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DP-1302

CURIUM PROCESS DEVELOPMENT

II-2. RECOVERY OF CURIUM AND AMERICIUM BY SOLVENT EXTRACTION WITH TERTIARY AMINES

W. E. PROUT, H. E. HENRY, H. P. HOLCOMB,
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for Plutonium and Uranium

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CURIUM PROCESS DEVELOPMENT

II-2. RECOVERY OF CURIUM AND AMERICIUM BY SOLVENT EXTRACTION WITH TERTIARY AMINES

by

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ABSTRACT

A solvent extraction process for separating and purifying kilogram quantities of curium and americium from irradiated plutonium-aluminum alloy targets was adapted and demonstrated. The process was tested extensively in miniature solvent extraction equipment to obtain design data for a large pilot production facility that was installed and operated in shielded caves at Savannah River Laboratory. The process (Tramex) employs three cycles of solvent extraction with 30% tertiary amines in diethylbenzene.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying curium-244 produced in Savannah River reactors. The series is being issued under the general title, *Curium Process Development*. Following the general title, a Roman numeral designates the subject area of the report, and an Arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report.

Subject areas in this series are:

I. Chemical Process Description
II. Chemical Processing Steps
III. Analytical Chemistry Support
IV. Equipment Development and Testing

Reports issued in this series include:

I. *General Process Description* by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009)

II-1. *Separation of Americium from Curium by Precipitation of* $K_3AmO_2(CO_3)_2$ by G. A. Burney (USAEC Report DP-1109)

III-1. *Analytical Techniques for Characterizing Solvent* by R. Narvaez (USAEC Report DP-1010)

III-2. *Identification of Solvent Degradation Products* by D. L. West and R. Narvaez (USAEC Report DP-1016)

III-3. *Analytical Control* by E. K. Dukes (USAEC Report DP-1039)

III-4. *Evaluation of Potential Hazards from Chlorination of Amines and Ammonia* by D. L. West, M. L. Hyder, G. A. Burney, and W. E. Prout (USAEC Report DP-1142)

III-5. *Qualitative Determination of DEB in Air* by B. Tiffany (USAEC Report DP-1230)

III-6. *Characterization of Emulsions Formed in Curium Solvent Extraction* by D. A. Brown and A. L. Marston (USAEC Report DP-1215)

IV. *Equipment Development and Testing* by A. A. Kishbaugh, H. Bull, G. W. Gibson, and L. F. Landon (USAEC Report DP-1146)

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INTRODUCTION

A program was undertaken at Savannah River to produce and purify several kilograms of ^{244}Cm for evaluation as a radioisotopic heat source.[1] The sequence of nuclear reactions to produce ^{244}Cm is shown in Figure 1; the irradiation stages for production of ^{244}Cm are depicted graphically in Figure 2. The general chemical processing scheme was described in the first report of this series (DP-1009).

In the first-stage irradiation, ^{239}Pu either fissions or captures neutrons to produce heavier actinide isotopes. The mixture of plutonium isotopes was separated from rare earth fission products, purified, and fabricated into targets for a second irradiation, in which a portion of the plutonium isotopes was converted to ^{242}Pu, ^{243}Am, ^{244}Cm, and heavier nuclides.

Plutonium targets from the second irradiation were dissolved in nitric acid,[2] and the plutonium was recovered and purified by solvent extraction with 3.5 vol % tributyl phosphate (TBP) in kerosene.[3] Aluminum, trivalent actinides, and fission products remain in the aqueous waste stream. The trivalent actinides and lanthanides were separated from aluminum and the non-actinide fission products by batch extraction with 50 vol % TBP in kerosene[4] in the Savannah River separations facilities.

This report describes the adapting and testing of a solvent extraction process for the separation and purification of americium and curium from the actinide-lanthanide concentrate from batch solvent extraction. As shown in Figure 3, the tertiary amine solvent extraction process, which was conceived at Oak Ridge National Laboratory,[5,6] consists of three cycles of solvent extraction with a mixture of n-octyl and n-decyl tertiary amines in diethylbenzene. The first amine extraction converts the nitrate solution from the separations plant to a chloride system[7] suitable for rejection of lanthanide fission products in the two following solvent extraction cycles. Californium is separated in the second cycle. The third cycle is included to provide additional decontamination of americium and curium from ^{144}Ce and other lanthanide fission products.

This solvent extraction process was subsequently applied in a large pilot production facility to purify ∿1.5 kg of ^{244}Cm and ∿0.7 kg ^{243}Am. The ^{244}Cm produced met the radioactive purity specifications given in the initial report of this series (DP-1009). Although product quality was good, the rate of production was slow. The exacting analysis requirements for process control, and maintenance problems caused by the high concentrations of chloride in the extraction system made continuous multicycle operation impractical.

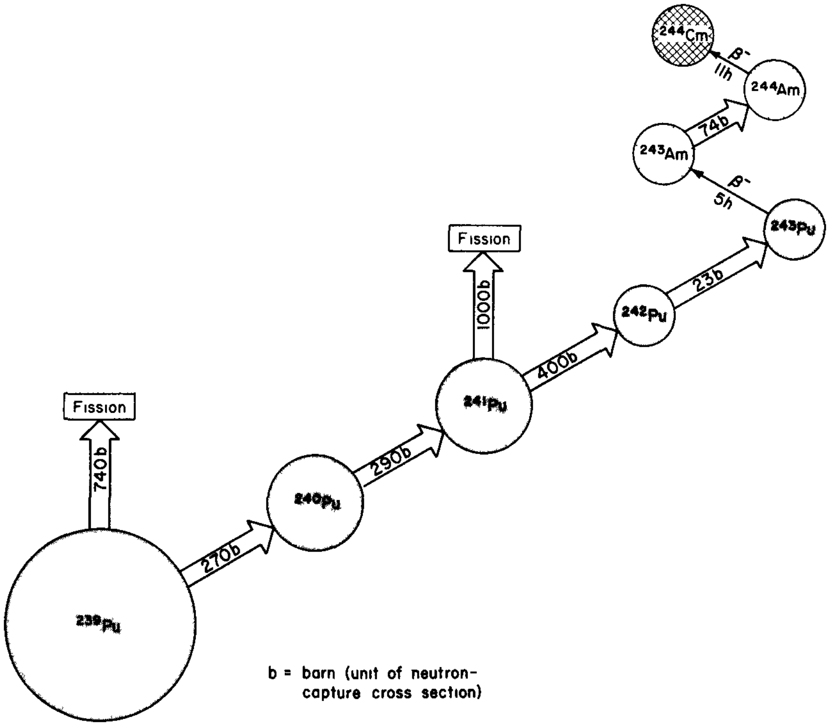


FIGURE 1. Production of ^{244}Cm by Successive Neutron Captures

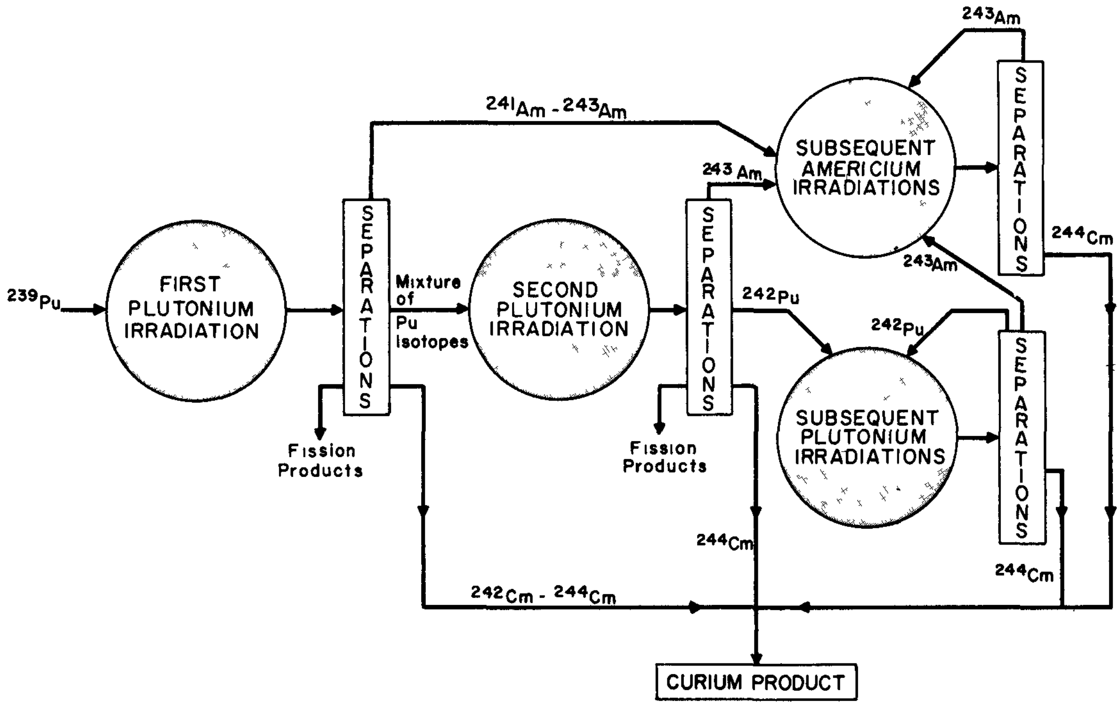
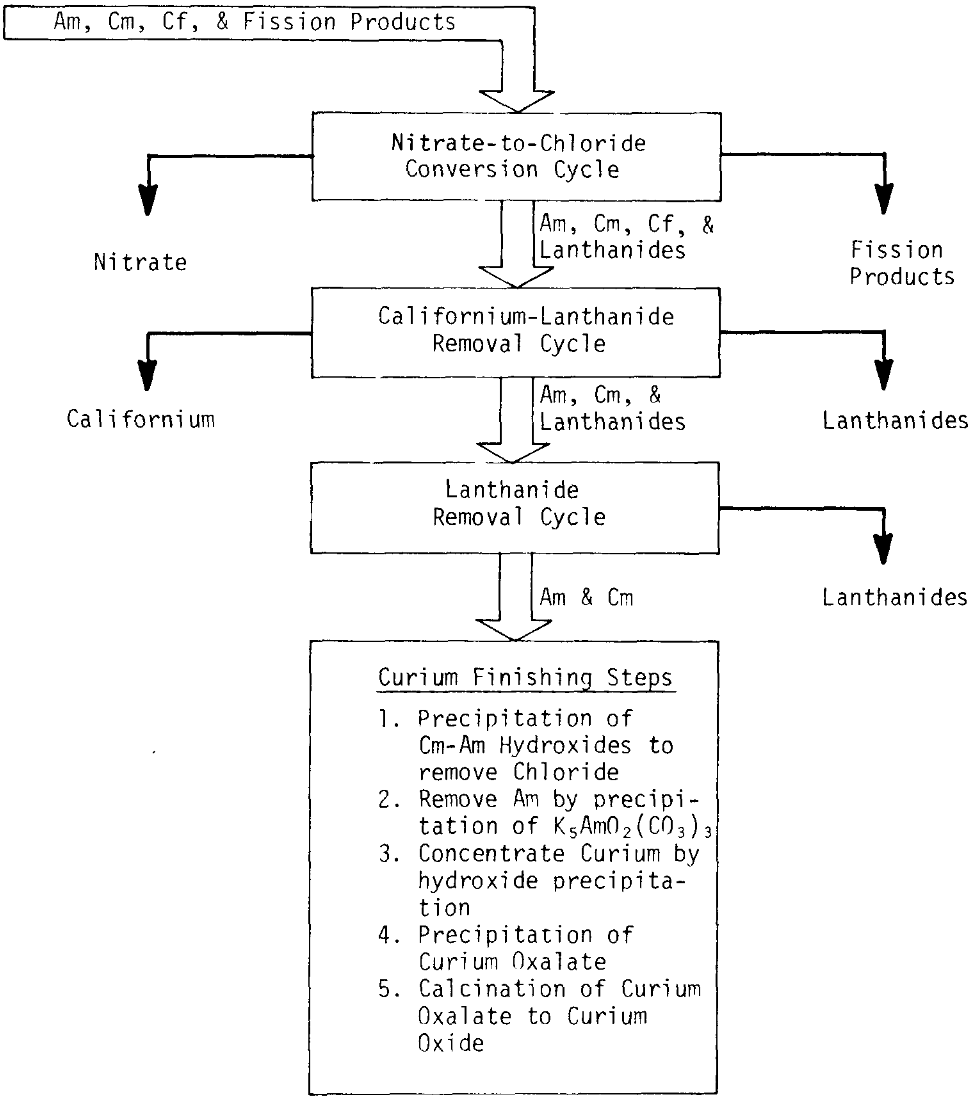


FIGURE 2. Curium Production Program



Curium Finishing Steps

1. Precipitation of Cm-Am Hydroxides to remove Chloride
2. Remove Am by precipitation of $K_5AmO_2(CO_3)_3$
3. Concentrate Curium by hydroxide precipitation
4. Precipitation of Curium Oxalate
5. Calcination of Curium Oxalate to Curium Oxide

FIGURE 3. Processing Steps to Purify Curium

SUMMARY

A solvent extraction process was adapted and demonstrated for the separation and purification of mixed curium-americium and californium produced from ^{239}Pu in successive reactor irradiations at Savannah River. The process uses three cycles of solvent extraction with a mixture of tertiary amines in diethylbenzene.

In the development program, all process steps were satisfactorily demonstrated in laboratory test facilities with miniature mixer-settlers. In the first cycle, the recovery efficiency for curium, americium, and californium was >99%; >99.9% of the ruthenium and cerium was rejected. In the second cycle, americium, curium, and californium recoveries were 98, 98, and 90% respectively, and >99.8% of the lanthanides and >99% of the remaining ruthenium and zirconium-niobium were rejected. In the third cycle, americium and curium recovery efficiency was >99%. Rejection of ^{144}Ce and ^{154}Eu across the three solvent cycles was >99.99%.

In pilot tests with miniature solvent extraction equipment, the high levels of radiation in chloride process solutions generated hypochlorous acid and caused oxidation of cerium to Ce(IV), which is not separated from Am-Cm in the second and third extraction cycles. The addition of Sn(II) to the feed solution or 2,5-ditertiarybutylhydroquinone to the tertiary amine extractant reduced the cerium to Ce(III) without adversely affecting the overall process. Also, the degradation of the tertiary amine - diethylbenzene solvent was studied; process performance did not deteriorate when the solvent was recycled ten times in each cycle.

DESCRIPTION OF FEED

In Savannah River separations facilities, irradiated Al-Pu alloy target elements were dissolved in nitric acid; the plutonium was separated and purified by countercurrent solvent extraction with 3.5 vol % tributyl phosphate (TBP) in kerosene, and a transplutonium actinide-lanthanide concentrate was isolated from the plutonium-recovery waste raffinate by batch extraction with 50 vol % TBP and evaporation. The composition of this actinide-lanthanide concentrate is given in Table I.

TABLE I

Composition of Actinide-Lanthanide Concentrate

	Concentration		Concentration
^{244}Cm	2 g/ℓ	^{154}Eu	$\sim$0.6 Ci/ℓ
^{243}Am	$\sim$0.9 g/ℓ	Total heat	$\sim$9 w/ℓ
^{252}Cf/^{244}Cm	$\sim 2 \times 10^{-6}$	HNO_3	$\sim$0.4M
Lanthanides	$\sim$8 g/ℓ	Al^{3+}	$\sim$1.4M
^{144}Ce-^{144}Pr	500 Ci/ℓ	Fe^{3+}	$\sim$0.16M
^{106}Ru-^{106}Rh	220 Ci/ℓ	Hg^{2+}	$\sim$0.12M
^{95}Zr-^{95}Nb	$\sim$2 Ci/ℓ	Total NO_3^-	$\sim$6M
^{110}Ag	$\sim$0.2 Ci/ℓ	SO_4^{2-}	$\leqslant$0.04M
^{137}Cs	$\sim$0.6 Ci/ℓ	PO_4^{3-}	$\leqslant$0.01M

Decontamination factors required for adequate purification from the limiting gamma-emitting fission products and from ^{252}Cf are summarized in Table II.

TABLE II

Decontamination Requirements for Curium for Isotopic Power Sources

Isotope	Feed Concentration, Ci/g ^{244}Cm	Product Concentration, Ci/g ^{244}Cm	Decontamination Factor
^{106}Ru-^{106}Rh	110	8×10^{-4}	1.4×10^{5}
^{144}Ce-^{144}Pr	250	2×10^{-3}	1.3×10^{5}
^{95}Zr-^{95}Nb	1	3×10^{-5}	3.3×10^{4}
^{154}Eu	0.3	1×10^{-5}	3.0×10^{4}
^{252}Cf	2×10^{-6} [a]	5.0×10^{-7} [a]	4

---

[a] g ^{252}Cf/g ^{244}Cm

Limits for nonradioactive impurities in the curium oxide product used for heat sources are summarized in Table III. Limits for nonradioactive impurities in the curium and americium oxide product for reactor target fabrication are shown in Table IV. These impurity limits are considered acceptable as to their effect on the fabrication and melting limits of the targets.

TABLE III

Maximum Impurity Limits for Heat Source Curium Oxide

Impurities	Concentration, wt % curium
Li, Na, K (Total)	0.1
Si, Zn (Total)	0.1
Fe, Cr, Ni (Total)	0.2
Any other single impurity, except Am and Zr	0.2
Total of all impurities, except Am and Zr	1.0
Including Am and Zr	3.0

TABLE IV

Maximum Impurity Limits for Am and Cm Oxide Mixture for Target Fabrication

Impurities	Concentration, wt % Am-Cm oxide
Li, Na, K (Total)	0.1
Si	0.05
Zn	3.0
Fe, Cr, Ni (Total)	0.2
Ta	0.4
Any other single impurity, except Zr	0.2
Total of all impurities, except Zn and Zr	1.0
Zr	5.0
Total of all impurities	7.0

NITRATE-TO-CHLORIDE CONVERSION CYCLE

Principal steps in the nitrate-to-chloride conversion cycle (Figure 4) are:

- *Feed Adjustment* consisting of evaporation to remove excess water, steam stripping if nitric acid must be removed, and addition of aluminum if insufficient is present.

- *Solvent Extraction* in two 16-stage, center-fed mixer-settlers. In the first mixer-settler (1A Bank), the actinides and lanthanides are coextracted with 30 vol % tertiary amine nitrates in diethylbenzene, and the organic phase is scrubbed with 7M lithium nitrate-1M lithium chloride solution. In the second mixer-settler (1B Bank), the actinides and lanthanides are selectively backextracted with 8M HCl and scrubbed with neutral 30% tertiary amines in diethylbenzene to remove entrained or residual nitrate. The nitrate ion remains in the spent solvent.

- *Solvent Washing* in three single-stage mixer-settlers. The spent solvent is washed consecutively with 1) water to remove some HCl, plutonium, and zirconium; 2) potassium carbonate-ethylenediaminetetraacetic acid (EDTA) to neutralize the acid in the solvent and to remove chloride, nitrate, iron, mercury, ruthenium, and the remaining zirconium; and 3) nitric acid to convert the tertiary amine to the nitrate form before recycle to the 1A Bank.

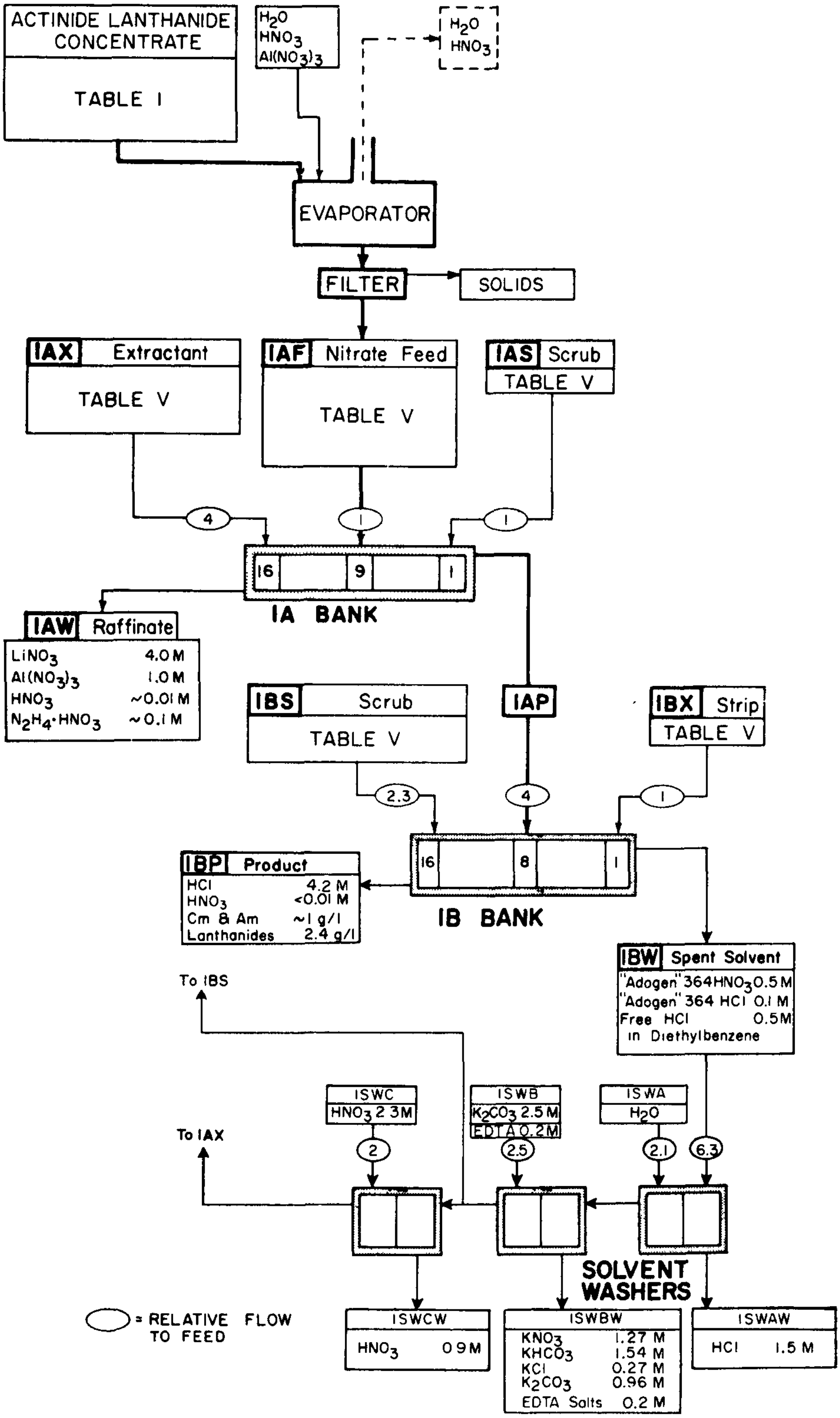


FIGURE 4. Nitrate-to-Chloride Conversion Cycle

FEED ADJUSTMENT

In feed adjustment, the actinide-lanthanide concentrate (Table I) from the separations plant is adjusted to meet feed (1AF) requirements for solvent extraction (Table V). The feed is adjusted by evaporation (to remove excess water) and steam stripping (to remove HNO_3). Aluminum nitrate could be added if an insufficient amount were present in the actinide-lanthanide concentrate. The limits necessary for safe evaporation and steam stripping of solutions that had been in contact with tributyl phosphate are: 1) $\leqslant 0.5$ wt % organic in the evaporator feed,[8] and 2) boiling temperature $\leqslant 125$°C.[9] Before attempting to transfer the adjusted solution through process piping, precautions must be taken to ensure that the freezing temperature of the solution (Figure 5) is below the ambient temperature, and to ensure that the solution is not acid-deficient (to prevent precipitation of metal hydroxides). The evaporator product solution is filtered; any solids should be determined to be free of curium before discarding.

For effective steam stripping, the $Al(NO_3)_3$ concentration was increased to $\sim$40 wt %, and the excess HNO_3 was removed by adding water at a rate equal to the boil-off rate. The necessity to concentrate before steam stripping is illustrated by the vapor-liquid equilibria in Figure 6. Below $\sim$40 wt % $Al(NO_3)_3$, the relative volatility of HNO_3 is too low; above $\sim$40 wt % $Al(NO_3)_3$, the relative volatility of HNO_3 is greater than unity, and the HNO_3 concentration in the condensate is greater than the concentration in the bottoms. Compositions during a typical evaporator-stripping sequence (calculated assuming no reflux of condensate and using the equilibria of Figure 6 and solution density data of Figure 7) are summarized in Figure 8. Evaporation of 1 lb of a typical evaporator feed to 0.525 lb, followed by steam stripping at 40 wt % $Al(NO_3)_3$ with 0.9 lb water will produce a solution, 2.6M $Al(NO_3)_3$ and <0.6M HNO_3, which can be diluted to the approximate limits for solvent extraction. Boiling point and specific gravity data, summarized in Figures 7 and 9, were used to monitor the course of the evaporation.

Reflux of condensate must be minimized to prevent excessive evaporation requirements. Refluxed condensate absorbs HNO_3 from vapor and returns it to the evaporator bottoms where the HNO_3 must be revolatilized by additional stripping. Laboratory studies showed that reflux must be <4% to prevent increasing the evaporation requirement >40%.

TABLE V

Nitrate-to-Chloride Conversion Cycle Operating Limits
(Cocurrent efficiency of mixer-settlers >80%)

Variables	Limits		
	Nominal	Minimum	Maximum
1. Temperature, °C	Ambient	-	50.
2. Flow rates (relative to 1AF=1)			
a. 1AX	4.0	3.6	4.4
b. 1AS	1.0	0.9	1.1
c. 1BS	2.3	2.0	2.6
d. 1BX	1.0	0.9	1.1
e. 1SWA	2.1	1.3	-
f. 1SWB	2.5	2.3	-
g. 1SWC	2.0	1.9	2.1
3. 1AF composition			
a. $Al(NO_3)_3$, M	2.0	1.8	[c]
b. HNO_3, M[e]	0.25	0.1	0.4
c. Sodium, M	-	-	[c]
d. Iron, M	-	-	0.20
e. Curium, g/ℓ[h]	1	-	2.8
f. Lanthanides, M	0.08	-	0.20[g]
g. Mercury, M	0.06	-	0.10
4. 1AX composition			
a. "Adogen" 364•HNO_3, M	0.61	0.59	0.63
b. Free HNO_3, M[e]	0.1	0.01[d]	0.2
5. 1AS composition[h]			
a. Lithium nitrate, M	7.0	6.8	7.2
b. Hydrazine nitrate, M	0.2	-	-
c. Lithium chloride, M[d]	1.0	0.75	1.25
6. 1BS composition			
a. "Adogen" 364, M	0.61	0.59	0.63
7. 1BX composition			
a. HCl, M	8.0	7.5[f]	8.5
8. 1SWA composition			
a. H_2O	-	-	-
9. 1SWB composition[h]			
a. K_2CO_3, M	2.5	2.4	2.6
b. EDTA, M[g]	0.2	0.18	0.22
10. 1SWC composition			
a. HNO_3, M	2.3	1.75	3.25
11. Entrainment			
a. 1A Bank			
1. Aqueous/organic, %	0.4	-	1.0
2. Organic/aqueous, %	1.0	-	1.0
b. 1B Bank			
1. Aqueous/organic, %	<0.1	-	3.0
2. Organic/aqueous, %	0.1	-	1.0
c. Solvent washer A[a]			
1. Aqueous/organic, %	0.2	-	3.0
2. Organic/aqueous, %	0.1	-	1.0
d. Solvent washer B[a]			
1. Aqueous/organic, %	0.2	-	1.0
2. Organic/aqueous, %	0.1	-	1.0
e. Solvent washer C[b]			
1. Aqueous/organic, %	0.4	-	1.0
2. Organic/aqueous, %	0.1	-	1.0

---

[a] Organic flow through solvent washers A and B can vary ±20%.

[b] Organic flow through solvent washer C can vary ±10%.

[c] See Figure 10

[d] Prevent precipitation of mercury with hydrazine

[e] See Figure 11

[f] Reference 10

[g] Tetrasodium salt

[h] For curium concentration of >1 g/ℓ, the LiCl in the 1AS and the EDTA in the 1SWB should be increased proportionately so that the sum of the molar concentrations of LiCl and $LiNO_3$ in the 1AS total 8.

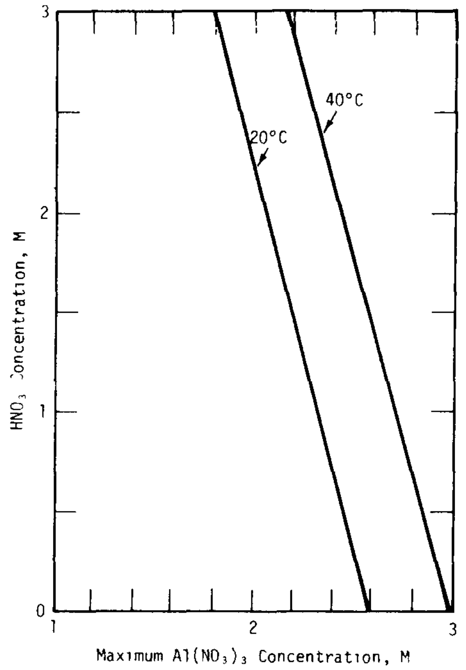


FIGURE 5. Solubility of $Al(NO_3)_3$ in Solutions of HNO_3

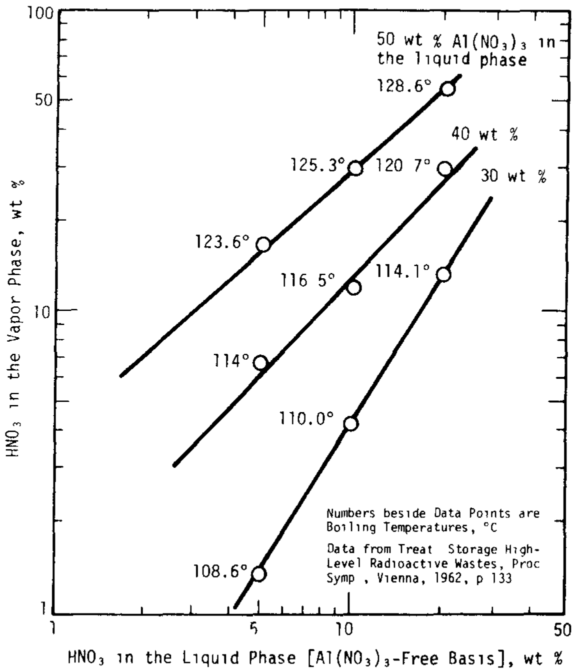


FIGURE 6. Vapor-Liquid Equilibria of HNO_3 from $Al(NO_3)_3$ Solutions

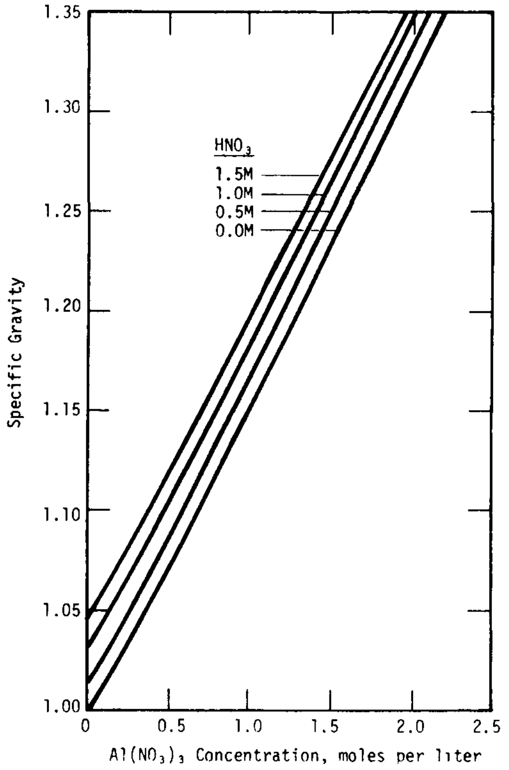


FIGURE 7. Specific Gravity of Al(NO$_3$)$_3$-HNO$_3$ Solutions

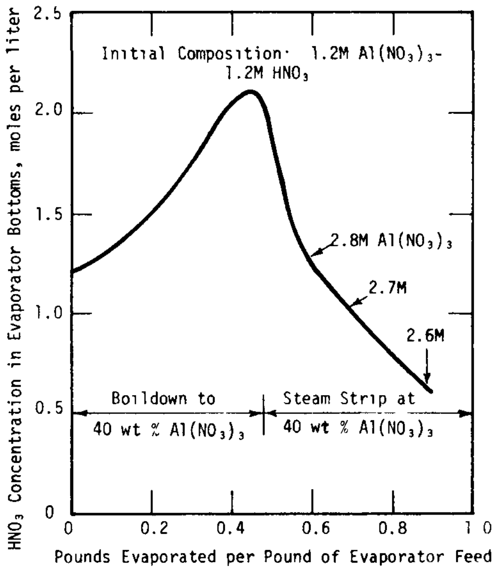


FIGURE 8. Solution Composition During Evaporation

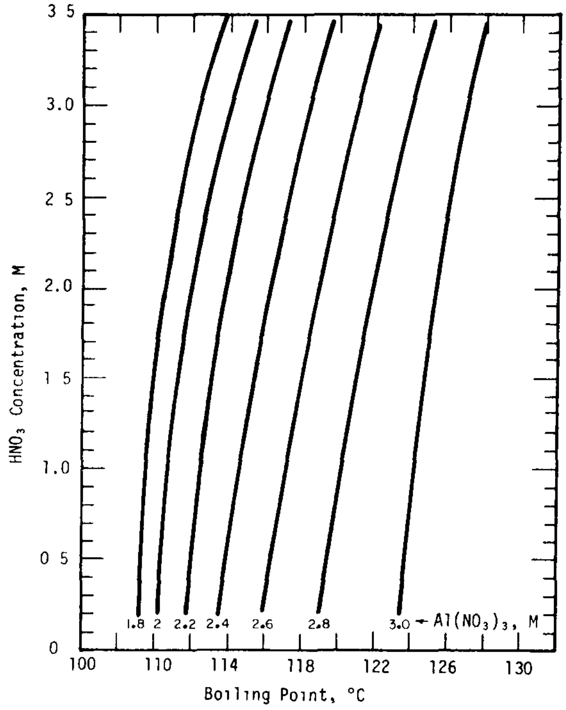


FIGURE 9. Boiling Points of $Al(NO_3)_3$-HNO_3 Solutions

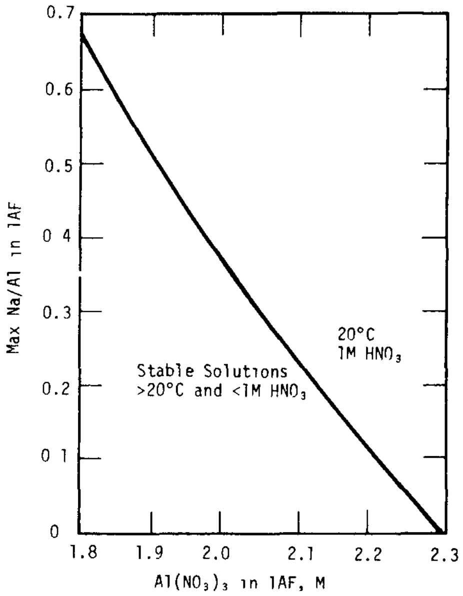


FIGURE 10. $Al(NO_3)_3$ in 1AF

SOLVENT EXTRACTION AND SOLVENT WASHING

The trivalent actinides and lanthanides (along with other actinides, >90% of the ruthenium, and ∿10% of the zirconium) are coextracted with 0.61M (30 vol %) tertiary amine nitrates in diethylbenzene (1AX), and scrubbed with 7M $LiNO_3$ - 1M LiCl - 0.2M hydrazine solution (1AS) in the 1A Bank. The actinides and lanthanides are selectively back-extracted into 8M HCl (1BX) in the 1B Bank and scrubbed with 0.61M neutral tertiary amines in diethylbenzene (1BS). Zirconium, ruthenium, plutonium, iron, mercury, and nitrate ion remain in the spent solvent (1BW). Before recycle to the mixer-settlers, the solvent is washed consecutively with:

- Water to remove HCl, plutonium, and zirconium.
- Potassium carbonate - EDTA to neutralize the acid in the solvent and to remove chloride, nitrate, iron, mercury, and the remaining zirconium. Neutral solvent is recycled as 1BS.
- Nitric acid to reconvert the amine to the nitrate form before recycle as 1AX.

Potassium carbonate is used in the washer because the potassium hydrogen carbonate ($KHCO_3$) in the spent wash is much more soluble than the corresponding sodium salt. With K_2CO_3, solvent containing 0.01M iron and 0.01M zirconium can be washed without forming precipitates; however, 25% of the mercury is retained by with the solvent. With EDTA (tetrasodium salt of ethylenediaminetetraacetic acid), all of the iron and mercury is removed from the solvent without forming solids.

Hydrazine is used in the scrub stream (1AS) to the 1A Bank to decrease degradation of diethylbenzene. With 0.2M hydrazine in the 1AS, only about 0.1% of the diethylbenzene is destroyed per exposure hour (∿0.05% per cycle of use). Also, a more effective separation from ruthenium is obtained with hydrazine (but no LiCl) in the scrub; without hydrazine the decontamination factor was ∿500, and ∿7% of the ruthenium in the feed (1AF) was retained by the recycled solvent. With hydrazine, the decontamination factor was >1000, and only ∿0.7% of the ruthenium was retained by the solvent. LiCl is used in the 1AS to prevent iron hydroxide from precipitating in the low-acid extraction section and to prevent mercury from precipitating as a hydrazine addition compound in the scrub section of the 1A Bank.

The 1AW stream contains hydrazine, and both the 1AW stream and the K_2CO_3 washer waste may contain hydrazoic acid, an explosive compound when concentrated either as vapor or in acid solutions.[11] Although the concentration of hydrazine is below hazardous limits, precautions must be taken to ensure that hydrazoic acid does not accumulate. To prevent its accumulation, hydrazine or HN_3 solutions must either be neutralized and sent directly to waste storage without evaporation, or be treated in acid solution with excess nitrous acid to destroy hydrazine and hydrazoic acid completely before evaporation.

Three streams (1AW, 1BP, and the aqueous waste from the first solvent washer) may require recycling. They are recycled as follows:

- 1AW is recycled as 1AF after adjustment (without evaporation). The concentration of $LiNO_3$ is equivalent to 1/3 its concentration of $Al(NO_3)_3$ for purposes of the limits in Table V.
- 1BP containing >0.01M NO_3^- and no metal cations in significant concentration (other than actinides and lanthanides) is recycled to the center of the 1B Bank as an aqueous feed (1BF); the rate should not exceed ∿50% of the 1BX rate, and the total nitrate molar addition rate in recycle should not exceed 10% of the amine addition rate via the 1BS stream.
- Aqueous waste from the first solvent washer is adjusted to ∿5M HCl and recycled to the center of the 1B Bank; or if low in nitrate, it can be combined with the product stream (1BP). If recycled to the center of the 1B Bank, the rates should be limited by the same criteria as for recycle 1BP.

OPERATING CONDITIONS

Operating conditions and corresponding limits for the nitrate-to-chloride conversion cycle are summarized in Table V. These limits were calculated from distribution data to provide satisfactory process performance when all variables are simultaneously at their most adverse limits. The limits that are interdependent, and the criteria used to establish numerical values for each are summarized in Table VI.

TABLE VI

Criteria for Establishing Numerical Limits in Table V

Limit of Variable in Table V	Interrelated Variables and Limits (See Table V)		Bases for Establishing Numerical Value of Limit
	Variables at Their Minima	Variables at Their Maxima	
Temperature			
Maximum	-	-	*a*
Flow Rates			
1AX			
Minimum	3a,4a,5a	2b,2g,3b,3c,3f,4b,10a,11e1	*b*
Maximum	2c,6a	-	*c*
1BS			
Minimum	6a	2a,3b,3f,4b,5a,11a1	*c*
Maximum	-	2a	*d*
1SWA			
Minimum	9a,2f	2a,2c,7a,11b1	*e*
1SWB			
Minimum	9a	2a,2c,3b,3f,4a,4b,5a,7a, 11a1,11b1,11c1	*f*
1SWC			
Minimum	-	2a,4a,4b,11d1	*g*,*h*
Maximum	2a,4a,4b	11e1	*g*,*h*
1AS and 1BX			
Minimum Maximum	-	-	*i*
Compositions			
1AF			
Minimum	2a,4a,5a	2b	*b*
Maximum	2a,2c,4a,4b	4b	*b*,*j*
1AX			
Minimum	3a	3c,3d,10a	*b*,*k*
Maximum	2c,10a	3b	*b*,*j*
1BS			
Minimum	-	2a,3b,3f,4b,5a,11a1	*c*
Maximum	-	-	*i*
1SWB			
Minimum	2f,2e	2a,2c,11c1	*f*
Maximum	-	-	*i*
1SWC			
Minimum	4b,2g	9a,11d1,2a,3d	*l*
Maximum	2a	4b,2g	*l*
1AX and 1BX			
Minimum Maximum	-	-	*i*

---

a. Flashpoint of diethylbenzene

b. Extraction factor for curium ≥ 1 in 1A Bank

c. Total amine $\geqslant$ total nitrate in 1B Bank

d. Organic-to-aqueous ratio in 1B Bank $\leqslant 7$

e. Minimize K_2CO_3 in 1SWB

f. Neutralization of all the acid in the spent solvent

g. Convert neutralized solvent to amine nitrate

h. Adjust free HNO_3 content of solvent to give extraction factor for curium ≥ 1 in 1A Bank

i. Operating experience

j. Total nitrate $\leqslant$ total amine in 1B Bank

k. Prevent precipitation of iron in 1A Bank

l. Necessary to meet 1AX composition limits for free HNO_3

DESIGN DATA

The basic operating conditions for the nitrate-to-chloride conversion cycle were designed to obtain a curium yield of greater than 99.9% with decontamination factors of >1000 for removal of zirconium and ruthenium. In addition, the concentration of nitrate in the curium product stream (1BP) was not to exceed 0.01M since the presence of nitrate ion in the curium feeds to the succeeding solvent extraction cycles interferes with the separation of actinides from lanthanides.

The most significant extraction reactions that occur in the nitrate-to-chloride conversion cycle can be represented by the following concepts:

- Formation and decomposition of amine nitrate in the solvent washers

$$R_3N + HNO_3 \rightleftarrows R_3N{\bullet}HNO_3$$

$$R_3N{\bullet}HNO_3 + K_2CO_3 \rightleftarrows R_3N + KHCO_3 + KNO_3$$

- Polymerization of amine nitrates

$$p\ R_3N{\bullet}HNO_3 \rightleftarrows (R_3N{\bullet}HNO_3)_p{\bullet}HNO_3,\ p = 2,3,\text{---}$$

- Formation of extractable nitrate complexes

$$M(NO_3)_{x-1}^{\,3-(x-1)} + NO_3^- \rightleftarrows M(NO_3)_x^{\,3-x}\ ,\ x \geqslant 1$$

- Extraction of complexes by amine nitrate extraction in 1A mixer-settler

$$M(NO_3)_{\bar{x}}^{\,3-\bar{x}} + (\bar{x}-3)H^+ + y\ R_3N{\bullet}HNO_3 \rightleftarrows M(NO_3)_3(R_3N)_y$$

$$\bullet\ (HNO_3)_{y-z+\bar{x}-3} + 3HNO_3$$

- Stripping of extracted nitrate complexes into HCl, and simultaneously exchanging chloride for nitrate in the amine salt

$$M(NO_3)_3(R_3N)_y(HNO_3)_{y-z+\bar{x}-3} + (\bar{x}+z)\ R_3N{\bullet}HCl$$

$$+ (3+z-\bar{x})\ HCL \overset{HCl}{\rightleftarrows} M^{3+} + 3Cl^- + (y+\bar{x}-z)R_3N{\bullet}HNO_3$$

where

$\bar{x}$ = the average stoichiometry of the extracted nitrate complexes

y = the combining ratio of the metal complexes with amines

z = the stoichiometry of the anion exchange reaction

Although the numerical values of $\bar{x}$, y, and z have not been determined, the empirical data presented below along with these extraction concepts were used in specifying design data.

Distribution Coefficients

In the nitrate-to-chloride conversion cycle, a mixture of n-octyl and n-decyl tertiary amine nitrates in diethylbenzene extracts curium and cerium from an aqueous solution of lithium nitrate, aluminum nitrate, and hydrazine. Nitric acid is also extracted, but lithium, aluminum, and hydrazine are not. Distribution coefficients of cerium, curium, and nitric acid depend on the concentration of lithium, aluminum, and hydrazine in the aqueous phase. The analytical expressions that relate distribution coefficients to concentrations are given in Table VII. These expressions were obtained by a least squares fit of distribution data determined experimentally at this and other laboratories.[12,13]

TABLE VII

Equations for Distribution Coefficients in the Nitrate-to-Chloride Conversion Cycle

(Organic phase: 30% tertiary amine nitrate in DEB)

Nitric Acid

$$D_a^o = \exp\,[-0.239 - 7.07(H_O) + 0.517(NO_3^-) - 1.06(Al) - 15.4(Ce_O) - 3.26(N_2H_4) + 3.27(H_O)(Al)]$$

Curium

$$D_a^o = \exp\,[-4.41 - 16.4(H_O) - 37.9(Ce_O) + 1.29(NO_3^-)]$$

Cerium (Aqueous phase: 8M $LiNO_3$)

$$D_a^o = \exp\,[+7.55 - 14.1(H_O) - 46.9(Ce_O)]$$

where

D_a^o = the distribution coefficient

H_O = the "free" nitric acid molarity in the organic phase

NO_3^- = the nitrate molarity in the aqueous phase (excluding HNO_3)

Al = the aluminum molarity in the aqueous phase

Ce_O = the cerium molarity in the organic phase

N_2H_4 = the hydrazine molarity in the aqueous phase

Flowsheet Design

A wide range of flowsheet conditions including variations of aqueous and organic feed rates and compositions, and mass transfer efficiencies were evaluated using steady-state calculations.[14] Combinations of flowsheet conditions that yield acceptable process performance of the 1A Bank are illustrated in Table V and Figures 11 and 12. The maximum allowable concentrations of iron, lanthanides, and nitric acid in $Al(NO_3)_3$ - HNO_3 feeds are interrelated and also depend on the concentration of excess HNO_3 in the solvent (1AX) fed to the 1A Bank as shown in Figure 13. The interrelations of Figure 13 also apply to feeds that contain $NaNO_3$, if the HNO_3 in the 1AX is decreased by 0.027M per mole of Na^+ in the feed (1AF). Sodium has the net effect of decreasing the allowable concentrations of lanthanides in the feed. The detrimental effect of each 1M Na^+ in the feed can be compensated by decreasing the acid in the 1AX by 0.02M.

Iron(III) is not extracted in the 1A Bank under normal conditions. However, at high concentrations of iron in the feed (1AF), the acidity of the solvent (1AX) must be sufficiently high to prevent the precipitation of iron hydroxide in the low-acid extraction section of the 1A Bank. Excessive concentrations of nitric acid in the 1AX must be avoided, however, to prevent reflux of curium in the scrub section and curium loss to the waste raffinate (1AW) as shown in Figure 13.

To avoid precipitation of mercury-hydrazine addition compound and iron hydroxide in the 1A Bank, lithium chloride can be added to the lithium nitrate-hydrazine scrub solution (1AS). When iron(III) and mercury(II) are complexed by the chloride, hydrazine can be retained in the 1AS to maintain highly efficient removal of ruthenium, and the normal excess acidity of 0.01-0.08M is adequate in the 1AX. The complexed iron and mercury are extracted with the tertiary amine nitrate solvent (1AX) and are removed from the spent solvent (1BW) by the K_2CO_3 - EDTA wash solution.

The quantity of nitric acid used in the third solvent washing step is adjusted to maintain the excess nitric acid in the washed solvent (1AX) within the operating limits of Table V before recycle to the 1A Bank. Operating limits for the third solvent washer were established from the HNO_3 equilibrium distribution data shown in Figure 14.

Nitric acid present in $Al(NO_3)_3$ feeds is slowly destroyed by radiolysis and must be periodically replenished to ensure that the solution does not become acid deficient. The calculated loss rate from the data shown in Figure 15 is 0.013 molecules HNO_3 per 100 eV of energy absorbed.

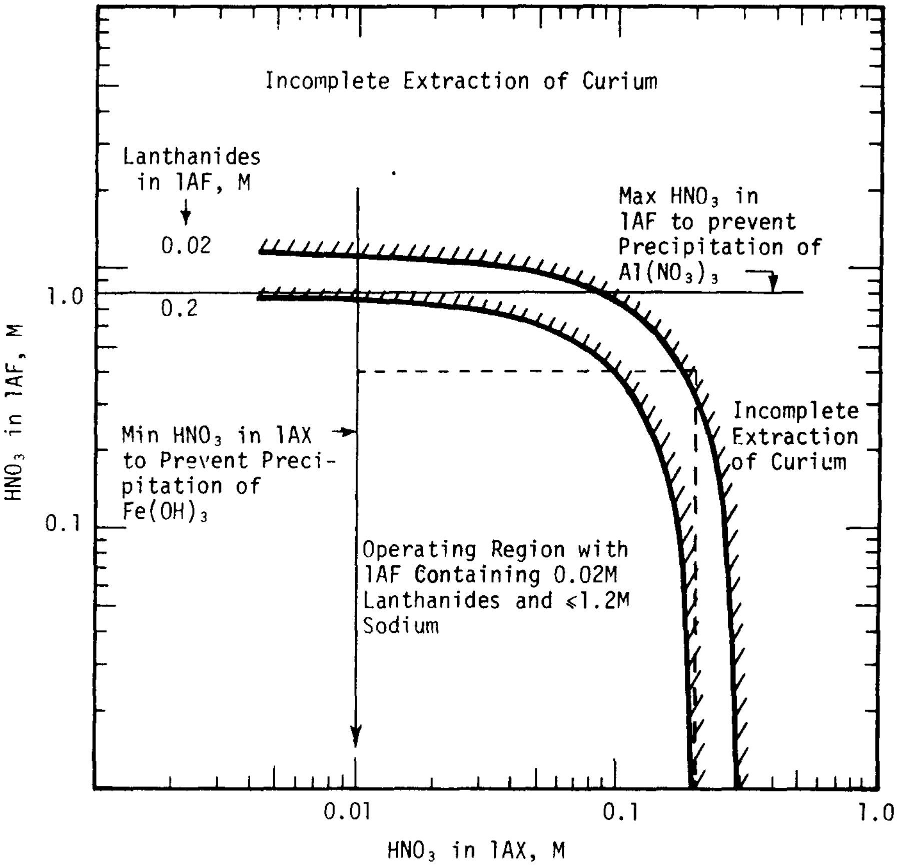


FIGURE 11. Operating Limits of Nitric Acid in Feed (1AF) and Extractant (1AX)

Flowsheet Conditions

Stream	Relative Flow	Composition
1AF	100 ±5%	$Al(NO_3)_3$, Variable HNO_3, Variable Lanthanides, <0.5M Iron, <0.1M Curium, ∿2g/l
1AS	200 ±5%	$LiNO_3$, 7.8-8.2M N_2H_4, ∿0.2M
1AX	800 ±5%	$R_3N{\cdot}HNO_3$, 0.6-0.62M HNO_3, 0.03-0.1M in DEB

>80% mass-transfer efficiency

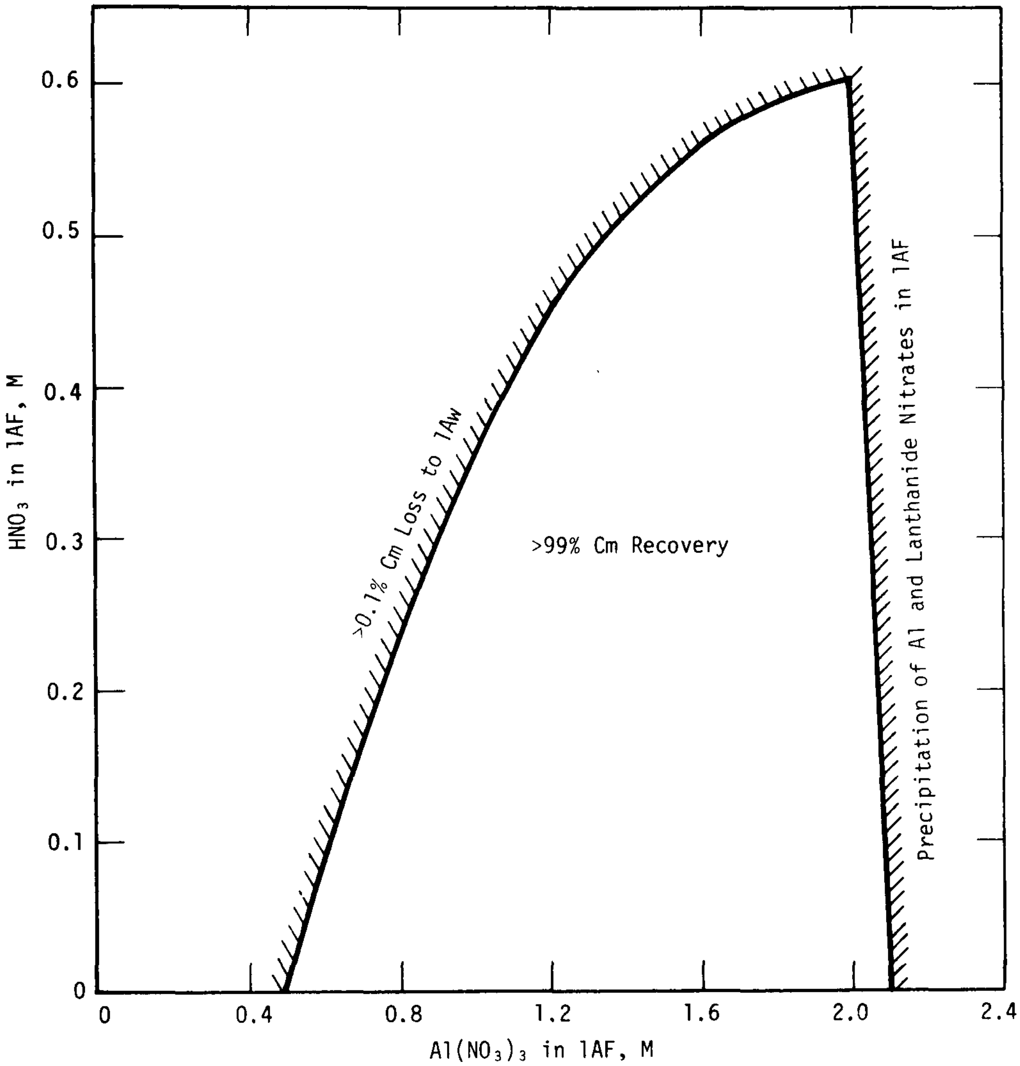


FIGURE 12. Operating Region for the Extraction Mixer-Settler of the Conversion Cycle

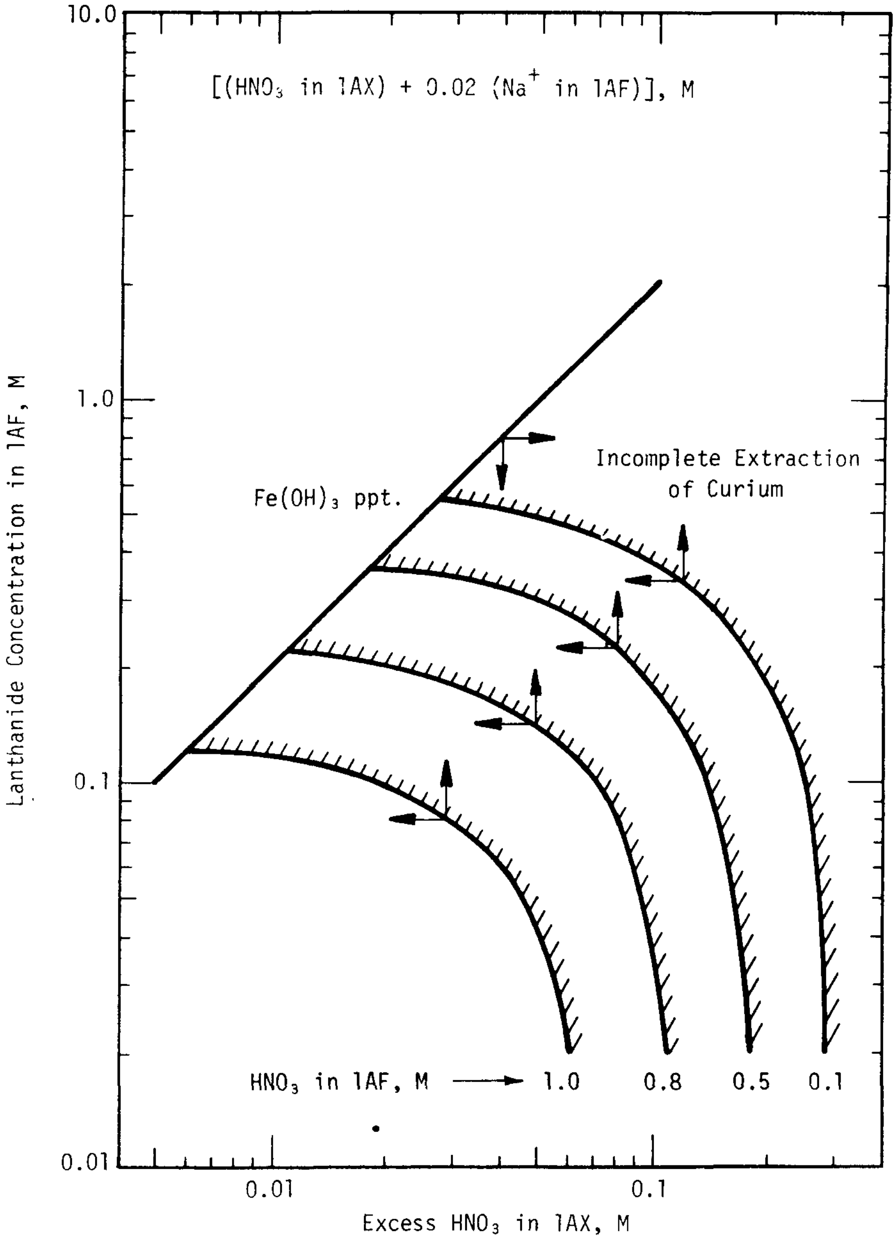


FIGURE 13. Limits of Iron, Lanthanides, Sodium, and HNO_3 in Feed to the Conversion Cycle

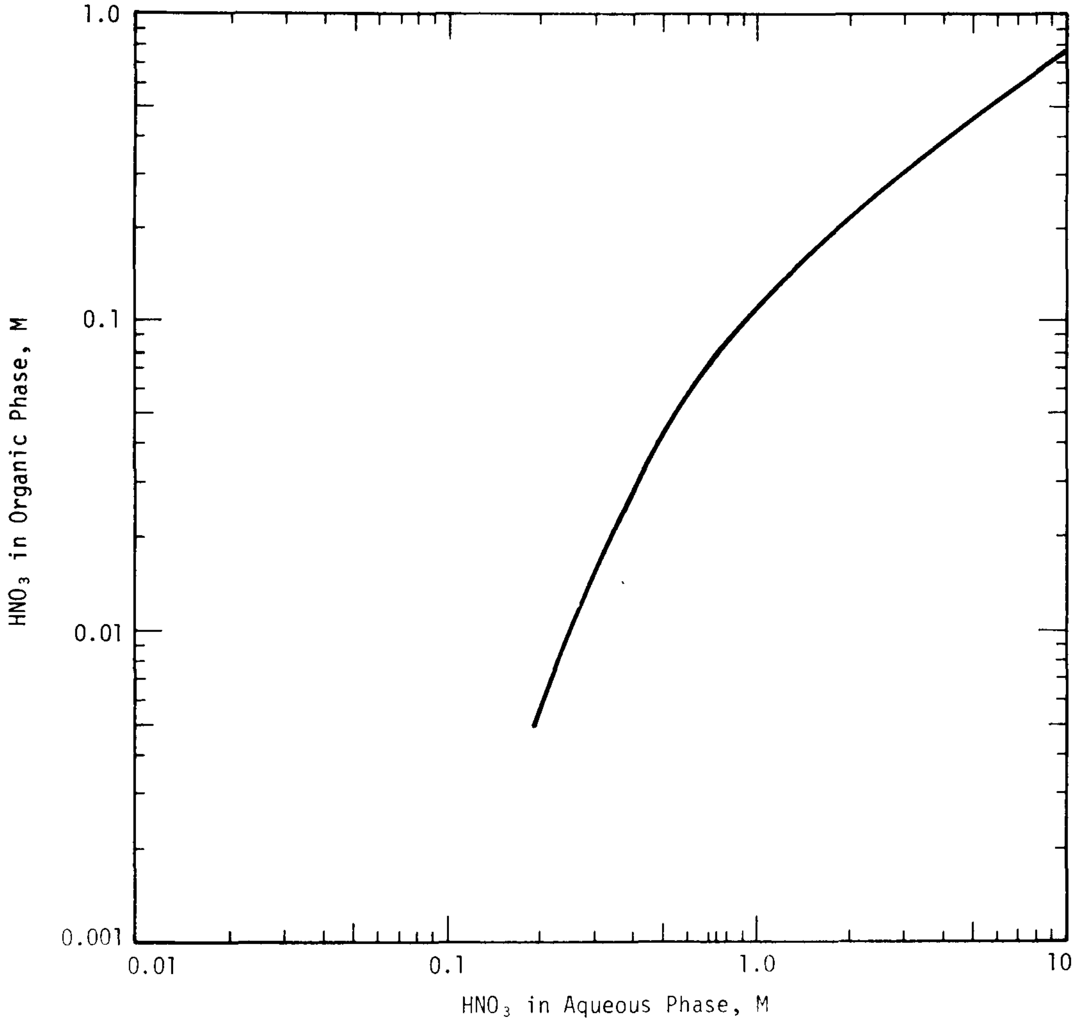


FIGURE 14. Distribution of HNO_3 Between Aqueous Solutions and 30% Tertiary Amine Nitrate in Diethylbenzene at 25°C

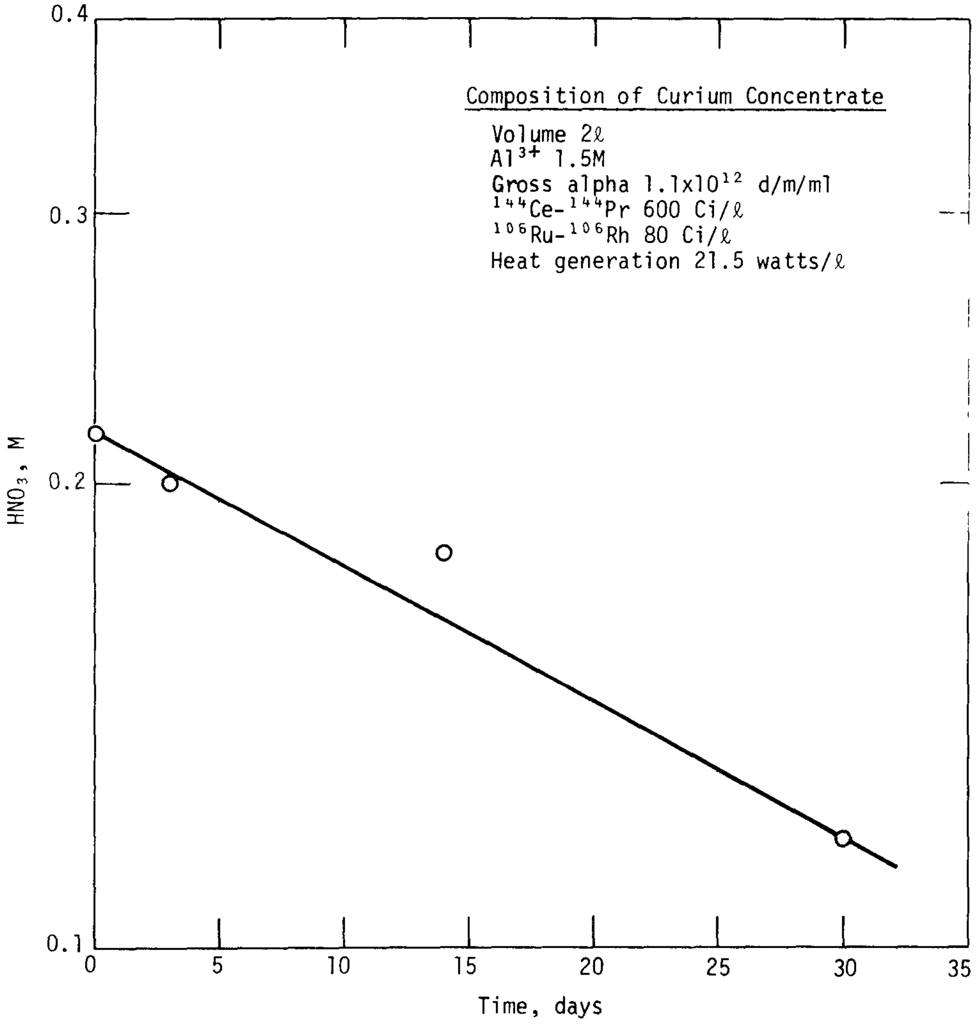


FIGURE 15. Radiolysis of Nitric Acid in Curium Concentrate

MINIATURE PILOT PLANT RESULTS

The conversion cycle was successfully demonstrated in miniature mixer-settlers with curium concentrate from the separations plant. In these tests the loss of curium was insignificant (<0.01% to 1AW and <0.17% to the spent organic, 1BW); the decontamination factor for removal of ^{106}Ru-^{106}Rh was >1000; the product (1BP) contained <0.01M HNO_3, and no detectable degradation products were accumulated in the washed solvent. The ^{95}Zr-^{95}Nb in the product was too low to measure the factor for its removal. Other test findings are:

- Excessive curium can leak to the aqueous waste of the 1A Bank, or iron can precipitate in the extraction section of the mixer-settler, unless the concentrations of nitric acid in the feed (1AF) and extractant (1AX) are adjusted to compensate for high concentrations of sodium, iron, and lanthanides in the feed.

- The use of hydrazine in the scrub stream (1AS) to the 1A Bank prevents accumulation of gross quantities of solids (believed to be caused by degradation products of diethylbenzene) in the K_2CO_3 solvent washer.

- The use of LiCl in the scrub stream (1AS) prevents precipitation of mercury hydrazine addition compound and iron hydroxide.

- The addition of EDTA to the potassium carbonate solvent wash solution aids in removing mercury and iron from the spent solvent and in preventing formation of solid material in the solvent washer.

- No degradation products of tertiary amine reached detectable quantities with ten repetitive uses of the solvent when hydrazine was used in the 1AS.

As indicated above, the temperature of the liquid leaving the condenser must be maintained <50°C to prevent excessive hydrogen chloride in the nitrogen purge gas (dry N_2) from flowing to the off-gas system. The N_2 purge, which is required to prevent accumulating radiolytically formed hydrogen in the condenser (as described below), decreases the effectiveness of the condenser and requires a large enough alkaline scrubber in the off-gas system to remove hydrogen chloride (as well as Cl_2) at the maximum rate that HCl is swept from the condenser. An updraft condenser is more efficient for removing hydrogen chloride than conventional downdraft condensers normally used in plant evaporators.

CALIFORNIUM-LANTHANIDE REMOVAL CYCLE

In the californium-lanthanide removal cycle (Figure 16), a mixture of tertiary amine hydrochlorides in diethylbenzene preferentially extracts trivalent actinides from trivalent lanthanides in concentrated lithium chloride feed in the 2A Bank and, in the 2B Bank, separates californium by selectively back-extracting the americium and curium. Principal steps in the californium-lanthanide removal cycle are:

- *Feed Adjustment* consisting of partial neutralization with LiOH, evaporation to remove excess water and HCl, and addition of LiCl if an insufficient amount is present.
- *Solvent Extraction* in two 16-stage, center-fed mixer-settlers. In the first mixer settler (2A), the trivalent actinides are extracted with 30 vol % tertiary amine hydrochlorides in diethylbenzene and scrubbed with 11M LiCl solution to separate the trivalent lanthanides. In the second mixer-settler (2B), americium and curium are selectively back-extracted with ∿9M LiCl, and californium is retained in the organic phase.
- *Solvent Washing* in three single-stage mixer-settlers. The spent solvent is washed consecutively with 1) dilute HCl to recover californium, 2) NaOH to neutralize the solvent, and 3) HCl to form the amine hydrochloride before recycle to the mixer-settlers.

FEED ADJUSTMENT

Feed solutions for the californium-lanthanide removal cycle are adjusted to contain ∿11M LiCl and ∿0.35M HCl, starting with ∿6M HCl solution from the conversion cycle, or other combinations of LiCl-HCl solutions, such as from recycle. The steps for the adjustment include addition of LiOH and LiCl, evaporation to remove excess water and HCl, and addition of HCl or water, if necessary. The solution is filtered, and the vapor space over the feed is purged continuously during storage to remove radiolytically formed hydrogen and chlorine. Subsequent adjustment also may be required periodically to compensate for radiolysis of HCl or for excessive dilution by water absorbed from moist gas that may leak into the feed system.

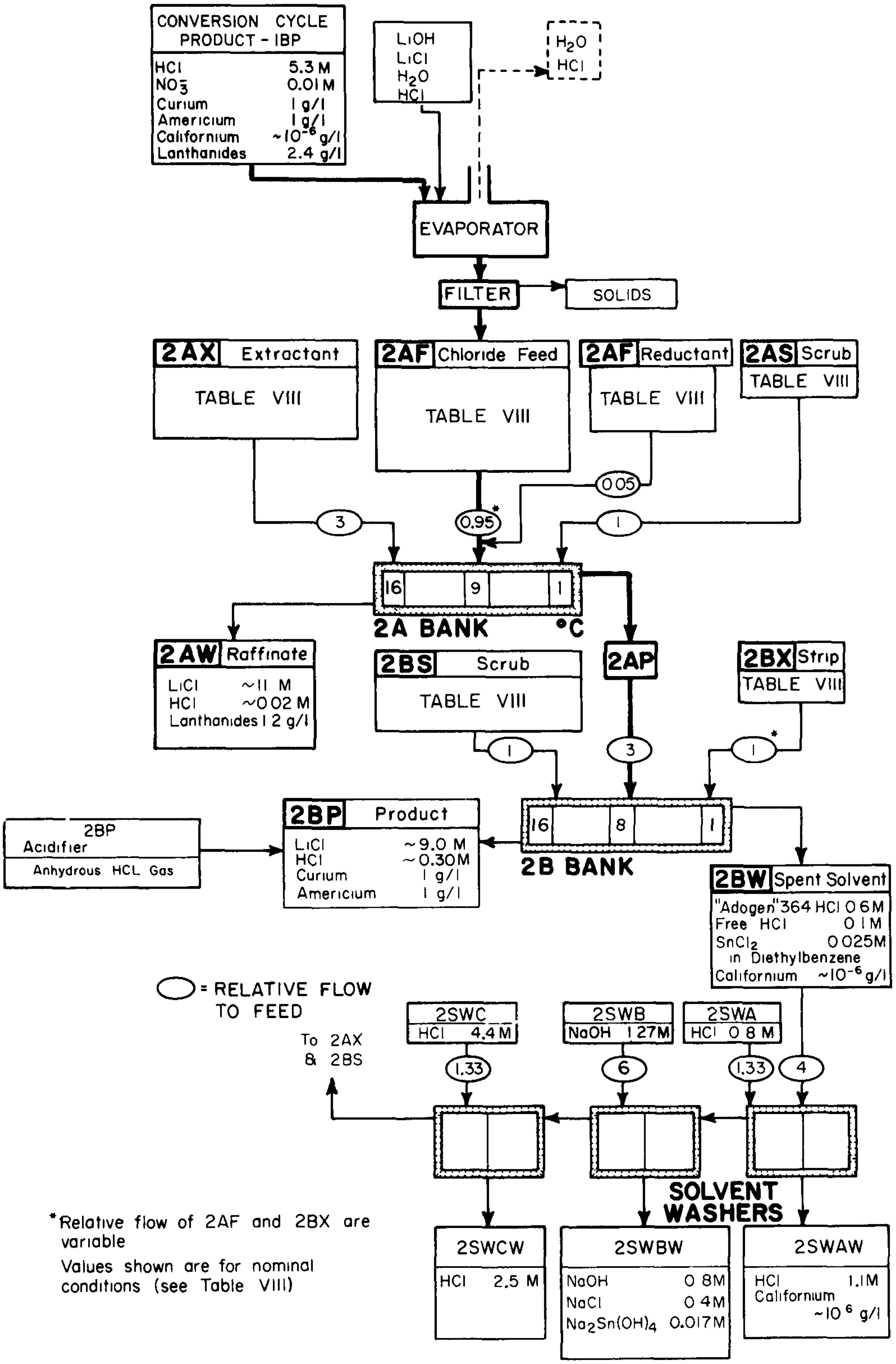


FIGURE 16. Californium-Lanthanide Removal Cycle

The vapor-liquid equilibria of H_2O and HCl over concentrated LiCl solutions affects the ability to adjust and maintain the proper concentration. These equilibria are summarized in Figures 17, 18, and 19 for conditions of principal interest. The significance of the data to process design and operation is discussed in the following paragraphs.

Partial Neutralization of HCl Before Evaporation

The hydrochloric acid (in 1BP solution from the conversion cycle) should be neutralized with LiOH to concentrations defined in Figure 20 to ensure that volatilization of HCl (enhanced at high LiCl concentrations as shown in Figure 17) relative to volatilization of water (depressed at high LiCl as shown in Figure 18) is not so great that most of the HCl is absorbed at the condenser in the subsequent evaporation step. If HCl volatilization is excessive, large quantities of HCl gas could be discharged into the off-gas system.

The limits summarized in Figure 20 are for the condition that the partial pressure of HCl over the condensate at temperatures up to 50°C will be $\leqslant 20$ mm Hg. This partial pressure is obtained over condensate containing 8.2M HCl (no LiCl) at 50°C; Figure 20 presents the LiCl - HCl binaries that yield condensates containing 8.2M HCl. The limits are not significantly changed by using a slightly different criterion; for example, the concentration of allowable HCl in the condensate could be increased to only $\sim$9M HCl by raising the allowable partial pressure to 50 mm Hg, or by decreasing the condensate temperature to 35°C while maintaining the 20-mm limit.

Evaporation

Practically all of the hydrochloric acid is distilled into the evaporator condensate, and subsequent acid adjustment can be made on the assumption that no acid remains in the feed solution. Specific gravities and boiling points, which are useful in monitoring the extent of evaporation, are summarized in Figures 21 and 22 and Reference 21, Figure 3.6.

Calculated and measured variation in acid during evaporation of typical solutions are shown in Figure 23. The difference between the calculated and experimental results is attributed to reflux of condensate in the experimental evaporator; reflux was not included in the calculations.

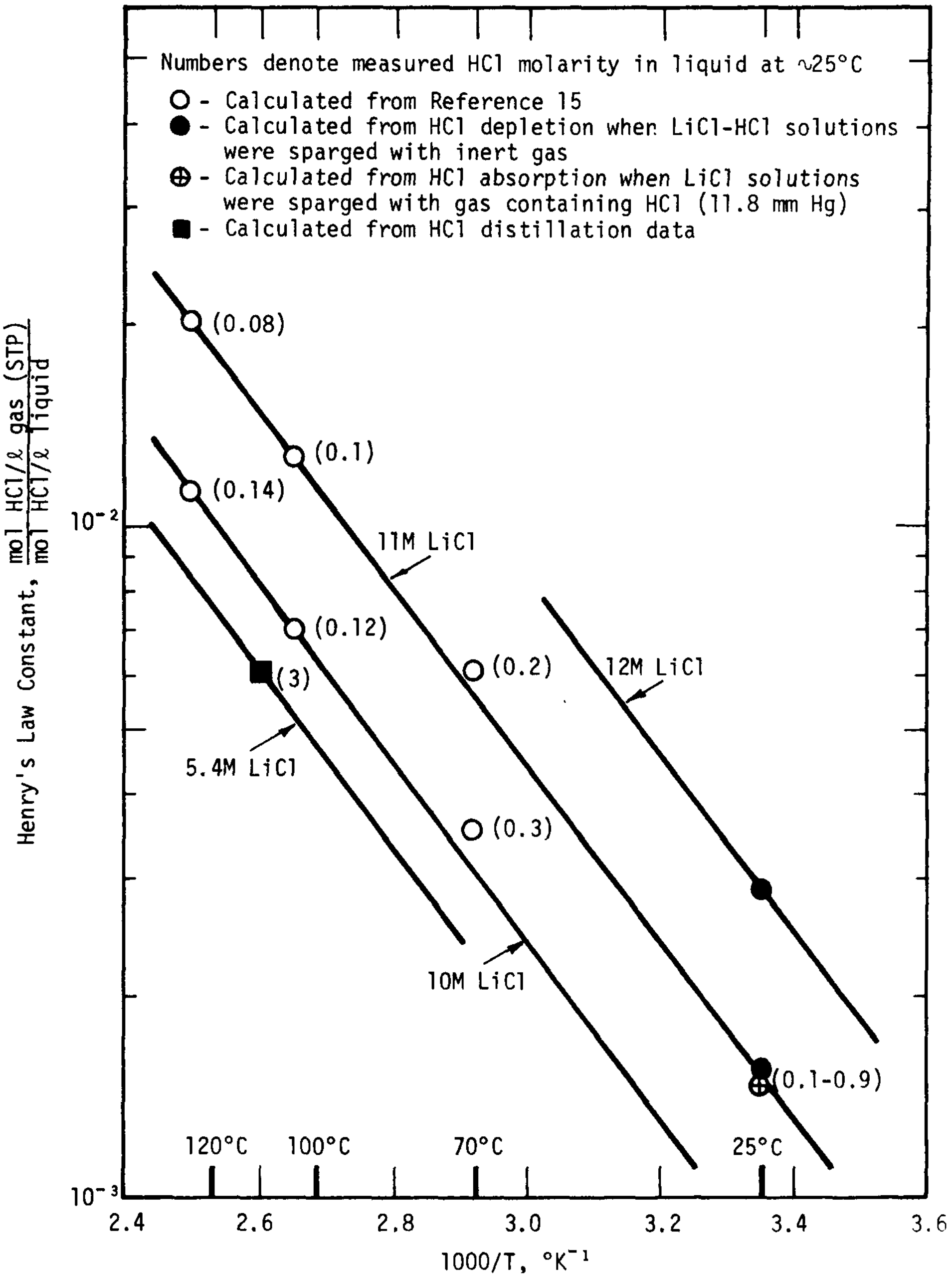


FIGURE 17. Vapor-Liquid Equilibria for HCl in LiCl Solutions

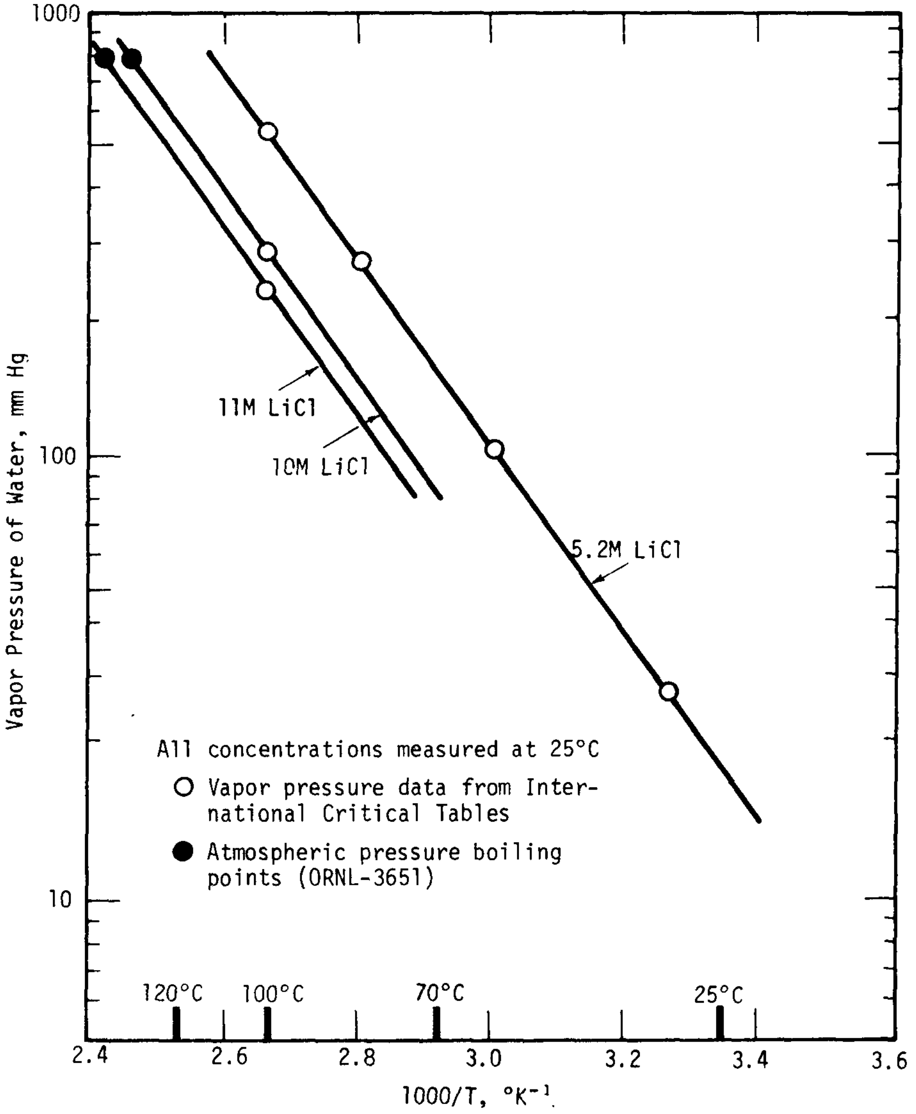


FIGURE 18. H_2O Vapor Pressure Over LiCl Solutions

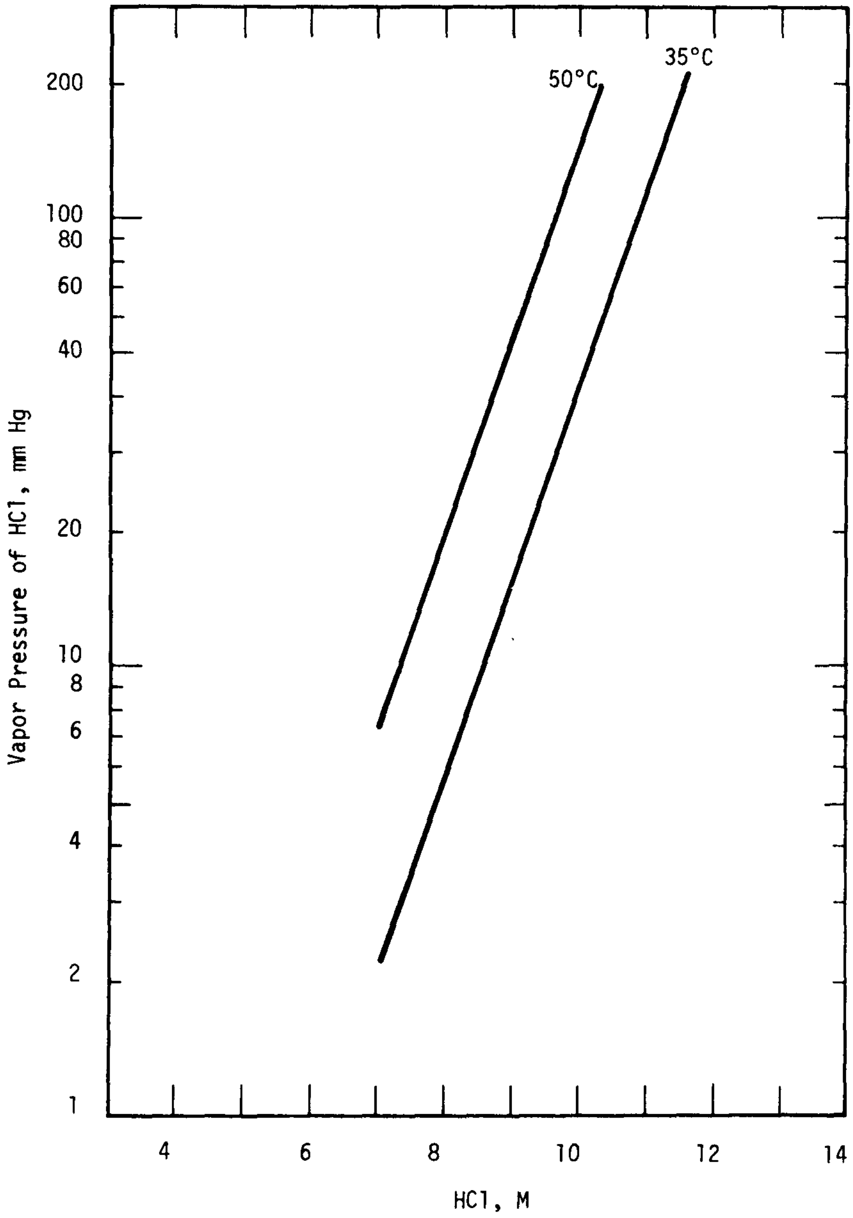


FIGURE 19. Partial Pressure of HCl Over Aqueous Solutions

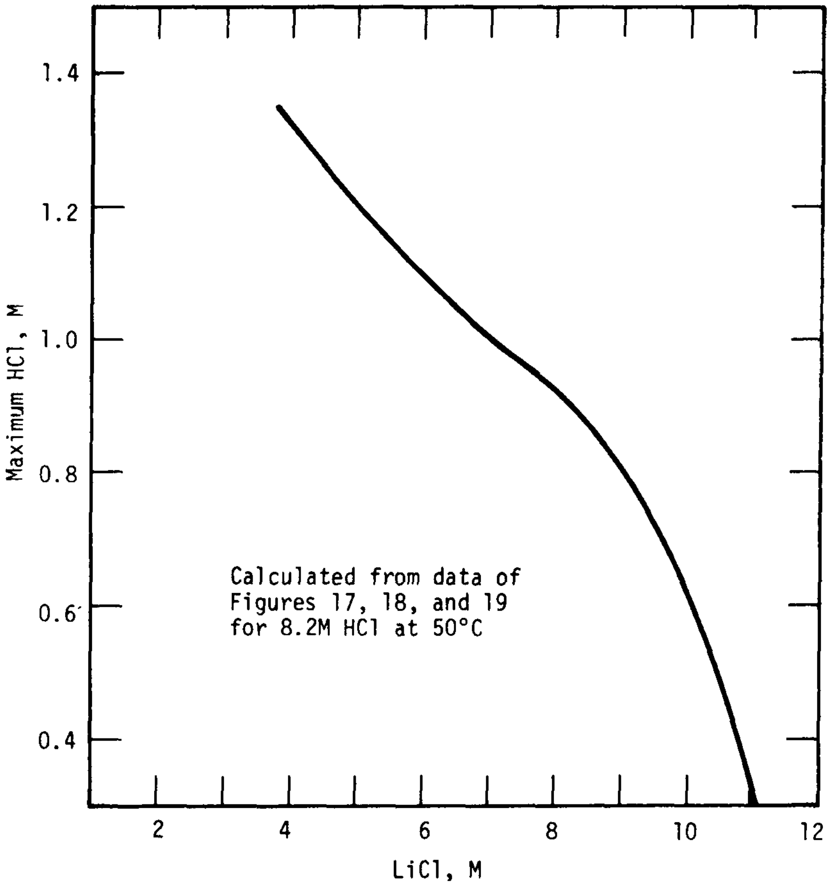


FIGURE 20. Tolerable HCl in Evaporator Feed

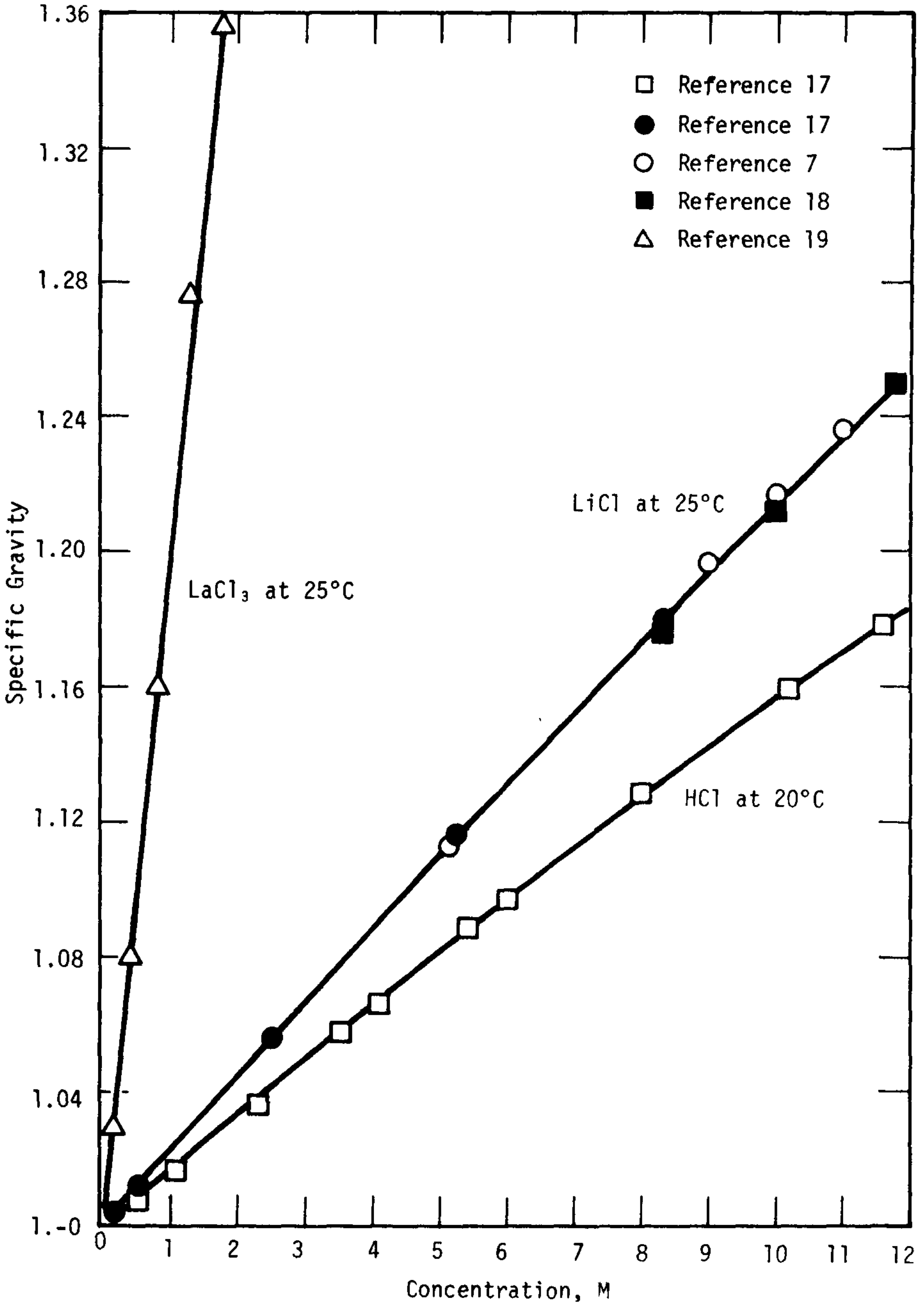


FIGURE 21. Specific Gravities of Solutions of HCl, LiCl, and $LaCl_3$

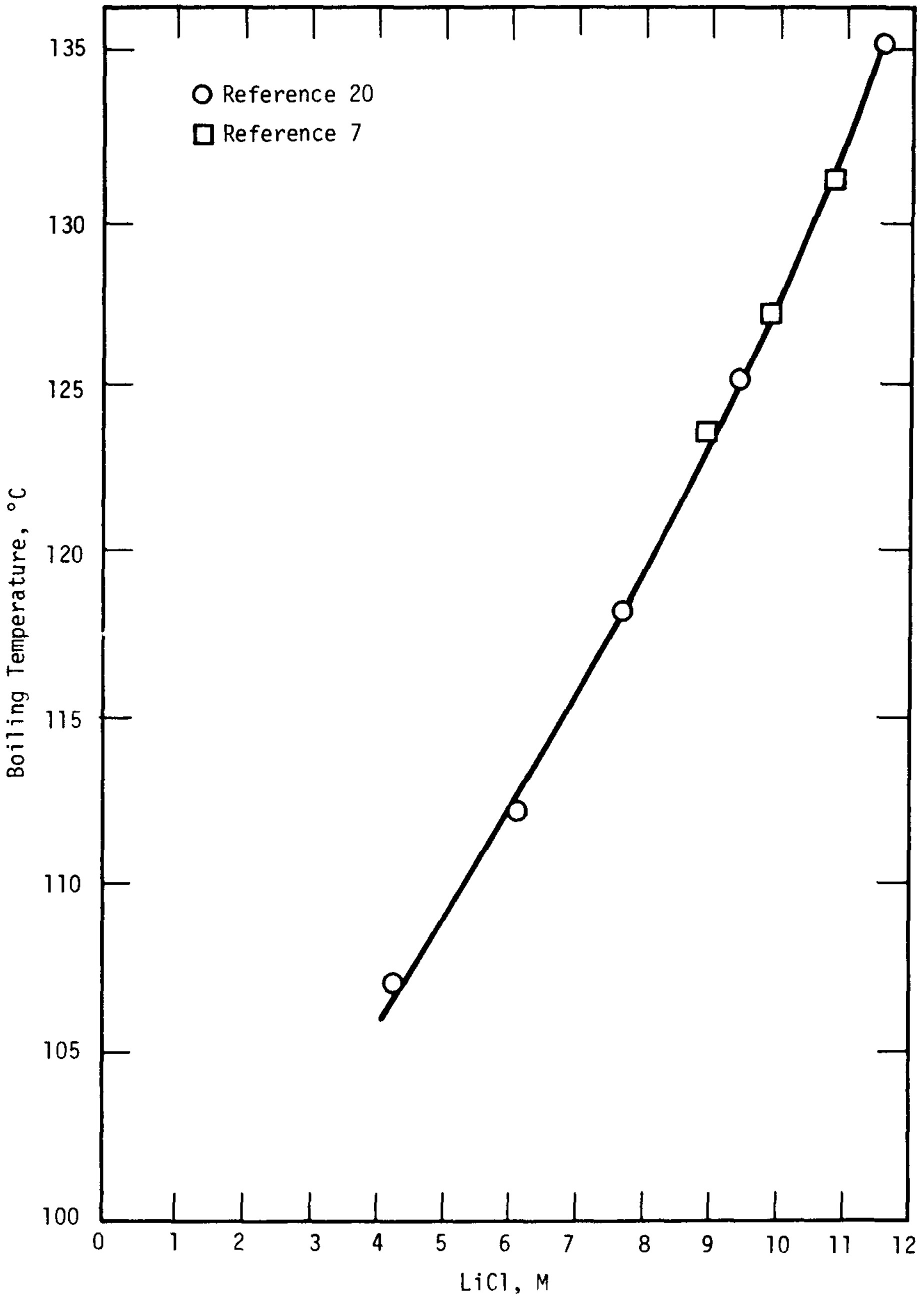


FIGURE 22. Effect of LiCl on Boiling Temperature

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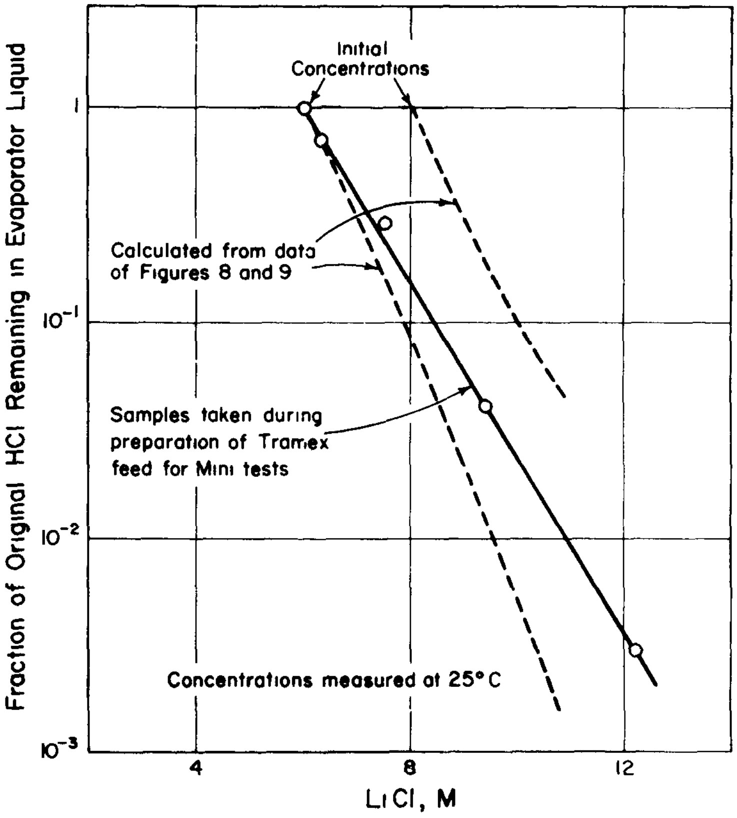


FIGURE 23. Distillation of HCl

Final Adjustment of HCl Concentration

Hydrochloric acid can be added most conveniently as hydrogen chloride gas to replenish acid lost by evaporation of LiCl solution or to readjust for acid loss by radiolysis. The frequency of readjustment is determined from operating experience; the expected loss rate corresponds to approximately G_{HCl} = 2 molecules per 100 eV of energy absorbed. The data of Figure 24 show that hydrogen chloride is easily absorbed in LiCl - HCl solutions by passing either pure or diluted hydrogen chloride through a simple dip tube sparger. Calculations indicate that equilibrium is very nearly attained, and that the transport properties that determine the rate of absorption are very favorable with a simple sparging device.

The use of HCl gas is convenient for adjusting the acidity of concentrated LiCl solutions (2AF and 2BP) without increasing the volume; however, the absence of potentially hazardous impurities (such as 1,1-dichlorethylene) must be verified for anhydrous HCl before use in solution adjustments. Several small flashes of light were observed while hydrogen chloride gas was being added to adjust the acidity of 9M LiCl product solution (2BP). The flashes occurred in the nitrogen atmosphere above the solution in 1-liter glass bottles. Investigations indicated that the flashes were caused by reaction of radiolytically generated chlorine with 1,1-dichloroethylene, a 1% contaminant in the HCl. The mechanism that allowed the dichloroethylene and chlorine to become concentrated in the nitrogen atmosphere in the bottles is as follows:

- Before addition of the HCl gas, the solution became saturated with radiolytic chlorine.
- Upon addition, the HCl was absorbed readily in solution, and the partial pressure of chlorine approached 1 atm.
- The resulting mixture of chlorine and dichloroethylene accumulated in the vapor space and ignited.

Excess hydrochloric acid can be removed by bubbling air or other noncondensable gas through LiCl solutions. Typical data showing acid depletion with sparging are illustrated in Figure 25. As in the case of absorption, gaseous hydrogen chloride is in equilibrium with acid in solution, and consequently transport properties for desorption are favorable. Also, the quantity of air required to remove a known amount of acid can be predicted readily.

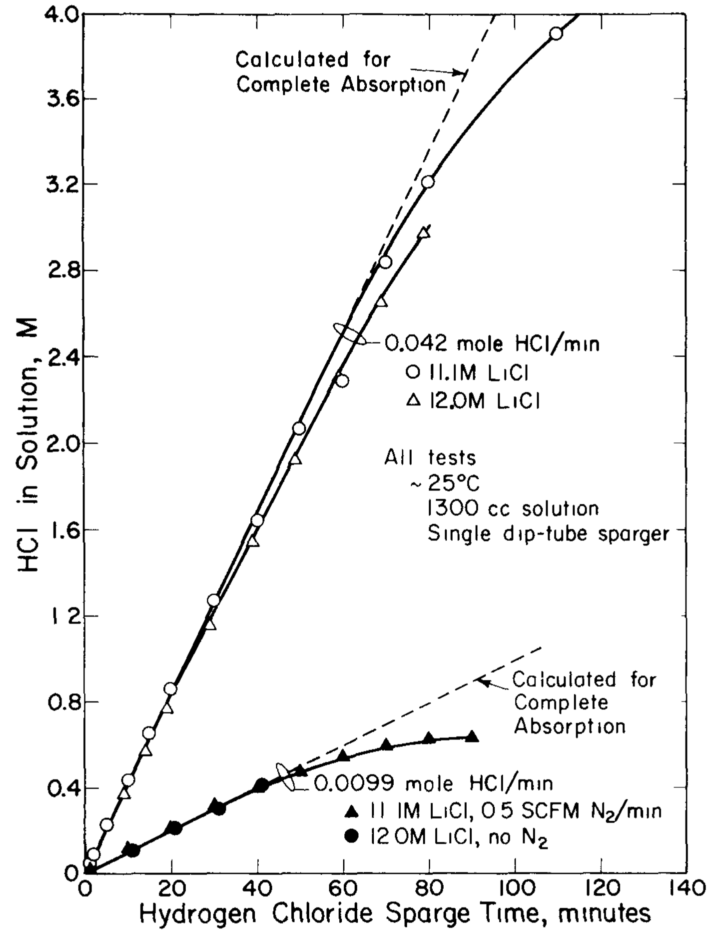


FIGURE 24. Absorption of HCl in Concentrated LiCl Solutions

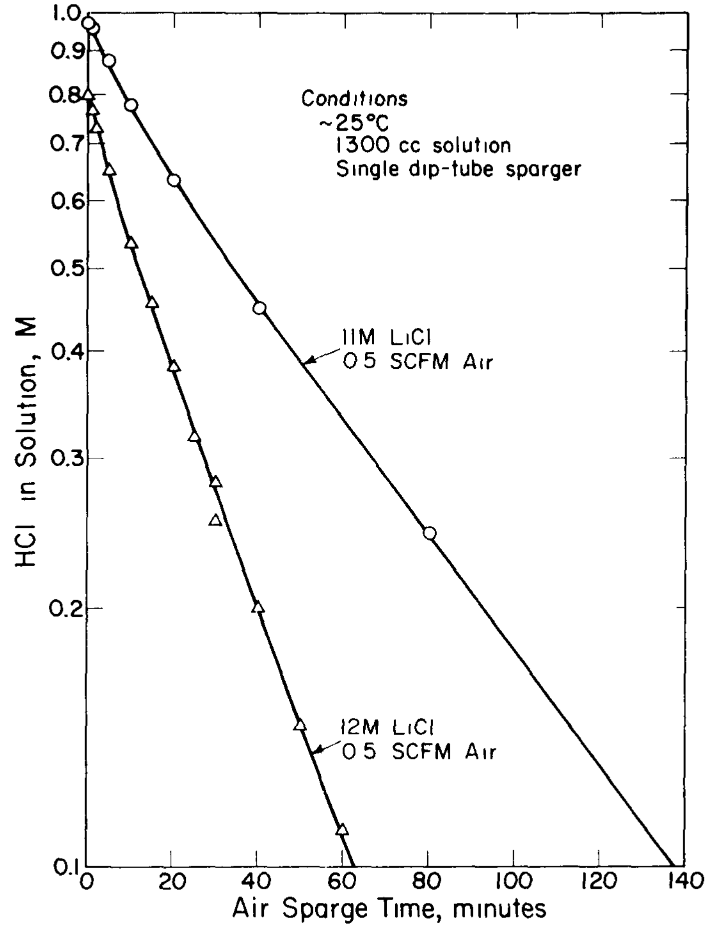


FIGURE 25. Removal of HCl from LiCl Solutions

Acid adjustment with concentrated hydrochloric acid is impractical because the accompanying water dilutes the LiCl. For example, adjusting with 12M HCl would dilute the LiCl about 3% and would necessitate controlled overconcentration during evaporation. Also, readjustments to compensate for radiolysis would cause further dilution and could necessitate re-evaporation.

Mixing Contents of Tanks

Mixing with air sparge is mechanically simple and maintenance free. Prior experience indicates that effective mixing can be obtained with volumes of sparge gas only one or two times the volume of solution being mixed. The HCl volatilization data of Figure 17 and the sparging results of Figure 25 indicate that loss of HCl to the sparge gas will be small; for example, the loss of HCl from 11M LiCl at 25°C will be $\leq 0.13\%$ for each solution volume of air.

Purge of Radiolytic Hydrogen

The vapor space above adjusted feed solutions in tanks should be purged to maintain the concentration of radiolytically formed hydrogen below its explosive limit. The major radiolytic reactions are:

$$2\,HCl \rightarrow H_2 + Cl_2$$

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$

The equilibrium is influenced by diffusion of gases from solution. Other undefined reactions leading to retention of O_2 and Cl_2 are known to occur, as illustrated by measurements at ORNL[15,21] which showed that:

- The gases evolved during radiolysis were rich in H_2.
- Chemical changes in solution composition after periods of radiolysis can lead to rapid evolution of gases rich in Cl_2 and O_2.

The required purge rate to decrease H_2 below 2% in the vapor space over adjusted feed is ∿15 cc/min for each watt of energy absorbed by the solution. This purge rate was established on the basis of tests indicating that:

- Radiolysis of HCl in 11M LiCl corresponds to $G_{-HCl} \cong 2$ molecules per 100 eV absorbed.
- The gases formed contain approximately equal quantities of O_2 and Cl_2.

Monitoring of the H_2 concentration is recommended because higher radiolysis rates have been observed under certain circumstances; for example, $G_{-HCl} \geq 10$ at concentrations of HCl >1M.[12,15]

Because its flow must be continuous, purge gas should be dehumidified sufficiently to prevent excessive dilution of the LiCl by condensation of water. Extrapolation of the data of Figure 18 indicates that the vapor pressure of water over 11M LiCl at 25°C is ∿8 mm Hg, corresponding to a relative humidity of 33% at 25°C, which is less than the 50-80% humidity in the atmosphere. For this reason, storage tanks for solutions of LiCl should not be exposed to moist atmospheres, if dilution cannot be tolerated.

Decreasing HOCl in Aged Feed

Miniature mixer-settler tests of the separation of lanthanides from actinides by solvent extraction with tertiary amine hydrochlorides showed poor rejection of cerium due to radiolytic generation of chlorine and subsequent oxidation of cerium(III) to cerium(IV) by hypochlorous acid. Therefore, to reduce hypochlorous acid-dissolved chlorine, either stannous ion is added to the feed shortly before solvent extraction, or the organic-soluble reductant 2,5-ditertiarybutylhydroquinone (DTBH) is added to the solvent (2AX and 2BS). The quantity of reductant must be adequate to reduce all hypochlorous acid and dissolved chlorine. As shown in Table VIII, the quantity of reductant is adequate to reduce all HOCl (∿0.01M) in equilibrium with chlorine at ½-atm partial pressure.

Less reductant is required if aged solutions are sparged with gas before solvent extraction. The results of Figure 26 show that HOCl can be removed without vaporizing excessive HCl. After removal, the Cl_2 and HOCl will again increase; HOCl will be formed at ∿0.00037 mole per watt-hour producing saturation of a solution containing ∿8 w/ℓ in ∿3 hours.

TABLE VIII

Californium-Lanthanide Removal Cycle Operating Limits
(Cocurrent efficiency of mixer-settlers >80%)

Variables	Limits		
	Nominal	Minimum	Maximum
1. Temperature	Ambient	-	50°C
2. Flow rates (relative)			
a. 2AF	0.95	*a*	*a*
b. 2AF'	0.05	0.047	0.053
c. 2AX	3.0	2.85	3.15
d. 2AS	1.0	0.95	1.05
e. 2BS	1.0	0.95	1.05
f. 2BX	1.0	*b*	*b*
g. 2SWA	1.33	1.27	1.40
h. 2SWB (if 2AF' is used)	6.0	5.8	-
(if DTBH is used)	2.0	1.8	2.2
i. 2SWC	1.33	1.25	1.60
3. 2AF composition			
a. LiCl, M	11.2	10.8	11.6
b. HCl, M	0.35	0.25	0.40
c. Curium, g/ℓ	1.05	-	-
d. Lanthanides, M	0.02	-	0.10
4. 2AF' composition (reductant)			
a. LiCl, M	10.2	9.8	11.2
b. HCl, M	0.35	0.3	0.4
c. $SnCl_2$, M	2.0	*c*	2.2
5. 2AX composition			
a. "Adogen" 364•HCl, M	0.61	0.59	0.63
b. Free HCl, M	0.025	0.01[d]	0.05[d]
c. Secondary amine, %	-	-	4
d. DTBH[e], M	-	0.04	-
6. 2AS composition			
a. LiCl, M	10.9	10.8	11.0
7. 2BS composition			
a. "Adogen" 364•HCl, M	0.61	0.59	0.63
b. Free HCl, M	0.025	0.01[d]	0.05[d]
c. Secondary amine, %	-	-	4
d. DTBH[e], M	-	0.04	-
8. 2BX composition			
a. LiCl,[f] M	8.98	8.85	9.11
9. 2SWA composition			
a. HCl, M	0.8	0.5	1.1
10. 2SWB composition			
a. NaOH, M	1.27	1.0	1.3
11. 2SWC composition			
a. HCl, M	4.4	4.2	4.6
12. Entrainment			
a. 2A Bank			
1. Aqueous/organic, %	0.0	-	1.0
2. Organic/aqueous, %	0.5	-	1.0
b. 2B Bank			
1. Aqueous/organic, %	0.0	-	1.0
2. Organic/aqueous, %	0.1	-	1.0
c. Solvent washer A[g]			
1. Aqueous/organic, %	0.2	-	3.0
2. Organic/aqueous, %	0.1	-	1.0
d. Solvent washer B[g]			
1. Aqueous/organic, %	-	-	1.0
2. Organic/aqueous, %	-	-	*h*
e. Solvent washer C			
1. Aqueous/organic, %	0.4	-	1.0
2. Organic/aqueous, %	0.1	-	1.0

---

a. Variable, depending on the HCl content of 2AX, 2AF', and 2AF, 2AF flow is adjusted to produce a 2AP containing 0.18M HCl.
b. See Figure 29
c. Undetermined — depends on HOCl and dissolved Cl_2 in 2AF (Calculations indicate the minimum value to be ∿0.4M $SnCl_2$).
d. See relative flow of 2AF and 2BX
e. 2,5-Ditertiarybutylhydroquinone. Use only if 2AF' is omitted from flowsheet.
f. See Figure 28
g. Organic flow through solvent washers can vary ±20%.
h. Normally expected to be <1%, however, experience has shown that provision should be incorporated in the waste handling system to remove excess solvent before evaporation.

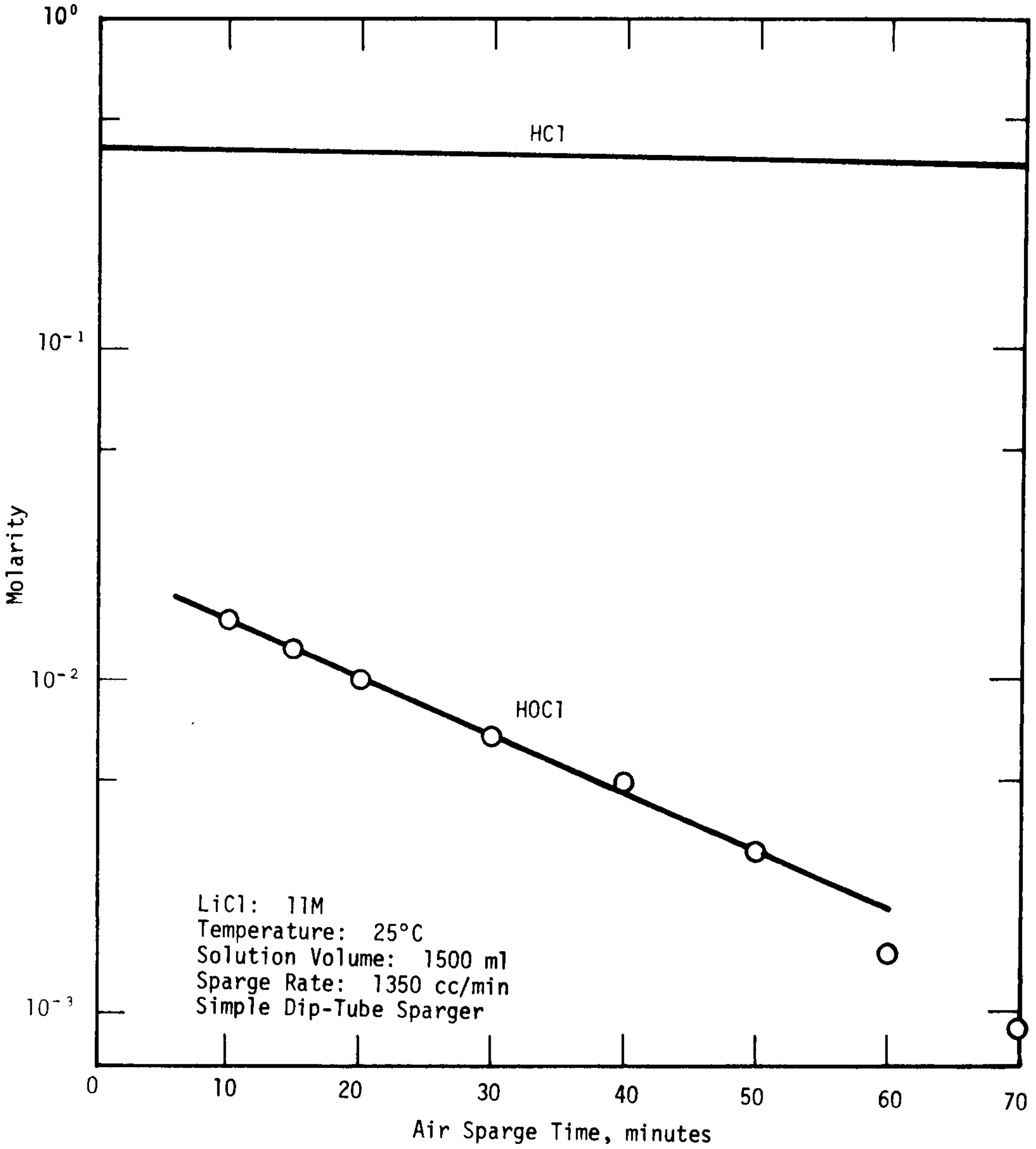


FIGURE 26. Removal of HOCl by Air Sparging

Filtration of Adjusted Solution

After adjustment, the evaporator solution is filtered to remove entrained solids. If material balance assays indicate that curium is carried by the solids, the filter must be backflushed to the evaporator with ∿8M HCl and the slurry combined with the next feed batch.

SOLVENT EXTRACTION

Before solvent extraction, the adjusted feed is continuously treated with Sn(II), or DTBH is used in the organic streams during extraction to destroy excess HOCl and dissolved Cl_2. The trivalent actinides are selectively extracted with 0.61M (30 vol %) tertiary amine hydrochlorides in diethylbenzene and scrubbed with 11M LiCl in the 2A Bank. The trivalent lanthanides are not extracted and leave in the waste raffinate (2AW). In the 2B Bank, americium and curium are selectively back-extracted into ∿9M LiCl leaving californium in the spent solvent (2BW) as well as Sn(II) and Sn(IV) if tin is used as the reductant. Before recycle, the solvent is consecutively washed with:

1. Dilute HCl to remove ^{252}Cf, ^{95}Zr-^{95}Nb, and residual ^{244}Cm. This stream which contains the ^{252}Cf is evaporated, and the ^{252}Cf is purified by rapid ion exchange elution chromatography with α-hydroxyisobutyrate.

2. NaOH to neutralize the solvent and to remove Sn and ^{106}Ru-^{106}Rh.

3. HCl to form the amine hydrochloride before recycle as 2AX and 2BS.

Stannous Chloride Reductant

The Sn(II) must be metered into the 2AF stream rather than added to the feed tank. If added to the feed tank, the quantity of Sn(II) required would have to be sufficient to reduce all the HOCl - Cl_2 formed during storage and processing as well as all the HOCl - Cl_2 at the equilibrium partial pressure of Cl_2 over the solution. For reasonable storage times the total tin added could back-salt curium excessively in the 2A mixer-settler, which would produce high levels of reflux or product loss. By metering Sn(II) continuously, it is not consumed in the feed tank; the quantity consumed in the 2A mixer-settler is small, and only the quantity [<0.1M Sn(II)] required to reduce the Ce(IV), Cl_2, and HOCl at the equilibrium partial pressure of Cl_2 need be added.

2,5-Ditertiarybutylhydroquinone Reductant

Pilot process experience using Sn(II) as the reductant showed that solids formation in the NaOH solvent washer (2SWB) gave rise to hydraulic problems causing processing difficulties. Data from Oak Ridge indicated that 2,5-ditertiarybutylhydroquinone (DTBH) could be used in place of Sn(II). DTBH is a commercially available, organic-soluble solid that is added to the 2AX and 2BS as makeup. Its oxidation product (quinone) is also soluble in the solvent system; however, neither the quinone or hydroquinone is removed in the solvent washing system. Thus, DTBH can be used as reductant only when the solvent is used on a once-through basis. However, a three-fold reduction in waste volume from the 2SWB is obtained since high concentrations of NaOH are no longer needed to form stannate or stannite complex ions.

Three streams (2AW, 2BP, and the aqueous waste from the first solvent washer) may require recycling as follows:

- 2AW is recycled as 2AF after adjustment to the limits given in Table VIII.
- 2BP or other LiCl solutions containing no other metal cations (other than actinides or lanthanides) in significant concentration are recycled to the evaporator and adjusted to the feed specifications given in Table VIII.
- Aqueous wastes from the first solvent washer or other HCl streams are recycled to the evaporator.

OPERATING CONDITIONS

Operating conditions and corresponding limits, calculated to provide satisfactory process performance when all variables are simultaneously at their most adverse limits, are summarized in Table VIII. Some of the limits are shown graphically in Figures 27, 28, and 29. The variables that are interdependent and the criteria used to establish numerical values for each are summarized in Table IX. The numerical values are predicted on the following bases.

2A Bank

- Cocurrent mass transfer efficiency is ≥80%.
- All flow rates are accurate to ±5%.
- Analyses of HCl in 2AX, 2AF, and 2AF' are accurate to ±5%.

2B Bank

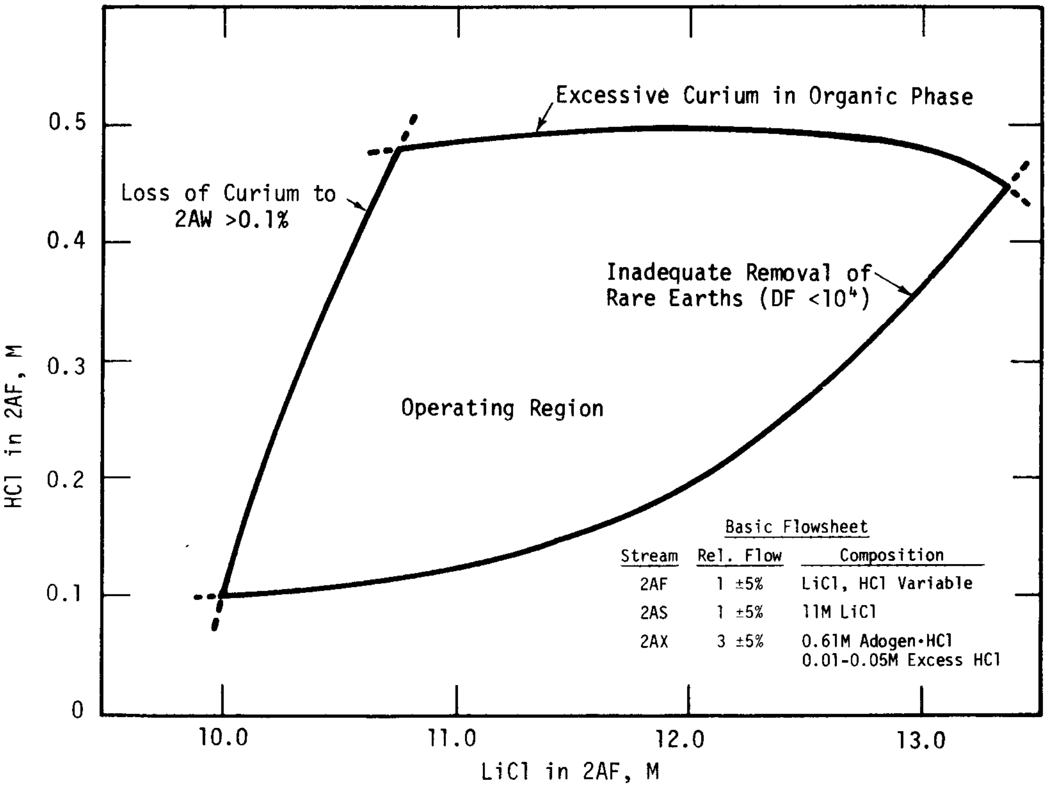
- Cocurrent mass transfer efficiency is ≥80%.
- 2AP and 2BS flow rates are accurate to ±5%.
- 2BX flow rate is accurate to ±2%.
- HCl content of 2BS is accurate to ±5%.

The limits in Figure 27 are less restrictive than those in Table VIII because the latter are for all variables at their most adverse values. If operating experience warrants, the limits in Table VIII can be expanded, subject to limits of operating region boundaries of Figure 27.

The effect of HCl concentration in the 2AP and LiCl in the 2BX on the separation of californium and curium in the 2B mixer-settler are shown in Figure 28. For a given concentration of LiCl in the 2BX, separation increases as the concentration of HCl in the 2AP increases, but californium refluxes (californium reflux is defined as the ratio of californium concentration in the mixer-settler to californium concentration in the 2AP being >1). Also, the maximum (0.218M) and minimum (0.095M) concentrations of HCl entering the 2B mixer-settler (via 2AP) is controlled by salting conditions (HCl and Sn, if used, in organic phase) in the scrub section of the 2A mixer-settler where the trivalent lanthanides are separated from actinides without excessive reflux of curium.

Figure 28 illustrates the rigorous operating controls needed to separate californium and curium adequately. Variations of ±0.24M from an optimum value of 9.05M LiCl in 2BX and variations of ±0.02M from an optimum value of 0.18M HCl in 2AP can be allowed without deviating from separation specifications. The 2A mixer-settler conditions should be controlled to provide 0.18M ±10% HCl in 2AP. The 0.18M HCl in the 2AP can be maintained by adjusting the flow of the 2AF on the assumption that all the HCl entering the 2A mixer-settler extracts with the 2AP.

Figure 29 presents the flow of the 2BX that must be maintained to compensate for variations in the HCl content of the 2BS stream. Although the concentration of HCl in the 2BS is nominally 0.025M, the limits in Table VIII allow this value to vary from 0.01 to 0.05M, and such variation must be compensated by the 2BX flow to ensure the latitude in operation represented by Figure 28.



Basic Flowsheet

Stream	Rel. Flow	Composition
2AF	1 ±5%	LiCl, HCl Variable
2AS	1 ±5%	11M LiCl
2AX	3 ±5%	0.61M Adogen·HCl 0.01-0.05M Excess HCl

FIGURE 27. Californium-Lanthanide Removal Cycle: Operating Region for 2A Bank

TABLE IX

Criteria for Establishing Numerical Limits in Tables VIII and XI

Limit of Variable in Tables VIII and XI	Interrelated Variables and Limits (See Tables VIII and XI)		Bases for Establishing Numerical Value of Limit (See Footnotes)
	Variables at Their Minima	Variables at Their Maxima	
Temperature			
Maximum	-	-	*a*
Flow Rates			
2AX			
Minimum	3a,5a,6a	2a,2d,2j,3b,5b,11a,12e1	*b*
Maximum	2a,2d,2j,3b,5b,11a	3a,5a,6a	*c*
2SWA			
Minimum	2i,10a	2c,2e,3b,4c,5a,5b,7a,7b, 8a,12b1	*d*
Maximum	-	-	*e*
2SWB			
Minimum	-	2c,2e,3b,4c,5a,5b,7a,7b, 9a,12c1	*f*
Maximum	-	-	*g*
2SWC			
Minimum	11a	2c,2e,3a,3b,3d,5a,5b,7a, 7b,10a,12d1	*h,i*
Maximum	2c,2e,3a,3b,3d,5a,5b,7a, 7b	11a,12e1	*h,i*
2AS, 2BX, and 2AF'			
Minimum Maximum	-	-	*e*
Compositions			
2AF			
Minimum	2d,5b,11a	2c,2j,5a,6a	*b*
Maximum	2c,2j,5a,6a	2d,5b,11a	*c*
2AX			
Minimum	2d,3a,11a	2j,3b,6a	*b*
Maximum	2j,3b,6a	2d,3a,11a	*c*
2BX			
Minimum	2b,4c	2c,2e,3b,5a,5b,7a,7b	*j*
Maximum	2c,2e,3b,5a,5b,7a,7b	2b,4c	*k*
2SWA			
Minimum	-	-	-
Maximum	2i,11a	-	*d*
2SWB			
Minimum	-	2b,2c,2e,4c,5a,5b,7a,7b, 9a,12c1	*f*
Maximum	11a	-	*g*
2SWC			
Minimum	2j,5b	2c,2e,10a,12d1	*l*
Maximum	2c,2e	2j,5b	*l*
2AS and 2BS			
Minimum Maximum	-	-	*e*

---

a. Flashpoint of diethylbenzene

b. Extraction factor for curium >1 in 1A Bank

c. Extraction factor for lanthanides <1 in 1A Bank

d. Minimize NaOH in 2SWB

e. Operating experience

f. Neutralization of all the acid in the spent solvent

g. Minimize HCl in 2SWC

h. Convert neutralized solvent to amine chloride

i. Adjust free HCl content of solvent to give extraction factors of >1 for curium and <1 for lanthanides in the 2A Bank

j. Extraction factor for curium <1 in 2B Bank

k. Extraction factor for californium >1 in 2B Bank

l. Necessary to meet 2AX and 2BS composition limits for free HCl

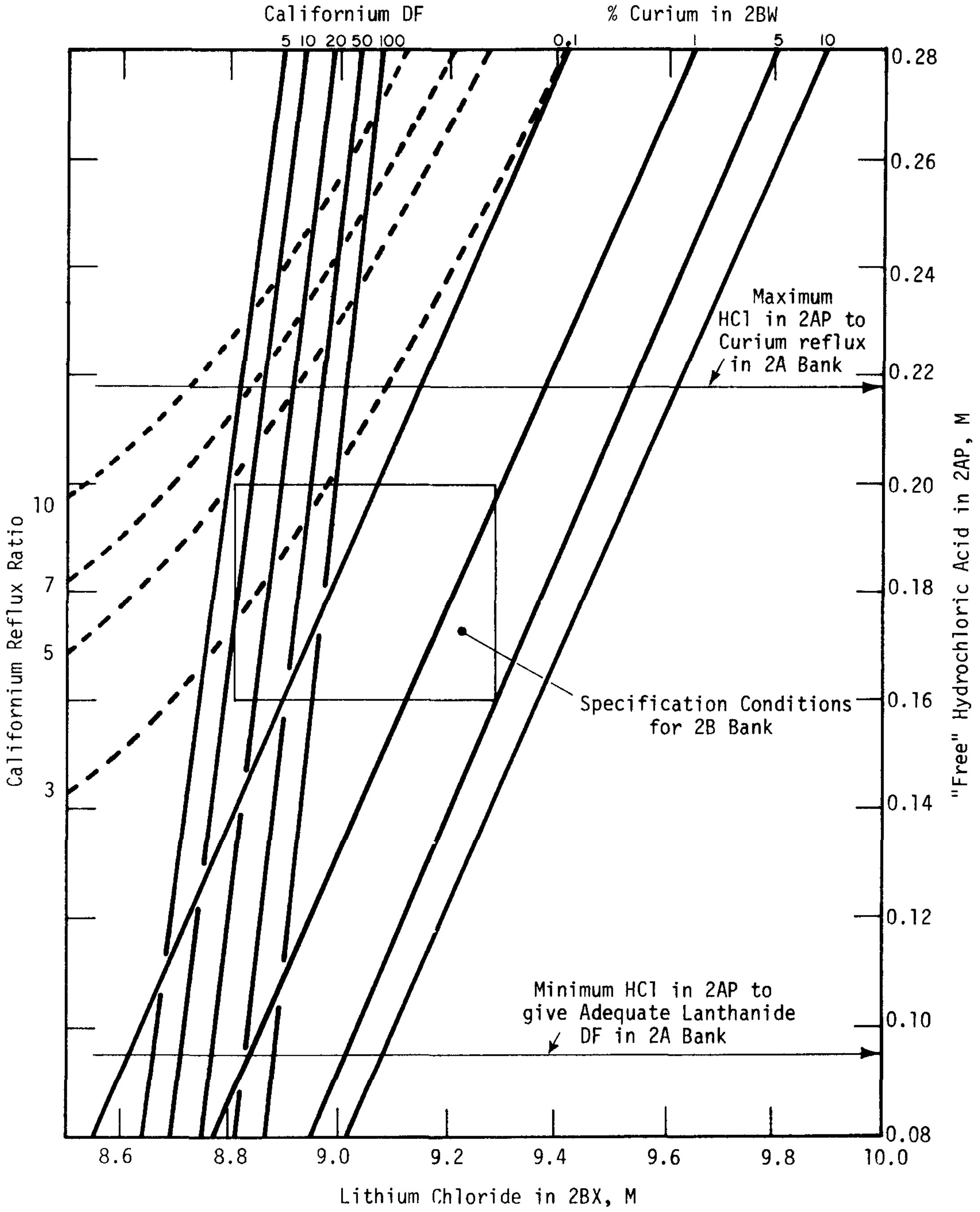


FIGURE 28. Operating Limits for 2B Bank with 0.01-0.05M "Free" HCl in 2BS

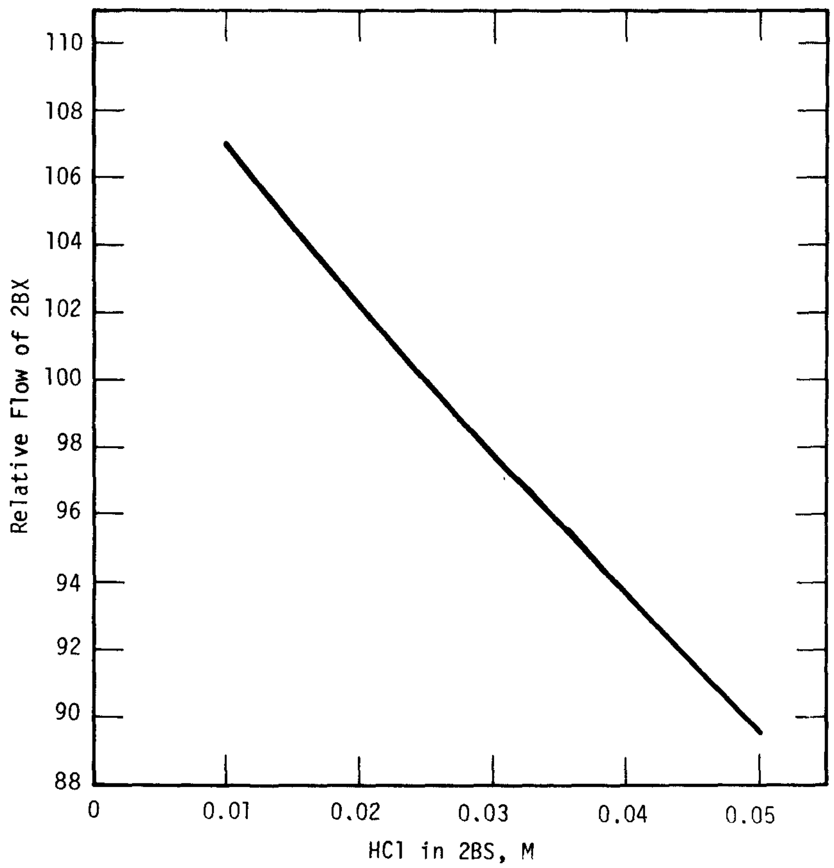


FIGURE 29. Limits of HCl in 2BS and Flow of 2BX

DESIGN DATA

The basic operating conditions for the californium-lanthanide and lanthanide removal cycles were designed to obtain a curium yield of greater than 99.9% with decontamination factors of >10 and >1000 for removal of californium (in californium removal cycle) and trivalent lanthanides (in each cycle), respectively.

The last two extraction cycles are an adaptation of ORNL's Tramex Process.[5] The Tramex process, which is based on the tertiary amine extraction of transplutonium elements from concentrated lithium chloride solution, was the first solvent extraction process developed specifically to separate trivalent lanthanides and actinides as groups. The difference in the relative extractabilities of the actinides and lanthanides is of the order of 100 in a single extraction.[22] The feasibility of separating the trivalent actinides from lanthanides and separating californium from americium-curium by multistage extraction was the basis for selecting the Tramex process for the last two cycles for the pilot production unit.

The most significant extraction reactions that occur in the two chloride salting cycles can be represented by the following:

- Formation and decomposition of amine hydrochloride in the solvent washers

$$R_3N + HCl \rightleftarrows R_3N\bullet HCl$$

$$R_3N\bullet HCl + NaOH \rightleftarrows R_3N + H_2O + NaCl$$

- Polymerization of amine salt

$$pR_3N\bullet HCl + HCl \rightleftarrows (R_3N\bullet HCl)_p\bullet HCl$$

- Formation of extractable chloro complexes

$$M(Cl)_{x-1}^{3-(x-1)} + Cl^- \rightleftarrows M(Cl)_x^{3-x}\ ,\ x \geqslant 1$$

- Extraction of complexes by amine hydrochloride extractant in 2A mixer-settler

$$M(Cl)_{\bar{x}}^{3-\bar{x}} + (\bar{x}-3)H^+ + yR_3N{\bullet}HCl \rightleftarrows M(Cl)_3(R_3N)_y$$
$$+ (HCl)_{y-z+\bar{x}-3} + zHCl$$

- Stripping of extracted complexes into HCl

$$M(Cl)_3(R_3N)_y(HCl)_{y-z+\bar{x}-3} + (\bar{x}-y)R_3N{\bullet}HCl$$
$$+ (3+z-\bar{x})HCl \overset{HCl}{\rightleftarrows} M^{3+} + 3Cl^- + (y+\bar{x}-z)R_3N{\bullet}HCl$$

where

$\bar{x}$ = the average stoichiometry of the extracted chloride complexes

y = the combining ratio of the metal complexes with amine

z = the stoichiometry of the anion exchange reaction

Although the numerical values of $\bar{x}$, y, and z have not been determined, the empirical data presented below and the extraction equations summarized above can be used to specify design data over a wide range of conditions.

Distribution Coefficients

Phase equilibrium data (at 25°C) for the tertiary amine hydrochloride system with americium, curium, californium, europium, and hydrochloric acid were determined in the presence of lithium chloride, stannous chloride, and stannic chloride. These data[23] were combined with data in the literature, correlated, and expressed mathematically.[14] Equations for equilibrium distribution are presented in Table X, where H_O is the equilibrium acid concentration in the organic phase (molar), Li is the aqueous lithium chloride concentration (molar), Sn is the organic stannous or stannic chloride concentration (molar), and D_a^o is the equilibrium distribution coefficient (organic concentration divided by aqueous concentration). These equations were used to represent extraction of HCl, lanthanides, and actinides in establishing design data; however, caution should be exercised in extrapolating these equations beyond the range of experimental data (9-11M LiCl and 0-0.4M H_o).

TABLE X

Equations for Distribution Coefficients in the Californium-Lanthanide Removal Cycle

(Organic phase: 30% tertiary amine hydrochloride in diethylbenzene)

HCl

$$D_a^o = \exp\ [-7.4(H_o) + 0.85(Li) - 6.23]$$

Americium

$$D_a^o = \exp\ [-11.4(H_o) + 1.97(Li) - 18.73]$$

Curium

$$D_a^o = \exp\ [-10.35(H_o) + 1.675(Li) - 15.965 - 6(Sn)(Li) + 52(Sn)]$$

Californium

$$D_a^o = \exp\ [-10.35(H_o) + 1.675(Li) - 14.02 - 6(Sn)(Li) + 52(Sn)]$$

Europium

$$D_a^o = \exp\ [-11.5(H_o) + 1.865(Li) - 22.115]$$

The extractability of the trivalent actinides and lanthanides is strongly dependent on the chloride concentration of the aqueous phase and extracted hydrochloric acid. Distribution coefficients increase as the salt concentration increases (D_a^o is a function of the $\sim$16th power of the chloride salt concentration) and decrease with an increasing concentration of free acid phase ($\sim$2nd power), which is competitively extracted into the organic phase.

Effect of Nitrate Ion

Tertiary amine is a base that may form a salt in the organic phase by extracting an acid from an aqueous phase:

$$R_3N + H^+ + A^- \rightleftarrows R_3N \bullet HA$$

The amine acid salt $R_3N \bullet HA$ can undergo anion exchange with another anion present in the aqueous phase; the order of preference is $ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$. Under these conditions, the presence of an anion with a preference higher than chloride for salt formation may be detrimental in a chloride extraction system. For example, the presence of nitrate in LiCl feeds decreases the actinide-lanthanide separation factors. Consequently, because feeds for the californium-lanthanide removal cycle are prepared from nitrate solutions, methods for nearly complete removal are required (nitrate-to-chloride conversion cycle). As illustrated in Figure 30, the distribution coefficient for americium and europium increase rapidly with increasing nitrate concentration, while the separation factor decreases steadily. To ensure adequate separation of the trivalent actinides from lanthanides in the californium and lanthanide removal cycles, a limit of $\lesssim$0.01M nitrate was established for LiCl feeds.

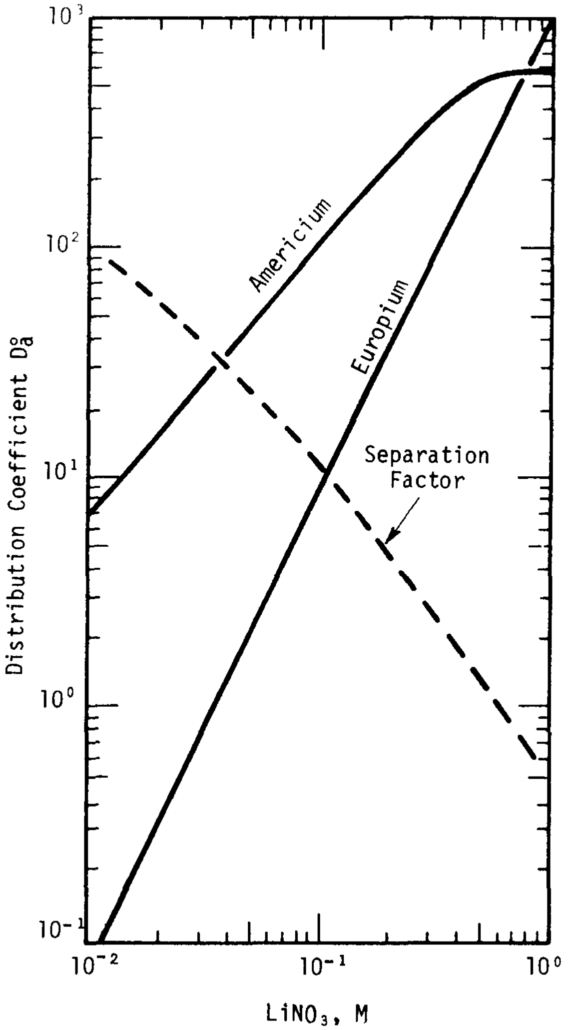


FIGURE 30. Effect of Nitrate on the Extraction of Americium and Europium from 11M LiCl with 30% Tertiary Amine

MINIATURE PILOT PLANT RESULTS

In miniature mixer-settler tests, the product (2BP) contained >95% of the curium, and decontamination factors for ^{252}Cf, ^{106}Ru-^{106}Rh, ^{95}Zr-^{95}Nb, and ^{144}Ce-^{144}Pr were >10, ∿50, >>40,* and >1000, respectively. Process performance did not deteriorate when solvent was recycled ten times. Because the Sn(II) forms interfacial precipitates in the alkaline washer, and because these precipitates are accompanied by organic entrainment in the aqueous waste stream, provision was made to:

- Remove solids from the washer
- Remove entrained organic from the waste before evaporation

Solvent Recycle

The tertiary amine extractant is used as the hydrochloride salt, which is formed by contacting the amine with hydrochloric acid. After each use in the process, the solvent is washed with water or dilute HCl and then with NaOH before reacidifying with HCl and recycling to the mixer-settlers. Operating limits for the third solvent washer were established from the HCl equilibrium distribution data shown in Figure 31.

Although both chemical and radiation damage limit the effective lifetime of the solvent, the following evidence indicates that rapid degradation of the solvent occurred in the solvent washer system [when NaOCl was used in the first washer to oxidize Sn(II) to Sn(IV)] rather than in the radiation field of the 2A Bank. The concentration of secondary amines increased to the point of precipitation at ∿4 vol % in six to eight solvent recycles during both tracer and full level tests. This degradation was up to 14 times as rapid as was measured during stagnant irradiation tests under simulated 2A Bank conditions. In both tests in which diethylbenzene and tertiary amines were exposed separately to hypochlorite, diethylbenzene was degraded to yield alcohols and other oxygenated compounds, and tertiary amines were degraded to secondary amines. Both the aromatic and amine degradation products resulted in up to 2-fold increase in times of phase separation, and when the secondary amine concentration increased to >4 vol % of the total solvent (amine plus diethylbenzene), the amine precipitated (presumably as amine hydrochloride salt) so that the mixer-settlers could not be hydraulically operated.

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* No detectable ^{95}Zr-^{95}Nb in 2BP.

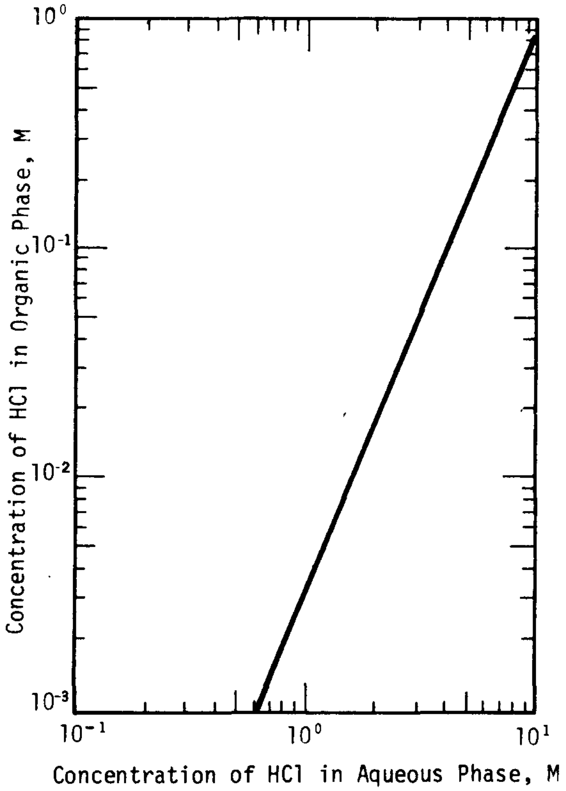

FIGURE 31. Equilibrium Distribution of HCl Between Organic and Aqueous Phases Without LiCl at 25°C

Miniature mixer-settler tests of the californium removal cycle showed that removal of Sn(II) as tin hydroxide in the alkaline washer (second washer) without prior oxidation (in the first washer with NaOCl) eliminated the rapid chemical oxidation of the solvent. Radiolytic degradation of the tertiary amine hydrochloride corresponded to ∿0.3% per cycle. Extrapolation of the results of two tests (Figure 32) indicates that the solvent would probably have been useful for 30 to 40 passes before radiolytically formed secondary amines reached ∿4%. Secondary amines are precipitated when they exceed 4% at which concentration the solvent must be replaced. The concentration of tertiary amine would need to be adjusted after ∿10 passes to maintain it within the range of 30 ±1%, the allowable design limit.

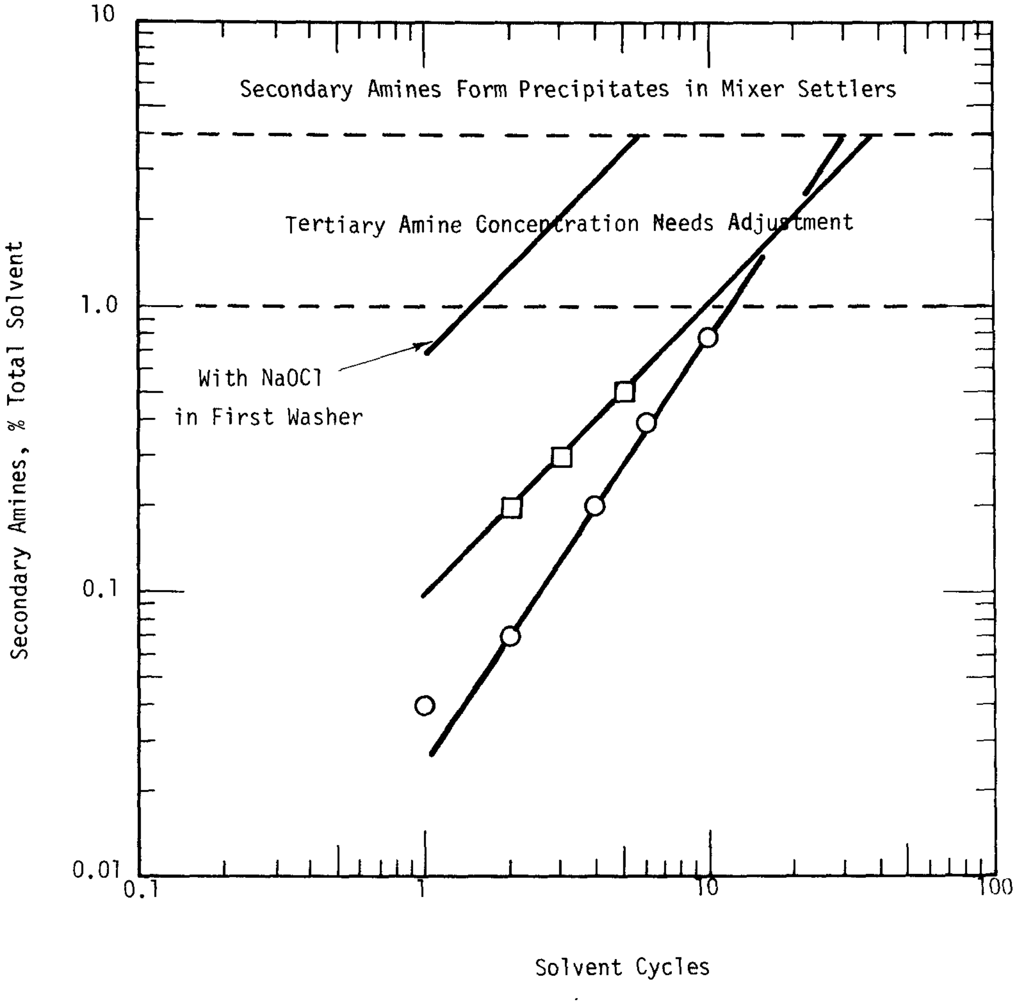

FIGURE 32. Degradation of Tertiary Amine Hydrochloride Solvent During Californium-Lanthanide Removal Cycle

Effect of Temperature

In initial tests of the californium removal cycle, the 2A Bank was operated at 50°C because ORNL data indicated that the efficiency for scrubbing of lanthanides was significantly lower at 25°C than the efficiency for extraction of curium. Analyses of 2A Bank stage concentration of ^{244}Cm and ^{144}Ce from tests made at 50 and 30°C showed that the efficiency for scrubbing cerium is equal to the efficiency for extracting curium, and the removal of cerium was the same at both temperatures. The observations were confirmed in batch tests, illustrated in Figure 33, which showed that the distribution coefficients of curium and cerium do not change appreciably between 25 and 50°C.

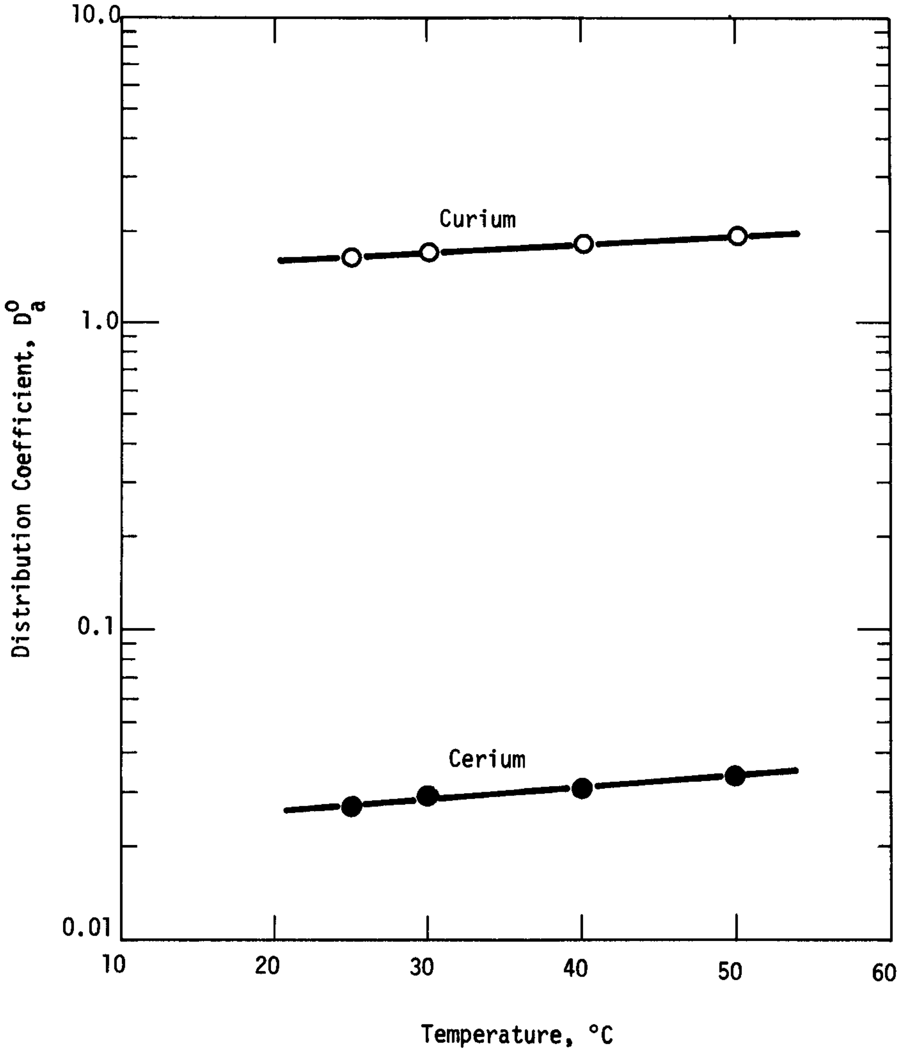

FIGURE 33. Effect of Temperature on Extraction of Curium and Cerium

LANTHANIDE REMOVAL CYCLE

In the lanthanide removal cycle (shown in Figure 34), a mixture of tertiary amine hydrochlorides in diethylbenzene preferentially extracts trivalent actinides from residual trivalent lanthanides in concentrated lithium chloride feed. Principal steps in the lanthanide removal cycle are the same as those for the californium-lanthanide removal cycle: feed adjustment, solvent extraction, and solvent washing.

FEED ADJUSTMENT

Feed solution for the lanthanide removal cycle is adjusted to ∿11.0M LiCl and 0.35M HCl, starting with ∿9M LiCl and ∿0.3M HCl from the californium-lanthanide removal cycle product stream (2BP). The steps for the adjustment include addition of LiCl and LiOH, evaporation to remove excess water and HCl, and addition of HCl or water, if necessary. The solution is filtered, and the vapor space over the feed is purged continuously during storage to remove radiolytically formed hydrogen. Details for these steps are identical with those for the feed adjustment step for the californium removal cycle except that neutralization of the HCl in the 2BP is not necessary.

SOLVENT EXTRACTION

Filtration and treatment of the adjusted feed with Sn(II), if used as the reductant for Ce(IV), is identical with those steps in the californium-lanthanide removal cycle. The alternative reductant, 2,5-ditertiarybutylhydroquinone (DTBH), can be used in the place of Sn(II) when once-through solvent is incorporated in the flowsheet.

Curium and americium are extracted from residual quantities of trivalent lanthanides with 30 vol % (∿0.6M) tertiary amine hydrochlorides in diethylbenzene, scrubbed with 11M LiCl in the 2A mixer-settler, and back-extracted into 8M HCl in the 3B mixer-settler [Sn(II) and Sn(IV) remain in the spent solvent (3BW)]. Before recycle, the solvent is washed consecutively with H_2O, NaOH, and HCl.

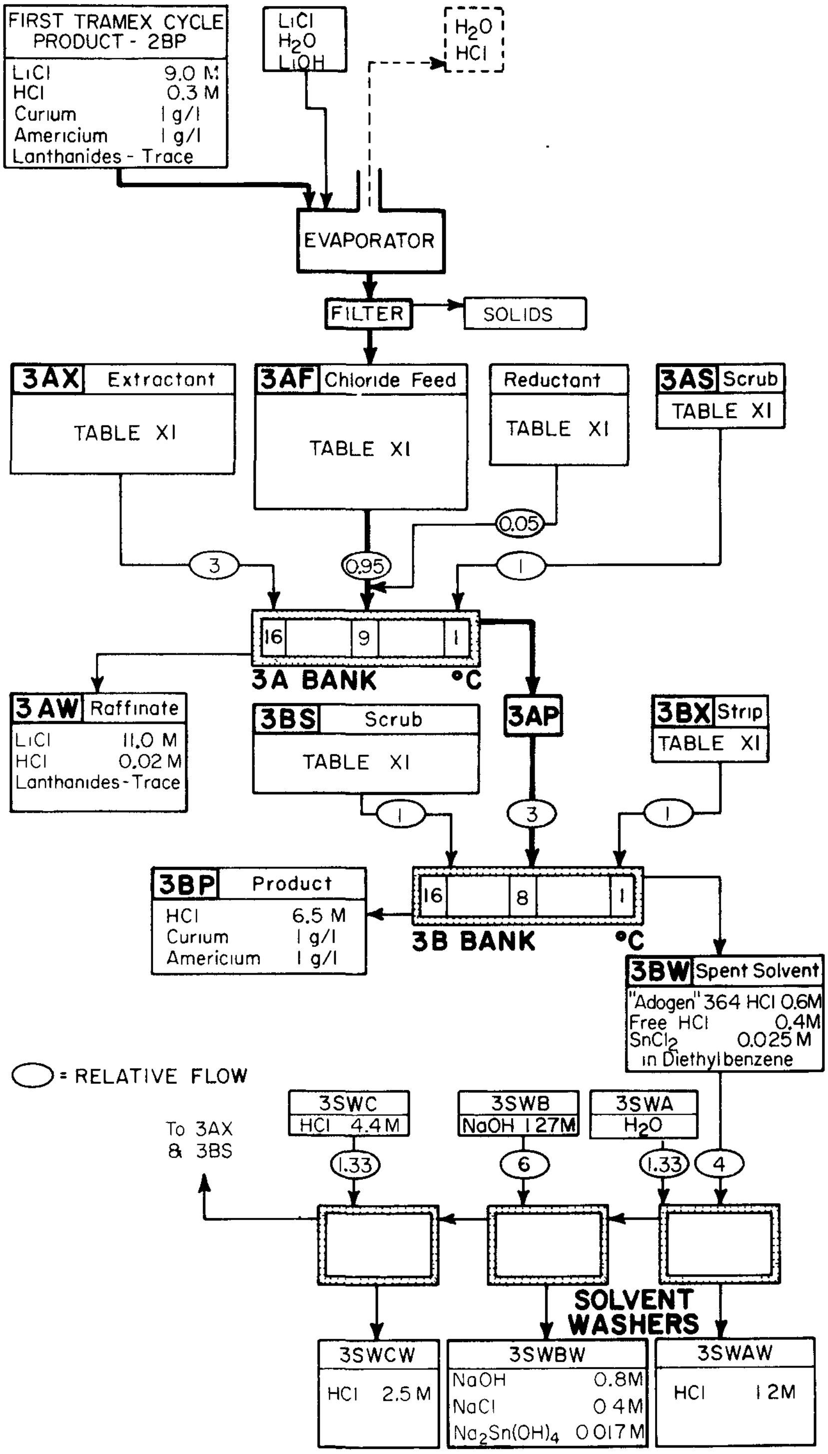

FIGURE 34. Lanthanide Removal Cycle

Three streams (3AW, 3BP, and the aqueous waste from the first solvent washer) may require recycling. They are recycled as follows:

- 3AW is recycled as 3AF after adjustment to the limits given in Table XI.
- 3BP is recycled to the evaporator where the HCl content is reduced by neutralization with LiOH, LiCl is added, and the solution is evaporated to the feed specifications given in Table XI.
- Aqueous wastes from the first solvent washer or other HCl streams are recycled to the evaporator.

OPERATING CONDITIONS

Operating conditions and corresponding limits, calculated to provide satisfactory process performance when all variables are simultaneously at their most adverse limits, are summarized in Table XI. The design and basic operating conditions for the lanthanide removal cycle are identical with the californium-lanthanide removal cycle, except that HCl is used to back-extract curium and americium in the 3B Bank instead of LiCl (used in 2B Bank to separate californium). The interdependent variables and the criteria used to establish numerical values for each are summarized in Table IX.

TABLE XI

Lanthanide Removal Cycle Operating Limits

(Cocurrent efficiency of mixer-settlers >80%)

Variables	Limits		
	Nominal	Minimum	Maximum
1. Temperature	Ambient	-	50°C
2. Flow rates (relative)			
a. 3AF	0.95	0.90	1.00
b. 3AF'	0.05	0.047	0.053
c. 3AX	3.0	2.85	3.15
d. 3AS	1.0	0.95	1.05
e. 3BS	1.0	0.95	1.05
f. 3BX	1.0	0.95	1.05
g. 3SWA	1.33	1.27	1.40
h. 3SWB (if 3AF' is used)	6.0	5.8	-
(if DTBH is used)	2.0	1.8	2.2
i. 3SWC	1.33	1.25	1.60
3. 3AF composition[a]			
a. LiCl, M	11.2	10.8	11.6
b. HCl, M	0.35	0.25	0.40
c. Curium, g/ℓ	1.05	-	-
4. 3AF' composition (reductant)			
a. LiCl, M	10.0	9.8	11.2
b. HCl, M	0.35	0.3	0.4
c. SnCl$_2$, M	2.0	[b]	2.2
5. 3AX composition			
a. "Adogen" 364•HCl, M	0.61	0.59	0.63
b. Free HCl, M	0.025	0.01	0.05
c. Secondary amine, %	-	-	4
d. DTBH[c]	-	0.04	-
6. 3AS composition			
a. LiCl, M	10.9	10.8	11.0
7. 3BS composition			
a. "Adogen" 364•HCl, M	0.61	0.59	0.63
b. Free HCl, M	0.025	0.01	0.05
c. Secondary amine, %	-	-	4
d. DTBH[c]	-	0.04	-
8. 3BX composition			
a. HCl, M	8.0	7.5	8.5
9. 3SWA composition			
a. H$_2$O	-	-	-
10. 3SWB composition			
a. NaOH, M	1.27	1.0	1.3
11. 3SWC composition			
a. HCl, M	4.4	4.2	4.6
12. Entrainment			
a. 3A Bank			
1. Aqueous/organic, %	0.0	-	0.3
2. Organic/aqueous, %	0.5	-	1.0
b. 3B Bank			
1. Aqueous/organic, %	0.0	-	1.0
2. Organic/aqueous, %	0.1	-	1.0
c. Solvent washer A[d]			
1. Aqueous/organic, %	0.2	-	3.0
2. Organic/aqueous, %	0.1	-	1.0
d. Solvent washer B[d]			
1. Aqueous/organic, %	-	-	1.0
2. Organic/aqueous, %	-	-	[e]
e. Solvent washer C[d]			
1. Aqueous/organic, %	0.4	-	1.0
2. Organic/aqueous, %	0.1	-	1.0

---

[a] See Figure 27

[b] Undetermined - depends on amount of HOCl and dissolved Cl$_2$ in 3AF (Calculations indicate that the minimum value is $\sim$0.4M SnCl$_2$)

[c] 2,5 Ditertiarybutylhydroquinone. Use only if 3AF is omitted from flowsheet.

[d] Organic flow through solvent washers can vary ±20%.

[e] Normally expected to be <1%, however, experience has shown that provision should be incorporated in the waste handling system to remove excess solvent before evaporation.

PILOT PLANT RESULTS

In miniature mixer-settler tests, the product (3BP) contained 99% of the curium. The only significant gamma activity was that from ^{244}Cm and ^{239}Np (the daughter of ^{243}Am). No residual ^{95}Zr-^{95}Nb, ^{106}Ru-^{106}Rh, ^{144}Ce-^{144}Pr, or ^{154}Eu was detected. The feasibility of increasing the rate of processing and decreasing the volume of waste was demonstrated with feeds (3AF) containing 7 g ^{244}Cm/liter, seven times the specified concentration.

In the large pilot production facility, typical composition of purified curium oxide produced from the product (3BP) of the three amine extraction cycles is given in Table XII.

TABLE XII

Typical Composition of Purified Curium Oxide

Fission Product Impurities

	Ci/g ^{244}Cm
^{144}Ce-^{144}Pr	3.3×10^{-4}
^{106}Ru-^{106}Rh	2.4×10^{-5}
^{95}Zr-^{95}Nb	4.0×10^{-6}
^{154}Eu	7.3×10^{-6}
^{137}Cs	3.4×10^{-6}

Elemental Impurities (ppm in Cm_2O_3)

	ppm		ppm
Li	<50	Al	<25
Na	50	Sn	1000
K	25	Cd	<50
Si	<25	B	<10
Zn	<250	Ag	25
Fe	150	Cn	<10
Cr	50	Mg	<10
Ni	25	Mo	250
Am	4200	Mn	<10
Zr	7000	Co	<50
Ca	10	Pb	50
		Ta	1000

Characteristics

Melting Point	2070°C
Weight Loss on Ignition	3%

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