccurate, or that the balance meter, the beam trimmer, or the cell holder may be out of position. The control laboratory personnel have been reminded that a careful check of these possibilities while the samples are still in the cell could eliminate many of the less satisfactory analyses and improve the precision.

The x-ray method has now been adopted as the official method of plutonium assay of the Fabrication Process metal shapes with recommendations for reruns and/or resamples whenever one of the following conditions is not met (2):

- a) A maximum analytical range between dissolutions of 0.48%.
- b) A minimum plutonium content of 98.5%.
- c) Summations of all elements to fall between 99.67% and 100.33%.

References

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THE DETERMINATION OF THE TIN CONTENT OF AL-SI -- F.A. Scott

A method of analysis using solution potential measurements has been established which is capable of estimating the tin content of a sample of Al-Si in the range 0 to 0.4% to within $\pm 0.01\%$. It has been demonstrated that a similar method can be established for Al-Si samples containing from 0.5 to 3.6% tin. Details of the procedure for the estimation of the tin content of a sample of Al-Si by the measurement of its solution potential has been described previously (1). The method was modified by the addition of 4 g/l of sodium nitrate to the etching bath. This permitted a more precise estimation of the tin in the range of 0.2%. Figure 22 is a plot of the tin content of Al-Si samples versus their solution potential in a bath 1 normal in sodium chloride and containing 4 g/l of sodium nitrate. The potential measurements on any single sample are reproducible to ± 10 millivolts. The estimate of tin content in the neighborhood of 0.2% is then reproducible to within $\pm 0.01\%$. The addition of sodium nitrate to the etching bath did not decrease the interference caused by lead.

By a reduction in sodium chloride concentration and an increase in sodium nitrate concentration in the etching bath, the slope and position of the potential versus tin concentration curve can be shifted to permit measurements in the range from 0.5 - 3.6% tin, as shown in Figure 23.

In the previous discussion, it has been indicated that the presence of tin markedly increases the solution potential of aluminum and Al-Si. There is then a possible need for the study of the effect of the tin introduced into the surface of the slug jacket during welding on the slug rupture rate. To indicate a need or lack of need for such a study, a review was made of the tin contents of the canning baths in which ruptured slugs were canned.

The date of canning of each rupture through 1952 was estimated as nearly as possible by John Little of the Applied Research Sub-Section. The records of tin analysis on the Al-Si canning and dip baths for the above days were examined for the following facts:

1. Maximum indicated tin content in the canning bath.
2. Minimum indicated tin content in the canning bath.
3. Maximum indicated tin content in the dip bath.
4. Minimum indicated tin content in the dip bath.
5. A complete change of metal in either canning or dip bath.

The above-mentioned figures were compared with similar figures for days in which no ruptured slugs were canned. None of the features were outstanding on the days in which the ruptured slugs were canned. This indicates that the present tin content of the canning baths is not a major factor contributing to slug rupture. It also tends to minimize the need for a study of the effect of tin on the corrosion of slug jackets.

0142-107A

0142-108

FIGURE 23
 SOLUTION POTENTIALS OF AISI IN
 0.1 N NaCl CONTAINING
 8 G/L NaNO₃

0142-109

THE IDENTIFICATION OF THE ANGULAR INCLUSIONS PRESENT IN HANFORD URANIUM -- F.A. ScottSummary

Hanford uranium contains minute angular inclusions which affect the microstructure, reactivity, and other important factors controlling the serviceability of the metal. The chemical nature of these inclusions is not known with certainty. This investigation is an attempt to obtain information concerning their chemical nature. Small quantities of the inclusions have been isolated by chemical means. The x-ray diffraction patterns and chemical analyses of the isolated materials have been determined. The most probable compounds present in the isolated materials are UO, UC, UN, C, and water. As yet no attempt has been made to establish the mechanism by which these compounds survive or arise during the isolation of the material from the matrix.

Experimental

Minute angular inclusions have been observed microscopically for some time in the uranium used at Hanford (2). Procedures for the preparation of metallographic samples used to count these inclusions have been established (3) and are in routine use (4, 5).

No investigation of the chemical nature of these inclusions has come to the author's attention. A.H. Compton (6) reports the separation and identification as UC of inclusions from uranium carbon alloys. He reports two separation methods which were successful. 1) The solution of the metal matrix in a hydrochloric acid-hydrogen peroxide mixture, followed by a gravity separation of the inclusions and any oxide formed. 2) The conversion of the metal to the hydride, followed by the removal of the inclusions with the aid of a sieve. It was reported that particles less than 37 microns in diameter were difficult to separate by the latter procedure.

In the course of this investigation, inclusions present in uranium have been separated from the matrix by the following procedures:

- (A) The displacement of the uranium with copper, using an ammonium chloride cupric acetate solution (7).
- (B) The electrolytic solution of the uranium, using a high current density and a citric acid electrolyte (5).
- (C) The solution of the uranium in an anhydrous solution of hydrogen chloride in methanol.
- (D) The solution of the uranium in a hydrochloric acid-hydrogen peroxide solution (8) (100 ml. distilled water, 20 ml. conc. hydrochloric acid, and 10 ml. 30% hydrogen peroxide).

By microscopic examination, the materials isolated by the above procedures were found to be between 50 and 70% opaque cubes, ranging in size from 1 - 10 microns on an edge and averaging between 3 and 4 microns on an edge. The remaining material was a mixture of other opaque angular particles and translucent irregularly shaped particles. The ratios of the various type particles and the per cent of the original uranium remaining depended upon the procedure used for the isolation, the purity of the original uranium, and the duration of the isolation treatment.

0142-110

Table I lists the methods used to isolate inclusions and the analyses of the material isolated by each procedure. The calculated nitrogen and carbon contents are obtained as the product of the analysis and per cent residue. They are smaller than the measured values. This indicates that during the isolation treatments some of the compounds of these elements are converted to gaseous or soluble forms. The carbon contents of residues isolated by procedures C-2 and E-2 are too high to permit all of the carbon to be present as any known uranium carbide. This high carbon content could arise from carbon present in the original uranium as elementary carbon, or from the decomposition of uranium carbide by water to form graphite and a complex mixture of hydrocarbons (8, 9, 10, 11). The hydrocarbons would be removed during the drying procedure by the ether wash, but the graphite should remain. The presence of graphite is not evident in the x-ray diffraction patterns of samples C-2 and E-2. The analysis of the sample isolated by the electrolytic procedure (C-2) indicates the presence of some element not analyzed for. A qualitative spectrographic analysis of the residue from an ignition of this material did not indicate the presence of any elements in quantity except uranium and calcium.

The x-ray diffraction patterns of the materials isolated by the various procedures are similar to each other and indicate the material has a face-centered cubic lattice with a lattice constant of $4.88 \text{ \AA}$. The lattice constants of the systems UO, UN, and UC are all within a few hundredth's of an Angstrom unit of the value. The material isolated by the electrolytic process exhibits, in addition to the previously mentioned face-centered cubic pattern, a weak, unidentified, diffraction pattern. The material isolated by copper displacement B-2 exhibits a weak diffraction pattern which may be attributed to UO_2 . The absence of lines of the diffraction patterns of compounds such as UC, UN_2 , U_3O_8 , etc., prohibit the presence of these compounds.

Table II lists computed chemical compositions for the isolated materials made by assuming the elements to be combined in the form of UN, UO, C, and H_2O . The oxygen contents listed in Table I were obtained by difference and therefore are the least reliable of the values at hand. In the computations for Table II, no use was made of these values. Except in the case of the sample isolated by electrolysis (C-2), the stoichiometric balance, as indicated by column 8, is within the error of the analysis. The failure to remove water by storage over P_2O_5 in the cases of the "dry" samples was unexpected and does not support the assumption that the hydrogen is present as water.

The infrared absorption spectra and the chemical properties of the isolated inclusions and samples of uranium carbide, nitride, and oxide of known composition will be investigated to more definitely establish the nature of the isolated material.

TABLE I

ANALYSES OF ISOLATED URANIUM INCLUSIONS

Isolation Method	Sample No.	% Residue	Analysis of Residue						Calc. % N in orig. U	Calc. % C in orig. U	Meas. % N in orig. U	Meas. % C in orig. U
			% U	% C	% N	% H	% O (by diff.)	% Other				
Cu displacement	B-2 wet*	0.5	80.3	6.23	0.62	0.30	10.9	1.66	0.003	0.03	0.0057	0.048
Cu displacement	B-2 dry**	0.5	80.9	6.30	0.63	0.29	10.2	1.66	0.003	0.03	0.0057	0.048
Electrolytic with citric acid elec- trolyte	C-2	--	21.6	36.1	1.42	2.32	38.6	--	--	--	--	--
HCl-H ₂ O ₂ Soln.	E-2 wet*	0.1	71.8	16.3	0.81	0.83	10.3	--	0.0008	0.016	0.0057	0.048
HCl-H ₂ O ₂ Soln.	E-2 dry**	0.1	77.6	14.4	0.80	0.68	6.5	--	0.008	0.014	0.0057	0.048
HCl-Methanol Soln. D-1		--	88.4	2.8	0.94	--	--	--	--	--	0.0057	0.048

*Dried by alcohol ether wash.

**Dried by alcohol ether wash followed by storage in vacuum over P₂O₅ for 5 days.

TABLE II

CALCULATED COMPOSITION OF ISOLATED URANIUM INCLUSIONS

<u>Isolation Method</u>	<u>Sample No.</u>	<u>% UN</u>	<u>% UO</u>	<u>% UC</u>	<u>% H₂O</u>	<u>% Cu</u>	<u>Total</u>
Cu displacement	B-2 wet*	11.3	74.3	6.2	2.7	1.66	96.1
Cu displacement	B-2 dry**	11.3	75.0	6.3	2.6	1.66	96.9
Electrolytic citric acid electrolyte	C-2	22.9	0	36.13	21.81	--	80.40
HCl-Methanol Soln.	D-1	16.9	77.3	2.8	--	--	--
HCl-H ₂ O ₂ Soln.	E-2 wet*	14.6	61.9	16.3	7.6	--	100.3
HCl-H ₂ O ₂ Soln.	E-2 dry**	14.4	68.8	14.3	6.2	--	103.7

*Dried by alcohol ether wash.

**Dried by alcohol ether wash followed by storage in vacuum over P₂O₅ for 5 days.

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0142-114

DETERMINATION OF CALCIUM IN TBP FEED SOLUTION -- H.H. Van Tuyl

The new specifications for calcium and sodium in uranic oxide require an improvement in the product with respect to calcium purity. To determine the source of calcium in the final product, calcium analysis of the feed solution was requested. Since both sodium and uranium are present in approximately equal amounts in the feed solution, the separation of the major constituents from the impurity elements does not appear possible with existing methods. The only spectrographic method available for this problem was the direct copper spark method, wherein the sample is converted to the chloride, evaporated on copper electrodes, and sparked directly. This method was selected for the determination of calcium, even though large amounts of total solids would be present on the electrodes.

Direct copper spark analyses were made with from 1 to 100 ul. of feed solution, corresponding to 0.06 to 6 mg. of uranium. The samples were compared with standards containing equal amounts of uranium and sodium. Analyses with the different sample sizes, both with and without spikes, all indicated that the calcium concentration was about 2000 ppm. These analyses demonstrate that the copper spark method may be used with up to 10 mg. of total solids per electrode pair if the standards and samples are in the same matrix.

ANALYSIS OF PROCESS TUBE FILM -- H.H. Van Tuyl

Corrosion of process tubes and slugs has increased alarmingly with increased power levels in the piles. In an attempt to determine the cause of this corrosion, the Process Unit scraped the film from process tubes and submitted the film for spectrographic analysis.

Since no facilities were available for arc excitation of beta radioactive samples, only spark spectrographic analyses were used. When the samples were reacted with hydrochloric acid, metallic aluminum chips or shavings were observed in each of the samples. A small part of each sample was insoluble in hydrochloric acid.

Portions of the samples were evaporated on silver electrodes for the determination of aluminum, iron, and copper. Other portions were evaporated on copper electrodes for the determination of other elements. Since no sample weights were available, the results were based on the aluminum content as determined spectrographically. All results are believed to be within a factor of five of the true values.

Table I lists the analyses of films from the 105-DR Pile, which uses dichromate-ferroflocc treated water. The samples were all taken from the same process tube and are listed in order from front to rear face. Table II lists the analyses of films from 105-F Pile, which uses alum treated water. The samples were not taken from the same process tube, but they are listed in order from front to rear face. Table III lists the elements which were not detected in film from either pile, along with approximate sensitivity limits.

Chromium might come from the dummy slugs, copper from impeller blades, zinc from 72 S aluminum, and iron from water. The film from both piles is largely aluminum oxide in the front part of the tubes, but other elements increase in concentration toward the downstream end.

TABLE ICOMPOSITION OF PROCESS TUBE FILM, 105-DR PILE

<u>Element</u>	<u>Sample Number</u>				
	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>
Al	100	100	100	100	100
Ca	0.5	0.5	0.5	0.5	0.5
Cd	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
Cr	0.2	0.1	0.1	0.1	50
Cu	1	1	2	2	10
Fe	2	5	10	10	10
Ga	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
Mg	L 0.1	L 0.1	L 0.1	L 0.1	L 0.1
Mn	0.5	0.2	0.1	0.1	0.2
Ni	0.1	0.05	0.05	0.05	0.2
Pb	L 0.05	0.1	0.2	0.1	0.2
Sn	1	L 0.5	L 0.5	L 0.5	L 0.5
Sr	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01
Ti	2	0.5	0.2	0.1	0.1
Zn	0.5	0.5	1	20	50
Zr	L 0.1	L 0.1	L 0.1	L 0.1	L 0.1

L = less than.

TABLE IICOMPOSITION OF PROCESS TUBE FILM, 105-F PILE

<u>Element</u>	<u>Sample Number</u>							
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Al	100	100	100	100	100	100	100	100
B	0.02	0.005	L 0.005	L 0.005	L 0.005	L 0.005	0.005	0.01
Ca	0.2	0.5	0.05	L 0.02	L 0.02	0.2	1	1
Cd	0.02	L 0.02	L 0.02	L 0.02	L 0.02	0.1	0.1	0.2
Cr	2	0.2	0.1	0.1	0.2	5	10	10
Cu	5	5	5	1	2	5	10	10
Fe	10	10	20	5	2	10	20	20
Ga	0.02	0.01	0.01	0.01	0.01	0.02	0.05	0.05
Mg	1	0.2	0.2	0.5	1	0.5	0.5	0.5
Mn	0.05	0.05	0.05	0.1	0.05	0.05	0.1	0.1
Ni	0.02	0.02	0.02	0.05	0.02	0.05	0.1	0.05
Pb	0.5	0.05	0.02	0.05	L 0.02	0.5	0.2	0.1
Si	10	10	5	2	5	10	10	20
Sr	0.005	0.002	0.001	0.001	L 0.001	0.005	0.01	0.005
Ti	0.1	0.02	0.05	0.1	0.05	0.1	0.2	1
Zn	10	1	1	2	2	10	20	10
Zr	0.05	0.05	0.05	0.1	0.05	0.1	0.1	0.1

L = less than.

TABLE III

ELEMENTS NOT DETECTED IN FILM

<u>Element</u>	<u>Sensitivity</u>	<u>Element</u>	<u>Sensitivity</u>	<u>Element</u>	<u>Sensitivity</u>
Ag	0.01	In	0.02	Sb	0.2
As	0.2	K	0.2	Th	0.05
Au	0.02	La	0.01	Tl	0.02
Be	0.0001	Li	0.2	U	0.2
Bi	0.05	Mo	0.1	V	0.01
Cb	0.01	Na	0.1	W	0.05
Ce	0.05	Pd	0.01	Y	0.01
Co	0.05	Pt	0.05		

COMPARISON OF URANIC OXIDE ANALYSES -- H.H. Van Tuyl

Differences in spectrochemical analyses of uranic oxide by Hanford and K-25 have been observed in a number of cases. In an effort to determine the extent of these discrepancies and to determine which site was more accurate, K-25 obtained samples of uranic oxide from Harshaw, Mallinckrodt, and Purex purification processes and submitted identical aliquots of these samples to Hanford, KAPL, Mallinckrodt, and the K-25 control laboratories for detailed analyses. At Hanford these samples were analyzed by the carrier distillation method in the 234-5 and 3706 Bldg. laboratories and by the TBP extraction-copper spark method by Analytical Research. The results of these Hanford analyses are listed in Table I. The three Hanford methods appear to be in good agreement, except for calcium, sodium, and aluminum. The values reported by the other sites on these samples have been published (1, 2, 3).

TABLE I

COMPARISON OF HANFORD ANALYSES

<u>Element</u>	<u>Harshaw</u>			<u>Mallinckrodt</u>			<u>Purex</u>		
	<u>234-5</u>	<u>3706</u>	<u>TBP</u>	<u>234-5</u>	<u>3706</u>	<u>TBP</u>	<u>234-5</u>	<u>3706</u>	<u>TBP</u>
Al	L 1	5	2	5	20	2	20	20	20
Ca	50	L 50	40	100	L 50	10	100	L 50	20
Cr	5	L 5	4	2	L 5	2	20	5	10
Fe	20	40	20	L 10	L 10	4	100	25	100
Mg	5	2		2	1		5	5	
Mo	L 20	L 5	L 2	L 20	L 5	L 2	L 20	L 5	L 2
Na	L 10	50	20	L 5	20	L 20	50	200	100
Ni	L 5	10	2	L 5	L 5	L 0.4	50	20	20
Si	5	11		20	23		50	35	
P	L 200	L 20		L 200	L 20		L 200	50	

References

- (1) Rider, B.F. to Hurd, F.W., "Comparative UO_3 Analyses," GEH-20328, 12/11/52 (Secret).
- (2) Work, J.B. to Hurd, F.W., "Comparative UO_3 Analyses," HW-27363, 3/10/53 (Secret).
- (3) Hurd, F.W., "Comparative UO_3 Analyses," KLI-1845, 12/9/52 (Secret).

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