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**LABORATORY STUDIES OF THE PENTAETHER
PROCESS FOR THE RECOVERY AND
DECONTAMINATION OF URANIUM**

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February 16, 1951

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LABORATORY STUDIES OF THE PENTAETHER PROCESS
FOR THE RECOVERY AND DECONTAMINATION OF URANIUM

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February 16, 1951

ABSTRACT

The desirable properties of pentaether as a solvent in a process for uranium extraction from an experimental dissolver solution have been illustrated. These include: (a) excellent uranium recovery, (b) fission product decontamination to a level of 1.57 above the natural uranium background by the use of a 16-stage center-fed batch countercurrent mixer-settler, a 1-stage batch strip-extraction, and ruthenium distillation, (c) good decontamination from ionic cerium, barium and lanthanum, (d) excellent stability when in contact with 2M nitric acid and a high level of beta, gamma and alpha radiation.

As a disadvantage of the process, ruthenium must be eliminated in a separate step, either prior to or after any continuous uranium extraction process. The behavior of zirconium is still open to question since ionic zirconium proved to be extractable but zirconium present in solution was not.

The presence of two types of ruthenium species in a column product stream was shown. Distribution coefficients (organic phase concentration divided by aqueous phase concentration) of 6 and 0.1 were tentatively assigned to these two species.

Steady-state uranium and nitric acid equilibrium curves have been obtained for various possible flow patterns in countercurrent center-fed columns.

INTRODUCTION

The feasibility of the use of pentaether (dibutoxytetraethyleneglycol) as a solvent for the recovery and decontamination of uranium has been reported from this laboratory^{1,2,3} and the conclusions of the experimental work reported here have been anticipated in a report of recent origin by two of the above authors. Therefore, the work reported herein bears largely on the question of the recovery and decontamination of uranium using pentaether as the solvent extraction agent in a continuous flow system. Of prime importance is the question of purity of the pentaether and its stability; consequently, this was the first point of attack.

In order to work with _____ dissolver solution and to gain the maximum amount of information expeditiously, it was advantageous (and necessary) to work on a small laboratory scale using a countercurrent batch method for the simulation of continuous contacting equipment. It is believed that this method of attack, in conjunction with supporting laboratory studies of continuous contacting equipment, has yielded sufficient data to support the conclusions drawn in the recent evaluation report on the subject of this process.

PHYSICAL-CHEMICAL PROPERTIES OF PENTAETHER

Commercial pentaether was obtained from Carbon and Carbide Chemical Company as a light yellow-brown, viscous, high-boiling liquid which decomposes when heated at atmospheric pressure. It has a purity of about 80-90 percent, the main impurities being monobutoxytetraethyleneglycol and tetraethyleneglycol. It is thought to be produced as a by-product of the carbitols and cellosolves.

Even though previous investigation of the properties of pentaether has indicated that it is unstable when in contact with dilute solutions of aqueous nitric acid, it was thought this might be due to impurities rather than to the pentaether itself. Therefore commercial pentaether was purified using vacuum batch distillation. The center cut was completely water-white and had a boiling range of 192.4°C to 192.6°C (neglecting stem corrections) at 10 mm. total pressure. The low-boiling fraction had a slight yellow-brown color while the bottoms had a dark brown color which deepened progressively throughout the distillation.

An examination of the infra-red transmission spectra of commercial pentaether showed absorption bands indicating the presence of hydroxyl groups at 3480 cm^{-1} , keto groups at 1710 cm^{-1} , and acids, esters, and doubly bonded carbon atoms at about 1620 cm^{-1} . An ultra-violet absorption spectra showed an absorption peak which suggested an impurity such as a β -diketone. None of these absorption peaks were present in the center cuts from the distillation and their absence was used as a criteria of purity. Figure 1 shows representative percent-transmission curves for both commercial and purified pentaether.

In the presence of $16M\text{ HNO}_3$ distilled pentaether will decompose slowly with the formation of a slight yellow-brown color in about two hours, changing to blue-green over a period of three days. A slow gas evolution takes place during the decomposition and the presence of nitrous acid was confirmed by the sudden evolution of nitrogen upon the addition of sulfamic acid. In contact with $8M\text{ HNO}_3$, purified pentaether must decompose only very slowly at room temperature, since even after one year of standing over $8M\text{ HNO}_3$ it remains essentially water

FIG 1

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white, and no gas was observed during that time. There is an immediate and rapid reaction between 16M HNO_3 or 8M HNO_3 and commercial pentaether; the pentaether darkens and turns brown with evolution of gas.

Preliminary single batch experiments were performed using an experimental dissolver solution to test the stability of pentaether under intense radiation. 1.5 ml. of distilled pentaether was mixed with 1.5 ml. of

solution having a β - γ activity of 1.2×10^9 c/m/ml, an α -activity of 7×10^6 c/m/ml, and concentrations of 1.37M uranium and 0.23M HNO_3 . Under these conditions approximately half of the uranium present was extracted into the pentaether at equilibrium. After mixing for three minutes, the β - γ activity of the pentaether phase was found to reach 1.0×10^7 c/m/ml, which is 0.82 percent of the fission product activity in the feed. This activity level was not increased by further stirring for 90 minutes, or by standing 14 hours and again stirring for 30 minutes. It was therefore concluded that three minutes' mixing is sufficient to reach a stable equilibrium. Settling time after each mixing was observed to be 10-15 seconds. No color change was observed in the pentaether during the experiments described.

A similar experiment with commercial pentaether however, showed that it continued to extract β - γ activity until approximately ten percent was in the organic phase after twenty hours of contacting with intermittent stirring. Distilled pentaether which had been used in a countercurrent batch extraction of uranium from dissolver solution was stripped with water, 2M NaOH, 0.1M HNO_3 , and finally with water again. An infra-red transmission spectrogram was obtained on this pentaether and, except for the hydroxyl group absorption because of the water saturation, was identical with that of the initial distilled

pentaether. It thus appears that distilled pentaether is stable, within the limits of detection, with respect to decomposition in the presence of intense radiation.

There is no detectable difference in the extraction of uranium with either commercial or distilled pentaether.

BATCH COUNTERCURRENT OPERATIONS WITH "COLD" URANIUM AND NITRIC ACID

The purpose of the following experiments was to determine the true steady-state equilibrium distribution of uranyl nitrate and nitric acid under various operating conditions of countercurrent extraction columns. This information is necessary to determine efficiencies in equipment such as packed or pulsed columns where equilibrium conditions are not attained.

It has been shown⁵ that the operation of a continuous countercurrent column can be simulated by the appropriate movement of phases in a bank of individual batch extractors. A bank of eleven 60 ml. separatory funnels was used to give twenty-two (total) equilibrium stages in two columns according to the flow pattern shown in Figure 2.

Four runs were made with this separatory funnel column using varying stream compositions, flow rates and numbers of stages in each section. These conditions are summarized in Table I, and the stagewise steady-state uranium and nitric acid distributions, and the resulting phase volumes, distribution coefficients, and X-Y diagrams may be found in the Appendix.

FLOW PATTERN FOR BATCH EXTRACTION COLUMNS

FIG. 2

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Table I

Flow Conditions for Batch Column Runs

Run	1	2	3	4
Stream Compositions				
IF (H ₂ O)				
MU	2.00	2.18	2.18	2.18
MHNO ₃	0.46	-0.09*	-0.09*	-0.09*
IX (PE)				
MHNO ₃	1.97	2.50	1.92	1.55
IS (H ₂ O)	H ₂ O	H ₂ O	H ₂ O	H ₂ O
IIX (H ₂ O)	H ₂ O	H ₂ O	H ₂ O	H ₂ O
Stream Volumes (ml.)				
IF	10	10	10	10
IX	20	20	20	20
IS	5	5	5	5
IIX	17	17	18	18
Length of Sections (Stages)				
Extracting	7	9	9	11
Scrubbing	9	5	7	5
Re-extraction	6	8	6	6
Temperature at Final Mixing	21.5°C	20.0°C	18.8°C	30.0°C

*Acid Deficient

The distribution of uranyl nitrate into pentaether as a function of nitric acid concentration is shown in Figure 3, reproduced here from UCRL-649. It can be seen that at low concentrations of uranium and

Fig. 3

nitric acid (i.e., low salting strength) the distribution coefficient of uranium is very low. This condition imposes a requirement that the pentaether extractant be 1-2M in nitric acid in order to maintain high salting strength in the dilute uranium region of the extraction column. Figures 22 and 29 show that an increase in nitric acid from 1.92M to 2.50M in the extractant stream lowers the uranium loss by more than a factor of ten.

For the scrub, pure water is used since the high concentration of uranium in the scrub section is sufficient to maintain the salting strength. It is of interest to note that the uranium concentration remains practically constant throughout the scrub section, dropping only in the last stage or two where the water scrub dilutes it. This behavior is particularly advantageous since it means that any number of scrub stages may be added to the column (should fission product behavior require them) without affecting the loss from a given number of extracting stages. Figure 4 represents a typical X-Y diagram for an extraction column; the uranium behavior in the scrub section is explained by the appearance of a pinch point as the feed plate is approached through the scrub section. It may be noted that three of the runs were performed using acid-deficient uranium feed; these were of interest in view of the possibly improved separation with respect to fission products which might be obtained with active dissolver solution under these conditions.

In the re-extraction column, high salting strength is undesirable and nitric acid is not added. At present, it is felt that scrubbing will not be necessary in the re-extraction column since experiments to be described later show fission products other than ruthenium are

FIG. 4

MU 1369

not extracted with uranium in the extraction column.

The flow rates used in these experiments were chosen so as to permit minimum volumes of solutions, and, thus maximum uranium concentrations, consistent with the available distribution coefficients.

The distribution of uranium and nitric acid in an equilibrium counter-current contactor may be calculated from the data of Figure 3, by material balance calculations based first on an assumed uniform nitric acid concentration and then on a readjusted stagewise nitric acid concentration obtained from the approximate uranium concentrations just determined. The stagewise uranium concentrations as shown in Figure 22 have been calculated in this manner and agree with the actual values within experimental error. It is felt that the close check between experimental and calculated column behavior is sufficient to place reliance on further calculations without the necessity of experimental verification.

A series of batch equilibrium determinations were made as a function of temperature. 2.3M uranyl nitrate solutions containing 0.34M HNO_3 were equilibrated with pentaether in thermostatted baths; the resulting data are shown in Table II and Figure 5.

The final concentrations used in these experiments are approximately those which were obtained in the scrub section of the column; since the shift of E with temperature was small it is felt that operation of the columns should not be too sensitive to changes in temperature. Other work^{2,3} indicates that the temperature effect on E may be larger in the dilute region which will be found in the extracting section of the first column.

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FIG. 5

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Table II
Variation of Uranium Distribution with Temperature

Temperature, °C	Concentration; M		E_a^0
	Organic Phase	Aqueous Phase	
15.1	1.13	1.21	0.933
18.3	1.12	1.22	0.917
20.8	1.12	1.24	0.903
23.0	1.12	1.25	0.895
24.7	1.11	1.23	0.902
28.8	1.11	1.26	0.880

DECONTAMINATION STUDIES

Batch Extractions*

Identification of Fission-Product Activity Extracted from Experimental Dissolver

Solution

An aluminum absorption curve of β - γ activity was determined on the pentaether phase from the radiation stability experiment described previously. A hard beta component with a maximum range of about 1700 mg Al/cm² was found to be present, and accounted for about 70 percent of the total activity. This component was ascribed to Rh¹⁰⁶ in the Ru¹⁰⁶ β^- (1.0 yr.) $\rightarrow$ Rh¹⁰⁶ β^- (30 s.) $\rightarrow$ Pd¹⁰⁶ chain. In view of the

*A description of the equipment used for batch extraction experiments may be found in the Appendix.

likelihood that ruthenium is the principal contaminant in the organic phase, it was distilled in a stream of nitrogen gas with KMnO_4 and H_3PO_4 present. Approximately 99 percent of the total activity was obtained as distillate; aluminum absorption curves indicated that this was a mixture of Ru^{103} and Ru^{106} . An aluminum absorption curve of the residue remaining after the distillation indicated that approximately 85 percent of the residual activity could be ascribed to Ru^{106} . Resolution of the additional activity was virtually impossible since the soft radiations from the residue were attenuated by the presence of compounds of phosphorus, manganese and uranium in the final sample, and since the specific activity of the residue was low. It is felt, however, that this activity may be ascribed to the presence of Ru^{103} and the natural UX activity.

The behavior of the activity in the pentaether phase, upon equilibrating with an aqueous natural uranium solution, was investigated next. This procedure should indicate the effect of stripping in a continuous-flow column. The following feeds were used:

Table III

Batch Re-Extraction of Pentaether
Previously Contacted with Dissolver Solution

Phase	Volume	Composition		
		$\beta\text{-}\gamma$ (c/m/ml)	Uranium (M)	HNO_3 (M)
Organic	1 ml.	1.0×10^7	1	0.12
Aqueous	1 ml.	Natural activity only	1	0.34

These two phases were mixed in an extractor of the type illustrated in Figure 12. β - γ activity was measured as a function of time in the aqueous phase. Again, three minutes' stirring proved sufficient to reach a gross equilibrium distribution. The resulting activity of the aqueous phase was 7.0×10^6 c/m/ml.

Behavior of Ruthenium. A series of experiments was carried out on a uranium-rich pentaether extract phase in which ruthenium accounted for 99 percent plus of the total activity. (This phase was a composite IP stream obtained from a countercurrent column run to be described in a later section.)

After the IP solution had stood for ten days, a short batch experiment indicated the rate of return of ruthenium to an aqueous natural uranium solution. Table IV gives the conditions of the experiment, and Table V gives the activity in the two phases as a function of time of mixing.

Table IV
Batch Re-extraction of Ruthenium

Phase	Volume	Composition		
		β - γ (c/m/ml)	U (M)	HNO ₃ (M)
Organic	1 ml.	8.0×10^5	0.7	1.0
Aqueous	1 ml.	Natural activity	0.5	0

Four minutes' stirring appears sufficient to reach an effective "equilibrium" distribution ratio E_a^0 , which is approximately two times the half-life for the extraction.

Table V

Rate of Re-Extraction of Ruthenium

Time of Mixing (min.)	$\beta\text{-}\gamma$ (c/m/ml $\times 10^{-5}$)		E_a^0
	Organic	Aqueous	
0.4	8.0	1.8	4.4
0.6	8.0	2.1	3.6
2	8.0	2.2	3.4
3	7.0	2.4	2.9
4	6.0	3.0	2.2
34	6.0	2.7	2.2

A study of multiple re-extraction was then carried out by the scheme shown in Table VI.

Table VI

Series of Extractions Performed on Uranium
Solutions Carrying Ruthenium

Organic Phase (IP) containing 0.7M U, 1.0M HNO_3

Mix with equal volume aqueous phase containing 0.5M U, no HNO_3

Organic Phase (IIO)
Discard

Aqueous Phase (IIA)

Mix with equal volume organic
phase containing 0.5M U, no HNO_3

Aqueous Phase (IIIA)
Analyze as a function
of time, then discard

Organic Phase (IIIO)
Mix with equal volume
of aqueous phase con-
taining 0.5M U

Organic (IVO)
Analyze

Aqueous (IVA)
Analyze

On the basis of the previous experiment, the first re-extraction was carried out by stirring for 4.5 minutes. The activity of the IIO phase was assumed to be the same as obtained in the previous experiment and reported in Table IV. In the second re-extraction, stirring over a period of 16 hours indicated that equilibrium was reached in less than one minute, with a half-life for transfer of about 0.2 minutes.

Analyses for β - γ activity in the various phases are listed in Table VII. Some of these were estimated by difference.

Table VII

Activity Levels for Uranium-Ruthenium Solutions
From Extractions Reported in Table VI

	β - γ (c/m/ml $\times 10^{-5}$)
Organic IP	8.0
Organic IIO	5.0
Aqueous IIA	3.0
Aqueous IIIA	2.2
Organic IIIO	0.9
Organic IVO	0.6
Aqueous IVA	0.3

Additional batch studies made with the uranium-pentaether-nitric acid-water system have indicated that, for times of an hour or less, the distribution coefficients for ruthenium are relatively insensitive to uranium and nitric acid concentrations.

The results obtained indicate that ruthenium is divided into several distinct chemical species similar to those reported by Elliott and Miles⁶ for ruthenium in the hexone extraction system. However, the data of

Table VII may be interpreted in an over-simplified manner by assuming that only two species are present, that the coefficient for each is constant throughout the series of extractions, and that not enough time was allowed for inter-conversion of species.

The data are sufficient to provide four simultaneous equations containing four separate unknowns.

Let x = activity of organic-soluble species $(Ru)_A$ in IP solution, in c/m/ml,

y = activity of aqueous-soluble species $(Ru)_B$ in IP solution, in c/m/ml,

A = distribution coefficient for $(Ru)_A$, with $A > 1$, and

B = distribution coefficient for $(Ru)_B$, with $B < 1$.

The following equations can be written:

$$x + y = 8.0 \times 10^5$$

$$\frac{x}{1+A} + \frac{y}{1+B} = 3.0 \times 10^5$$

$$\frac{Ax}{(1+A)^2} + \frac{By}{(1+B)^2} = 8.5 \times 10^4$$

$$\frac{Ax}{(1+A)^3} + \frac{By}{(1+B)^3} = 2.8 \times 10^4$$

Trial-and-error solution yields

$$(Ru)_A = x = 5.6 \times 10^5 = 70\% \text{ of total Ru in IP}$$

$$(Ru)_B = y = 2.4 \times 10^5 = 30\% \text{ of total Ru in IP}$$

$$A = 6.0$$

$$B = 0.09$$

Despite the many assumptions involved in arriving at these values, they tend to indicate that the behavior of ruthenium in pentaether is not significantly different from that in hexone. The rate data given in Table V indicate qualitatively that the organic-soluble component $(Ru)_A$ has a two-minute half-life for interphase transfer at the stirring speed of the experiment, provided

the water-soluble component is assumed (from the data on extraction of II A) to have an 0.2-minute half-life for transfer. It is therefore concluded that ruthenium will be the limiting activity in a decontamination process using pentaether as the solvent. Postulated equilibria between extractable and non-extractable species of ruthenium suggest that the stripping section in a column would be ineffective with respect to ruthenium. A practicable number of scrub stages can be expected to give a promising (10^6 - 10^7) DF with respect to all other fission products under these experimental conditions.

Batch Countercurrent Operations with Active Solutions

Batch countercurrent column manipulations were carried out in a manner similar to those used for "cold" uranium, except that the volumes of solution used were on a one to two milliliter scale and the remotely controlled extractors employed were mounted in a shielded Berkeley box. A more complete description of the equipment may be found in the Appendix. Behavior of Uranium in the Remotely Controlled Equipment. In order to verify that uranium behaved in the remotely controlled equipment as in the larger "separatory funnel" column, a run was made using a "synthetic dissolver solution" with "cold" uranium and identical results were obtained. It is therefore believed that fission product data obtained with "hot" solutions are representative also of their behavior on a larger scale.

Experiments with Dissolver Solutions. In all experiments active solutions were used as feed, with only minor dilution for adjustment of nitric acid and uranium concentration to desired levels.

In the first experiment with the equipment all twenty stages were used as either extraction or scrub stages. The flow used is indicated in the following diagram, and analyses of the feeds and product are given in Table VIII. The dissolver solution used was somewhat more than one year old.

Table VIII

Compositions in First Extraction of Dissolver Solution

Stream	Phase	Volume, (ml.)	Composition		
			$\beta\text{-}\gamma$ (c/m/ml)	U (M)	HNO ₃ (M)
IX (Solvent)	Org.	3	0	0	1.00
IS (Scrub)	Aq.	1	0	0	1.45
IF (Feed)	Aq.	1	2.2×10^8	2.0	0.50
IP (Product)	Org.	1	1.6×10^6	0.6	0.97
IW (Waste)	Aq.	2	2.6×10^8	~0.01	2.84

The distribution of $\beta\text{-}\gamma$ activity in the column after reaching steady-state was measured and is reported in Table IX.

Table IX
Decontamination in First Extraction Column

Stage	$\beta\text{-}\gamma$ (c/m/ml $\times 10^{-6}$)		E_a^0
	Organic	Aqueous	
1	0.5	260	0.02
3	2.8	440	0.06
7	2.5	25	0.10
8	4.8	31	0.15
10	2.8	11	0.25
12	3.2	4.5	0.71
14	3.0	2.3	1.3
16	2.1	1.8	1.2
18	1.6	1.3	1.2
19	1.7	0.9	2.0
20	1.5	0.6	2.5

In the belief that ruthenium might account for a major portion of the activity carried into the organic phase, RuO_4 distillations were carried out by A. Kaminski of this laboratory on the organic and aqueous phases of stage 20 and the aqueous phase of stage 16. Results are shown in Table X.

Table X
Ruthenium Analyses in First Extraction

Stage Number	Phase	% Beta Distilled as RuO_4	% of Residual Beta Identified as Ru^*	% Non-Ru Activity of Gross Beta
16	Aqueous	98	>90	<0.2
20	Aqueous	98	>80	<0.4
20	Organic	85	>90	<1.5

*Identification by aluminum absorption curve.

The efficiency of the scrub section is indicated by the variation of activity in the pentaether phase as a function of stage number, which is shown in Table IX and also plotted in Figure 6. Although the batch experiments reported above suggested that only a small number of scrub stages were needed, later experiments indicated that the relative inefficiency of the scrub section was due to a salting effect of the high acid concentration (1.45M) in the scrub stream, or to an accompanying shift of the ruthenium species. A DF of 79 was achieved in the extraction column where

$$DF = \frac{\text{c/m/ng U of } \beta\text{-}\gamma \text{ activity in feed stream}}{\text{c/m/ng U of } \beta\text{-}\gamma \text{ activity in product stream.}}$$

During the course of two and one-half solvent throughputs, enough product stream was collected to be used as feed in a stripping column in which five extractors were used to simulate ten stages. The following flowsheet was used for the stripping column:

Table XI lists the compositions of the principal streams, and Table XII shows the distribution of activity in the column.

Table XI
Compositions in Re-extraction Run

Stream	Volume (ml.)	Composition		
		$\beta\text{-}\gamma$ (c/m/ml $\times 10^{-5}$)	U (M)	HNO ₃ (M)
IIP (Aq.)	2	2.5	0.33	0.5
IIX (Aq.)	6	0	0	0
IIS (Org.)	3	0	0	0
IIF (Org.)	1	8.0	0.7	1.0

FIG. 6

MU 1370

Table XII
Decontamination in Re-extraction Run

Simulated Stage	$\beta\text{-}\gamma$ (c/m/ml $\times 10^{-5}$)		E_a^0
	Organic	Aqueous	
10'	0.6	2.0	0.28
9'	2.7	1.8	1.48
7'	0.7	1.9	0.38
5'	2.4	2.1	1.55
3'	3.3	1.4	2.30

Figure 7 is a plot of $\beta\text{-}\gamma$ activity as a function of stage number. This plot indicates that, within experimental limits, only three scrub stages are needed.

In the stripping column, the DF was 1.7, and the over-all DF in extraction and re-extraction was 134.

Ruthenium distillations were carried out on the aqueous phase of stage 10', i.e., the IIP stream. Ninety-eight percent of the activity in this solution distilled as ruthenium. The residue was all ruthenium, UX_1 and UX_2 within the experimental error of the aluminum absorption curve, and the desirability of removing ruthenium in a separate operation, by distillation or otherwise, appears to be established. The residual activity after distillation amounts to 4.0×10^3 c/m/ml; this gives an over-all DF, including ruthenium decontamination by distillation, of $\sim 10^4$. These runs therefore establish the feasibility of using pentaether for uranium recovery provided the ruthenium is removed in a separate step.

The presence of two or more species of ruthenium, as found by

FIG. 7

MU 1371

several investigators⁶ would explain the fact that ruthenium shows an appreciable E_a^0 when in the organic phase and an appreciable $1/E_a^0$ when in the aqueous phase, the E 's varying with hydrogen ion concentration but all being of the same order of magnitude. The uranium concentration of the IIP stream used in the DF calculation was only estimated, and not measured directly; the limits set on ruthenium concentrations in distillates, residues, and phases of stages in the column are governed by factors such as self-absorption, statistics on low-counting samples, and inherent inaccuracies in the identification of activities by absorption curves.

The results obtained in the two runs just described indicate that the scrubbing efficiency could be improved considerably by decreasing the acid in the scrub stream. This would shift hydrolysis equilibria, and negate the considerable salting effect of nitric acid which was encountered here.

Ozonized Dissolver Solution in the Batch Column. A mixture of 10 ml. of 4-month old solution with a uranium concentration of 2.0M and 6 ml. of approximately one-year old solution with a uranium concentration of 1.4M was "ozonized" with four percent ozone in oxygen at 97°C for approximately forty hours.

A description of the equipment and procedure used may be found in the Appendix.

The "ozonized" solution was used as feed for the simulated column with all other conditions identical to those of the previous Column I run solution. The compositions and volumes of the feed streams are shown in Table XIII and the analyses of the stages at steady state are given in Table XIV.

Table XIII

Feed Compositions in Extraction of Ozonized Dissolver Solution

Stream	Phase	Volume (ml.)	Composition		
			β - γ (c/m/ml)	U (M)	HNO ₃ (M)
IX	Org.	2	0	0	2.0
IS	Aq.	0.5	0	0	0
IF	Aq.	1	1.6×10^9	2.0	0.25

Table XIV

Decontamination of Ozonized Dissolver Solution

Stage Number	β - γ (c/m/ml $\times 10^{-7}$)		E_a^0
	Organic	Aqueous	
1	1.0	80.	0.012
3	20.	170.	0.12
5	19.	60.	0.32
7	45.	290.	0.16
9	20.	6.0	3.3
11	0.60	0.70	0.86
13	0.34	0.37	0.92
15	0.44	0.18	2.4
16	0.31		
(strip)	—	0.07	

Figure 8 indicates graphically the behavior of activity as a function of stage number. The effectiveness of the scrub section continues until

FIG. 6

MU 1372

stage 12, after which the activity remains essentially constant in the organic phase. Distillation of the pentaether phase of stage 15 under oxidizing conditions removed 99.1% of the activity. An aluminum absorption curve of the subsequent residue indicated that > ninety percent of its activity was also due to ruthenium. This shows an upper limit of 0.1 percent of the β - γ -activity in the 15th stage of this column is due to non-ruthenium activity. Decontamination factors were achieved as shown in Table XV.

Table XV

Ruthenium Decontamination Factors	
Decontamination Step	DF
Column I	178
Column II	3.1
Ruthenium Distillation	114
Over-all	62,700

Decontamination yielded a product which had an activity 1.57 times the natural uranium background, most of which is due to ruthenium. Little, if any, benefit was achieved by "ozonization" of the original feed solution.

Behavior of Other Isotopes

A number of the fission product isotopes considered to be of importance other than ruthenium, were investigated in the batch column.

Behavior of Cerium. Preliminary experiments showed that at low levels of activity, in the presence of uranium, Ce^{144} could not be differentiated by aluminum absorption curves from the Ru^{106} contamination which remained on the glass extraction vessels from previous work with ruthenium. Accordingly, seven extractors comprising the scrub section and part of the extraction section of the column were replaced with new ones, and it was hoped that any

contamination in the remaining three extractors would be of small consequence.

An old Ce^{141} , Ce^{144} tracer solution in which the Ce^{141} had essentially decayed out was diluted with stable cerium, precipitated as the hydroxide and dissolved in nitric acid. This solution was used in preparing a synthetic "dissolver solution," and fed to the column according the following flow scheme:

The compositions of feed and product streams attained after two feed throughputs are shown in Table XVI and the stagewise β - γ distribution is shown in Table XVII.

Table XVI
Flow Streams for Cerium Behavior

Stream	Phase	Volume (ml.)	Composition		
			β - γ (c/m/ml)	U (M)	HNO_3 (M)
IF	Aq.	1	2.4×10^6 *	2.00	0.50
IX	Org.	2		0	1.00
IS	Aq.	1/2		0	0
IP	Org.	2.3	170	0.87	0.26
IW	Aq.	1.3		0.02	1.45
IIX	Aq.	2.0		0	0
IIP	Aq.	2.3	90	0.87	0.20
IIW	Org.	2.0	90	~ 0.01	0.06

*Also contains 0.15M Ce^{+++} (stable)

Table XVII
Distribution of β - γ Activity for Cerium

Stage	β - γ (c/m/ml $\times 10^{-4}$)		E_a^0
	Organic	Aqueous	
2	0.60	140	0.004
4	0.60	60	0.010
6	2.9	16	0.190
8	0.17	37	0.005
10	0.05	9.0	0.006
12	0.26	2.3	0.010
14	0.17	1.1	0.020
<u>Strip Column</u>			
2'	0.009	0.007	1.3

Figure 9 shows the data of Table XVII graphically.

The data in Table XVI indicate that a DF of approximately 3600 was achieved in the first column. This figure is conservative since there is evidence that the activity remaining in stages 14-16 is ruthenium contamination. This is further shown in the virtual ineffectiveness of scrub after stage 14, indicating that all of an activity of low distribution coefficient has been scrubbed out, leaving another activity of high distribution coefficient in the organic phase. The experiments with ruthenium have shown it to behave precisely as this activity does; it is impervious to scrubbing and has the same extraction coefficient under similar experimental conditions.

It is therefore considered that cerium will not be limiting in the pentaether process.

FIG. 9

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Behavior of Barium and Lanthanum. Ba^{140} - La^{140} tracer from Oak Ridge was used to prepare a synthetic dissolver solution which was fed to the batch column. In this experiment, only Column I was run.

Feed compositions are shown in Table XVIII; the stagewise activity distribution at steady-state is given in Table XIX and shown in Figure 10.

Table XVIII
Compositions for Ba^{140} - La^{140} Experiment

Stream	Phase	Volume (ml.)	Composition		
			β - γ (c/m/ml)	U (M)	HNO_3 (M)
IF	Aq.	1.0	6.35×10^7	2.0	0.5
IX	Org.	2.0	0	0	2.0
IS	Aq.	0.5	0	0	0
IP	Org.	2.3	$\sim 9 \times 10^3$	~ 0.9 (calc.)	~ 0.25 (calc.)
IV	Aq.	1.3	8.8×10^5	~ 0.01	3.0

FIG. 10

MJ 1374

Table XIX

Stage β -Y Activity Distribution for Ba ¹⁴⁰ - La ¹⁴⁰			
Stage	β -Y (c/ml $\times 10^{-5}$)		E_a^0
	Organic	Aqueous	
1	8.8	560	0.0015
3	4.3	250	0.0019
5	2.0	430	0.00046
7	0.24	500	0.00036
9	0.12	21	0.0060
11	0.12	1.7	0.068
13	0.11	0.33	0.32
15	0.09	0.15	0.57

The DF for Column I from the data of Table XVIII is 3200. Assuming as before (on the basis of aluminum absorption curves) that the residual activity in the last scrub state was ruthenium contamination, it is concluded that barium and lanthanum will not be limiting activities.

Behavior of Zirconium. Zr⁹⁵ tracer obtained from Oak Ridge was purified by extracting it into a benzene phase with TTA and re-extracting into nitric acid. Synthetic dissolver solution was spiked with this tracer and fed to the batch column using the same flow pattern as for cerium. Because of the continued difficulties with ruthenium in the barium-lanthanum experiment, all ten of the extractors were replaced for this run. Compositions of the feeds are shown in Table XX and the steady state β -Y distribution is shown in Table XXI and Figure 11.

FIG. 11

MJ 1375

Table XI
Feed Compositions for Zirconium Experiment

Stream	Phase	Volume (ml.)	Composition		
			β -Y (c/m/ml)	U (M)	HNO_3 (M)
IF	Aq.	1.0	3.2×10^6	2.26	0.215
IX	Org.	2.0	0	0	2.00
IS	Aq.	0.5	0	0	0
IIX	Aq.	2.0	0	0	0
IIP	Aq.	~2.3	2.9×10^5	~0.9 (calc)	~0.25 (calc)

Table XII
Stagewise Activity Distribution In Zirconium Experiment

Stage	β -Y (c/m/ml $\times 10^{-5}$)		K_a^0
	Organic	Aqueous	
1	1.6	21	0.76
3	1.6	15	0.11
5	1.9	17	0.11
7	5.0	22	0.22
9	4.7	8.7	0.54
11	4.2	5.7	0.73
13	3.8	4.3	0.89
15	3.6	3.5	1.0
Stripping			
1'	3.5	2.9	1.2
3'	0.70	2.4	0.29

From the data of Table XI, the overall DF for column I and II is 4.3.
These results are surprising in view of the quite different zirconium

behavior.

It was postulated therefore that the zirconium in the solutions was present as a polymerized or other unextractable species. In order to check this, Er^{95} tracer was allowed to stand for three weeks in synthetic dissolver solution of 0.3M HNO_3 , in the hopes that the zirconium would polymerize or otherwise approach the state of zirconium in solution. This synthetic solution was then fed to the batch column exactly as before. Within experimental error however, results were identical to those reported above. It can only be concluded therefore, that the behavior of ionic Er^{95} tracer used in these experiments does not represent the behavior of zirconium in solution. Although decontamination with respect to zirconium was satisfactory, its decontamination is unsatisfactory with respect to solutions which have had different chemical histories.

APPENDIX

Experimental

Chemicals. For all experiments, technical grade (Carbide and Carbon) penta-ether was distilled at 10 mm and the center cut, boiling at 192.4-192.6°C, was used.

Reagent grade (Baker and Adamson) nitric acid was used in all experiments.

For adjustment of the uranium concentration of the available dissolver solution, and for preparation of synthetic dissolver solutions, commercially pure uranium nitrate hexahydrate (Mallinckrodt) was used. Equilibrium with respect to U^{IV} and U^{VI} existed in this uranium stock.

Analyses. Counting for β - γ intensities was done with Geiger-Müller end-window tube counters with Asperex Type C tubes containing argon and one percent chlorine at a total pressure of 13 cm. of mercury. These counters had an effective geometry of five percent with a counting efficiency of essentially one hundred percent for beta particles and about one percent for gamma rays. β - γ counts as reported in this paper are given directly as observed with correction for coincidence and background, but no attempt has been made to report actual disintegration rates. Gamma counting was accomplished by using 2760 mg Al/cm² absorber.

Isotope identification in the organic and aqueous phases was considered reliable only if accomplished by chemical methods; aluminum absorption curves, while giving valuable information were considered too unreliable for positive identification.

Three types of uranium analyses were employed:

- (1) A gravimetric method was used which consists of

igniting an aliquot to about 850°C and then weighing the residue as U_3O_8 .

(2) A UO_2^{++} peak in nitric acid at about $4120 \text{ \AA}$ was established with an extinction coefficient of 8.6. Beer's law was shown to hold at this wave length. In all cases, one centimeter Correx cells were used with a Beckman spectrophotometer.

(3) Uranium concentrations were also determined by the colorimetric method of Smith et.al.⁷ with l-ascorbic acid.

Nitric acid concentrations were determined by titration with sodium hydroxide to a potentiometric endpoint using a Beckman pH meter. The masking of the endpoint due to uranium hydrolysis was eliminated by complexing the uranium with oxalate.⁸ The results were reproducible and accurate to within one percent.

Ozonization. For the "ozonization" of solution to remove ruthenium, ozone was produced by electrolysis of a 7% sulfuric acid solution at a temperature of approximately 5°C . An internally cooled platinum electrode was used, and cell and electrode dimensions were such that a potential difference of 15 volts gave a current of 20 amperes. This temperature and cell geometry yielded approximately 150 cc per min of an ozone-oxygen mixture with 4% by volume of ozone. For the ozone analysis, the gas mixture was bubbled through a KI solution buffered at pH 8 with a phosphate buffer. After passing through the KI solution the gas stream volume was measured by a wet test gas meter.

"Ozonization" of solution was carried out in a 50 ml centrifuge cone with a glass sidearm; a bubbler tube with a capillary tip extended to a point $1/4$ inch from the bottom of the

solution. The centrifuge cone was partially immersed in a hot water bath kept at approximately 97°C. The RuO_4 gas was collected in a sodium bisulfite solution which reduced the ozone as well as the RuO_4 . A second trap in series was filled with a KI solution which became colored with KI_3 when the reducing strength of the first trap was exhausted.

Special Equipment Used - General. To accommodate the high levels of radioactivity used, all work with active solution was in "dry boxes" of the Berkeley type with lead-glass windows and 3/4"-1" lead shielding on three sides. All transfers of solutions and mounting of samples for β - γ counting were accomplished by means of a remotely-controlled pipettor.

Batch Extractions. Figure 12 shows the type of extractors used. The extractor proper had a total volume of ~7 ml. and was equipped with a propeller-shaped agitator. It had a sidearm for introduction of solutions and a bottom stopcock for separation of phases.

Batch Countercurrent Extraction Column.

(1) Experiment with "cold" uranium. A bank of eleven 60 ml. separatory funnels was set up in a row and measured volumes of aqueous and penta-ether solutions were fed in their proper sequence according to a set pattern for the experiment. The operations were repeated until analyses showed that a steady-state distribution of concentrations had been achieved. This generally required a minimum of 25 movements of the two phases in each stage. A description of the mechanics of operation of such countercurrent batch extractors has been reported.⁵

Samples of both phases in each funnel were then analyzed for uranium and nitric acid content by the methods described above.

(2) Experiments with active solutions. Ten glass extractors with

- a - PIPETOR
- b - TRANSFER PIPET
- c - ARC OF EXTRACTORS
- d - INDIVIDUAL PIPET HOLDERS AND STIRRER MOTORS

FIG. 12

SIMULATED COUNTER CURRENT MIXER-SETTLER EQUIPMENT.

individually controlled stirrer motors and ten pipets were set up as shown in Figures 13 and 14. The total volume which could be used was four ml. per extractor. The various liquid phases were moved from extractor to extractor by means of the remote-controlled pipettor in a manner analogous to that used for the "cold" experiments, and the sequence of operations was continued until steady-state had been achieved.

Each phase of each extractor was then separately stored in 3 ml. stoppered bottles in order to prevent a change in isotope distribution between phases due to the radioactive decay of extractable or non-extractable species. Aliquots ranging in size from 10 λ to 100 λ were mounted on glass or platinum plates for counting.

Uranium - Nitric Acid Steady-State Equilibrium and Operating Curves as Determined by Batch Column. As mentioned previously, stagewise uranium and nitric acid distributions, volumes, X-Y diagrams, and uranium and nitric acid distribution coefficients are shown in Figures 15 through 41.

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FIG. 13 -

VIEW OF INSIDE OF DRY BOX CONTAINING SIMULATED
COUNTER CURRENT MIXER-SETTLER EQUIPMENT.

02 945

a - STIRRER MOTORS
b-c EXTRACTORS

FIG. 14
BATCH EXTRACTORS

4094

-50-

FIG. 15

MU 1376

FIG. 16

MU 1377

FIG. 17

MU578

FIG. 18

MU 1379

FIG. 19

MU 1380

4094

-55-

FIG. 20

MU 1381

FIG. 21

MU 1392

4094

-57-

FIG. 22

MU 1383

4094

-58-

FIG. 23

MU 1384

FIG. 24

MU 1385

4094

-61-

FIG. 26

MU 1367

4054

-62-

FIG. 27

MU1308

FIG. 28

MU 1389

4094

-64-

FIG. 29

MU1390

4094

-65-

4094

-66-

FIG. 31

MU 1392

4094

-67-

FIG. 32

MU 1393

4094

-68-

FIG. 33

MU 1394

4094

-69-

FIG. 34

MU 1395

4094

-70-

FIG. 35

MU1396

4034

-71-

4094

-72-

FIG. 37

MU 1398

4094

-73-

FIG. 38

MU 1399

4094

-74-

FIG. 39

MUI400

4094

-75-

FIG. 40

MU 1401

4054

-76-

FIG. 41

MU 1402

4094

-77-

FIG. 42

MU 1402