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LABORATORY RECORD
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1954

PROGRESS REPORT

AUGUST, 1952 THROUGH JANUARY, 1953

J. R. Flanary
H. J. Groh, Jr.
L. E. Line, Jr.
V. J. Reilly

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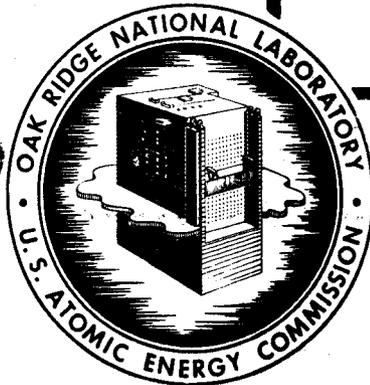
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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

PUREX PROCESS LABORATORY DEVELOPMENT PROGRESS REPORT,

AUGUST, 1952 THROUGH JANUARY, 1953

J. R. Flanary
H. J. Groh, Jr.
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V. J. Reilly

DATE ISSUED:

JUL 17 1953

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0.0 ABSTRACT

This report describes further laboratory development of the Purex process for the six-month period ending January 31, 1953. The results of comprehensive studies of solvent degradation and regeneration, continued investigation of final purification steps for the uranium product, and miscellaneous process experimental work are presented.

1.0 INTRODUCTION

For the past six months, a major portion of the Purex laboratory work has dealt with process problems which have materialized during the final phase of pilot-scale process evaluation and demonstration at ORNL. Repetitive operation of the ORNL Purex pilot plant with highly irradiated Hanford metal of minimum 60 days cooling has been accompanied by visible evidence of solvent deterioration, which has made the solvent reconditioning operation exceedingly troublesome. Through the combined efforts of the Chemical Development and the Pilot Plant Sections most of the solvent recovery problems have been resolved. However, the laboratory group has continued the study of solvent chemistry in order to gain more basic knowledge of solvent behavior in the Purex system, as understood here and at other sites.

Further study of the adsorption of radioactive zirconium and niobium on silica gel has resulted in significant improvement in decontamination and bed capacity. The prospect of continuous plant-scale operation of an "infinite capacity" silica gel bed for the tail-end treatment of uranium product appears quite promising.

Investigation of the effect of process variables (e.g., denitration, nature and extent of metallic impurities) on the reactivity of uranium trioxide, produced from Purex uranyl nitrate, during conversion of the oxide to uranium tetrafluoride has been started. Attention has been given to the foaming problem encountered during calcination of uranyl nitrate from TBP systems and to ferric sulfate solubility in acid evaporator residues.

Appreciation is expressed to G. R. Wilson and J. H. Edgerton for analytical work done by them during the course of this work.

2.0 SUMMARY

Solvent Studies. Sodium hydroxide was again demonstrated to be superior to sodium carbonate as a solvent decontaminating agent. Comparison of the decontamination obtained with 1 M and 0.1 M Na_2CO_3 showed no advantages of the more concentrated carbonate solution. Superior decontamination factors obtained in laboratory studies over those obtained in the pilot plant were attributed to the presence of entrained material in the solvent, which was allowed to settle out in the laboratory experiments before the decontamination was carried out. In the continuous process used in the pilot plant, the settling does not occur.

Studies on the emulsion that formed in solvent washed with water showed that the emulsion can be broken with as little as 10^{-3} M HNO_3 in the aqueous phase. The presence of a small amount of sodium carbonate in the aqueous phase also breaks the emulsion. The substance that causes the emulsion to form could not be removed by exhaustive washing with sodium hydroxide, sodium carbonate, or nitric acid. When the volume ratio favors the aqueous phase, emulsions form much more readily, and are much more stable than when an excess of organic is present.

The inorganic fraction of the interfacial sludge that accumulated in the pilot plant water wash column was found to be a mixture consisting principally of calcium, aluminum, silicon, and corrosion products.

Centrifugation of the second uranium cycle product stream was shown to be slightly effective in reducing the carryover of radioactive insoluble materials into the uranium product, but the small gain in decontamination is considered not to be worth the added operating cost.

Decontamination experiments with used Purex solvent have indicated that much of the iodine present is irreversibly fixed by the solvent. Further work using radioiodine has demonstrated that the diluent combines chemically with iodine under conditions existing in the process, whereas TBP does not. These experiments have demonstrated that the diluent has an appreciable capacity for reacting with iodine.

Uranium Product Tail-End Treatment. No positive conclusions were reached as to the cause of the variations in the adsorption efficiency of silica gel for zirconium and niobium from different batches of uranium product concentrate. However, the results of the experiments that were carried out indicated that the presence in the solution of orthophosphoric acid, DBP, or MBP does not cause the variable behavior of the silica gel.

A column of 60- to 80-mesh silica gel was shown to have four times the capacity for the uranium product solution as 20- to 40-mesh, and to give greater decontamination. Rough calculations indicate that advantage may be taken of the decay of the adsorbed zirconium and niobium on the bed in such a way that a fine-mesh silica gel column of practical size can be used with no regeneration of the silica gel being needed.

Foaming during Denitration. Further studies have indicated that, when uranyl nitrate product is dehydrated and denitrated at a rate comparable to that experienced in plant-size equipment, excessive foaming does not occur in the presence of as much as 400 parts of DBP per million of uranium. The presence of 50 to 200 parts of TBP per million of uranium causes uneven boiling but no foaming.

Solubility of Ferric Sulfate in Acid Evaporator Residues. The results of preliminary studies indicated that both nitric and sulfuric acids markedly depress the solubility of ferric sulfate.

3.0 SOLVENT STUDIES

V. J. Reilly and L. E. Line, Jr.

Increase of the activity level of the Purex pilot plant demonstration runs during operation with 600-Mwd Hanford metal cooled only 60 days has been paralleled by certain problems associated with solvent recovery. Contrary to experience in runs with longer cooled material, the first-cycle solvent effluent (ICW) in these runs has proved to be exceedingly difficult to decontaminate to an acceptable level. When irradiated uranium cooled only 60 days is processed, the problem of I^{131} pickup and retention by the solvent stream becomes especially acute.

The appearance of interfacial matter in the solvent recovery columns suggested the possibility that this condition is associated with the loss of decontamination efficiency. Aside from this, such column emulsions are operationally undesirable, and may conceivably affect the main line process performance.

Conclusions drawn from results of preliminary experiments on these problems are of a tentative nature, but they should provide a base for further investigation.

The solvent decontamination procedure used in the pilot plant at the time of these experiments consisted in washing the used solvent with one-fifth volume of 0.5 M Na_2CO_3 in a pulse column (S1 column for first-cycle solvent, S2 column for second-cycle solvent), followed by a one-fifth volume water wash in a spray tower.

3.1 Solvent Decontamination

Experiments on decontamination of first-cycle used solvent (ICW) from Purex pilot plant runs confirmed previous results⁽¹⁾ which had shown that 0.1 M $NaOH$ is superior to sodium carbonate as a solvent-decontaminating

agent by a factor of about 2 (see Table 3-1). The difference is not considered great enough, however, to warrant changing to caustic decontamination. Comparison of results with 0.1 M (1%) and 1 M (10%) Na_2CO_3 showed no or only slight superiority of the more concentrated carbonate (see Tables 3-1, 2, and 3). In view of this fact, there is probably no advantage in using the more concentrated carbonate solution in pilot plant decontamination. In laboratory studies on the ICW from HCP-7, beta decontamination factors of ~ 8 and gamma decontamination factors of ~ 10 were obtained with both 0.1 M and 1 M Na_2CO_3 . Similar results were obtained with HCP-16 ICW. In the pilot plant beta and gamma factors of 3, each, were obtained with 1 M Na_2CO_3 . The apparently higher factors obtained in the laboratory are probably due to the fact that, after being washed, the solvent was allowed to settle over the weekend, and when analyzed contained little or no entrained material (see Sec. 3.2). In the continuous solvent-recovery equipment in the pilot plant, there was essentially no holdup of washed solvent, and entrained particles had not settled out when the organic was analyzed. With ICW from runs HCP-14 and 16, the gamma decontamination and phase separation were slightly better with 1 M Na_2CO_3 than with 0.1 M.

In the experiments on the ICW from HCP-14, appreciable decontamination was still being obtained after 20 min contact between the solvent and the carbonate. Such a lag in the completion of the decontamination is not always observed. No explanation for this behavior is offered.

It should be noted that the irradiated uranium processed in runs HCP-14 and 16 had been cooled for only 60 days. That processed in the other runs mentioned had cooled for 90 to 120 days.

The equivalence of two 10-min washes to one 20-min wash with sodium carbonate is shown in Tables 3-2 and 3. Other experiments were carried out which showed the equivalence of three 10-min washes and one 30-min wash with carbonate.

Table 3-1

Laboratory Decontamination of First-Cycle Used Solvent
(from Pilot Plant Run HCP-7) with Sodium Hydroxide and
Sodium Carbonate

Samples of ICW were contacted with decontamination reagent indicated; at intervals shown, portions were removed and analyzed for beta and gamma activities

Initial beta activity: 15,500 c/m/ml

Initial gamma activity: 10.7 mv/ml^(a)

Sample No.	Decontaminating Reagent	Stirring Time (min)	Activity of Solvent after Treatment	
			Gross β (c/m/ml)	Gross γ ^(a) (mv/ml)
1	0.1 M NaOH	5	1,280	0.4
		10	1,180	
		33	890	
2	0.1 M Na ₂ CO ₃	5	2,170	1.05
		10	2,130	
		30	2,240	
3	1 M Na ₂ CO ₃	5	1,610	1.10
		10	2,110	
		35	2,100	

(a) Readings on ionization chamber in Building 3550.

Table 3-2

Laboratory Decontamination of First-Cycle Used Solvent
(from Pilot Plant Run HCP-14) with Sodium Carbonate

Samples of ICW contacted with reagents for times shown, and portions then analyzed, within 2 min of end of stirring, for gamma activity

Initial gamma activity: 57 mv/ml^(a)

Sample No.	Treatment	γ Activity ^(a) of Solvent (mv/ml)	
		After Wash with 0.1 M Na ₂ CO ₃	After Wash with 1 M Na ₂ CO ₃
1	20-min wash with carbonate	26	18
2	First 10-min wash with carbonate	42	36
	Second 10-min wash with carbonate	26	18
	Third 10-min wash with carbonate	20	11
2a	1-min water wash following third carbonate wash	8	6.5
2b	10-min wash with 0.1 M NaOH following third carbonate wash	5.2	---

(a) Readings on Building 3550 ionization chamber.

Table 3-3

Laboratory Decontamination of First-Cycle Used Solvent
(from Pilot Plant Run HCP-16^(a)) with Sodium Carbonate

Samples of ICW contacted with reagents for times shown, and portions then analyzed, within 2 min of end of stirring, for gamma activity

Initial gamma activity: 1200 mv/ml^(b)

Treatment	γ Activity ^(b) of Solvent (mv/ml)	
	After Wash with 0.1 M Na_2CO_3	After Wash with 1 M Na_2CO_3
First 10-min wash with carbonate	394	345
Second 10-min wash with carbonate	290	240
Third 10-min wash with carbonate	260	200
10-min wash with 0.1 M NaOH following third carbonate wash	180	150
1-min water wash following caustic wash	116	---

(a) In run HCP-16, 60-day-cooled material was processed.

(b) Readings on Building 3550 ionization chamber.

Washing the solvent with water and/or sodium hydroxide following the carbonate wash gives further decontamination (Tables 3-2 and 3). Since nitric acid is effective in removing entrained activity from the used solvent (see Sec. 3.3.2), its effect on the carbonate-treated solvent from HCP-16 was tried. The gamma activity increased from about 200 to 420 mv/ml when the solvent was washed with 0.1 M HNO_3 . This was undoubtedly due to the redissolving of activity which had plated out on the walls of the container. Centrifugation of the carbonate-washed solvent accomplished no additional decontamination. This is not in agreement with results of other recent runs, in which a large amount of activity was removed from the solvent by allowing it to settle (see Sec. 3.2).

Washing the HCP-16 ICW for 1 hr with 0.1 M Na_2S at 75°C reduced the gamma activity from 1200 to 53 mv/ml, which is comparable to results obtained with hot caustic. Washing with 0.1 M H_2O_2 -- 0.1 M NaOH at 75°C reduced the activity to 180 mv/ml. Further washing with water had no effect with either reagent. Neither of these reagents is recommended for process use.

Since the bulk of the residual activity was found to be iodine (see Sec. 3.1.1), repetitive washing with a mixture of 0.1 M Na_2CO_3 + 0.1 M KI was tried and found to be no more effective than carbonate alone. Treatment with 1% NaOCl was ineffective, while sodium methoxide was no better than sodium hydroxide.

3.1.1 Nature of Activity Remaining in Treated Solvent

Scintillation spectrometer analyses of solvent that had been washed with various reagents showed that only a small fraction of the activity remaining in the solvent is due to ruthenium, zirconium, and niobium (see Table 3-4). The bulk of the activity is due to iodine.

Decay measurements on the HCP-16 ICW and radiochemical analyses of the untreated solvent indicated that 60 to 75% of the gamma activity in the untreated solvent was iodine, which gives a combined ruthenium-

Table 3-4

Nature of Activity Remaining in Treated Solvent

Estimated by means of the scintillation spectrometer

Solvent Treatment	% of Gross γ ^(a)		Estimated ^(b) γ Activity (mv/ml)		
	Ru	Zr-Nb	Ru	Zr-Nb	I ^(c)
30-min sodium carbonate wash, followed by centrifugation	9	0	37	0	400
30-min sodium carbonate wash, followed by 10-min sodium sulfide wash at room temperature	10	3	12	4	104
60-min sodium sulfide wash at 75°C	10	3	5	1.5	44
60-min sodium hydroxide—hydrogen peroxide wash at 75°C	3	0	5	0	162

(a) The remainder of the activity is iodine.

(b) Scintillation spectrometer results converted to millivolts per milliliter for comparison with other results reported.

(c) Iodine γ activity taken by difference.

niobium-zirconium activity of about 400 mv/ml for this ICW. This is somewhat lower than the amount encountered in other recent solvent batches, which again bears out the difference between this batch and previous ones.

Results of caustic washing experiments show that a large part of the iodine in the ICW is chemically bound rather than dissolved molecular iodine. Organic iodine compounds could be formed in the solvent by direct iodination when the organic phase is contacted with the IAF or by addition of HI across double bonds. There is some evidence that direct addition could occur under Purex conditions (see Sec. 3.1.2).

Caustic washing of the organic at elevated temperature removed much of the iodine during the first time interval. A 100-ml sample of ICW from run HCP-16 was stirred with 75 ml of 0.1 M NaOH at 60-65°C; at intervals the mixture was allowed to settle for several minutes and 10-ml portions were removed and analyzed by scintillation spectrometer (see Table 3-5). The activity of the unwashed sample of ICW (zero time) was found to be almost 100% iodine, which is surprising. There was a sharp drop in the iodine beta activity of the solvent during the first 5 min of washing, followed by a very slow drop over the remainder of the hour. The sharp drop may be due to the removal of molecular iodine, while the slow decrease may be attributed to the sluggish hydrolysis of the organic iodine compounds at the elevated temperature.

3.1.2 Investigation of Possible Methods of Formation of Iodine Compounds

In order to elucidate the nature of the organic iodine compounds found in used solvent, as well as to determine possible methods of formation, several simpler solvents were treated with either iodine or hydriodic acid in nitric acid, then washed at room temperature with 0.1 M NaOH to remove dissolved reagents before analysis. I^{131} tracer was used to simplify the iodine determination. The total iodine concentration in the aqueous medium

Table 3-5
Iodine Removal from Pilot Plant ICW by Caustic Washing
at 60 to 65°C

Stirring Time (min)	Iodine $\beta^{(a)}$ (d/m/ml)	Gross $\gamma^{(b)}$ (mv/ml)
0	30.2×10^6	1360
5	3.86×10^6	128
10	2.85×10^6	100
30	2.28×10^6	74
60	1.67×10^6	58

(a) Activity in organic determined directly by scintillation spectrometer.

(b) Readings on Building 3550 ionization chamber.

was about 1 g/liter. In these experiments, molecular iodine was found to react extensively with commercial hexane; about 70% of the iodine present was taken up by the hexane in 1 hr at room temperature when the aqueous phase was 5 M in HNO_3 . Hexane that had been washed with concentrated sulfuric acid before being treated with iodine did not absorb an appreciable amount. Under the same conditions, commercial benzene (not washed with sulfuric acid) absorbed no iodine. Amsco 123-15 absorbed 40% of the iodine present; Amsco 125-90, 73%, and Amsco 190-10, 94%. After eight washes with concentrated sulfuric acid, Amsco 123-15 took up 20% of the iodine present, or about 0.2 g of iodine per liter of solvent. The iodine thus picked up is not removed by washing with 0.1 M caustic at 75°C. Therefore, the kerosene diluent appears directly responsible for the pickup of radioiodine in the Purex process.

The hydriodic acid did not react readily with any of the solvents that added molecular iodine rapidly under the same conditions. These results indicate that the iodine pickup by the Purex solvent might be minimized by judicious choice of solvent diluent or by providing conditions in the IAF for conversion of the iodine to some form other than molecular iodine.

3.2 Change in Activity of ICW with Time

Comparison of the beta and gamma activities of untreated ICW samples submitted by the pilot plant for analysis with those of corresponding samples submitted by the Chemical Development Section showed considerably higher values for the pilot plant samples (see Table 3-6). It is thought that these higher values are due to the presence of radioactive particulate matter, which slowly settles out when the solvent is allowed to stand.

Since the time lapse of about six weeks between the two sets of analyses is about one half-life in terms of the predominating kinds of activity (ruthenium, niobium, and zirconium), the differences in the pilot plant and laboratory sample analyses are much greater than can be

accounted for on the basis of decay. Measurements made of the gross gamma activity as a function of time with a sample of ICW from run HCP-15 immediately after it was obtained from the pilot plant (see Table 3-7) showed that over a 9-day period the loss in activity due to 8-day iodine is only a fraction of the total loss.

To determine whether the loss in activity on standing was due to plating out on the walls of the glass container, a 250-ml sample of this same solvent was allowed to stand for 11 days. The activity of the undisturbed sample (see Table 3-8) was considerably less than the activity after thorough mixing. As shown in Table 3-8, most of the original activity of this sample of ICW is associated with droplets and/or particulate matter which slowly settle out. Some of the activity was attracted to the glass but was not strongly held there, as shown by the activity recovered by rinsing the walls with fresh solvent, and by the small amount removed by the nitric acid.

Pilot plant solvent from runs HCP-6 through 14 also contained a large amount of activity which settled out on standing. However, neither treated nor untreated solvent from runs HCP-1 through 5 and from run HCP-16 showed the presence of activity-carrying foreign matter.

Table 3-6

Comparison of Beta and Gamma Activities of Laboratory
and Pilot Plant Samples

Run	β Activity (c/m/ml)		γ Activity ^(a) (mv/ml)	
	Laboratory	Pilot Plant	Laboratory	Pilot Plant
HCP-7	15,500	96,000	10.7	490
HCP-8A	20,400	123,000	27.8	1020
HCP-8B	19,500	80,000	30.0	2720

(a) As determined on Building 3550 ionization chamber.

Table 3-7

Decrease in Gross Gamma and Iodine Activity
of ICW (HCP-15) with Time

Time	Gross γ (mv/ml)	Iodine γ (mv/ml)
0	962	\sim 50
5 min	896	
10 min	853	
4 days	198	
9 days	148	25

Table 3-8

Adsorption of ICW (HCP-15) Activity on Walls of Container

Original ICW activity: about 960 mv/ml

Solution	Gross γ (mv/ml)
1. After standing for 11 days and before thorough mixing of contents	154
2. After thorough mixing	847
3. Rinse of walls with fresh TBP-Amsco mixture (calculated to ICW volume)	168
4. Rinse of walls with hot 8 M HNO_3 for 2 hr (calculated to ICW volume)	4
Total, items 2-4	<hr/> 1019

3.3 Phase Distribution of Activity in Treated Solvent

Several samples (100 to 250 ml) of solvent that had been treated with Na_2CO_3 in the pilot plant (S2P) were cloudy when received. When these were allowed to stand for several days, 1 to 2 ml of aqueous phase collected at the bottom, and streaks of white interfacial material formed. Results of experiments carried out on these samples indicated that much of the activity remaining in the S2P after the decontamination treatment is associated with this interfacial material (see Table 3-9).

Measurements were made of the gross beta activity of the organic phases and of the whole samples after thorough mixing. With two exceptions (S2P-1 and 7), the mixed samples showed an activity 5 to 10 times higher than that of the organic phase alone, and it was concluded that the activity did not follow the organic when the two phases separated. The volume of the separated aqueous phase was only about 1% of the volume of the organic, so that if the activity followed the aqueous, the aqueous activity would be 500 to 1000 times that of the organic. However, no decontamination factors this high have ever been obtained under the most favorable laboratory conditions, and it therefore appears that the activity must reside on the interfacial material.

3.3.1 Identification of Interfacial Sludge

A sample of the interfacial material was recovered by centrifuging the sludge and washing several times with hexane to remove solvent and with water to remove residual sodium carbonate. A preliminary scintillation spectrometer examination indicated the activity to be largely niobium. Spectrographic analysis showed calcium to be very strong; iron and chromium strong; silicon, manganese, and aluminum moderate; and only traces of uranium and sodium. The material appears to be essentially a mixture of calcium, aluminum, silicon, and corrosion products.

Table 3-9
Activities of Separated Organic Phase and Mixed Sample of
Sodium Carbonate-Treated Solvent

S2P Sample No.	Gross β Activity (c/m/ml)	
	Separated Organic Phase	Mixed Sample
1	3,390	3,770
2	3,830	37,400
3	3,690	19,400
4	4,240	20,400
5	2,550	27,100
6	10,200	128,000
7	5,070	13,200
8	3,660	18,900
9	2,760	15,800

3.3.2 Effect of Nitric Acid on Interfacial Activity

Nitric acid does not remove appreciable gamma activity from carbonate-treated solvent that has been allowed to settle prior to being washed with nitric acid. It was found to remove considerable activity from certain lots of solvent (i.e., from HCP-11) that had not been allowed to settle, but the decontamination of the mixed solvent with nitric acid was somewhat less than the decontamination obtained by settling alone (see Table 3-10). The experiments consisted in washing 25-ml portions of the carbonate-treated solvent (S2P) samples by shaking with equal volumes of 0.1 M HNO_3 and allowing to settle for 1 min. The gross gamma activities of the samples were compared with those of the untreated samples. Similar determinations were made, before and after nitric acid treatment, on solvent that had been allowed to settle for several days. [It has been noted elsewhere (Sec. 3.1) in this report that neither a dilute acid wash nor centrifugation had any beneficial effect on carbonate-washed solvent from pilot plant run HCP-16.]

3.4 Formation and Discharge of Emulsions

3.4.1 Effect of Volume Ratios

It has been observed in the pilot plant that, when ICW is washed with sodium carbonate in a pulse column, the phases disengage easily; in the water-wash column, which follows the carbonate-wash column, an emulsion is formed. Brief exploratory laboratory work indicated that, when the volume ratio of aqueous to organic is greater than 1, there is, under certain conditions, a tendency to emulsify, which is absent when the volume ratio is in favor of the organic. These findings were consistent with the pilot plant observations; namely, the volume ratio favors the organic in the carbonate-wash column, where no emulsion is formed, but the water-wash column, where emulsification occurs, is operated with the aqueous phase continuous, so that the volume ratio of aqueous to organic is considerably higher than 1. However, further

Table 3-10

Effect of Nitric Acid on Interfacial Activity of
Carbonate-Treated Solvent from Run HCP-11

25-ml volumes of carbonate-treated solvent (S2P) thoroughly mixed and contacted with equal volumes of 0.1 M HNO₃; same samples allowed to settle several days and treated similarly; gamma activities of both mixed and settled solvent measured before and after nitric acid treatment

Sample No.	γ activity ^(a) (mv/ml)			
	Mixed Organic		Organic Settled Several Days	
	Before HNO ₃ Treatment	After HNO ₃ Treatment	Before HNO ₃ Treatment	After HNO ₃ Treatment
1	---	---	4.4	4.64
2	456	4	---	---
3	911	6.24	---	---
4	1181	43.3	4.48	2.96
5	389	8.09	2.88	3.12
6	771	11.2	6.00	3.2

(a) Readings on ionization chamber in Building 3550.

experiments have indicated that ICW and sodium carbonate solution mixed in any proportions separate readily. Also, ICW that has not been previously contacted with carbonate separates readily from a mixture with water in any proportions.

Other experiments showed that either ICW or IEW (used solvent from the second uranium cycle), after being contacted with alkaline solution, emulsifies readily when mixed with equal or greater volumes of either water, sodium hydroxide, or calcium hydroxide but does not readily form an emulsion with half its volume of these reagents. The emulsions, when formed in these experiments, did not separate completely for an hour or more. The similar behavior of ICW and IEW indicates that radiation damage is not a factor in the Purex process in the formation of the emulsifying agent, as the IEW has received only an infinitesimal radiation dose.

3.4.2 Presence of Nitric Acid

Experiments to determine the effect of nitric acid on phase separation indicated that the presence of nitric acid greatly shortens the time required for disengagement of the phases, but that the acid concentration is not critical (see Table 3-11).

In studying the effect of nitric acid, a 25-ml sample of solvent (S2P-1) that had been treated with 1 M Na_2CO_3 in the pilot plant was shaken with an equal volume of various reagents. The phases were allowed to separate and the disengagement time, i.e., the time between the end of stirring and the disengagement of the phases, was observed. The aqueous reagents used successively on the same sample of solvent were 0.1 M Na_2CO_3 and three separate portions of distilled water. By the end of this treatment, any nitric acid that might have remained in the solvent after the pilot plant treatment was presumably removed. A volume of 0.1 M HNO_3 was next added, followed by three separate portions of distilled water. Measurements of the nitric acid concentration of the solvent after each reagent had been withdrawn showed progressively

Table 3-11

Effect of Nitric Acid on Phase Separation

25 ml of solvent that had already been treated with 1 M Na₂CO₃ (S2P-1) stirred with 25 ml of each of aqueous reagents mentioned below, in order given; disengaging time of phases following each treatment noted

Aqueous Reagents Used	HNO ₃ Concentration ^(a) in Organic at Equilibrium (M)	Disengaging Time (sec)
0.1 M HNO ₃	---	62
Distilled water	---	73
Distilled water	---	150
Distilled water	---	150
Distilled water	---	150
0.1 M HNO ₃	0.083	39
Distilled water	0.014	44
Distilled water	0.0023	45
Distilled water	---	90
Distilled water	---	100
1 M HNO ₃	0.83	36
Distilled water	---	34
Distilled water	---	40

(a) Calculated, using D.C. (O/A) for HNO₃ of 0.2.

decreasing acidity. A volume of 1 M HNO_3 was then added, followed by two separate portions of distilled water. The disengagement time dropped sharply when nitric acid was added, and the time was not very different in the presence of 0.002 M HNO_3 from that in the presence of 0.8 M. The disengagement time was short as long as any appreciable nitric acid remained in the solvent.

Sodium carbonate was also found to break the emulsion once it had formed, but not at such low concentrations as in the case of nitric acid.

3.4.3 Removal of DBP and MBP from Uranium-Containing Solvent

Quantitative removal of DBP from fresh solvent by a single short 0.1 M Na_2CO_3 wash was demonstrated⁽³⁾ earlier, but removal of either DBP or MBP in the presence of uranium had not been demonstrated.

In the following experiments the uranium method⁽²⁾ for determining small amounts of DBP in an organic phase was used. This procedure utilizes the complexing action of DBP for uranium, in stoichiometric amounts, with direct analysis of the organic phase for uranium to indicate the quantity of DBP present. It is believed to be reliable with as little as 0.001% DBP in the organic.

In order to determine whether DBP would be quantitatively removed by a sodium carbonate wash, pure DBP was added to a level of about 800 ppm to 30% TBP—Amsco that contained only 1 ppm of DBP originally; the solution was then equilibrated with 0.002 M $\text{UO}_2(\text{NO}_3)_2$ solution. The organic containing the DBP and its associated uranium was washed four times, 1 min for each wash, with equal volumes of 0.1 M Na_2CO_3 . The aqueous washes and final organic were analyzed for DBP (by determining the uranium present), with the following results:

First carbonate wash	800 ppm DBP removed
Second aqueous wash	5.7 ppm DBP removed
Third aqueous wash	1.0 ppm DBP removed
Fourth aqueous wash	Below limit of detection
Organic after fourth wash	Below limit of detection

Therefore, within the limits of accuracy of the analytical method, about 99% or more of the uranium was removed by the first carbonate wash.

Another experiment confirmed this result. After the organic (containing 800 ppm of DBP with its associated uranium) had been washed for 1 min with 0.1 M Na_2CO_3 and then with water, the organic was re-equilibrated with the dilute uranium test solution. It was found then to contain uranium equivalent to 2 ppm of DBP, while a blank of fresh solvent contained 1 ppm. Thus a DBP decontamination factor of 400 to 800 was achieved in this single carbonate wash.

Several experiments were carried out with MBP. In rather small amounts (about 30 ppm of MBP in the organic phase), quite a heavy precipitate formed at the interface with 0.002 M uranyl nitrate. After the solvent was contacted with 0.1 M Na_2CO_3 , the precipitate was readily discharged, and the uranium dissolved in the aqueous phase. Analysis of the organic phase showed essentially no uranium, indicating the absence of uranium-complexed MBP. Uncomplexed MBP should be even more readily removed by an alkaline wash than is DBP.

Three samples of ICW from run HCP-16 were analyzed for DBP by measuring their uranium content. One was washed three times with water to remove TBP-complexed uranium and then equilibrated with 0.002 M uranium. The uranium analysis indicated 1 ppm of DBP, which is at the lower limit of detection of the method. The other two samples were washed three times with 0.002 M uranium (also to remove TBP-complexed uranium) and, upon analysis for uranium, were indicated to contain 6 ppm of DBP, roughly 5×10^{-4} % DBP by volume. This is lower than had been expected.

3.5 Activity Entrainment in Second-Uranium-Cycle Extractor

Emulsification in the second-uranium-cycle extractor might result in carryover of activity (associated with the emulsifying agent) by the solvent stream (DU), which could limit uranium decontamination. Since the amount of liquid entrained in the DU stream is small (about 0.3%, as indicated by iron determinations) and the aqueous phase at the last scrub stage is at roughly the same activity level as the organic product, any change in activity on filtering or centrifuging would be due to removal of solid or liquid retained in the organic from the neighborhood of the feed stage. Results of experiments carried out on second-cycle solutions indicated that some benefit would be gained in product decontamination by centrifuging the DU stream or the EU stream. However, the benefit is probably not worth the cost of the operation.

A sample of DU from run HCP-15 was centrifuged. The decrease in activity (see Table 3-12) may not appear significant when the fraction removed is considered, but the amount corresponds to roughly six times the gamma tolerance in the uranium. If most of this should go with the uranium and be converted to a form not removable by filtration or centrifugation, it would be a very important contributor to product gamma activity. In order to determine whether the activity removed from the DU by centrifugation would go with the uranium product or the organic waste if not removed, samples of the aqueous uranium product (EU), both flowing stream and concentrate, and of the organic waste (EW) were also centrifuged. The results (see Table 3-12) indicated that the amount of gamma activity separated by centrifuging the DU is about equally split between the EU and EW. A fairly good material balance was obtained. The amount of material removed from the EU concentrate by centrifuging was small.

The data do not confirm or disprove the hypothesis that filtration of the EU concentrate (which is done to some degree when a silica gel tail-end absorber is used) will be as effective as centrifuging the EU flowing stream.

Table 3-12
Reduction in Activity of Second-Uranium-Cycle Streams
by Centrifugation

Solutions centrifuged for 10 min in International
Clinical Centrifuge

Stream	γ Activities ^(a)			
	(mv/ml)		(mv/g U)	
	Uncentrifuged	Centrifuged	Uncentrifuged	Centrifuged
DU	6.05	4.8	67.2	53.3
EU, fs No. 1	1.32	0.96	22.0	16.0
No. 2	2.20	1.76	36.7	29.3
EU, conc.	7.02	6.5	17.6	16.2
EW No. 1	1.60	1.0	17.8	11.1
No. 2	1.32	0.92	---	---

(a) Readings on Building 3550 ionization chamber.

4.0 URANIUM PRODUCT TAIL-END TREATMENT

V. J. Reilly

Previous experience^(4,5) in the adsorption of zirconium and niobium from several pilot plant batches of EU concentrate has indicated the presence of more than one chemical form of zirconium and niobium, the different species exhibiting different affinities for the silica gel. The relative proportions of these forms have varied significantly from batch to batch, leading to erratic behavior in adsorption efficiency. Further work has been done in an effort to determine the nature of these species, the means of converting them to more readily adsorbed species, and the effect of particle size on adsorption capacity and efficiency.

4.1 Effect of Refluxing and of the Presence of Impurities on Zirconium and Niobium Adsorption by Silica Gel

The effects on the decontamination factors of refluxing the feed and of the presence of MBP, DBP, TBP, and orthophosphoric acid were studied in an attempt to gain an insight into the variations in adsorbability of zirconium and niobium found in previous runs. Control runs were made under identical conditions except for the treatment of the feed. Decontamination factors for both zirconium and niobium (see Table 4-1) in feed that was refluxed prior to being passed through the column were about half what they were in the control run. The addition of DBP and MBP, 200 parts per million parts of uranium, to the unknown amount already present appeared to reduce the decontamination factors somewhat, especially those for niobium. The addition of inorganic orthophosphate increased the decontamination slightly, but the amount was insignificant in comparison with the batch-to-batch variations. The removal of DBP by scrubbing six times with 5% TBP in Amsco and of TBP by scrubbing with Amsco had no effect on zirconium adsorption, but the niobium decontamination was about half that obtained in the control run. The reproducibility of these experiments is probably not better than $\pm 50\%$; some of the effects therefore may not be real.

Table 4-1

Effect of Feed Treatment on Zirconium and Niobium Decontamination by Silica Gel

Silica gel column: 20 cm high, 1 cm² in cross-sectional area;
 filled with 20- to 40-mesh Davison refrigeration-grade silica gel
 Temperature: room Solution flow rate: 1 ml/m/cm²

Run No. (a)	EU Concentrate	HNO ₃ (N)	Uranium (g/liter)	γ Activity ^(b) (c/m/ml)		Pretreatment	Effluent Vols. per Column Vol.	Instantaneous Decontamination Factors ^(c)			
				Zr	Nb			Zr		Nb	
								Control	Treated	Control	Treated
22(C) 24(T)	HCP-15	0.59	286	8,000	7,800	Feed refluxed for 3 days	15 70 140 260	18 13 8 5	9 7 4 3	47 25 13 6	30 12 7 6
25(C) 27(T)	HCP-17	0.65	345	8,300	5,000	Feed spiked with 200 parts each of DBP and MBP per million parts of U	15 70 140 165 260	5.5 4.8 4.3 2.7	5.3 3.4 3.0 3.1	17 13 10 5.5	20 6 3 5
30(C) 31(T)	HCP-19	0.83	470	23,000	21,000	Feed spiked with 200 parts of orthophosphate per million parts of U	15 70 140	3.4 2.8 3.0	5.2 3.6 4.0	4.5 4.2 4.3	7.5 5.4 5.2
30(C) 33(T)	HCP-19 ^(d)	0.83	470	19,000	28,000	Feed treated to remove DBP and TBP	15 70	3.4 2.8	3.3 2.3	4.5 4.2	2.6 2.1

- (a) C = Control run; T = Treated.
- (b) Determined by scintillation counting.
- (c) Activity of feed / activity of grab sample of effluent.
- (d) Run 33 was made on HCP-19 EU concentrate about four weeks after the control run 30 and the treated run 31. The differences in the initial zirconium and niobium activities are due to decay.

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One of the variables that was not held constant for these runs was the effective age of the solutions at the time of adsorption. For example, run 33 was processed through the adsorber four weeks after its control, run 30, and in that time about half the original niobium decayed and was replaced with new niobium from the decay of the zirconium. This fresh niobium would be expected to behave in a manner that is dependent only on the chemical composition of the solution and not on its previous history. The possibility had been considered that the low-acid conditions (i.e., $<1 \text{ M}$) in the slug dissolver or in the CU and EU evaporators were responsible for the formation of the less readily adsorbed species, but the poor decontamination obtained with the freshly formed niobium in this run make such an explanation unlikely to be correct.

The results of run 33 prove conclusively that DBP is not the material responsible for formation of nonadsorbable zirconium and niobium, since the decontamination was poor in this series in which DBP was not present in significant amounts. The only compound in the group TBP, DBP, MBP, and orthophosphoric acid not cleared by these experiments of responsibility for poor decontamination is monobutyl phosphoric acid.

Other chemicals which may be responsible for the poor decontamination, but which were not investigated in this series of experiments, are fluoride and oxalate, which are occasionally introduced into the pilot plant system as decontaminating agents. Oxalate is used in regeneration of the pilot plant silica gel column, and may be present as a result of back-mixing or poor washing. Both would be expected to interfere with adsorption, and therefore with decontamination, because of their value as eluting agents for the spent silica gel. In recent experiments⁽⁶⁾ on the resin-coupling process for plutonium, zirconium and niobium were not significantly adsorbed on Dowex-50 in runs HCP-16 through 19. Corollary experiments showed that 0.005 M or less HF in the ion-exchange resin feed would result in their passage through the column.

4.2 Effect of Particle Size of Silica Gel on Zirconium and Niobium Decontamination

The use of finer mesh silica gel was investigated, control runs being made with 20- to 40-mesh material. The decontamination with 60- to 80-mesh silica gel was significantly greater than that in the control runs (see Table 4-2). The capacity of the column appeared to be greater than 800 volumes of solution per column volume, but this may have been due in part to radioactive decay on the bed (see Sec. 4.4).

4.3 Pressure Drop Data

An important consideration in the use of fine-sized silica gel in the column is the increase in back pressure which occurs. The pressure drops through the columns used for runs 26 and 28 were measured with the solutions treated by the column, namely with a solution of uranium concentration, in two cases, of 345 g/liter and in a third, of 490 g/liter. The pressure drops shown in Table 4-3 include the head of the solution in the bed itself. The viscosities of these solutions at 25°C have been calculated from a formula given by Hanford⁽⁹⁾ as 2.19 and 3.2 centipoises for the 345- and 490-g/liter solutions, respectively. The ratio of the viscosities is thus 1.45. If the pressure drop obtained with the more concentrated solution is divided by 1.45, to make it comparable with that of the less concentrated solution, the resultant value, when plotted on a graph of pressure drop versus flow rate, will fall on a straight line through the two points plotted on the same graph for the less concentrated solution. Thus, pressure drops at other flow rates and at other concentrations may be estimated from the data presented. The pressure drops found are not prohibitively high for the use of such fine-sized silica gel.

4.4 Infinite-Capacity Silica Gel Column for Zirconium and Niobium Adsorption

The high capacity found with the fine-sized silica gel has raised the possibility that the column may be designed so that no regeneration is needed. This is achieved when the amounts of zirconium and niobium on

Table 4-2

Effect of Silica Gel Particle Size on Decontamination of Zirconium and Niobium

Silica gel column: 20 cm high, 1 cm² in cross-sectional area;
 filled with 20- to 40-mesh Davison refrigeration-grade silica gel
 Temperature: room

Run No.	EU Concentrate	HNO ₃ (N)	Uranium (g/liter)	γ Activity ^(b) (c/m/ml)		Column Height (cm)	Flow Rate (ml/m/cm ²)	Effluent Vols. per Column Vol.	Instantaneous Decontamination Factors ^(c)			
									Zr		Nb	
				Zr	Nb				20 to 40 mesh	60 to 80 mesh	20 to 40 mesh	60 to 80 mesh
22(C) 23(F)	HCP-15	0.59	286	8,000	7,800	20	1.0	15	18	21	47	61
								70	13	13	25	53
								140	8	16	13	47
								165	---	---	---	56
								260	5	15	6	55
								375	---	9	---	~40
								600	---	15	---	
25(C) 26(F)	HCP-17	0.65	345	8,300	5,000	23.5	1.1	15	5.5	7	17	15
								70	4.8	7	13	15
								140	4.3	---	10	---
								165	---	7	---	15
								260	2.7	---	5.5	---
								375	---	7	---	15
								600	---	7	---	15
800	---	7	---	15								
29(C) 28(F)	HCP-18	1.05	490	12,600	8,400	39.4	3.0	70	3.3	38	4	~150
								165	3	15	4	40
								375	---	4	---	25
								600	---	3.5	---	10
								800	---	3	---	10

(a) C = control runs, 20- to 40-mesh silica gel; F = fine-sized, 60- to 80-mesh silica gel.

(b) Determined by scintillation counting.

(c) Activity of feed / activity of grab sample of effluent.

Table 4-3

Pressure Drop through a Column of Fine-Mesh Silica Gel

Grain size: 60 to 80 mesh

Temperature: 25°C

Uranium Concentration of Solution (g/liter)	Flow Rate (ml/m/cm ²)	Pressure Drop (lb/in. ² /ft of column)
345	0.35	1.0
345	0.78	2.06
490	1.75	2.96

the column are such that their decay rates are equal to the rate of their addition in the feed. Rough calculations (see Sec. 9.0) have indicated that, with a capacity (excluding decay) of 600 volumes per column volume, a column 20 in. in diameter and 18 ft high will have infinite capacity for a feed of 3 metric tons of uranium per day.

The decontamination obtained in such a bed will depend on the relative amounts of zirconium and niobium in the feed. With a zirconium decontamination of 10, the effluent zirconium plus niobium activity will be roughly one-third the zirconium feed activity over a fairly wide range. Greater decontamination for niobium is possible with a somewhat larger column, but the niobium will grow back in to some extent on further decay of the zirconium. At transient equilibrium, there will be 2.3 times more niobium than zirconium activity. For more details, see Sec. 9.0.

5.0 FOAMING DURING DENITRATION

V. J. Reilly

In September, 1951, 2740 lb of uranium [as $\text{UO}_2(\text{NO}_3)_2$ solution] accumulated from early Purex pilot plant runs was shipped to Mallinckrodt (St. Louis) for large-scale conversion to uranium trioxide. Their preliminary buildown of the Purex uranium product solution ($\sim 1.9 \text{ M}$ uranium and 0.6 M HNO_3) to nearly 100% uranyl nitrate proceeded smoothly. However, with the inception of denitration, violent foaming occurred in the pot, resulting in the overflow of 340 lb of uranium before the heat could be reduced. Subsequent laboratory investigation⁽⁷⁾ at ORNL revealed that small quantities of DBP and TBP (the latter undergoing hydrolysis during evaporation and denitration) present in the uranium product solution were responsible for the foaming phenomenon.

By the installation of after-separators on the uranium strip columns, the ORNL pilot plant has reduced solvent entrainment to a minimum. Incidental to its primary purpose, the silica gel adsorption column effectively filters

out the solvent-containing sludge that appears in the uranium product (IEU) after evaporation to 1.9 M uranium. Subsequent large-scale denitrations of the pilot plant uranium product have indicated that these measures are sufficiently effective to reduce foaming to a manageable level.

Coincident with these developments, some laboratory effort was put forth to determine the DBP concentration that could be tolerated without excessive foaming. At KAPL,⁽¹⁰⁾ with extremely rapid evaporation rates and on a laboratory scale, serious foaming occurred with less than 50 parts of DBP or TBP per million of uranium, whereas prior ORNL experience with a flask denitrator at moderate evaporation rates indicated that significant foaming would not occur with less than 450 parts of DBP. It was planned to evaluate the effect of smaller amounts of DBP in this apparatus, which is believed to approach more closely the conditions prevailing in a full-scale denitrator.

The effect of TBP was studied with uranyl nitrate solutions to which were added 50, 100, and 200 parts of TBP per million of uranium immediately prior to evaporation (starting at about 700 g of uranium per liter, 0.4 to 0.9 N in HNO_3). The presence of TBP at all concentrations tested appeared to cause uneven boiling in the temperature range 110 to 115°C, which on two occasions caused liquid to spew over into the receiver. However, very little effect on foaming was noted. With 200 parts of TBP per million of uranium, there was not sufficient foam at 150 to 160°C to cover the surface; above this temperature the foam died down.

The effect of DBP was studied on uranyl nitrate solutions to which were added 200, 300, and 400 parts of DBP, as an aqueous solution, per million of uranium. At 400 parts and below, there was no significant amount of foam at 140 to 170°C (i.e., less foam than required to cover the surface), but there was more tendency for the solution to boil unevenly in the range 110 to 115°C than with pure uranyl nitrate solution. UO_3 from two different sources was used in the preparation of the uranyl nitrate solutions, and DBP from two different sources was used at 400 ppm.

The effect of aging the uranyl nitrate-DBP solution for 18 hr before evaporation was investigated, and solutions containing only 0.1 mole of HNO_3 per mole of uranium as well as neutral uranyl nitrate solutions were tried in addition to the normal HNO_3/U mole ratio of 0.5. None of these variations had any significant effect on the foaming. When 600 parts of DBP was added per million of uranium, considerably more trouble was experienced with uneven boiling in the range 110 to 115°C, and at 150 to 170°C, 0.75 to 1.0 in. of foam was present, covering the surface. In all these experiments, the evaporation rate was such as to go from 100% uranyl nitrate hexahydrate to the inception of denitration in about 50 min.

The large difference between the effect of DBP in the apparatus used here and that used at KAPL may be due entirely to the large difference in the rate of evaporation between the two tests. It appears that our conditions approach much more closely those occurring in plant-size equipment. A sample of uranyl nitrate solution taken from the Harshaw pot just prior to the final boildown in the recent test with Purex process material was denitrated in the laboratory apparatus. Less than 0.5 in. of foam, not completely covering the surface, was present at 160 to 170°C. In the plant denitrator, some foam was present at this stage, and the heating rate was reduced to about half for 1 hr until the foam subsided. On this basis, 0.75 to 1 in. of foam may represent an undesirable level in plant equipment.

6.0 REACTIVITY OF URANIUM TRIOXIDE

H. J. Groh, Jr.

The "reactivity test," developed by K-25 as part of an extensive program to investigate the reactions of uranium trioxide,⁽⁸⁾ has been reported to be a useful gauge of the reactivity of uranium trioxide, i.e., of the extent of its conversion to uranium tetrafluoride under conditions similar to those employed in the K-25 feed plant. Correlation between

the index of reactivity of a given oxide as obtained in this laboratory test and the plant behavior of the same oxide is reported as being excellent.

In view of the apparent dependence of the extent of conversion of UO_3 to UF_4 on such matters as the presence of small amounts of ionic impurities and the physical properties of the UO_3 , the laboratory reactivity test has been proposed as a suitable "use" test for recovered UO_3 . The apparatus for the test has been set up according to the recommendations of K-25, and work has been done to gain experience with the method as well as to simplify and standardize the procedure.

Conclusions drawn from results of work done at K-25 have suggested that the uranyl nitrate denitration procedure used in producing UO_3 affects the reactivity of the oxide. It is desirable, therefore, to have a standard laboratory denitration procedure, preferably one giving an oxide of the same reactivity as that produced by plant-scale denitration. For this purpose a laboratory-scale denitration reactor was fabricated.

6.1 Laboratory Reactivity Test

The apparatus used for the reduction and hydrofluorination of uranium trioxide consists of a furnace through which tank hydrogen and hydrogen fluoride gases can be passed over samples of oxide contained in a nickel boat. A 17-in. length of 1.5-in.-i.d. nickel pipe placed in an electric tube furnace serves as the reaction chamber. The pipe is closed at one end except for the gas inlet and a thermocouple well, and can be closed at the other end by a threaded nickel cap. The exit gases escape by a side takeoff at the threaded end and are passed through a soda lime trap before being discharged. The gas inlet is connected through a 0.020-in. leak orifice and needle valve to a manifold supplying tank hydrogen, nitrogen, and anhydrous hydrogen fluoride. The reaction vessel is a four-compartment nickel boat with overall dimensions 1 by 1/2 by 4-1/2 in. The four compartments are cut into the 4-1/2- by 1-in. face, and each of

these chambers is 2 by 5/16 and 1/4 in. deep. Each compartment is about half-filled by a 3-g sample of UO_3 . For the method of direct weighing of the samples before and after reaction, four detachable nickel boats were made. One of these could be placed in each compartment of the larger vessel. Each of these boats weighs about 5 g.

The orifice size (0.020 in.) and needle valve setting were adjusted to give flow rates of ~ 400 std cc/min of hydrogen fluoride and ~ 1600 std cc/min of H_2 . Through the course of the experiments, these flow rates were not found to vary significantly.

The procedure used in treating the samples (identical with that in use at K-25) was the following:

1. Into two of the compartments (diagonally opposite) of the boat, 3-g samples of the oxide in question are weighed. Into the other two compartments 3-g samples of standard oxide are weighed.* If the method of direct weighing is to be used, the samples are weighed accurately on an analytical balance.
2. The loaded boat is placed in the cold furnace, the hydrogen flow is started, and heating of the furnace is begun.
3. After 30 min the temperature of the furnace reaches $590^\circ C$, where it is maintained for 1.5 hr more.
4. After a total reduction time of 2 hr, the hydrogen flow is cut off and the HF flow is begun and continued steadily for 30 min at $590^\circ C$.
5. While the HF flow is continued, the system is cooled with an air jet on the outer side of the furnace. After 15 min of cooling, the temperature should drop to $\sim 125^\circ C$. A flow of nitrogen is then used to flush the HF from the system.

* At present Mallinckrodt UO_3 is being used at K-25 as a reference standard. Some of this oxide has been transferred to ORNL for use in the present work.

6. The samples are removed, pulverized, and analyzed for UF_4 , UO_2 , and UO_2F_2 . If analysis is to be done gravimetrically, each boat plus its contents is weighed before the sample is removed.

With the reduction and hydrofluorination reaction conditions described, the product will be a mixture of UF_4 , UO_2 , and UO_2F_2 . In the time provided, almost complete reduction of UO_3 to UO_2 will be accomplished, and the percentage of UO_2F_2 is thus small (1 to 5%). The UF_4/UO_2 ratio will vary widely, owing, presumably, to small amounts of impurities and differences in physical properties of the initial uranium trioxide sample.

In Table 6-1 are presented representative data obtained with several different oxides chosen to cover a wide range of reactivities. The reaction mixtures containing UO_2 , UF_4 , and UO_2F_2 were analyzed by standard procedures for (1) total uranium, (2) total fluorine, (3) U(IV), and (4) the portion insoluble in saturated ammonium oxalate solution, that is, UO_2 . The percentages given in the table were calculated from analyses 1, 2, and 3. The "ammonium oxalate--insoluble" analysis (4) was found to vary unaccountably and could not be regarded as quantitative. Modifications in the analytical procedure, especially longer digestion periods, will probably correct these variations. The percentages of UF_4 given in the "weight gain" column are those obtained by use of the relation

$$\% UF_4 = 714 - 8.09 (\% U \times w/W)$$

where $\% U$ = $\%$ of uranium in original UO_3 sample as obtained by analysis,
 w = weight of initial UO_3 sample, and
 W = weight of product.

This method assumes complete reduction of UO_3 to UO_2 and thereby introduces a small error proportional to the amount of UO_2F_2 .

The variation of the UF_4 in the Mallinckrodt (M) samples from 70 to 90% emphasizes the need for a control on each unknown sample. The reactivity ratio values for the samples agree qualitatively with the behavior of these oxides at K-25 (exact data are lacking). The HW sample was taken from an

Table 6-1

Laboratory Reactivity of Uranium Trioxide from Various Sources

Sample No. (a)	UO ₂ F ₂ (%)	UO ₂ (%)	UF ₄ (%)	UF ₄ by Wt. Gain Procedure (%)	Reactivity Ratio, R/r	
					Analytical	Wt. Gain
H-2	4.4	40	54.7	---	0.68	---
M-4	2.6	18	80	---		
H-3	4.9	43.2	52.2	---	0.70	---
M-9	1.6	23.8	74.6	---		
H-4	5.5	35.5	59.5	---	0.68	---
M-11	0.8	11.6	87.3	---		
HW-1	3.7	46.5	49.7	---	0.70	---
M-5	2.6	27	70.5	---		
HW-3	4.9	40.4	55.2	---	0.68	---
M-10	1.4	17.3	81.2	---		
HW-4	4.9	45.9	49.8	52.8	0.55	0.61
M-13	3.3	6.8	90.0	87		
HW-5	7.5	46.5	46.4	47.9	0.54	0.58
M-14	4.1	11.4	85.4	82.2		
HX-1	1.1	2.1	96.8	---	1.14	---
M-12	1.0	14.5	84.6	---		
HX-2	---	---	96.8	100	1.13	1.18
M-15	4.7	10.4	85.6	84.4		
HX-3	---	---	99.2	98	1.16	1.20
M-16	1.8	13.6	85.1	81.5		
P-1	0.6	17.9	81.6	81.8	0.96	0.98
M-17	1.4	14.0	84.9	83.8		
P-2	0	24.2	76.0	74.5	0.96	0.96
M-18	1.5	19.7	79.2	78		

(a) See text for meaning of prefixes on sample numbers.

(b) The reactivity ratio, R/r, is the % UF₄ in the unknown sample divided by the % UF₄ in the standard Mallinckrodt sample run adjacent to the unknown in the boat.

old Hanford product known to be of low reactivity; HX was a laboratory-hydrated UO_3 ; P was an oxide prepared by denitration of Purex process uranyl nitrate; H was an oxide of undetermined origin, probably containing impurities.

Comparison of the reactivity ratios obtained from analytical results with those obtained by the weight-gain procedure indicates that within the limit of applicability of the test the simpler weight-gain method should suffice. That is, the average precision in the reactivity ratio determinations is no better than 5%, while the average error introduced by the weight-gain method is about 7%. As expected, the lower the reactivity of an oxide, the greater is the difference between the reactivity ratio values obtained by the two methods. In general, it is recommended that the reactivity test be relied upon for no greater than 10% accuracy.

On a routine basis, the weight-gain method should reduce the processing time per sample from 8-10 hr to about 3-4 hr.

6.2 Denitration Equipment

A 100 ml capacity denitration pot has been constructed from type 347 stainless steel. This reactor is electrically heated (Glas-Col mantle) and is equipped with an anchor type stirrer operated at 100 rpm. This apparatus will be used to study the denitration reaction with particular regard to the reactivity of the oxide produced.

7.0 SOLUBILITY OF FERRIC SULFATE IN ACID EVAPORATOR RESIDUES

Ferric sulfate and sulfuric acid are formed in equimolar amounts by the decomposition of ferrous sulfamate during evaporation of the acid wastes from the Purex process for recovery of the nitric acid. Information on the solubility of ferric sulfate in the acid evaporator residues is of interest in the determination of the acid concentration factor that may be obtained during acid recovery without precipitation of any of the constituents of the solution. Results of preliminary experiments at

Table 7-1

Solubility of Ferric Sulfate in Nitric Acid--Sulfuric Acid Mixtures

Temp. (°C)	HNO ₃ (M)	H ₂ SO ₄ (M)	Ferric Sulfate Solubility (g of Fe per liter)
Room	6.18	0.37	23.3
	8.75	0.25	11.8
	10.97	0.13	6.8
100	10.91	0.37	6.5
105	9.19	0.50	17.2
	9.40	0.50	15.4
108	6.06	0.34	51.0
	6.09	0.31	59.1
	7.19	0.61	40.6
	7.19	0.37	49.7
	8.44	0.16	27.1
	8.48	0.12	28.1
	8.68	0.12	26.0
111	10.51	0.09	12.3
	10.55	0.04	12.0
	10.68	0.37	7.15
	10.91	0.37	7.08
112	11.05	0.0	10.8

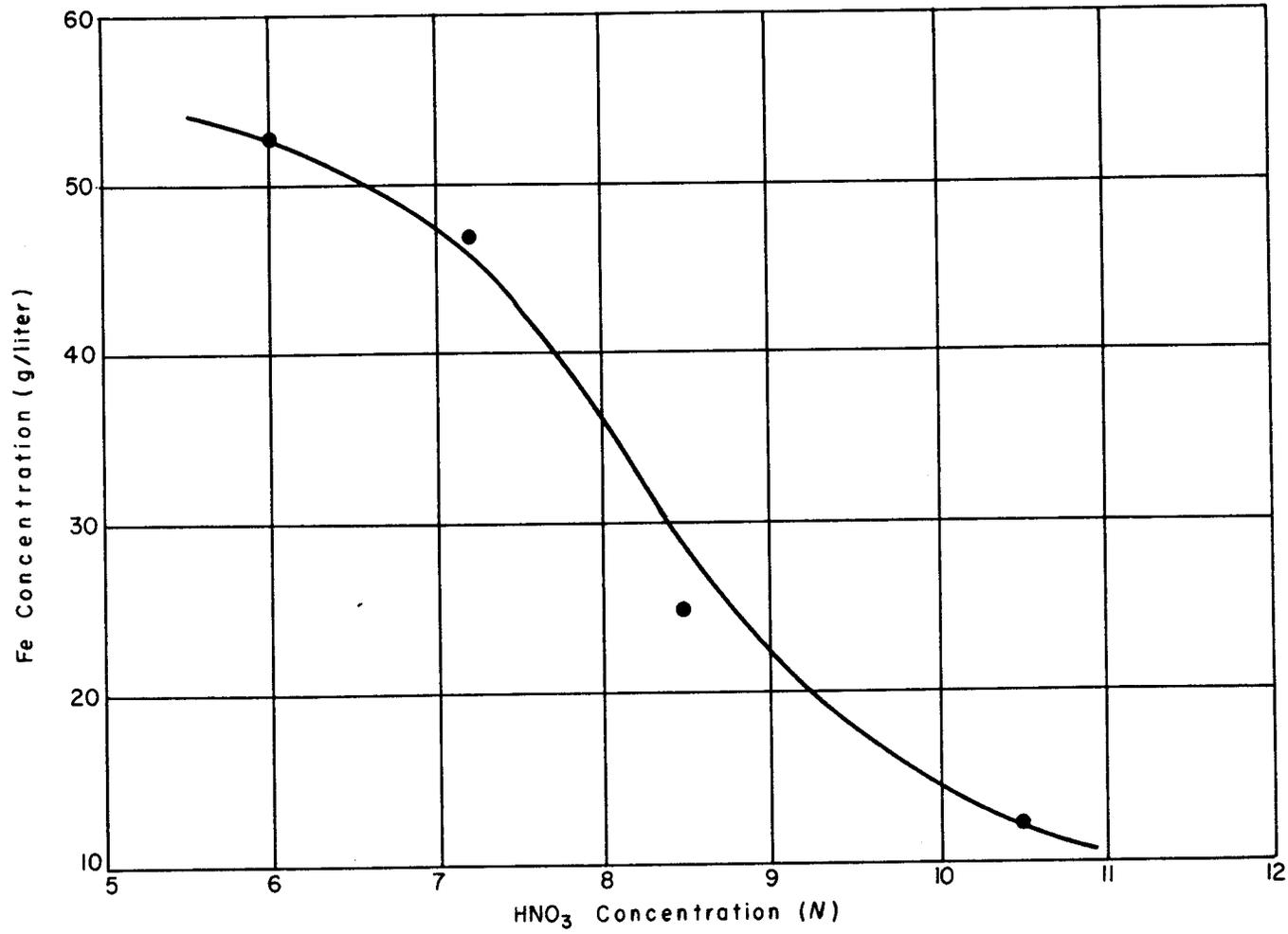


Fig. 7-1 SOLUBILITY OF $Fe_2(SO_4)_3$ IN HNO_3 AT THE BOILING POINT, IN PRESENCE OF H_2SO_4 FROM DECOMPOSITION OF $Fe(NH_2SO_3)_2$
(2 moles of Fe per mole of H_2SO_4)

various temperatures (see Table 7-1) indicate that both nitric acid and sulfuric acid have a strong depressing action on ferric sulfate solubility. The measured solubilities were used to estimate the amount of ferric sulfate that can just remain in solution, in the presence of equimolar amounts of sulfuric acid, in nitric acid at the boiling point (see Fig. 7-1).

The effect of sodium nitrate was not considered in these experiments, and the information therefore is of limited value at present. Sodium nitrate is also expected to exert a depressing effect on the ferric sulfate solubility.

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9.0 Appendix

CALCULATIONS ON A SILICA GEL BED SIZED TO OBLVIATE REGENERATION

The regeneration of the silica gel bed may be eliminated if the decay of zirconium and niobium on the bed is equal to the rate of their addition in the feed. If niobium is the principal contaminant, the calculation is fairly straightforward, leading to a moderately small bed because of its rather short half-life of 37 days.

If zirconium is present in roughly comparable amounts, however, the parent-daughter relationship must be considered. Since the holdup time of the activity on the bed must be fairly long to accomplish the objective desired, the niobium/zirconium ratio may be taken as that at transient equilibrium; specifically, 2.3 times as much niobium activity will be present as zirconium. This, of course, will not be the case if zirconium and niobium have different affinities for silica gel. Experimentally, it has been found that niobium is removed with a greater decontamination factor, so that if we use the transient equilibrium ratio, we will be on the safe side.

If we assume that 90% of the zirconium is adsorbed, with a capacity of 600 volumes of feed per bed volume in the absence of decay, we can consider the column has been "saturated" with zirconium without decay. Then, if decay is taken into consideration, removal of zirconium by decay will be equal to the zirconium feed rate less the small amount not adsorbed:

$$\text{Amount of Zr on column} = 0.9 \times Zr^0 \times 600 \times V,$$

where Zr^0 is the zirconium activity per unit volume in the feed, 0.9 is the fraction of zirconium activity retained by the column, and V is the column volume. Then,

$$\text{Rate of decay of Zr in column} = \lambda_{Zr} (0.9 \times Zr^0 \times 600 \times V),$$

where λ_{Zr} is the decay constant for zirconium. The rate of zirconium feed, at steady state, will have to be equal to this figure plus that leaving in the effluent. Thus,

$$R \times Zr^0 = \lambda_{Zr} (0.9 \times Zr^0 \times 600 \times V) + 0.1 R Zr^0,$$

and

$$V = \frac{R}{600 \lambda_{Zr}}$$

where R is the flow rate of both feed and effluent. For a bed handling 3 metric tons of uranium per day, R will be 7500 liters/day and $\lambda_{Zr} = 0.0107 \text{ day}^{-1}$; V is found to be 1170 liters. This volume will be contained in a 20-in.-diameter column, about 18 ft high. This column cross-section will provide a linear flow rate which is consistent with decontamination and capacity specifications used in these calculations.

With the assumptions made, the effluent of this bed will contain one-tenth the feed concentration of zirconium. If the niobium activity in the feed is about five times or less the zirconium activity, the niobium activity in the effluent will be 2.3 times the zirconium activity owing to the transient equilibrium. Present data indicate that the zirconium decontamination factor may not be increased much beyond 10, which means that additional column length beyond the value found in the preceding paragraph will be ineffective for removal of zirconium. However, additional removal of niobium is likely, giving less niobium than the transient equilibrium value. It is not very profitable to reduce the niobium activity much below the equilibrium value, though, as it will grow back in as the product ages. The overall niobium plus zirconium decontamination factor may be estimated as a function of the relative activities of the two species in the feed:

Activity ratio in feed, Zr/Nb	Overall D.F. (Nb + Zr)
∞	3
1	6
0.5	9
0.2	18