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Solvent Extraction of Transuranium Elements

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Summary

Steady-state and unsteady-state digital computer programs, processed on an IBM 7072 computer, were used to obtain the concentration profiles for hydrochloric acid, curium, americium, and europium for a 16-stage liquid–liquid extraction process which is the final purification step in the production of curium 244. The equilibrium data were in the form of empirical equations which were suitable for the computer solutions.

The steady-state program, a trial-and-error procedure based on a mass balance and an equilibrium and efficiency condition written for each stage, was used to investigate the effect of changing the system variables on the separation.

The unsteady-state program is based on mass balances and an equilibrium condition for each stage and was used to obtain the unsteady-state buildup of the transuranium concentration profiles for a step change in the transuranium feed concentrations.

SOLVENT EXTRACTION OF TRANSURANIUM ELEMENTS

Emphasis on the production and purification of the transplutonium elements has been brought about because of interest in curium 244 as a long-lived heat source in space equipment. Curium 244 is produced by extended radiation of plutonium to obtain americium, which in turn converts to curium 244 (2). Tertiary amine extraction is then used to purify americium and curium from the remaining fission products, mainly europium. This investigation concerns only the purification step of the process.

The final step of the purification process is a 16-stage liquid–liquid extraction process in which curium and americium are separated from europium. The process consists of countercurrent organic and aqueous streams and an aqueous feed. The organic stream, a mixture of the tertiary amines, tri-*n*-octylamine and tri-*n*-decylamine, strips americium and curium from the aqueous feed. This mixture of tertiary amines is produced under the trade names Adogen 364 and Alamine 336 by Archer-Daniels-Midland Co. and General Mills, Inc., respectively.

In this work digital computer programs, written in Fortran language and processed on an IBM 7072 digital computer, were used to investigate the steady-state and unsteady-state concentration profiles for the process. These programs were based on a mass balance and an equilibrium and efficiency condition for each stage of the process.

PREVIOUS WORK

Treybal (5) presents the equations for countercurrent extraction with an internal feed and without reflux. The steady-state trial-and-error calculations of this work are based on these equations, written for the case of insoluble extract and raffinate. The Murphree tray efficiency written for either the raffinate or extract is also taken from Treybal.

Moore (3) has shown that the anionic species of the trivalent actinide elements are extracted preferentially from the lanthanide elements when an aqueous solution is brought into contact with a tertiary amine. The mechanism of the extraction appears to be

$$2R_3N + 2H^+ + MCl_5^{2-} = (R_3NH)_2MCl_5 \qquad (1)$$

A tertiary amine is applicable for liquid extraction since it and its metal chloride complex are essentially insoluble in aqueous solutions. Experiments by Moore (3) indicated that lithium chloride provided a source of chloride ions and the highly hydrated lithium ion reduced the concentration of free water, promoting the formation of an anionic chloro-complex species of the actinide elements. Further experiments by Moore (3) showed that addition of dilute hydrochloric acid solution to the aqueous lithium chloride solution definitely inhibited the extraction of europium, whereas it only slightly affected the extraction of americium.

An indication of the separation that can be expected was shown in

TABLE 1

Equations for Equilibrium Distributions at 25°C
(30 vol. % Adogen 364 or Alamine 336) (*4*)

Component	Equation
HCl	$E_a^0 = \exp(-7.4y_{i,\mathrm{HCl}} + 0.85L - 6.23)$
Am	$E_a^0 = \exp(-11.4y_{i,\mathrm{HCl}} + 1.97L - 18.73)$
Eu	$E_a^0 = \exp(-11.5y_{i,\mathrm{HCl}} + 1.865L - 22.115)$
Cm	$E_a^0 = \exp(-10.35y_{i,\mathrm{HCl}} + 1.675L - 15.965 - 6SL + 52S)$

a 5-stage batch countercurrent experiment by Baybarz and Weaver (*1*). In experiments in which americium 241 and europium 152 tracers were used, 99.0% of the americium 241 was extracted and 99.90% of the europium 152 rejected. This is an overall separation factor of 120.

Roth and Henry (*4*) have reported the equilibrium data, obtained from batch experiments, required for the design of this final purification process. For analytical investigations of the process, mathematical representations of the equilibrium data were made. These are shown in Table 1.

PROCESS DESCRIPTION

A flow sheet of the process is shown in Fig. 1 with relative flow rates and entering compositions. The entering concentrations of

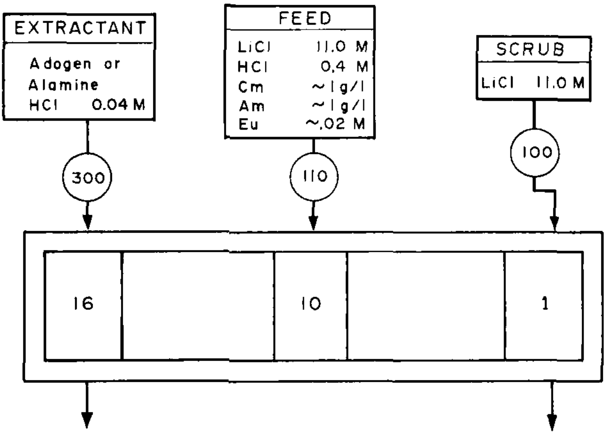

FIG. 1. Flow sheet for purification process.

the curium, americium, and europium used are 0.1846×10^{12} counts/min, 0.41×10^{9} counts/min, and 0.21×10^{8} counts/min, respectively. The curium and americium concentrations are given in α-activity counts per minute and the europium concentration is in γ-activity counts per minute. The entering feed stream and entering aqueous phase also contain a combined stannous and stannic chloride concentration of 0.033 M.

STEADY-STATE PROGRAM

The steady-state program is based on a mass balance and an equilibrium and efficiency condition written for each stage. It consists mainly of two sections—the first section for calculation of the hydrochloric acid concentration profiles and the second section for calculation of the particular transuranium concentration profile. The transuranium equilibrium expression is dependent upon the hydrochloric acid concentration at the stage of calculation.

For calculation of the hydrochloric acid, curium, and americium concentration profiles, an estimate of the exiting organic phase concentrations of each was made. The stage-by-stage calculation was then performed using these estimates. Next, the calculated entering organic phase concentration was checked against its known value to either confirm or disprove the estimate. If the initial estimate was confirmed, the calculation was complete; if the initial estimate was disproved, a new estimate was made.

The europium concentration profile was obtained in a similar manner, with an initial estimate being made for the exiting aqueous phase.

The program was written in a manner such that the concentration of the system variables could be altered to determine their effect on the concentration profiles. The program was also capable of beginning and ending the process with any stage in the top and bottom of the process, respectively. This allowed investigation of an abbreviated number of stages.

UNSTEADY-STATE PROGRAM

The unsteady-state program was written assuming that the separation was performed by a mixer–settler type of operation. It consists mainly of a mass balance about each mixer and a mass balance and equilibrium condition for each settler. The method uses known concentrations at a given time to predict concentrations at some future time.

Assuming that the flow rates and the acid concentration profiles throughout the process are at steady state, consider stage *m* in the bottom of the mixer–settler process, shown in Fig. 2(a) for time *t*.

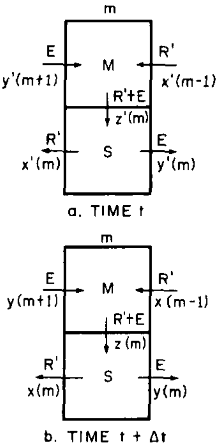

FIG. 2. Unsteady-state conditions at stage *m*.

Next, assume that each stream indicated by the arrows in Fig. 2(a) is allowed to flow at its respective flow rate and concentration for a length of time Δt. After the time t has elapsed, flow is halted, the mixer becomes well mixed, and the settler comes to equilibrium. The new concentrations for stage m at time $t + \Delta t$ are shown in Fig. 2(b).

The concentrations associated with the mixer and the settler at time $t + \Delta t$ may be calculated from the concentrations at time t. For example, a mass balance about the mixer at time $t + \Delta t$ gives

$$z(m) = FT[y'(m+1)E + x'(m-1)R']/(R'+E) + (1 - FT)z'(m) \quad (2)$$

the new well-mixed concentration in the mixer.

Therefore, if a concentration profile for some time t is known, then the concentration profile at future times $t + \Delta t$, $t + 2\Delta t$, $t + 3\Delta t$, · · · may be found.

The program was used to obtain the unsteady-state concentration buildup from zero throughout initially to the steady-state value for a step change in the feed concentration at time *t*.

DISCUSSION OF RESULTS

The steady-state results for the hydrochloric acid, curium, americium, and europium for the normal operating conditions, the conditions of Fig. 1, are shown in Figs. 3, 4, 5, and 7, respectively.

The hydrochloric acid concentration is important only as it affects the transuranium concentration profiles. The large drop in hydrochloric acid concentration across the feed stage, as shown in Fig. 3, accounts for the large change in the equilibrium distribution coefficient for the curium, americium, and europium across the feed stage, as shown in Figs. 4, 5, and 6, respectively.

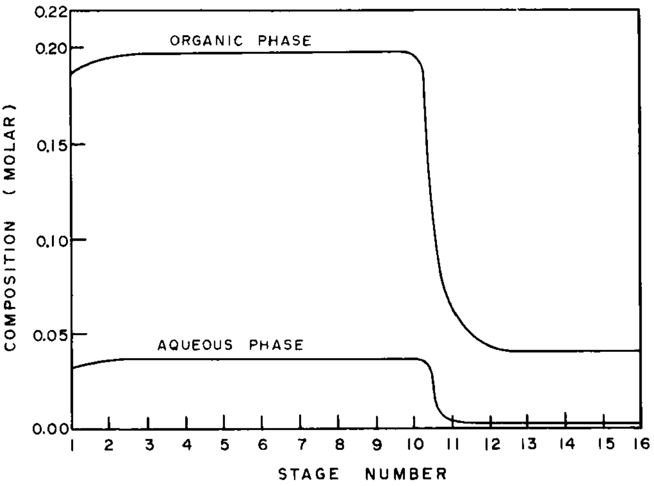

FIG. 3. Steady-state hydrochloric acid profile.

Changing the hydrochloric acid feed concentration, the aqueous lithium chloride concentration, the combined aqueous stannous and stannic chloride concentration, and the stage efficiency had negligible effect on the exiting concentration of the curium, americium, and europium, but did shift the concentration within the process.

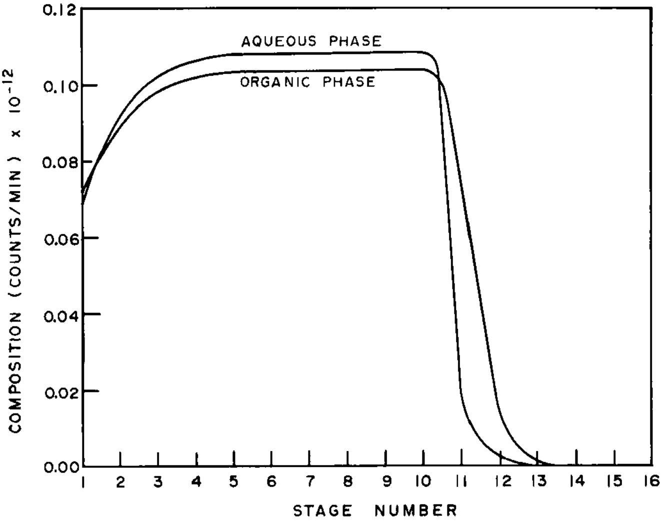

FIG. 4. Steady-state curium profile.

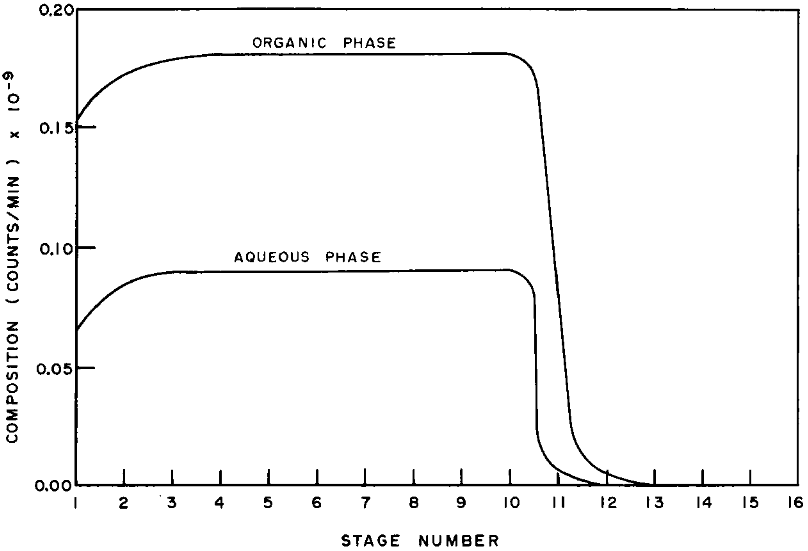

FIG. 5. Steady-state americium profile.

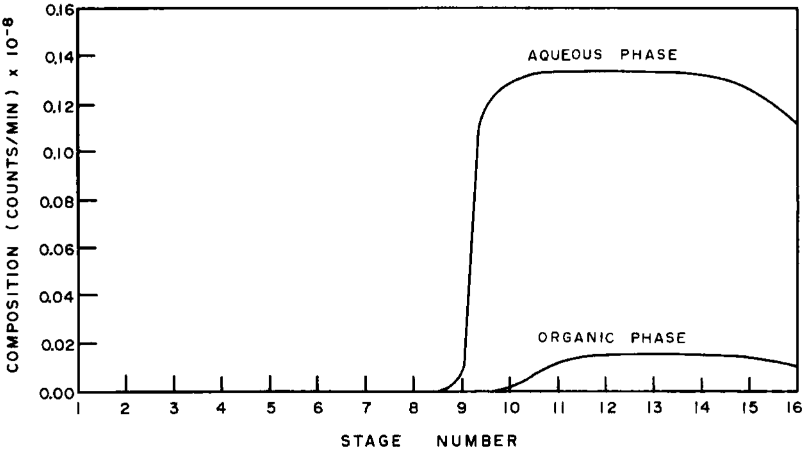

FIG. 6. Steady-state europium profile.

To determine whether all 16 stages were actually needed to effect the separation, concentration profile calculations were made for abbreviated columns. This investigation showed that removal of the first 6 stages does not significantly affect the separation.

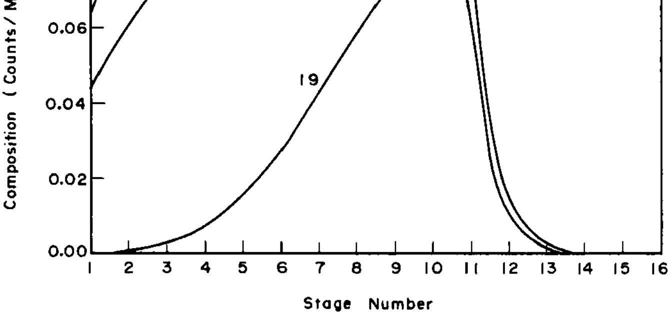

FIG. 7. Unsteady-state curium profiles for $FT = 0.50$ at total times of 19, 57, 95.

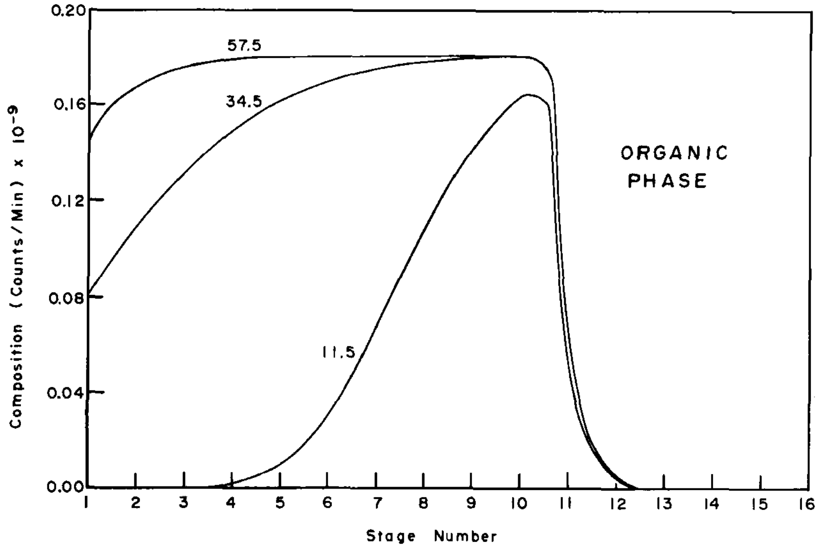

FIG. 8. Unsteady-state americium profiles for $FT = 0.50$ at total times of 11.5, 34.5, 57.5.

The unsteady-state concentration profiles were allowed to build up until approximately 95% of the exiting organic phase concentration was reached for the curium and americium and until approxi-

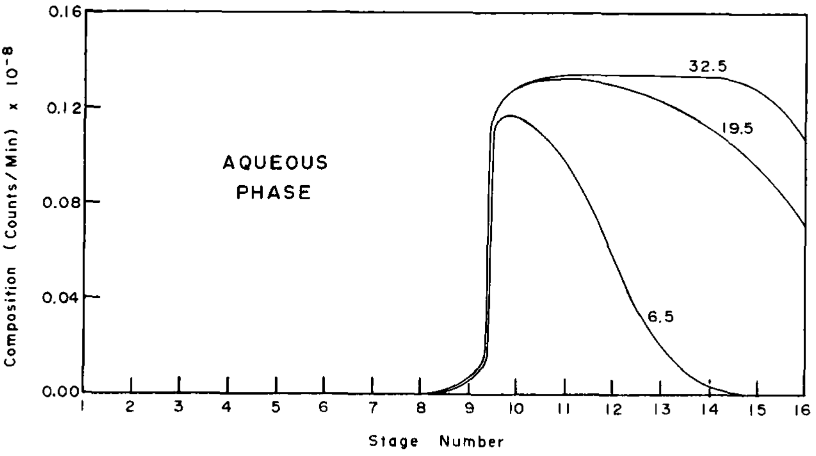

FIG. 9. Unsteady-state europium profiles for $FT = 0.50$ at total times of 6.5, 19.5, 32.5.

mately 95% of the exiting aqueous phase concentration was reached for the europium. The investigation was made for various values of *FT*. The size of *FT* did not seem to significantly affect the unsteady-state buildup. The concentration profiles for the curium, americium, and europium for $\frac{1}{5}$, $\frac{3}{5}$, and $\frac{5}{5}$ of the time required to reach approximately 95% of their steady-state exiting concentrations for $FT = 0.50$ are shown in Figs. 7, 8, and 9, respectively. From these three figures, the longest time required to reach approximately 95% of the exiting steady-state value is the 95 for the curium; therefore, all concentrations within the process should be at least 95% of their steady-state values at time equal to 95. The time here is in multiples of the holdup time *T*.

Nomenclature

E	relative organic phase flow rate throughout process
E_a^0	equilibrium distribution coefficient, $y_{i,j}/x_{i,j}$
FT	unsteady-state time increment, $\Delta t/T$
L	aqueous lithium chloride concentration (molar)
M	a trivalent actinide element
m	any stage in the bottom of the process
R'	relative aqueous phase flow rate for the bottom of the process
$R' + E$	sum of the relative organic and aqueous phase flow rates for the bottom of the process
R_3N	a tertiary amine
S	organic phase combined stannous or stannic chloride concentration (molar)
T	holdup time for any mixer or settler in the bottom of the process
$x(m)$	aqueous phase concentration for present time
$x'(m)$	aqueous phase concentration for past time
$y_{i,j}$	concentration of component *j* in the organic stream leaving stage *i*
$y(m)$	organic phase concentration for present time
$y'(m)$	organic phase concentration for past time
$z(m)$	overall concentration in the mixer at present time
$z'(m)$	overall concentration in the mixer at past time
Δt	actual unsteady-state time increment

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