DRAFT

CONF-800814--15

MASTER

**MULTIGRAM GROUP SEPARATION OF ACTINIDE AND LANTHANIDE ELEMENTS
BY LiCl-BASED ANION EXCHANGE***

E. D. Collins, D. E. Benker, F. R. Chatten,
P. B. Orr, and R. G. Ross

Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. It contains certain information which may be confidential. It is to be distributed only to those persons who are authorized to receive it. It is not to be distributed outside the agency or to the public. It is not to be used for any purpose other than that for which it was prepared. It is not to be reproduced or transmitted in any form or by any means electronic or mechanical, including photocopying and recording, or by any information storage or retrieval system, except as may be permitted in writing by the agency. It is to be destroyed when it is no longer needed for the purpose for which it was prepared.

To be presented at the Symposium on "Industrial-Scale Production - Separation - Recovery of Transplutonium Elements," 2nd Chemical Congress, ~~San Francisco~~, 1980, August 24-29.

L. S. Veyse

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the article.

*

Research sponsored by Office of Basic Energy Sciences, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

26

DO NOT TYPE ON THIS LINE

Start typing — 50
on this line.

MULTIGRAM GROUP SEPARATION OF ACTINIDE AND LANTHANIDE ELEMENTS
BY LiCl-BASED ANION EXCHANGE

E. D. Collins, D. E. Benker, F. R. Chattin,
P. B. Orr, and R. G. Ross

Do Not Type
Past this
Line

Start First — 35
Page Here.

A laboratory-scale, chromatographically-operated, LiCl-based anion exchange (LiCl AIX) process (1) was adapted to the multigram scale and has been used successfully in the Transuranium Processing Plant (TRU) at Oak Ridge National Laboratory (ORNL) for over ten years to separate lanthanide fission products from the transplutonium actinides and to partition americium and curium from the heavier elements. At the time of the process design studies for TRU, the LiCl AIX process was recognized as one of the few methods that had been used successfully in laboratory operations; however, the use of solid ion exchangers was considered impractical for the larger scale operations at TRU, primarily because of the localized heating and radiolytic gas generation that would occur. Thus, a continuously-operated solvent extraction process (Tramex) was developed to accomplish the actinide-lanthanide separation (2). This process was chemically similar to the anion exchange process because it utilized a mixed tertiary amine (primarily

Do Not Type
Below This
Line. — 1

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50 octyl and decyl) to extract transplutonium actinides from a concentrated LiCl solution.

Do Not Type
Past this
LineStart First
Page Here.

35 A second continuously-operated solvent extraction process (Pharex) was developed to partition the transcurium actinides from the americium and curium in the Tramex product (3). The Pharex process utilized 2-ethylhexyl phenylphosphonic acid as the extractant for the transcurium actinides. During early operations at TRU, the selectivity of the Pharex extractant was found to be severely reduced by the presence of zirconium ions which were introduced into the process solutions by corrosion of Zircaloy-2 equipment in TRU. At zirconium concentrations above 10 ppm, the achievable separation began to be diminished and at 100 ppm, a practical separation could not be made (4). Thus, a replacement for the Pharex process was needed and the LiCl AIX process was the most immediate alternative.

Temporary glass equipment was installed and the LiCl AIX process was successfully scaled to a useful level (5). Tramex product solutions, containing from 4 to 10 g of ^{244}Cm (11 to 28 W of decay heat) were processed initially, using a 38-mm-diam column containing 450 mL of Dowex 1-X8 anion exchange resin (Dowex 1-X10 is now used). Subsequently, a larger glass column, having a diameter of 50 mm and containing 1.2 L of resin, was used. Finally, the large glass column was replaced with a tantalum column of identical size. For this column, a loading capacity of 19 g of ^{244}Cm (54 W) or 35 g of total actinide mass

Do Not Type
Below This
Line.

1

<R3

<R4

<R5

Start typing — 50
on this line.

has been empirically established. Localized heating and cumulative radiation exposure of the resin is a problem although not as extensive as expected. Radiolytic gas generation has not caused any significant difficulty and downflow operation is used with little evidence of channeling. At the loading limits that have been established, three column loadings and elutions can be made successfully on each batch of resin.

Do Not Type
Past this
Line

Start First — 35
Page Here.

Process Chemistry

The LiCl AIX process is based on (1) the formation of anionic chloride complexes of the tripositive actinide and lanthanide metals in concentrated lithium chloride solutions, (2) the sorption of these complexes onto a strong base anion exchange resin contained in a column, and (3) the preferential chromatographic elution of the lanthanides as a group prior to elution of the actinides. Typical reactions involved in the complex formation and resin loading are:

At equilibrium, the activities (a) of the reacting species are related as follows:

$$(1a) \quad K_1 = \frac{(a_{MCl_5}^{-2})_{aq}}{(a_{M^{+3}})_{aq} (a_{Cl^{-}}^5)_{aq}}$$

Do Not Type
Below This
Line.

DO NOT TYPE ON THIS LINE

Start typing
on this line.

50

$$(2a) \quad K_2 = \frac{(a(R_3NH)_2MCl_5)_{org} (a_{Cl^-}^2)_{aq}}{(a_{(R_3NHCl)}^2)_{org} (a_{MCl_5-2}^5)_{aq}}$$

Do Not Type
Past this
LineStart First
Page Here.

35

where K_1 and K_2 are the equilibrium constants for the two reactions. The equilibrium distribution coefficient (K_d) for the trivalent metal, defined as the ratio of the activity sorbed on the resin to the activity in the aqueous phase at equilibrium, can be obtained by combination and rearrangement of equations (1a) and (2a):

$$(3) \quad K_d = \frac{(a(R_3NH)_2MCl_5)_{org}}{(a_{M+3})_{aq}} = K_1 K_2 (a_{R_3NHCl}^2)_{org} (a_{Cl^-}^3)_{aq}$$

Thus, for the divalent anionic complex illustrated, the distribution coefficient, K_d , varies directly with the second power of the activity of the functional amine group (quarternary ammonium chloride) of the resin and with the third power of the aqueous chloride activity. Similar equations can be written to show that the K_d dependence on the activity of the functional amine group is first power for monovalent anionic complexes, second power for divalent complexes (as illustrated), third power for trivalent complexes, etc. However, the dependency on the activity of the aqueous chloride is third power for all complexes. The latter effect was confirmed experimentally by

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50

Hulet, et al (1). Even though this is true, the dependency on the aqueous chloride concentration (rather than the activity) is much greater, since the activity coefficients increase rapidly with concentration in the region of interest. Baybarz and Weaver (2), in their studies of the Tramex system, found the K_d dependency to be proportional to the 17th power of the chloride concentration. Thus, the LiCl concentration in eluent solutions must be very carefully controlled to obtain the desired sorption and separations. Hulet, et al found that superior actinide-lanthanide group separations are obtained in the region of 10 M LiCl; below 8 M LiCl, the two series of elements tend to merge and above 10 M, the elution time becomes inconveniently long. Their study also showed that, by increasing temperature from 25 to 87°C, resin cross-linkage to 8 or 10% divinylbenzene, and LiCl concentration to >10 M, the sorption and selectivity were improved; however, increasing the HCl concentration above 0.1 M, caused a significant decrease of sorption.

Do Not Type
Past this
LineStart First —
Page Here.

35

The relative distribution coefficients shown in Fig. 1 suggest that the lanthanides could be separated as a group from the actinides and that the americium and curium could be partitioned from the heavier actinides. These data were obtained by Baybarz and Weaver (2) for the Tramex solvent extraction system but are applicable to the LiCl AIX system on a relative basis.

Do Not Type
Below This
Line.

1

< F1

DO NOT TYPE ON THIS LINE

Start typing _____ 50
on this line.

The comparative data obtained by Baybarz and Kinser (6), in their study of the behavior of contaminant ions in TrameX extraction (from 11 M LiCl solutions) and stripping (with 0.5-10 M HCl) have been useful for planning and interpreting results from LiCl AIX operations. The distribution coefficients (K_d 's) for the extraction of various ions of corrosion and fission product elements indicated that Ru^{+3} , Ce^{+3} , Eu^{+3} , Y^{+3} , Cr^{+3} , Ba^{+2} , and Sr^{+2} are sorbed more poorly than the tri-positive actinides, that Zr^{+4} , MoO_4^{-2} , Ni^{+2} , and Pb^{+2} behave similarly, and that Fe^{+3} , Co^{+2} , Mn^{+2} , Ti^{+4} , Cu^{+2} , Sn^{+4} , and Zn^{+2} are more strongly sorbed. Stripping K_d 's indicated that Ti^{+4} and Ni^{+2} are stripped with the actinides at any HCl concentration between 0.5-10 M. However, most of the extracted elements can be left on the resin during the stripping of the actinides. The effects of various anions were also determined by Baybarz and Kinser. Increasing nitrate concentration was shown to cause an increase in extraction K_d 's of both Am^{+3} and Eu^{+3} , but to cause a decrease in the separation factor between the two elements.

Process Equipment

Most of the equipment used at TRU for separating multigram quantities of actinides and lanthanides is contained on a compactly arranged equipment rack that is about 1 m wide and 2 m high. The rack is located within a heavily-shielded, but small hot cell (about 8 m³ of space) which is equipped with a viewing

Do Not Type
Past this
Line <R6Start First _____ 35
Page Here.Do Not Type _____ 1
Below This
Line.

DO NOT TYPE ON THIS LINE

Start typing
on this line.

50

window and a pair of master-slave manipulators. A schematic diagram of the equipment is shown in Fig. 2. The feed adjustment evaporator (25 L capacity) and waste collection tank (70 L capacity) are located in a remote tank pit and the eluent and resin addition tanks are located above the hot cell in a non-radioactive area. All of the equipment and piping which serve the feed and product solutions are built of glass or tantalum; these materials have provided excellent resistance to the highly corrosive, radioactive chloride solutions.

Start First
Page Here.

35

The calibrated, glass feed tank has a diameter of 102 mm and a capacity of 4.5 L. Solutions can be added to the tank via two routes: first, vacuum can be applied to the tank to motivate transfer of adjusted feed solution from the feed adjustment evaporator; and secondly, pressurized transfer of solution can be made from the eluent addition tank. A tantalum diaphragm pump is used to transfer solutions from the feed tank to the top of the ion exchange column. Flow rates are controlled by cycling vacuum and pressure against the diaphragm at a selected frequency; a discharge pressure of up to 200 kPa can be achieved.

The tantalum ion exchange column has a 50-mm diameter and is 76 cm long; it is heated to 70-80°C by hot water which is circulated through the column jacket. Resin supports inside the column are sintered tantalum discs. In the glass columns used previously, a spring-loaded plate was provided at the top

Do Not Type
Below This
Line.

1

Do Not Type
Past this
Line

CF2

DO NOT TYPE ON THIS LINE

Start typing
on this line.

50

of the column to prevent movement of the resin bed by rising bubbles of radiolytically generated gas; however, the plate was found to be unnecessary and was not provided in the present column.

Do Not Type
Past this
Line

Effluent solution from the ion exchange column is passed through an in-line alpha-detector which activates a count rate meter and recorder outside the cell. Inside the detector, the liquid flow is passed adjacent to a mylar film-covered window, which separates the liquid from the silicon diode detector.

In addition to the large waste collection tank, the column effluent liquid can be routed to either of five product collection tanks, each of which has a capacity of 7 L.

Operating Procedure

Resin Preparation and Loading. Batches of 200-400 mesh Dowex 1-X10 resin (chloride form) are classified to obtain a middle fraction having a wet particle size range of about 55-105 μm . The classified resin is treated with 6 M HCl to ensure that the chloride form has been maintained. A 1.3 L volume of the treated resin (measured after settling for 60 min) is slurried in water and transferred into the ion exchange column. The feed tank, pump, piping, column, and resin bed are conditioned by transfer of 3 column volumes of synthetic feed solution (12 M LiCl --0.1 M HCl) through the system. This avoids dilution of the actual feed solution by any dilute solution left in the equipment during previous operations.

1

Start First
Page Here.

35

Do Not Type
Below This
Line.

DO NOT TYPE ON THIS LINE

Start typing
on this line.

50

Feed Pretreatment. A two-step clarification process is used to eliminate problems with solids formation and to significantly reduce the amount of transplutonium elements diverted into rework solutions by inclusion with the solid material (7). In the first step, the feed solution, which is the product of a solvent extraction process, is washed with an organic diluent (diethylbenzene) to remove entrained organic extractant that would be degraded in the subsequent evaporation steps to a tar that could sorb a significant amount of the transplutonium elements. The second step is designed to remove insoluble amounts of aluminum, sodium, and zirconium which are typical impurities contained in the feed solutions. The treatment includes: (1) adjustment to a small volume of 12 M LiCl--1 M HCl, (2) filtration to remove the insoluble materials, (3) dilution by flushing the filter with 12 M LiCl--1 M HCl solution, and (4) readjustment to a larger volume of 12 M LiCl--0.1 M HCl. This treatment is based on the fact that the solubility of AlCl_3 is significantly lower in 12 M LiCl--1 M HCl than in 12 M LiCl--0.1 M HCl.

Do Not Type
Past this
LineStart First
Page Here.

35

Feed Adjustment. The feed solutions are adjusted to concentrations of 12.0 M LiCl and approximately 0.1 M HCl. The typical feed volume used for a single loading and elution of the resin is 3 L. Thus, when the loading is limited by total mass of the actinides (to 35 g), the concentration is about 12 g/L,

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing
on this line.

50

and when the limit is alpha-decay heat (54 W from 19 g of ^{244}Cm), the power density is 18 W/L.

Do Not Type
Past this
LineStart First
Page Here.

35

The specification for feed solution acidity is based on providing an HCl concentration high enough to prevent hydrolysis of the actinides and yet low enough to allow sorption of the actinides within a narrow band at the top of the resin bed. By using the maximum practical concentration of LiCl (12 M), the highest allowable concentration of HCl can be used. This is necessary because the acidity is continuously reduced by radiolytic destruction of the HCl at such a rapid rate (typically about 0.01 M/h) that the technique of acidity adjustment, sampling, analysis, and readjustment cannot be used. Thus, the acidity can not be firmly specified. The acceptability of the feed is achieved by using a proven procedure for adjustment and is judged by observation of the presence or absence of a precipitate.

The feed adjustment procedure includes (1) adding the required amount of LiCl (if necessary), (2) evaporating the solution until a temperature of 142.5°C is reached (this is the boiling point of 13 M LiCl), (3) cooling to 50°C and adding enough 12 M HCl to bring the feed solution acidity to 1 M, (4) digesting the solution at 120±0.5°C for 10 minutes (to dissolve hydrolyzed zirconium which is frequently present and to lower the acidity to about 0.1 M HCl), and (5) cooling to 50°C. The adjusted feed solution will remain stable for several

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing — 50
on this line.

hours which is enough time to complete the transfer to the ion exchange column.

Do Not Type
Past this
Line

Loading. The appropriate volume (usually 3 L) of adjusted feed is transferred to the feed tank and pumped to the ion exchange column at a flow rate of 2 L/h (equivalent to a superficial velocity of 280 $\mu\text{m/s}$ in the column). Elution of the resin is begun immediately after the loading is completed. A movable detector is used to measure the neutron profile in the column after the loading and at one-hour intervals during the elution. The position of the neutron peak (from ^{252}Cf) after loading, as illustrated in Fig. 3, can indicate resin damage or shrinkage at the top of the bed; a peak which is lower in the bed is usually observed when the resin is used for more than one loading and elution.

Elution. In general, the lanthanides are eluted first, using 4 column volumes of 10 M LiCl; then, 90-95% of the americium and curium is eluted, using 3 column volumes of 9 M LiCl. The remainder of the americium and curium is eluted along with all of the heavier actinides, using 2 column volumes of 8 M HCl. Finally, the column is flushed with 3 volumes of 0.8 M HCl to remove sorbed impurities, such as zirconium and plutonium. More precisely, the LiCl eluent solutions are adjusted to within 0.05 M of the desired concentration and are acidified to 0.10 ± 0.05 M HCl; hydroxylamine hydrochloride is

Start First — 35
Page Here.

Do Not Type — 1
Below This
Line.

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50

added (to a concentration of 0.1 M) as a reducing agent for any tetravalent cerium sorbed on the resin and methyl alcohol is added (to a concentration of 2.5% by volume) to suppress the rate of radiolytic destruction of HCl and the corresponding generation of radiolytic gases (8). Typically, the eluents are added to the feed tank in small portions and pumped to the column; thus, the eluents also serve to flush the feed system. The eluent flow rate is 1 L/h and the superficial column velocity is 140 $\mu\text{m/s}$.

Do Not Type
Past this
LineStart First
Page Here.

35

The progress of the actinide elutions are monitored by periodic measurement of the neutron profile of the column, as illustrated in Fig. 3, and by a continuous reading of the alpha-activity in the effluent solution from the column. A typical plot of the alpha-activity is shown in Fig. 4. These data are used to select the routing of the effluent solution into the proper collection tank. Although a discriminator is used, the alpha-detector is usually sensitive to some of the beta-gamma emissions from the lanthanide fission products. Practically, the detector response may vary because of radiation exposure, heat effects, or physical damage. Also, the process separations vary from run to run because of the extreme sensitivity to solution concentrations and because of accumulated radiation damage to the resin. Thus, the operating procedure requires routing the effluent solution into a "pre-curium" collection tank when the alpha-detector reading

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50

rises above the background. If the reading continues to increase, the flow is routed into the curium product tank. If the alpha-detector malfunctions and no response occurs, route selections are based on solution volumes.

Do Not Type
Past this
LineStart First
Page Here.

35

The location of berkelium, a beta emitter which cannot be monitored, can be estimated from the position of the californium in the column, as determined by the neutron peak (from ^{252}Cf), during the time that curium is in the effluent solution. Typical neutron peaks are shown in Fig. 3. By comparison of the relative distribution coefficients of the actinides shown in Fig. 1, the berkelium location is known to be about midway between californium and curium. The last 5-10% of the americium and curium is purposely routed into the transcurium element product tank to minimize the berkelium loss. Subsequently, this americium and curium is recovered in a second cycle LiCl AIX run.

Resin Damage, Replacement, and Storage. At the actinide loading limits described above, up to 3 loadings and elutions can be made on each batch of resin before accumulated resin damage occurs to an extent that adequate separations can no longer be made. The exposure of the resin after 3 loadings and elutions of 19 g of ^{244}Cm (a total of 57 g of ^{244}Cm or 162 W of decay heat) has been estimated to be 2.5 MGy (2.5×10^8 rads) at the top 15% of the resin bed and 1.5 MGy in the lower bed. This

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50 is in the range of exposure that typically causes considerable degradation to most anion exchange resins (9). Thus, in production operations at TRU, the resin must be replaced frequently.

Spent resin is transferred from the column through a 10-mm-diam tube to a resin storage tank. The flush water continuously overflows the storage tank through a screen to the ORNL Intermediate Level Liquid Waste System.

Start First —
Page Here.

35 Process Use in Production Campaigns

The LiCl AIX process was used for several years at TRU to treat product solutions from the continuous Tramex process to partition the americium and curium from the heavier elements and to provide additional decontamination from fission products. However, the continuous Tramex process was often plagued by malfunctions caused by feed solution instability and emulsion formation in the pulsed columns. During one campaign, a severe emulsion problem occurred and could not be overcome. As an expedient, a Tramex batch extraction was employed. The decontamination obtained from the lanthanide fission products was about 5-10 times lower than that usually obtained from the continuous multistage process. However, the remaining lanthanides were efficiently removed by the subsequent LiCl AIX process. These experiences showed that the combination of a Tramex batch extraction with the LiCl AIX process provided adequate decontamination of the transplutonium elements and required less

Do Not Type
Past this
Line

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50 time and effort than the previous method. Thus, the continuous version of the Tramex process was abandoned.

Do Not Type
Past this
LineStart First
Page Here. —

35 The process sequence now used is shown in Fig. 5. Since only about 5% of the fission products are disposed of in waste solutions from the Tramex batch extraction, that process serves primarily as a feed pretreatment for the LiCl AIX. The Tramex product contains about 95% of the transcurium elements and can be processed quickly to maximize the recovery of ^{253}Es , which has a 20 d half-life. As time permits, the "clean rework (RW)" can be processed to recover the remaining actinides.

The sequence of process steps shown in Fig. 5 produces 3 batches of spent resin (a total of about 4 L) and introduces about 50 kg of LiCl into the liquid waste system. The initial product recovery steps require about 2 weeks of operating time and the clean RW recovery requires another 2 weeks.

Process Results

A typical composition of feed solution and the fractional distribution of the feed solution components into the various exit streams are shown in Table I. The feed solution is usually the product of a Cleanex batch solvent extraction (10), a process in which most of the non-lanthanide fission products and macroscopic corrosion products are removed. However, the Cleanex process does not effectively remove residual aluminum from the target rod dissolution and introduces a significant

Do Not Type
Below This
Line. —

1

< 5

< T 1

< R 1

DO NOT TYPE ON THIS LINE

Start typing on this line.

50

TABLE 1. TYPICAL COMPOSITION OF FEED SOLUTIONS AND DISTRIBUTION OF COMPONENTS TO EXIT SOLUTIONS

Do Not Type Past this Line

Component	Amounts in Feed Solution	% Distribution to Exit Solutions			
		Products			F.P. Waste
		AmCm	BkCfEsFm	Rework ^a	
Part A: Transplutonium Elements					
²⁴³ Am	0.1 g	98	0.3 ^b	1.5	0.2
²⁴⁴ Cm (Total Cm)	20(50)g	98	0.3 ^b	1.5	0.2
²⁴⁹ Bk	35 mg	0.5	98	1.5	<0.1
²⁵² Cf	400 mg	0.05	99	1.0	<0.1
²⁵³ Es	2.5 mg	<0.1	99	1.0	<0.1
²⁵⁷ Fm (estimated)	0.8 pg	<0.1 ^e	99 ^e	1.0 ^e	<0.1 ^e

Part B: Fission Products					
⁹⁵ ZrNb	5 Ci	<1	(c)	<1	100 ^d
^{103,106} Ru	75 Ci	<0.1	(c)	<1	100 ^d
^{110m} Ag	10 Ci	0.3	(c)	<1	100
¹⁴⁰ BaLa	300 Ci	0.2	(c)	<1	100
^{141,144} Ce	2000 Ci	0.03	(c)	10	90
¹⁵⁶ Eu	1000 Ci	0.02	(c)	10	90
Gross Gamma	1x10 ¹⁵ c/m	0.03	(c)	10	90

Part C. Macroscopic Impurities					
Al	30 g	<1	<1	70	30
Na	60 g	<1	<1	90	10

- a Short-lived nuclides are lost by radioactive decay during typical 0.5 year storage of rework solution.
- b Recovered by subsequent process step.
- c Cannot be measured because of masking by ²⁵²Cf spontaneous fission spectrum.
- d Removed in Tramex solvent.
- e Assumed.

Start First Page Here.

35

Do Not Type Below This Line.

1

DO NOT TYPE ON THIS LINE

Start typing —
on this line.

50

amount of sodium salts into the product solution (NaOH is used to neutralize excess acidity in the Cleanex process). The aluminum and sodium impurities are only slightly soluble in concentrated LiCl solutions; however, the feed pretreatment filtration step, described above, has removed these insoluble impurities effectively.

Do Not Type
Past this
LineStart First —
Page Here.

35

In some production campaigns, the "clean" rework solutions, as well as the "dirty" rework has been stored for about six months and then processed along with the subsequent group of irradiated targets. However, during the storage period, small but significant amounts of the short-lived products, especially ^{253}Es and ^{257}Fm but also including some of the ^{249}Bk , have been lost by radioactive decay. Thus, the practice of reprocessing the "clean" rework solution immediately after the initial actinide recovery steps has increased product yields.

Conclusions

The laboratory-scale LiCl AIX process has been successfully adapted to the multigram scale and has been used effectively in transuranium element production campaigns to separate the lanthanide fission products from the transplutonium actinides and to partition americium and curium from the heavier elements. Corrosion of the tantalum and glass equipment has been negligible. Although radiolytic gas generation has not caused a problem, radiation exposure of the Dowex 1-X10 anion

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing — 50
on this line.

exchange resin does occur significantly. However, the 1.3-L resin bed can be used successfully to process up to 3 batches, each containing 19 g of ^{244}Cm (54 W of decay heat). The chromatographic elution process is controlled by use of an alpha detector in the column effluent line and by periodic measurement of the neutron profile of the column. The development and use of feed pretreatment and operating methods has enabled effective and dependable operation.

Do Not Type
Past this
Line

Start First — 35
Page Here.

Acknowledgement

This research was sponsored by the Office of Basic Energy Sciences, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

Literature Cited

1. Hulet, E. K.; Gutmacher, R. G.; and Coops, M. S.; "Group Separation of the Actinides from the Lanthanides by Anion Exchange," J. Inorg. Nucl. Chem., 17, 1961, 350-360.
2. Baybarz, R. D.; Weaver, B.; "Separation of Transplutoniums from Lanthanides by Tertiary Amine Extraction," ORNL-3185 (December 1961).
3. Leuze, R. E.; Baybarz, R. D.; Weaver, B.; "Application of Amine and Phosphonate Extractants to Transplutonium Element Production," Nucl. Sci. Eng. 17, 1963, 252-258.
4. Weaver, B., J. Inorg. Nucl. Chem., 30, 1968, 2223.

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing _____
on this line.

50

5. Baybarz, R. D.; Orr, P. B.; "Final Purification of the Heavy Actinides from the First Four Campaigns of the TRU Program," ORNL-TM-2083 (November 1967).

6. Baybarz, R. D.; Kinser, H. B.; "Separation of Transplutoniums and Lanthanides by Tertiary Amine Extraction II. Contaminant Ions," ORNL-3244 (February 1962).

7. Collins, E. D.; Bigelow, J. E.; "Chemical Process Engineering in the Transuranium Processing Plant," Proc. 24th Conf. Remote Syst. Technol., 1976, 130-139.

8. Baybarz, R. D., "Alpha Radiation Effects on Concentrated LiCl Solutions Containing HCl, and the use of Methanol as an Inhibitor of Acid Radiolysis," J. Inorg. Nucl. Chem., 27, 1965, 725-730.

9. Gangwer, T. E.; Goldstein, M.; Pillay, K. K. S.; "Radiation Effects on Ion Exchange Materials," BNL-50781, Brookhaven National Laboratory (November 1977).

10. Bigelow, J. E.; Collins, E. D.; King, L. J., "The "Cleanex" Process: A Versatile Solvent Extraction Process for Recovery and Purification of Lanthanides, Americium, and Curium," Actinide Separations, ACS Symp. Series, No. 117, 1980, 147-155.

Do Not Type
Past this
LineStart First
Page Here.

35

Do Not Type
Below This
Line.

1

DO NOT TYPE ON THIS LINE

Start typing — 50
on this line.

FIGURE TITLES

Figure 1. Relative distribution coefficients for actinides and lanthanides between Tramex solvent (30% Alamine-336 in xylene) and 11 M LiCl--0.02 M HCl.(2)

Figure 2. LiCl Anion Exchange Equipment

Figure 3. Neutron profiles of AIX column

Figure 4. Column effluent composition

Figure 5. Process sequence

Do Not Type
Past this
LineStart First — 35
Page Here.Do Not Type — 1
Below This
Line.

Figure 1. Relative distribution coefficients for actinides and lanthanides between Tramex solvent (30% Alamix-336 in xylene) and 11 M LiCl--0.02 M HCl (2)

Figure 2. LiCl anion exchange equipment

Figure 3. Neutron profiles of AIX column

Figure 4. Column effluent composition

Figure 5. Process sequence