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SEPARATION OF TRANSPLUTONIUMS FROM
LANTHANIDES BY TERTIARY AMINE EXTRACTION

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operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

Elements of the transplutonium group can be separated from those of the lanthanide group by extraction with tertiary amines from concentrated lithium chloride solutions. In laboratory-scale studies single-stage separation factors between the two groups were found to be ≥ 100 . Extraction varied with amine composition and concentration, diluent composition and acidity, and very greatly with salt concentration. Flowsheets were developed for processing transplutoniums to be produced by large-scale neutron irradiation of plutonium.

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1.0 INTRODUCTION

This report covers a study of the extraction of elements of the transplutonium and lanthanide groups by tertiary amine chlorides from aqueous chloride solutions.

The rapidly increasing rate of production of the heaviest elements by neutron irradiation of plutonium necessitates the development of new and improved methods for separating these elements from the fission-product rare earths which always accompany them. The trivalent transplutonium elements differ from each other only slightly in chemical properties, and in most chemical systems each of them behaves almost exactly like a corresponding element in the lanthanide series. Separations of the two groups have been accomplished by certain ion exchange resin systems: 13 N HCl—Dowex 50 (1-3), 20% ethanol-saturated HCl—Dowex 50 (4), NH_4SCN —Dowex 1 (5-7), and 11 N LiCl—Dowex 1 (8-11). These have all been small-scale batch separations. The extremely high level of radiation to be expected from projected quantities of these elements is likely to make the use of solid ion exchangers impractical. Since elements deposited on solid ion exchangers saturate narrow bands of the resins, localized heating and gas evolution will be inevitable.

Liquid-liquid extraction has several advantages over solid ion exchangers, since it may be made continuous and concentrations in all parts of the system are subject to control. Several extraction systems with limited application have been developed: mono-(2-ethylhexyl) phosphoric acid—LiCl (12), monoalkyl phosphoric acid—HCl (13,14), tributyl phosphate (TBP)—LiCl (15), and TBP— NH_4SCN (16). In all these systems there is a shift from the usual relations of the groups, but there is still an overlap. The only extraction system found thus far which provides complete separation of the groups is extraction by tertiary amines from concentrated chloride solutions. Moore (17) has described this system from an analytical viewpoint.

In the work reported attention was given to the effects on extraction of salt composition and concentration, acidity, reagent composition and concentration, diluent composition, extraneous anions, irradiation

of reagents, and physical behavior. Process flowsheets are presented which were devised and tested by multistage laboratory experiments.

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2.0 EXPERIMENTAL TECHNIQUES AND ANALYSIS

Most of the data were obtained by contacting organic and aqueous phases in separatory funnels. Tracer activity was introduced into the aqueous phases either as very small volumes of aqueous solution or by lightly drying small volumes of tracers in beakers and using the salt solutions to dissolve the deposits. The latter method was satisfactory except when the salt solution was lithium chloride with no acid. Since experiments with short contact times indicated that extraction was essentially simultaneous with mixing, long contact times were unnecessary. Separatory funnels were shaken vigorously by hand or for 10 min on mechanical shakers. They were centrifuged or allowed to stand until both phases were clear. Batch countercurrent experiments were performed with separatory funnels and continuous countercurrent experiments with mixer-settlers.

Samples of 1 or 2 ml of each phase were taken for analysis. Activities in the samples were measured by counting of alphas in proportional counters, betas in Geiger-Müller counters, and gammas in scintillation counters. Gammas were counted in vials while sample preparation was required for betas and alphas. Precipitation of fluorides with lanthanum carrier was satisfactory for activities in lithium chloride solutions, but salt mixtures containing aluminum required hydroxide precipitation with sufficient sodium hydroxide to redissolve the aluminum hydroxide. Mixtures of Eu-152 and Am-241 were analyzed by scintillation counting of the Eu-152 after shielding out the low-energy gammas of Am-241 with lead and counting the Am-241 alphas separately, or by differential scintillation spectrometry. The latter method allowed resolution of the 60-kev Am-241 gammas from the 122-kev

Eu-152 gammas as effectively as by lead shielding, but corrections had to be made for low-energy gammas from Eu-152 in counting the Am-241 gammas. Gamma spectrometry was useful in obtaining much more rapid analyses than were possible by the laborious alpha counting procedures. Curium-242 was determined by alpha counting. Californium-252 was measured by spontaneous fission counting, with no interference from other activities. The Bk-249, 90-kev beta, was measured by gas proportional counting of a very pure sample, care being taken to ensure that there was no cross contamination of alpha or other beta.

3.0 PROCESS TESTING AND EVALUATION

The separation factors between elements of the transplutonium group and those of the lanthanide group are so large that only a few stages are necessary to give separations too high to measure at concentrations used in this study. Unless the concentration of an element is extremely high in the feed, it may be undetectable in one of the effluents. Safety restrictions on the amount of activity allowable in laboratory locations limited the number of useful stages in the laboratory counter-current experiments.

Batch countercurrent experiments with more than 5 stages gave separations too large to measure within the restriction to 60 μ c of alpha activity in process at one time. In a 5-stage batch countercurrent experiment for the separation of Am-241 and Eu-152, the organic was 1 M triisooctylamine in diisopropylbenzene, and the aqueous phases were 8 N LiCl—2 N AlCl₃. Batch volumes of organic, feed, and scrubs were each 10 ml. Experimental inefficiency of transfer of such small volumes in funnels obviously decreased the separation. The experiment was continued through 50 cycles. Analyses of effluents near the end of the experiment showed that 99.0% of the Am-241 was extracted while 99.90% of the Eu-152 was rejected. An over-all separation factor of 10^5 corresponds to 4.8 stages with a single-stage factor of 120. Separation of the same magnitude should continue through additional stages; thus 10 stages should give a separation of 10^{10} . In processing

a typical mixture containing 90% lanthanides and 10% transplutoniums, chemically it should be possible to recover 99.99% of the transplutoniums with a purity of 99.999% in a 10-stage system.

In a proposed flowsheet for recovery of actinides (Fig. 1) the feed is 11 N LiCl containing a trace of HCl. The organic is 0.6 M Alamine 336 chloride in diethylbenzene or diisopropylbenzene. The scrub is 11 N LiCl—0.02 N HCl. The scrub/feed/extractant flow ratios are 1/1/3. The transplutoniums are extracted, rejecting the fission products and LiCl, and the pregnant organic is stripped with 1 N HCl to obtain the transplutonium product. The organic can be recycled after sodium carbonate washings and regeneration of the HCl amine salt with an HCl wash. In a batch countercurrent run under conditions similar to those in the proposed flowsheet, tracer Am-241 was 99.99% recovered (Table 1).

4.0 CHEMICAL BACKGROUND

4.1 Relative Extractability of Transplutoniums and Lanthanides

Tertiary amines separate the transplutonium element group from the lanthanide group by factors of the order of 100 in a single extraction. The relative extraction positions of the individual elements of both groups are shown in Fig. 2 for the system 0.6 M Alamine 336 chloride in xylene vs 11 N LiCl, 0.02 N HCl.

In this system the order of extractability of the transplutoniums is $Cf > Bk > Am \geq Cm$ and $Cf > Fm > Es$. Curium is the least extractable transplutonium element, and its reversal of order with americium in the atomic series is the same as in sorption by anion exchange resins from lithium chloride solutions (11). The considerable differences between some of these elements predicate the feasibility of intragroup separation by multistage extractions with amine-LiCl systems, e.g. Cf from Bk-Cm-Am and Bk from Am-Cm. Americium and curium are too nearly alike for practical separation in this way. The same is true of Cf-Es-Fm.

Fig. 1. Actinide-lanthanide separation flowsheet.

Table 1. Separation of Am-241 from Rare Earths by Batch Countercurrent Extraction with 0.8 M Alamine 336 from 11 N LiCl

Feed: 11 N LiCl—0.02 N HCl—5 g/liter rare earths, Eu-152 and Am-241 traced

Scrub: 11 N LiCl—0.02 N HCl

Extractant: 0.6 M Alamine 336—diethylbenzene

Scrub/feed/extractant flow ratio: 1/1/3

Stages: 6 scrub, 6 extraction

Am-241 recovery: 99.99%

Decontamination factor from rare earths: $>10^{4*}$

*Rare earth remaining below limit of detection.

Fig. 2. Extractability of actinides and lanthanides into 30% Alamine-336 in xylene from 11 M LiCl-0.02 M HCl.

The whole lanthanide group is much less extractable than the transplutonium, but differences between elements within the group are small. Of the lanthanides tested, europium is the most extractable. Extractability increased from lanthanum to europium and decreased from europium to lutetium. Analogy with behavior in various other chemical systems indicates that gadolinium may be slightly more extractable than europium.

The separation factor between the least extractable transplutonium, curium, and the most extractable lanthanide, europium, is of the order of 100. This makes possible a group separation with only a few stages, which is unparalleled by previous methods of actinide-lanthanide separation. With as few as 10 stages a separation factor of 10^{10} is available in a continuous countercurrent system.

4.2 Effect of Salt Composition and Concentration

The extractability of the transplutoniums and lanthanides is very strongly dependent on the chloride salt concentration of the aqueous phase. A minimum of approximately 10 N chloride is required in order

to obtain sufficient extraction with reasonable phase ratios. Only lithium and calcium salts have solubility in this range. Lithium chloride is preferred, as the viscosity is considerably less and the extractability of actinides is greater by a factor of ~30 than from calcium chloride. The practical use of LiCl is limited to about 12 N, with 11 N being now considered optimum. It is possible to have a mixed salt of AlCl_3 and LiCl, but at 11 N chloride concentration, the AlCl_3 must be limited to <0.5 N due to solubility limits. However, at 10 N chloride the range of AlCl_3 is considerably greater and 2 N AlCl_3 —8 N LiCl is quite stable and satisfactory for extraction.

The effect of salt concentration on extraction from LiCl was studied with Am-241 and 0.6 M Alamine-336 chloride in diethylbenzene from 8 to 11 N LiCl. Extraction of americium was proportional to approximately the 17th power of the salt concentration over the concentration range studied:

<u>Aqueous LiCl, N</u>	<u>Am E_a^0</u>	<u>Aqueous LiCl, N</u>	<u>Am E_a^0</u>
11	7.0	9.5	0.8
10.5	3.5	9.0	0.25
10.0	1.4	8.0	0.036

Additional work with 0.5 M Alamine-336 in diisopropylbenzene and in Amsco vs 7-11 N LiCl and 7-10 N ($\text{LiCl} + \text{AlCl}_3$) gave extraction dependences of 18th and 19th power on the chloride concentration (Table 2). At these very high concentration dependences it is difficult to establish precise power factors of the LiCl concentration. It may be said that the extractability of the transplutonium and rare earth elements is proportional to the 15-20th power of the chloride salt concentration. This high concentration dependence is reflected in variations in experimental extraction coefficients with small differences in the concentrations of separate batches of prepared aqueous solutions.

The most consistent experimental results were obtained with 8 N LiCl—2 N AlCl_3 with no excess acid in the amine or salt. The aluminum chloride had such a strong buffering effect that even a considerable

Table 2. Salt Concentration Dependence of Americium Extraction

Organic: 0.5 M Alamine 336 in DIPB; Amsco 125-82 + 5% TDA

Aqueous: 7-11 N LiCl, 7-10 N (LiCl + AlCl₃) (4/1 equivalent ratio)

Chloride (LiCl) Range, N	Power Dependence		Chloride (LiCl+AlCl ₃) Range, N	Power Dependence	
	DIPB	Amsco 125-82		DIPB	Amsco 125-82
7-8	20	16	7-8	16	17
8-9	14	20	8-9	19	18
9-10	19	21	9-10	20	22
10-11	23	17	7-10 (over- all)	18	19
7-11 (over- all)	18	19			

acid deficiency made no significant difference in results.

4.3 Effect of Acidity

The effect of acidity on extraction of Am-241 and Eu-152 by Alamine-336 chloride was measured at a constant 11.3 N total chloride (LiCl + HCl) concentration in the aqueous before contacting with an equal volume of the amine chloride solution. Initial acidities of the aqueous were varied from 0.1 to 1.0 N HCl. Over this range the distribution coefficient for americium was inversely proportional to the 1.75 power of the initial acidity, while that for europium was inversely proportional to the 1.3 power of the acidity (Fig. 3). Thus the separation factor decreased as the acidity increased.

Similar tests were made of extractions of Am-241 and Ce-144 by Alamine-336 from 8 N LiCl—2 N AlCl₃ with added acid. Americium extraction was inversely proportional to the 1.2 power of the acidity while cerium extraction was inversely proportional to the 0.7 power of the acidity. There was less effect on extraction from acid in the mixed salt than in pure LiCl.

Tertiary amine chloride solutions are usually prepared by contacting solutions of amines in diluents with more than enough hydrochloric acid to form the salt R₃N·HCl. A fraction of the excess acid is extracted

Fig. 3. Effect of acidity on extraction by 0.6 M Alamine 336.

by the amine chloride. This can be removed by a few stages of stripping with dilute lithium chloride. Further strippings will contain $\sim 0.001 N$ HCl from hydrolysis of the amine chloride.

The behavior of acid in an amine chloride—lithium chloride system depends on the concentrations of amine and aqueous salt solutions. Small amounts of acid were highly extracted by 0.5–1.0 M amine chloride solutions from concentrated lithium chloride. Therefore, in successive contacts with slightly acidified lithium chloride, the acidity of the amine continually increased, resulting in changes in americium extraction. Americium-241 distribution coefficients decreased rapidly with successive scrubs with 11 N $LiCl$ —0.05 N HCl and slowly with 11 N $LiCl$ —0.01 N HCl , but remained essentially constant with 11 N $LiCl$ —0.001 N HCl (Table 3). In view of the high extraction of hydrochloric acid, the amount of acid added to the system by the 11 N $LiCl$ —0.001 N HCl was probably insignificant compared with the unknown amount of excess acid already in the amine chloride.

Successive stages of extraction by amine chlorides from the same

Table 3. Effect of Acidity on Am-241 Extraction

Organic: 1 M TIOA in DIPB, contacted with 6 N HCl and 6 N LiCl

Aqueous: 11 N LiCl with added HCl

Scrub Stage	E_a^O			Scrub Stage	E_a^O		
	0.001 <u>N</u> HCl	0.01 <u>N</u> HCl	0.05 <u>N</u> HCl		0.001 <u>N</u> HCl	0.01 <u>N</u> HCl	0.05 <u>N</u> HCl
1	47	35	19	8	46	25	5.5
2	49	31	14	9	35	24	5.6
3	43	32	12	10	47	24	5.0
4	46	32	9.2				
5	45	31	8.1	11	47	23	2.3
				12		24	2.5
6	55	30	7.0	13			2.6
7	49	28	6.4				

aqueous salt solution were expected to deplete the acid in the aqueous solution. However, an 11-stage batch countercurrent extraction resulted in constant aqueous acidity throughout the system. A solution of 0.8 M Alamine-336 chloride in diisopropylbenzene had been prepared by contacting the amine solution first with 6 N HCl, then with 2 N LiCl, and finally with an equal volume of 11 N LiCl—0.05 N HCl. Aqueous feed and scrub for the countercurrent experiment were equal volumes of 11 N LiCl—0.05 N HCl. The system reached apparent equilibrium rapidly with 0.004 N HCl in the aqueous phase of all stages. In a similar experiment with 11 N LiCl—0.01 N HCl, the acidity left in the aqueous was 0.003 N. These experiments indicated that at low acidities nearly all the acid was extracted by the amine, and the excess acidity of the prepared amine was a major part of the acidity in the system.

Attempts were made to determine the concentration of excess hydrochloric acid in an amine chloride solution. Portions of 0.8 M Alamine-336 chloride solution in diisopropylbenzene, prepared as above with a final scrub with 11 N LiCl—0.01 N HCl, were contacted with multistage strips of 0.05, 0.5, 2, 6, and 11 N LiCl. Attempts to strip with pure water resulted in emulsions. Analyses of the strips showed a large effect of salt concentration, not only on the fractions of acid stripped by

successive strips but also on the apparent total amount of acid available for stripping (Table 4). There was considerably more excess HCl

Table 4. Stripping of HCl from Amine Chloride

Organic: 0.8 M Alamine-336 chloride plus HCl in DIPB

Stripping agents: 0.05, 0.5, 2, 6, and 11 N LiCl

A/O volume ratio: 1/1

Strip No.	HCl, N				
	0.05 N LiCl	0.5 N LiCl	2 N LiCl	6 N LiCl	11 N LiCl
1	0.062	0.057	0.055	0.037	0.0030
2	0.015	0.007	0.0046	0.009	0.0027
3	0.011	0.0045	0.0024	0.0030	0.0024
4	Emulsion	0.0035	0.0016	0.0011	0.0023
5		0.0030	0.0014	0.0009	0.0023
6		0.0029	0.0014	0.0004	0.0021
7		0.0026	0.0009		0.0019
8		0.0022			0.0017
9		0.0020			
10		0.0019			
11		0.0017			
12		0.0016			
13		0.0015			
14		0.0014			
15		0.0014			
16		0.0014			
Apparent Total	>0.08	~0.09	~0.06	~0.05	~0.02

than the 0.01 N planned in preparation of the amine solution. Alteration of original acidities by successive extractions or scrubbing was the cause of some inconsistencies in data on extraction of transplutoniums and lanthanides from lithium chloride solutions.

4.4 Effect of Reagent Composition

A variety of tertiary amines in a common diluent were compared as extractants of Am-241 from 8 N LiCl—2 N AlCl₃ (Table 5). Extraction coefficients increased as the size of the hydrocarbon groups decreased,

Table 5. Amine Composition Dependence

0.5 M amine in Solvesso-100; 8 N LiCl—2 N AlCl₃

Amine	E_a^0	
	Am	Eu
Trilauryl (dodecyl)	0.50	0.004
Alamine 336 (octyl and decyl)	0.64	0.006
Triisooctyl	1.02	0.008
Triisohexyl	1.35	
<u>n</u> -butyldidodecyl	1.0	
<u>n</u> -butyldidodecenyl	1.0	

and substitution of unsaturated for saturated groups had no effect in the one example tested. The amines differed considerably in physical properties and behavior. Trilauryl amine chloride separated as a solid from 0.5 M solution in Amsco 125-82 or diethylbenzene in contact with 1 N HCl at temperatures below 35°C. Alamine-336 was somewhat more compatible with Amsco 125-82 and gave no difficulties with aromatic diluents. All amines in Amsco 125-82 required modification with alcohol to prevent separation of a second liquid organic phase on contact with salt solutions. Triisohexylamine required the most alcohol and gave a second organic phase even in aromatic diluents on contact with dilute hydrochloric acid.

4.5 Effect of Reagent Concentration

Reagent concentration dependence for Am-241 extraction was studied with various concentrations of Alamine-336 chloride in diisopropylbenzene (DIPB) and in Amsco 125-82 modified with 0.4 mole of TDA per mole of amine. Aqueous solutions were both 11 N LiCl—0.01 N HCl and 8 N LiCl—2 N AlCl₃. Power dependence of extraction on concentration varied from 1.4 to 2.0 (Fig. 4). Results of corresponding extractions of Eu-152 were essentially parallel to those for Am-241. Extractions of Am-241 by TIOA (0.5 to 1.0 M) in DIPB from 8 N LiCl—2 N AlCl₃ were proportional to the 2.0 power of the amine concentration. It appears that aromatic

Fig. 4. Amine concentration dependence.

diluents give a higher reagent concentration dependence than aliphatics, but there are insufficient data to evaluate the influence of all factors.

4.6 Effect of Diluent Composition

The extraction of Am-241 and Eu-152 from 8 N LiCl—2 N $AlCl_3$ by 0.5 M triisooctylamine (TIOA) was studied with a variety of diluents (Table 6). Increasing the lengths of carbon chain substituents in aromatics increased extraction. The aromatics lighter than diethylbenzene are unsuitable because of flammability (flash point of diethylbenzene is 138°F). Some cyclic compounds gave good extraction, but decalin gave a third phase in contact with 1 N HCl. Amsco 125-82 appeared favorable but required up to 5% tridecanol to prevent third-phase formation on contact with concentrated salt solution and still more with 1 N HCl. The alcohol greatly decreased extraction. Straight-

Table 6. Diluent Composition Dependence

Extractant: 0.5 M TIOA

Aqueous: 8 N LiCl—2 N AlCl₃

Diluent	E_a^0		Separation Factor
	Am	Eu	
Benzene	0.27	0.0022	130
Toluene	0.45	0.0040	110
Xylene	0.65	0.0052	125
sec-Butylbenzene	0.83		
sec-Butylbenzene + 5% TDA	0.19	0.0020	95
Diethylbenzene	1.35	0.011	120
Diisopropylbenzene	1.8	0.015	120
Triethylbenzene	1.2		
Cyclohexane	1.8	0.025	70
Tetralin	0.07		
Decalin	3.5	0.029	120
Nonane + 5% TDA	0.79		
Hexadecane + 10% TDA	0.74		
Amsco G	0.13		
Amsco 123-15 + 5% TDA	0.49		
Amsco 125-82 + 5% TDA	2.5	0.03	80
Amsco 125-82 + 10% TDA	0.6		
Amsco 125-82 + 5% nonylphenol	1.0		
Solvesso-100	1.0	0.0077	130
Varsol + 10% TDA	0.45		
Shell E-2342 + 2% TDA	10.5	0.48	22
Shell E-2342 + 5% TDA	5.7	0.29	20
Shell E-2342 + 20% cyclohexane	20	0.8	25
Shell E-2342 + 20% xylene	14	0.6	23
Shell E-2342 + 20% diisopropyl- benzene	18	0.7	26
Dibutylcarbitol	0.06		
Diethylcarbitol	1.2		
Acetophenone	0.2		
Isophorone	0.3		
Carbon tetrachloride	0.001		
Pentachloroethane	<0.001		
Diisobutyl carbinol	<0.002		

chain aliphatics gave low extraction and poor phase compatibility. Shell E-2342, reported to contain some cyclic compounds, gave high extraction but required extensive modification by alcohol and gave greatly decreased Am/Eu separation factors. Extraction with other diluents was very poor except with diethylcarbitol, which is soluble in water and dilute HCl but not in concentrated salt solutions.

For use with 8 N LiCl—2 N AlCl₃, diisopropylbenzene appears to be the best choice based on extraction power, phase compatibility, and flash point (171°F). The high extraction power is useful but unnecessary with 11 N LiCl.

4.7 Effect of Organic Phase Modifiers

Amine chlorides in aliphatic diluents require the addition of a modifier, such as a long-chain alcohol, to prevent formation of two organic phases when in contact with either concentrated LiCl or dilute HCl solutions. The alcohol decreases extraction. Extractions of americium and europium by 0.5 M TIOA chloride in Amsco 125-82 decreased by a factor of 4 with an increase of tridecanol concentration from 5% (required to prevent third-phase formation with concentrated chloride solutions) to 10% (required to prevent third-phase formation with dilute HCl).

The effect of an alcohol on an aromatic diluent was tested by extractions of americium and europium by 0.6 M Alamine-336 chloride in xylene with added 2-ethylhexanol from 11 N LiCl. Extractabilities of americium and europium decreased sharply with increasing alcohol content (Fig. 5a). Distribution coefficients decreased by a factor of 3 to 4 with 5% and by a factor of 100 with 20% 2-ethylhexanol.

Aromatic diluents are preferred to aliphatics because, with those tested, maximum extractability may be obtained with no problem of phase stability.

4.8 Effect of Extraneous Anions

A tertiary amine is a base which may form a salt in the organic phase by extracting an acid from an aqueous phase:

Fig. 5. Effect of (a) isooctyl alcohol in xylene (constant 0.6 M Alamine 336) and (b) nitrate on extraction of americium and europium from 11 M LiCl .

where R_3N is an amine of high molecular weight; A^- is an anion of a simple acid or a complex metal acid, such as $AmCl_6^{3-}$; and o and a are the organic and aqueous phases, respectively.

The amine salt can undergo anion exchange with another anion present in the aqueous phase, the order of preference being $ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$ (18). 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.

The effect of nitrate on extractability of americium and europium by 0.8 M TIOA in xylene from 11 N LiCl was tested. Lithium nitrate was added in concentrations from 0.01 to 1.0 N to 11 N LiCl. The distribution coefficient for americium and europium increased very rapidly with increased nitrate concentration, while the separation factor decreased steadily (Fig. 5b). At 0.6 N $LiNO_3$ the americium and europium distribution coefficients were equal. At higher nitrate concentrations europium was more extractable than americium. Separation factors decreased from 100 at 0.01 N NO_3^- to approximately 10 at 0.1 N NO_3^- .

The preferential affinity of amines for certain anions can be used to remove an objectionable anion from an aqueous phase. A process was devised and tested in a mixer-settler to remove HNO_3 from a mixture of HNO_3 and HCl (Fig. 6). The feed, 5 N HCl—1 N HNO_3 , was contacted with twice its volume of neutral 0.6 M Alamine-336 in diethylbenzene in a continuous mixer-settler. In 7 stages the nitrate concentration of the aqueous decreased from 1.0 to <0.001 N. The raffinate from the extractor was 5 N HCl with no detectable trace of nitrate present. Neither transplutonium nor lanthanide elements are extracted by the amine from the acid solution. The raffinate can be readily converted to a concentrated LiCl solution, which can be fed to an amine chloride—LiCl system for group separation.

4.9 Effect of Radiation

Preliminary data on the radiation stability of Alamine-336 chloride in diethylbenzene indicate that irradiation at levels likely to be

Fig. 6. Nitrate removal flowsheet.

encountered in processing has no significant effect on separation power or on the chemistry of extraction. With very high irradiation there is an increase in phase separation difficulties. An 0.6 M Alamine-336 chloride solution in diethylbenzene was agitated with 11 N LiCl while exposed to Co^{60} irradiation up to 100 whr/liter. Up to 25 whr/liter no effect was observed except a change in the color of the organic phase from reddish orange to lime green. At 100 whr/liter the organic contained a gel-like emulsion. The distribution coefficients increased about 50% with 25 whr/liter irradiation, while the separation factor remained constant at about 120.

It was possible to clean up the reagent for reuse even after 100 whr/liter irradiation. Scrubbing the irradiated reagent with 1 M Na_2CO_3 and reconvertng to chloride restored it to its original condition with respect to distribution coefficients and physical characteristics.

4.10 Phase Separation

One problem encountered in the use of amine chloride and concentrated LiCl solutions derives from the high viscosity and surface tension

of the two solutions. The breaking time for the two phases after intimate mixing tends to be impracticably long, of the order of 3 min at room temperature (23°C). This creates problems when trying to operate the process in a mixer-settler, as the holdup volume must be large in order to provide sufficient time for the phases to separate and thus prevent flooding.

Two methods are available for reducing the breaking time: the use of surface-active agents and increase of temperature. A surfactant which reduces the surface tension of either phase also reduces breaking time. Of many surfactants investigated, only a few have been found which produce the desired effect. One of the best of these is Minnesota Mining and Manufacturing's surfactant FX-170. This is a nonionic fluorochemical with a solubilizing functional group. With 100-1000 ppm of FX-170 in the aqueous phase the breaking time was reduced from ~3 min to 30-40 sec. The surfactant had no effect on the distribution coefficients or separation factors of americium and the lanthanides.

Temperature has a considerable effect on the breaking time of the mixed phases. The breaking time for 0.6 M Alamine-336 chloride in diethylbenzene vs 11 N LiCl decreased considerably as the temperature increased:

Temp, °C	Breaking Time, sec	Temp, °C	Breaking Time, sec
23	210	60	50
30	180	70	30
40	120	80	20
50	70		

The increase in temperature also decreased the extractability of americium and rare earths, e.g. the distribution coefficient for americium decreased ~25% with a temperature increase from 30 to 60°C.

A combination of surfactant addition and a reasonable temperature increase permitted operation of the mixer-settlers without flooding.

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