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RECOVERY OF IRRADIATED URANIUM BY A

TWO-STAGE DIFFERENTIAL

EXTRACTION PROCEDURE

R. E. McHenry
J. C. Posey
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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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DATE ISSUED

MAR 21 1963

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CONTENTS

	Page
Abstract.....	1
Introduction.....	1
Theoretical Discussion.....	4
Equipment.....	8
Procedure.....	12
Results and Discussion.....	13
Laboratory Data.....	13
Uranium Distribution Coefficients.....	14
Zirconium-Niobium Distribution Coefficients.....	20
Contact Time.....	22
Europium Distribution Coefficients.....	23
Ruthenium Distribution Coefficients.....	24
Separation Factors.....	24
Stage Evaluation.....	25
Production Flowsheet and Results.....	28
Conclusions.....	30
Acknowledgments.....	31

RECOVERY OF IRRADIATED URANIUM BY A TWO-STAGE
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R. E. McHenry J. C. Posey P. S. Baker

ABSTRACT

The recovery of uranium from irradiated fuel and its simultaneous separation from fission products can be effected by a differential extraction procedure which requires only two stages. Tributyl phosphate is used as the organic extractant, and sulfate ion is used as a complexing agent in the aqueous phase to enhance separation of uranium from fission products.

In the first stage, sufficient extractant is used to obtain the required recovery of uranium. In the second stage, the extractant phase from the first cycle contains the uranium and a small portion of the fission products, and has now become the solvent phase. Sufficient aqueous extractant (3 M HNO_3 and 1 M H_2SO_4) is used in the second stage to obtain the required decontamination. The extracted uranium is then recycled to the first stage.

In a system employing a 30% TBP-Amsco organic phase and a 3 M HNO_3 -1 M SO_4^{2-} aqueous phase, a separation factor between uranium and zirconium-niobium of >1200 was obtained. This value was constant throughout the first stage. The separation factor between uranium and zirconium-niobium in the second stage was >600 . The separation factor for uranium and europium varied from 2500 to 400, depending upon the extent of uranium saturation in the organic phase. The separation factor for uranium and ruthenium was >5000 .

In one program, 15 kg of uranium was recovered with an overall efficiency greater than 99.5%. Decontamination factors were $>1 \times 10^6$. The decontamination factor between uranium and zirconium-niobium was approximately 1×10^4 .

INTRODUCTION

A process has been developed which requires only two solvent extraction stages for the recovery of uranium from irradiated fuel. Tributyl phosphate is used as the organic extractant, as in the Purex process,¹ but a complexing agent is added to the aqueous phase to enhance

¹J. R. Flanary and J. H. Goode, Recovery of Uranium from Sulfate Solution by Solvent Extraction with Tributyl Phosphate, ORNL-2615 (Nov. 18, 1958).

the separation from fission products. A differential extraction is used to obtain the high separation required.

The process was developed as a result of a need for the recovery of approximately 20 kg of U^{235} from irradiated fuel of Homogeneous Reactor Experiment No. 2. This limited objective necessitated complete amortization of the cost of the process equipment during the period of the recovery operation.

Solvent extraction processes for uranium recovery have generally been designed for continuous countercurrent multiple-stage operation. The design has usually been chosen on the basis of the most economical process which meets the criteria of the problem — such as scale and efficiency of operation, capital and operating costs, maintenance, and amortization. The most important criterion is that the process accomplish at least the minimum acceptable separation.

Continuous countercurrent multiple-stage operation is often used for obtaining high separation in those cases where the single-stage separation is low. This operation has many advantages over others, the one inherent advantage being that for a particular extraction a minimum amount of extractant is used. The high capital cost of the plant, however, makes it unsuitable for processing a small amount of feed material for a short period of operation. Since the present problem would allow only a small capital investment, other types of solvent extraction procedures which could give high separations were examined.

A traditional method for small laboratory-scale separations involves a pseudo-countercurrent, batch-type fractionation procedure.² In this type of operation, if N total extraction and scrubbing stages are required, then at least N vessels and at least N^2 contactings are required. Although the separation from a given number of stages is usually greater than in continuous countercurrent operation and the cost of each unit is low, the cost of such a process in remote applications is prohibitive if more than two or three stages are required.

In the problem at hand, because of cost considerations, both high separation and a minimum number of separation units were desirable. Hence,

²R. E. Treybal, Liquid Extraction, McGraw-Hill, New York, 1951.

various methods for increasing the separation attained in a single stage were examined. One approach is to increase the chemical selectivity of the process. This increase would be beneficial regardless of the mode of operation because of the increase in the separation. This ideal situation is not realized generally, and only limited effects are obtained.

It is well known that in separation processes other than solvent extraction the degree of separation attainable in one stage may be much higher than that attained simply by equilibration of two phases; the separation depends on the details of operation of the stage. For many years this fact has been applied to distillation and, more recently, to gaseous diffusion separations.³ Rayleigh⁴ first described quantitatively the simple batch distillation and showed that the overall separation could be many times greater than the ratio of the volatilities of the substances to be separated.

In general, most simple batch separations - with the exception of solvent extraction - are carried out differentially, and the stage separation factor is greater than the simple equilibrium separation factor. For most separations a differential method is usually the most straightforward. The attainment of good differential separation in solvent extraction, however, has not been described in the literature.

Varteressian and Fenske⁵ have discussed differential extraction under the heading of a "Cocurrent Infinite Stage." They describe mathematically an ideal system similar to the Rayleigh distillation. They do not discuss the means of accomplishing the ideal differential stage, nor do they consider many of the physical parameters that affect the operation of a differential solvent extraction stage.

The authors of this report had previously investigated differential extraction⁶ as a means of separating fission products into chemically

³H. D. Smyth, Atomic Energy for Military Purposes, Princeton University Press, Princeton, 1945.

⁴J. H. Perry, Chemical Engineering Handbook, 2d ed., p 1382, McGraw-Hill, New York, 1941.

⁵K. A. Varteressian and M. R. Fenske, Ind. Eng. Chem. 28, 1353 (1936).

⁶Unpublished memorandum to A. F. Rupp, July 26, 1961.

related groups and had developed the theory and demonstrated equipment that would accomplish a nearly ideal differential stage. On the basis of this work, differential extraction was chosen as the most promising approach to the present problem.

In this report a quantitative description of an operable differential solvent extraction stage is developed for a four- (or more) component system (including two solvents) in which the solvents are immiscible. A description of the process equipment for accomplishing a nearly ideal differential stage is given. The description and results of a number of laboratory experiments and production runs are also included.

THEORETICAL DISCUSSION

The flow diagram of a differential extraction stage is shown in Fig. 1. The mixing tank is filled with the original solution containing

Fig. 1. Flow Diagram of a Differential Extraction Stage.

the solutes to be separated. This solution does not leave the stage and is hereafter called the resident phase. A steady stream of the extractant, E, enters the mixing vessel, where it is thoroughly dispersed by vigorous agitation. A stream of the mixed phases is then circulated

through the settler, where the extractant is separated and leaves the stage. The other phase returns by gravity flow to the mixing vessel.

Any differential extraction system is easily described mathematically if certain simplifying assumptions are made:

1. That the mutual solubility of the two phases is negligible.
2. That because of a high circulation rate and small holdup in the settler the composition of the resident phase at any time is essentially uniform.
3. That the distribution coefficients of the substances being separated are constant. [The distribution coefficient D of a substance is defined as (concentration in extractant phase/concentration in resident phase).]
4. That the volumes of the phases do not change appreciably during extraction.

A differential volume of extractant, dE , enters the stage, and an equal volume (also dE) which has been contacted with the other phase leaves the stage. The resulting removal of an extractable solute is described by the following equation:

$$Y dE = -(S dX + H dY) , \quad (1)$$

where

Y = concentration of solute in the extractant phase,

X = concentration of solute in resident phase,

S = volume of the resident phase,

H = volume of extractant phase held up in dispersed form.

From the definition of the distribution coefficient, D , the following equation is apparent:

$$Y = DX . \quad (2)$$

By substituting DX for Y in Eq. (1) and integrating between the limits 0 and E , and X_1 and X_2 , Eq. (3) is obtained:

$$E = \left(\frac{S}{D} + H \right) \ln \frac{X_1}{X_2} . \quad (3)$$

The distribution coefficient has a different value for each of the solutes which is extracted. On the other hand, the values of E , S , and

H are the same for all solutes. Consequently, an effective differential extraction separation between extractable components cannot be obtained unless the value of H is small compared to S/D (this is best accomplished by reducing H as much as practical, since any increase in S/D requires an increase in E, the amount of extractant required).

In the limiting case in which H is negligible, the fractions of two different substances remaining in solution after the passage of any amount of E are related by Eq. (4), which is derived from Eq. (1) by assuming that D_A/D_B is constant, and that $H = 0$:

$$\ln \frac{X_{A1}}{X_{A2}} = \frac{D_A}{D_B} \ln \frac{X_{B1}}{X_{B2}}, \quad (4)$$

where

X_{A1} = initial concentration of component A in the resident phase,

X_{A2} = final concentration of component A in the resident phase,

X_{B1} = initial concentration of component B in resident phase,

X_{B2} = final concentration of component B in resident phase.

From this equation it can be seen that the degree of separation (not the amount of solvent required) depends upon the ratio of the distribution coefficients and is independent of their absolute values. (In many systems the absolute values of the distribution coefficients of different components vary greatly with concentration, but the ratio of the distribution coefficients is approximately constant.) On the other hand, when H is not negligible, or when the ratio of distribution coefficients is a function of concentration, an accurate calculation of the degree of separation requires either that Y be expressed as a function of X for each component, or that a stepwise integration of Eq. (1) be carried out.

The value of the important parameter H can be calculated from a material balance of the extractant entering and leaving the stage. The rate F at which the extractant enters the settler is equal to the rate at which it leaves the settler - assuming 100% efficiency and steady-state operation. This rate also equals the rate at which the extractant enters and leaves the stage. The equality is expressed by Eq. (5).

$$F = R \left(\frac{H}{H + S} \right), \quad (5)$$

where

F = rate of extractant flow into, through, and out of the system,
 R = rate at which mixed phases are pumped into settler.

By rearranging Eq. (5), the value of H is obtained directly:

$$H = \frac{FS}{R - F} \quad (6)$$

As shown by Eq. (3), a small value of H is required for good separation. This is best achieved by making R as high as practical, since the time required for the process will be increased if F is decreased. A change in S has no net effect when the parameters described by Eqs. (3) and (6) are considered. A high value of R can be used only if an efficient, high-throughput settler is used.

A two-stage differential extraction can be used for the separation of two components where both high recovery and high purity of the two are required. A batch of the original solution of the two substances, A and B, is placed in the stage 1 mixing tank. A stream of extractant is passed through until the concentration of A (the component exhibiting the higher distribution coefficient) has been reduced to any desired level. From Eq. (3) it can be seen that the amount of A left behind can be reduced to any required level by passing an appropriate amount of extractant through the stage.

At this point the resident phase from stage 1 is removed from the system. If the ratio of the distribution coefficients of the two components is comparatively high, this phase will contain most of substance B.

The accumulated extractant is now placed in the mixing tank of stage 2, where it becomes the resident phase. A stream of extractant is passed through in the same manner as in stage 1. If the extractant in stage 1 is an organic solution and the resident phase an aqueous solution, then the extractant in stage 2 will be an aqueous solution and the resident phase is the organic extractant from stage 1. The distribution coefficient D is again defined as: (concentration in extractant phase/concentration in resident phase). The relative sizes of the distribution coefficients of the two components will be reversed because of the reversal of the roles of the organic and aqueous phases; Eqs. (1) through (6)

will apply without alteration. As in the operation of stage 1, the extraction can be continued until the concentration of the more extractable substance (in this case component B) has been reduced to any desired level.

The material has now been separated into three portions. The first consists of a solution of substance A and the second of a solution of substance B; each is of specified purity with respect to the other. The third portion consists of the extractant which has passed through stage 2, containing some of both substances A and B. The third portion is stored in a separate tank until a sufficient quantity has been accumulated to make a full charge for stage 1, and it is then processed in the same manner as for the original material.

The effectiveness of differential extraction as compared to a simple batch extraction is illustrated by the following numerical comparison. A 10-liter batch of solution containing components A and B with distribution coefficients of 10 and 0.1, respectively, is extracted differentially with 10 liters of an extracting solution. A holdup, H , of 0.5 liter is assumed. At the end of the extraction, 99.87% of component A and 9.1% of component B will have been extracted [based on Eqs. (3) and (6)]. In contrast, if a simple batch extraction is made by contacting 10 liters of extracting solution as a unit with 10 liters of the original solution, only 90.9% of component A will be removed along with 9.1% of component B.

EQUIPMENT

The design criteria for the extraction equipment required that the two phases be thoroughly mixed in the mixer and efficiently separated at a high flow rate in the settler. In particular, the settler was required to separate the extractant as solvent-free as possible. This was made easier since the solvent was always the continuous phase in the dispersion.

It was also necessary that the settler reduce as far as possible the amount of extractant returning to the mixer. Otherwise a poor removal of the extractant would increase the value of H [see Eq. (6)] and thus reduce the effectiveness of the stage.

The laboratory equipment flow diagrams are shown in Fig. 2. The mixing vessel was a 2-liter beaker provided with a bottom discharge and agitated with a suitable laboratory mixer. The operating volume in the mixing vessel was 1350 ml. The circulating pump was required to pump 41 liters/hr (30 times the operating volume of the mixing vessel).

The design of the laboratory settlers is shown in Fig. 3. To promote efficient separation of the phases and to minimize the transfer of solute between the solvent phase and the extractant phase held up in the settler, the settlers were designed for laminar flow by keeping the Reynolds number well below the critical value for turbulent flow. Minimum dimensions for a conservative Reynolds number were chosen to reduce

Fig. 2. Flow Diagram of Two-Stage Apparatus.

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Fig. 3. Laboratory Settler Design.

the holdup of the phases in the settler. The inlet tube to the settler was also tapered to minimize turbulence. The settlers were mounted at a 45° angle, which was a reasonable compromise between the distance a drop of extract had to move to reach the stagnant layer near the surface of

the settler and the vector force which caused the extract phase to move toward the outlet. The level of the interface between the phases was adjusted by means of an adjustable weir. The extractant pump was a laboratory-size, diaphragm, metering pump.

The production equipment flow diagram for the production runs is shown in Fig. 4. This equipment was a fivefold scale-up of the laboratory equipment. The settlers are shown in Fig. 5. The weirs were operated by a motorized rack and pinion. Liquid levels in the vessel were indicated by manometers used with dip legs which were purged with a small flow of air.

Criticality control was maintained by means of ever-safe geometry. All of the equipment was mounted as a unit in a rack and then installed in a manipulator cell. The manipulators were used to operate the valves and samplers.

Fig. 4. Production Equipment Flow Diagram.

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Fig. 5. Production-Scale Settlers.

PROCEDURE

The aqueous feed solutions used in the laboratory differential extraction runs contained 75 g of uranium per liter as uranyl nitrate in 3 N nitric acid, and 0.0, 0.5, 1.0, or 2.0 M sulfuric acid. The behavior of radioactive fission products was simulated by the use of appropriate

radioactive tracers (Zr^{95} - Nb^{95} , $\text{Eu}^{152,154}$, or Ru^{106}). Approximately 2 mc of tracer per liter of solution was used, except as noted.

The organic solution used throughout the work was composed of 30 vol % of commercial TBP in Amsco diluent (Amsco 125-82, high-grade petroleum distillate). The TBP solution was equilibrated with 3 M nitric acid before use.

In typical laboratory runs, a charge of aqueous solution was placed in the mixing vessel (flow diagram a, Fig. 2). The circulating pump, the mixer, and the extractant feed pump were then started. The stream of uranium-bearing TBP emerging from the settler was sampled periodically. The aqueous stream returning to the pot was sampled simultaneously. The radioactive tracer concentrations in these samples were determined by gamma-ray scintillation counting. The uranium concentrations were determined by chemical analysis.

The extraction of the uranium with TBP was continued until the uranium concentration in the aqueous phase was reduced to the required value. The accumulated organic phase was then placed in the mixing vessel shown in flow diagram b, Fig. 2.

Most of the fission-product activity and a fraction of the uranium were extracted from the organic phase by an aqueous phase 3 M in HNO_3 and 0.0, 0.5, or 1.0 M in H_2SO_4 . The extraction was continued until the desired decontamination was obtained.

In the production flowsheet (Fig. 6) the aqueous phase from the second cycle was accumulated and recycled to the first cycle as feed solution. The conditions for the laboratory runs are shown in Table 1.

RESULTS AND DISCUSSION

Laboratory Data

The data taken during 22 laboratory runs are shown in Table 1. These runs were made (1) to determine the effect of several variables on the distribution coefficients for uranium and the fission products generally most difficult to separate from uranium, (2) to evaluate the effect of the several variables on the separation, and (3) to test the conformance of the equipment with theory.

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Fig. 6. Cell 14 Process Chemical Flowsheet.

The distribution coefficients for uranium and the radioactive tracers were compared by plotting logs of distribution coefficients as linear functions of logs of the residual capacities of TBP. (The capacity of the unreacted TBP was obtained by subtracting the uranium concentration in grams per liter in the TBP-Amsco phase from 130 g/liter, which is the maximum capacity of the TBP-Amsco phase assuming a 2 to 1 TBP/uranium stoichiometry.) Although this comparison does not consider the TBP which has reacted with nitric acid or the change in nitrate concentration due to uranyl nitrate extraction, there is no evidence of nonlinearity.

Uranium Distribution Coefficients

The relationship of the uranium distribution coefficient to residual capacity for various systems is shown in Fig. 7. It can be seen that the distribution coefficients for uranium are lowered by the addition of sulfate ion to the aqueous phase, with the effect for any given sulfate ion concentration being greater at low uranium concentrations. The data for

Table 1. Summary of Laboratory Runs

Run	S (liters)	E (ml)	F (liter/hr)	R (liters/hr)	NO ₃ ⁻ (M)	SO ₄ ²⁻ (M)	Y _U	130 - Y _U	D _U	D _{Zr}	Type of Extraction	Contact Time (min)
1	1.350	0	0.940	37.5	3.64	0					Forward	2.2
		79					105.0	25.0	1.42			
		366					102.0	28.0	1.82	0.09		
		557					100.0	30.0	2.44	0.093		
		812					94.0	36.0	3.76	0.078		
		1030					80.0	50.0	6.50	0.075		
		1290					33.0	97.0	18.30	0.213		
		1510					5.4	124.6	22.50	0.345		
2	1.350	0	0.468	37.5	3.64	0		28.0			Forward	4.4
		78					100	30.0	1.41			
		312					99.4	30.6	1.85	0.042		
		546					93.0	37.0	2.70	0.056		
		780					87.8	42.2	4.50	0.068		
		1010					69.2	68.0	11.00	0.134		
		1250					25.1	104.9	33.50	0.472		
		1480					5.5	124.5	68.00	0.355		
3	1.420	0	0.135	37.5	3.00	0					Backward	2.4
		54					73.0	57.0	8.02	0.245		
		106					72.0	58.0	8.10	0.345		
		187					71.0	59.0	8.26	0.448		
		261					70.5	59.5	8.50	0.547		
		328					70.0	60.0	8.65	0.660		
		374					69.0	61.0	8.75	0.745		
		441					68.5	61.5	8.90	0.970		
4	1.450	0	0.368	18.9	3.00	0	67.8	62.2	9.23		Backward	4.6
		11.3					67.6	62.4	9.35	0.117		
		33.8					68.3	61.7	9.28	0.160		
		73.1					67.5	62.5	9.20	0.270		
		101.0					67.8	62.2	9.23	0.570		
		129.5					67.8	62.2	9.23	0.430		

Table 1 (continued)

Run	S (liters)	E (ml)	F (liter/hr)	R (liters/hr)	NO ₃ ⁻ (M)	SO ₄ ²⁻ (M)	Y _U	130 - Y _U	D _U	D _{Zr}	Type of Extraction	Contact Time (min)
5	1.350	0	0.940	37.5	3.64	0.50					Forward	2.2
		350					97.2	32.8	2.36			
		595					90.2	39.8	2.34	0.0032		
		830					80.6	49.4	4.51	0.0040		
		1057					58.2	71.8	8.37	0.0065		
		1300					22.5	107.5	14.70	0.0160		
		1460					5.3	124.7	19.20	0.0140		
6	1.460	0	0.135	37.5	3.00	0.50					Backward	2.4
		27					63.5	66.5	5.70			
		95					62.3	67.7	5.70	0.044		
		162					62.0	68.0	5.80	0.042		
		230					61.0	69.0	5.90	0.053		
		297					60.0	70.0	6.00	0.066		
		364					59.0	71.0	6.10	0.084		
7	0.675	0	0.470	37.5	3.64	1.00	97.2	32.8	1.30		Forward	1.1
		122					92.0	38.0	1.53	0.0013		
		244					84.0	46.0	2.00	0.0016		
		366					75.0	55.0	2.78	0.0023		
		488					61.0	69.0	4.07	0.0034		
		610					40.0	90.0	6.67	0.0058		
		731					18.0	112.0	11.25	0.0082		
8	1.350	0	0.940	37.5	3.64	1.00					Forward	2.2
		314					88.1	41.9	1.55	0.0023		
		549					81.6	48.4	1.67	0.0012		
		784					74.2	55.8	2.43	0.0023		
		1020					63.0	67.0	3.75	0.0021		
		1252					42.1	87.9	6.21	0.0037		
		1440					24.2	105.3	10.80	0.0064		

Table 1 (continued)

Run	S (liters)	E (ml)	F (liter/hr)	R (liters/hr)	NO ₃ ⁻ (M)	SO ₄ ²⁻ (M)	Y _U	130 - Y _U	D _U	D _{Zr}	Type of Extraction	Contact Time (min)
9	1.350	0	0.468	18.9	3.64	1.00	96.0	34.0	1.26		Forward	4.4
		86					94.3	35.7	1.32			
		320					90.7	39.3	1.64	0.0026		
		554					85.4	44.6	2.28	0.0025		
		788					73.8	56.2	3.09	0.0026		
		1020					57.2	72.8	4.68	0.0038		
		1260					35.9	94.1	7.27	0.0063		
		1490					13.9	116.1	9.80	0.0082		
		1610					8.9	121.1	10.88	0.0085		
10	1.450	0	0.135	37.5	3.00	1.00					Backward	2.4
		66.5					69.2	60.8	3.26			
		140.0					68.2	61.8	3.35	0.014		
		224.0					67.2	62.8	3.48	0.020		
		266.0					66.0	64.0	3.63	0.015		
		349.0					65.0	65.0	3.71	0.019		
		405.0					64.0	66.0	3.90	0.013		
		445.0					63.0	67.0	3.94			
11	1.450	0	0.068	18.9	3.00	1.00					Backward	4.6
		41.6					62.7	67.3	3.82	0.0056		
		75.4					62.3	67.7	3.82	0.0063		
		109.0					62.0	68.0	3.82	0.0070		
		143.0					61.9	68.1	3.82	0.0032		
		178.0					61.5	68.5	3.82			
12	1.350	0	0.940	37.5	3.64	2.00	80.8	49.2	1.16		Forward	2.2
		480					68.0	62.0	1.63	0.0041		
		1000					48.0	82.0	2.86	0.0060		
		1465					22.0	108.0	4.78	0.0120		
		1940					4.5	114.3	5.40	0.0090		
		2550					0.51	129.4	7.30			
13	1.350	0	0.940	37.5	3.64	2.00	96.9	33.1	0.668		Forward	2.2
		235					92.0	38.0	0.697			
		480					88.0	42.0	0.786			
		730					84.3	45.7	0.858			
		1000					79.7	50.3	0.968			
		1240					76.6	53.4	1.170			
		1465					71.4	58.6	1.350			

Table 1 (continued)

Run	S (liters)	E (ml)	F (liter/hr)	R (liters/hr)	NO ₃ ⁻ (M)	SO ₄ ²⁻ (M)	Y _U	130 - Y _U	D _U	D _{Eu}	Type of Extraction	Contact Time (min)
14	1.350	0	0.940	37.5	3.64	0					Forward	2.2
		94					107.0	23.0	1.52	0.00130		
		329					103.0	27.0	2.20	0.00090		
		564					97.1	32.9	3.97	0.00135		
		800					82.4	47.6	6.86	0.00410		
15	0.950	0	0.250	37.5	3.00	0					Backward	1.5
		8					87.0	43.0	3.70	0.0068		
		75					86.0	44.0	3.90	0.0035		
		137					84.0	46.0	4.00	0.0073		
		200					83.0	47.0	4.26			
		250					82.0	48.0	4.40			
		312					81.0	49.0	4.60			
16	0.610	0	0.940	37.5	3.64	1.00	95.40	34.6	1.36	0.0011	Forward	1
		235					80.60	49.4	2.39	0.0014		
		472					45.90	84.1	6.07	0.0110		
		706					4.96	125.0	10.80	0.0320		
		800					1.68	128.3	14.00	0.0560		
17	1.350	0	0.940	37.5	3.64	1.00	93.0	37.0	1.24		Forward	2.2
		258					90.0	40.0	1.62	0.0008		
		486					84.0	46.0	2.13	0.0011		
		706					74.0	56.0	2.90	0.0026		
		940					59.0	71.0	4.20	0.0059		
		1190					33.0	97.0	7.00	0.0160		
		1410					11.8	118.2	9.30	0.0274		
		1620					3.5	126.5	11.70	0.0320		
18	0.950	0	0.250	37.5	3.00	1.00	55.7	72.5			Backward	1.5
		63					56.0	74.0	4.44	0.0054		
		125					55.0	75.0	4.51			
		192					54.2	75.8	4.59			
		250					53.5	76.5	4.61	0.0020		
		313					53.0	77.0	4.65	0.0027		
		375					52.0	78.0	4.64			
		438					51.5	78.5	4.94			

Table 1 (continued)

Run	S (liters)	E (ml)	F (liter/hr)	R (liters/hr)	NO ₃ ⁻ (M)	SC ₄ ²⁻ (M)	Y _U	130 - Y _U	D _U	D _{Eu}	Type of Extraction	Contact Time (min)
19	0.850	0	0.250	37.5	3.00	1.00	50.0	80.0	4.70		Backward	1.5
		63					50.0	80.0	5.00	0.013		
		125					49.3	80.7	5.00	0.015		
		188					48.3	81.7	5.10	0.019		
		250					47.4	82.6	5.30			
		312					45.9	84.1	5.20			
		375					45.6	84.4	5.30			
20	1.350	0	0.940	37.5	3.64	0	105.4	24.6	1.48	0.0006	Forward	2.2
		235					102.0	28.0	2.10	0.0003		
		470					90.6	39.4	3.10	0.0005		
		705					73.6	56.4	6.20	0.0009		
		940					35.3	94.7	25.40	0.0032		
		1175					3.6	106.4	45.00	0.0065		
										D _{Ru}		
21	0.610	0	0.940	37.5	3.64	1.00					Forward	1
		235					76.80	53.2	2.20	0.00073		
		470					46.60	83.4	7.30	0.00160		
		705					4.92	125.1	15.40	0.00270		
22	1.350	0	0.940	37.5	3.64	1.00	97.80	32.2	1.41	0.00035	Forward	2.2
		235					90.60	34.9	1.88	0.00076		
		470					83.00	47.0	2.43	0.00053		
		705					73.30	56.7	3.54	0.00099		
		940					51.80	78.2	4.90	0.00050		
		1175					25.20	104.8	9.30	0.00087		
		1410					6.99	118.3	11.70	0.00102

Fig. 7. Uranium Distribution Coefficient vs Function of Free TBP.

no sulfate in the aqueous phase tend to confirm the assumption that two TBP molecules react with each uranyl ion.

Zirconium-Niobium Distribution Coefficients

The data for the distribution coefficients of zirconium-niobium are shown in Figs. 8 and 9, representing forward extractions and back extractions respectively. The slope of the plots in Fig. 8 indicates approximately three TBP molecules reacting with each zirconium and niobium ion which is extracted. The addition of sufficient sulfate to give 0.5 M sulfate ion in the aqueous phase reduces the distribution coefficient of zirconium-niobium by a factor of ~30. A further increase in sulfate concentration up to 2 M reduces the distribution coefficient by an additional factor of ~2.

Fig. 8. Distribution Coefficients of Zr-Nb vs Function of Free TBP Concentration (Forward Extraction).

Fig. 9. Distribution Coefficient of Zr-Nb vs Function of Free TBP Concentration (Back Extraction).

Shown for comparison with the back extraction data in Fig. 9 is the correlation of the forward extraction data. As is the case for the forward extraction, the distribution coefficients are lowered by the addition of sulfate ion. The zirconium-niobium distribution coefficients

are higher on the back extraction, but the difference is reduced by increasing the contact time. A large difference in the forward and backward extraction of niobium has been reported by Brown *et al.*⁷ They noted that a large fraction of the niobium exists in an unextractable form at nitric acid concentrations of <6 M and that, when a back extraction is made, the extracted niobium exhibits a higher distribution coefficient than for the forward extraction. The data in Fig. 9 are consistent with these findings.

Contact Time

Experiments to determine the effect of contact time on the distribution coefficients of zirconium-niobium in a forward extraction indicate only a small change in the distribution coefficient with time. The changes were masked by the scatter of the data included in Table 1. If, at equilibrium, a large fraction of the zirconium-niobium exists in an unextractable form, then the change in the distribution coefficient produced by re-establishing equilibrium would be small. The effect of contact time on the back extraction is shown in Fig. 10. These data, as well as those in Fig. 9, suggest that the extractable zirconium-niobium very slowly reverts to the unextractable form.

⁷P. G. M. Brown *et al.*, Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958 17, 118 (1959).

Fig. 10. Distribution Coefficient of Zr-Nb; Back Extraction vs Contact Time.

Europium Distribution Coefficients

The distribution coefficients of europium are plotted in Fig. 11. The addition of 1 M SO_4^{2-} ion lowers the distribution coefficients by a factor of ~ 4.5 .

Fig. 11. Distribution Coefficient of Eu vs Function of Free TBP Concentration (Forward and Back Extraction).

Ruthenium Distribution Coefficients

The distribution coefficients of ruthenium are plotted in Fig. 12. The effect of SO_4^{2-} appears to be small.

Separation Factors

The separation factors D_U/D_{Zr} for uranium and zirconium-niobium as a function of the concentration of unreacted TBP (or uranium loading) are shown in Fig. 13. The separation factors are highest when the aqueous phase is 1 M in SO_4^{2-} , and they are constant in the forward extraction. The highest values for the back extraction were obtained at longer contact times.

Fig. 12. Distribution Coefficient of Ru vs Function of Free TBP Concentration (Forward Extraction).

Fig. 13. Uranium-Zr-Nb Alphas vs Function of Free TBP Concentration (Forward and Back Extraction).

Figure 14 shows that the separation factors between uranium and europium are better in the presence of 1 M SO_4^{2-} . When the concentration of unreacted TBP is high, the separation factor drops rapidly; however, during most of the differential extraction the organic phase is highly loaded with uranium, leaving little free TBP.

The separation factors between ruthenium and uranium are plotted in Fig. 15. The addition of SO_4^{2-} lowers the separation factor; however, these factors remain sufficiently high under all reasonable conditions to effect good separation between uranium and ruthenium.

Stage Evaluation

The conformance of the laboratory process with the theory of differential extraction was checked for run 5. The holdup was calculated from the measured flows by Eq. (6) and found to be 0.026 liter of organic phase per liter of aqueous phase. The relationship between the uranium concentration and amount of extractant passed through the stage was calculated from Eq. (7), which is based directly on Eq. (1).

$$E = \sum_E^O \Delta E = \sum_{Y(\text{final})}^{Y(\text{initial})} \frac{S\Delta X + H\Delta Y}{Y_{\text{av}}}, \quad (7)$$

Fig. 14. Uranium-Europium Alphas vs Function of Free TBP Concentration.

Fig. 15. Uranium-Ruthenium Alphas vs Function of Free TBP Concentration.

where ΔX and ΔY are the changes in the uranium concentration in the aqueous and organic phases which result from the passage of the volume ΔE of solvent through the system. All other symbols have been defined previously.

Values of ΔY were obtained by dividing the total change in Y into arbitrary intervals. The average of the initial and final values of Y for the interval is Y_{av} . Nine intervals of 10 g/liter each, one of 6 g/liter, and one of 4 g/liter were used. Values of X corresponding to the initial and final values of Y for the interval were calculated, using a plot of the distribution coefficient as a function of the concentration of unreacted TBP. The data for this plot were obtained during laboratory run No. 5. Values of ΔE were calculated from the corresponding values of ΔX , ΔY , and Y_{av} . The total extractant, E , required to reach a given value of X or Y was the sum of the values of ΔE for all the intervals between the initial and final values of X and Y .

As seen in Fig. 16, the points representing experimental results are very close to the calculated curve for 0.026 liter of organic holdup per

Fig. 16. Removal of Uranium by Differential Extraction (Calculated Curves and Experimental Points).

liter of aqueous phase. The use of point values of X and Y obtained during the run to obtain the relationship between X and Y eliminates any effect of analytical errors or lack of equilibrium.

The three calculated curves illustrate the effect of H (the volume of extractant dispersed in the aqueous phase) on E (the total volume of extractant required). The effect of the holdup becomes greater at low uranium loading as a result of the increase in D , the uranium distribution coefficient. This is predicted from Eq. (3).

The increase in the amount of solvent required in the region of low uranium concentration is particularly undesirable. Since the distribution coefficients of fission products increase as the uranium loading decreases, the amounts of fission products carried along with the uranium are more than directly proportional to the total amount of extractant required; hence the adverse effect of an increase in H is even greater than that predicted for an ideal system by Eq. (3).

The amount of zirconium-niobium carried along with the uranium was calculated from Eq. (8),

$$Y_{Zr(av)} = \frac{X_{Zr}}{E} \sum D_{Zr} \Delta E, \quad (8)$$

where

$Y_{Zr(av)}$ = concentration of zirconium-niobium in the accumulated TBP extract phase,

X_{Zr} = zirconium-niobium concentration in the aqueous phase (it changed less than 1% during the run).

The values of ΔE are those which had been calculated from Eq. (7) in determining the amount of solvent required to remove the uranium. Values of D_{Zr} corresponding to the values of ΔE were determined from Fig. 8, using the values for the average uranium loading in the TBP (Y_{av}) which had been used to calculate the values of ΔE .

Using a starting zirconium-niobium activity of 8.20×10^5 counts $\text{min}^{-1} \text{ ml}^{-1}$, a value of $Y_{Zr(av)}$ of 5.5×10^3 counts $\text{min}^{-1} \text{ ml}^{-1}$ was calculated. The observed value was 6.4×10^3 counts $\text{min}^{-1} \text{ ml}^{-1}$. The agreement is satisfactory in view of the comparatively low level of activity in the TBP and an uncertain correction required for uranium and uranium-decay products.

PRODUCTION FLOWSHEET AND RESULTS

The conditions for the production flowsheet were chosen from the data on separation factors shown in Figs. 12, 13, and 14. The volumes and flow rates, as well as the uranium flow, are shown in Fig. 6. The composition of the phases for both cycles is also shown.

The concentration of the sulfate ion complexing agent was 1 M. Although the distribution coefficients of most of the solutes were lowered by SO_4^{2-} , the separation factor (α) was enhanced for zirconium-niobium and the rare earths. The separation factors for ruthenium were lowered but remained sufficiently high to present no difficulty. It is expected that this flowsheet will also reduce the separation of the singly and doubly charged ions; however, these ions are never a problem in uranium separation.

The decontamination factors and recovery of uranium were calculated by using Eqs. (7) and (8) and the data in Figs. 7 through 12. These calculations are summarized in Table 2. As may be seen, the decontamination factor of zirconium-niobium could have been increased by increasing the contact time in the second cycle. This would have doubled the run time, however, and actually was not necessary because of the low zirconium-niobium content of the feed (Table 3).

The decontamination factor of any of the contaminants could have been increased as required by increasing the extractant volume and recycling in the second cycle. The amount of recycling that can be tolerated has practical limits. In the flow diagram in Fig. 6 one batch of every five is a recycle batch. The composition of the original feed material is listed in Table 3. Only the major activities are shown.

The decontamination factors for the major gamma activities obtained during the production runs are listed in Table 4. No activity other than zirconium-niobium was found in the product. The decontamination factors for Cs^{137} , Ce^{144} , and Ru^{106} are minimum values calculated by assuming that all the activity in the product was attributable to them. The decontamination factor for zirconium-niobium was $\sim 1.4 \times 10^4$, and the overall factor was $\sim 1.06 \times 10^6$.

An overall recovery of uranium was 99.5%. The major loss which occurred resulted from an operational error in one of the earlier runs.

Table 2. Calculated Recovery and Decontamination Using Two Differential Stages

Element	Decontamination Factor		
	Stage 1 ^a	Stage 2 ^b	Overall
Uranium recovery	99.9%		
Uranium recycle		3.4%	
Zirconium	1.5×10^2	3.6×10^2	5.4×10^4
		4.2×10^{5c}	6.24×10^7
Europium	7.1×10^1	5.9×10^6	4.2×10^8
Ruthenium	4.6×10^2	1.4×10^{12}	6.2×10^{14}

^aContact time: 2.2 min

Aqueous phase: 75 g of U per liter, 3.64 M HNO₃, 1 M H₂SO₄

Organic phase: 30% TBP-Amsco

Conditions:

S = 6 liters (aqueous phase)

R = 160 liters/hr

F = 4.2 liters/hr

E = 8.88 liters (organic extractant).

^bContact time: 2.4 min

Aqueous phase: 3 M HNO₃, 1 M H₂SO₄

Organic phase: 30% TBP-Amsco, 50.63 g of U per liter

Conditions:

S = 8.88 liters (organic phase)

R = 222 liters/hr

F = 1.13 liters/hr

E = 1.640 liters (aqueous extractant).

^cContact time: 4.8 min

Conditions:

S = 8.88 liters

R = 111 liters/hr

F = 0.563 liter/hr.

Table 3. Composition of Feed (Major Activities)

Activity	Uranium (mc/g)
Cs ¹³⁷	132
Sr ⁸⁹	49
Sr ⁹⁰	71
Ce ¹⁴⁴	491
Pm ¹⁴⁷	265
Ru ¹⁰⁶	0.32
Zr ⁹⁵	0.33
Nb ⁹⁵	0.46

Table 4. Gamma Decontamination Factors for Production Run

Activity	Counts per Gram		D
	Starting	Final	
Cs ¹³⁷	2.9×10^{11}	Not found	$>1 \times 10^7$
Ce ¹⁴⁴	10.9×10^{11}	Not found	$>1 \times 10^7$
Ru ¹⁰⁶	6.8×10^8	Not found	$>1 \times 10^7$
Zr ⁹⁵ , Nb ⁹⁵	1.8×10^9	$\sim 1.3 \times 10^5$	$\sim 1.4 \times 10^4$
Overall	1.38×10^{11}	1.3×10^5	1.06×10^6

CONCLUSIONS

The following conclusions are made from this report.

1. Differential extraction is an effective procedure for separation of uranium from fission products.
2. The equipment is inexpensive and simple.
3. Very short contact times can be used to reduce the damage to the organic phase during the extraction.
4. Differential extraction is a useful means of accomplishing good separation when the separation factors are high.

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