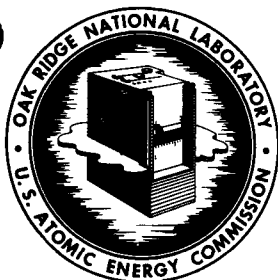


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SUBJECT: Anion Exchange Separation of Trivalent Actinides and Lanthanides

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FROM: M. H. Lloyd and R. E. Leuze

ABSTRACT

A process for separating americium and curium from rare earths by anion exchange based on selective chloride complexing has been developed and tested on a laboratory scale. The separation is accomplished by sorption of americium, curium, and rare earths on Dowex 1-10X resin from a solution of 8 M LiNO₃ followed by selective elution of rare earths with 10 M LiCl and americium-curium elution with 1 M LiCl. Laboratory demonstration of this process has given greater than 99.5% recovery of americium tracer containing no detectable amounts of rare earths.

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1.0 INTRODUCTION

Separation of americium and curium from rare earths by anion exchange based on selective chloride complexing has been developed and tested on a laboratory scale with tracer amounts of Am-241 and Cm-242 and macro amounts of mixed rare earths. This procedure is one step of the proposed multistage process shown in Fig. 1 for recovering Pu-242, Am-243, and Cm-244 from highly irradiated Pu-239. Plutonium-aluminum alloy that has been irradiated until all plutonium has either fissioned or been converted to Pu-242, Am-243, and Cm-244 is dissolved in nitric acid. Plutonium is recovered by tributyl phosphate extraction from an aqueous phase salted with aluminum nitrate and nitric acid. The plutonium is sent to either a second extraction cycle or anion exchange for additional decontamination. Americium and curium remaining in the aqueous raffinate are separated from aluminum and most of the fission products by tributyl phosphate extraction from neutral aluminum nitrate solution. All the trivalent rare earth fission products are also extracted under these conditions. The anion exchange procedure discussed in this paper is designed to take the mixture of americium, curium, and rare earths in a nitrate solution as feed and to remove most of the rare earths. Additional purification from the heavier rare earths can be obtained by extracting the rare earths into mono-2-ethylhexyl phosphoric acid¹ from concentrated lithium chloride solution. Purified Pu-242, Am-243, and Cm-244 will be used in research and as target material for production of heavier isotopes by neutron capture.

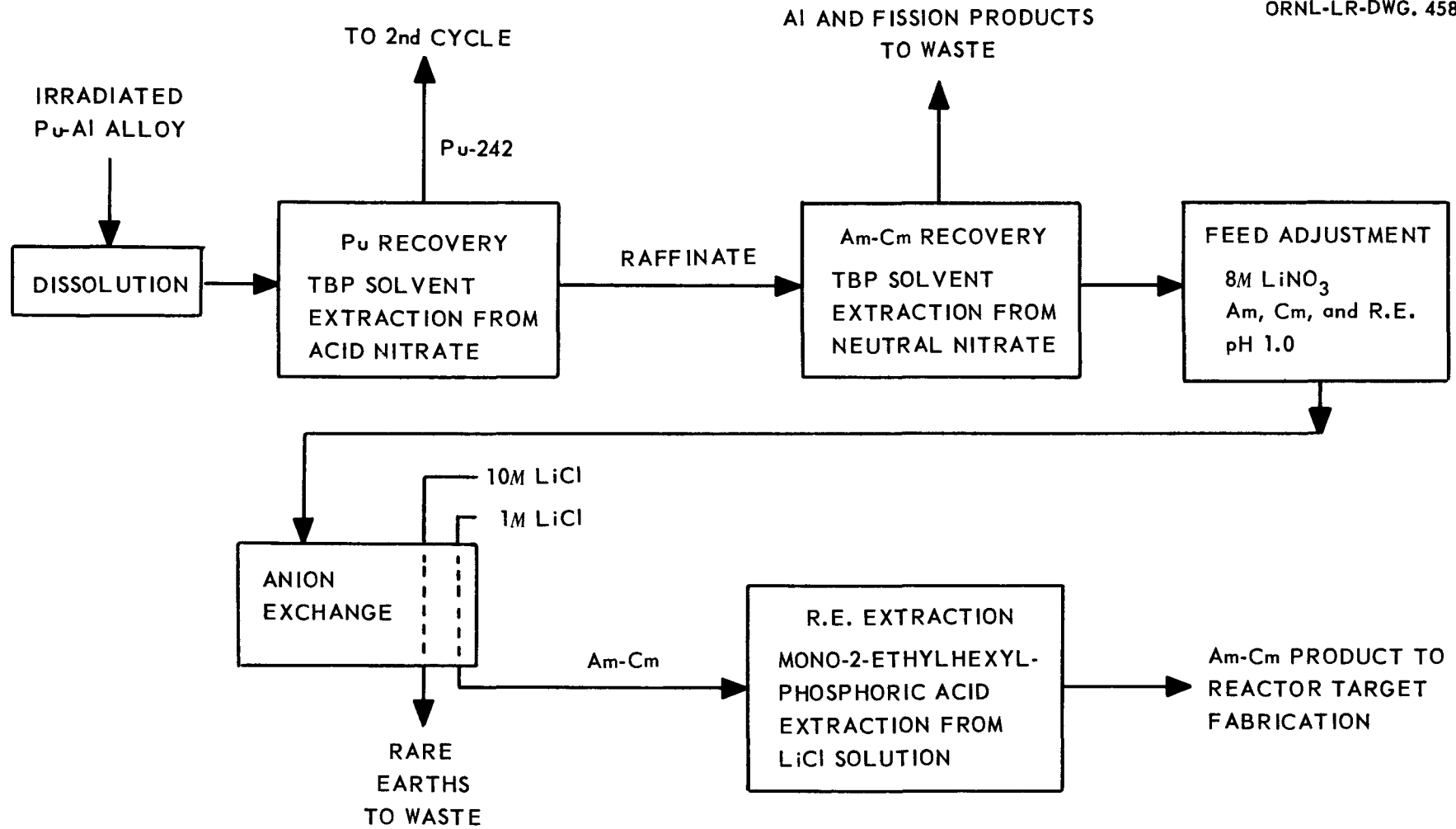


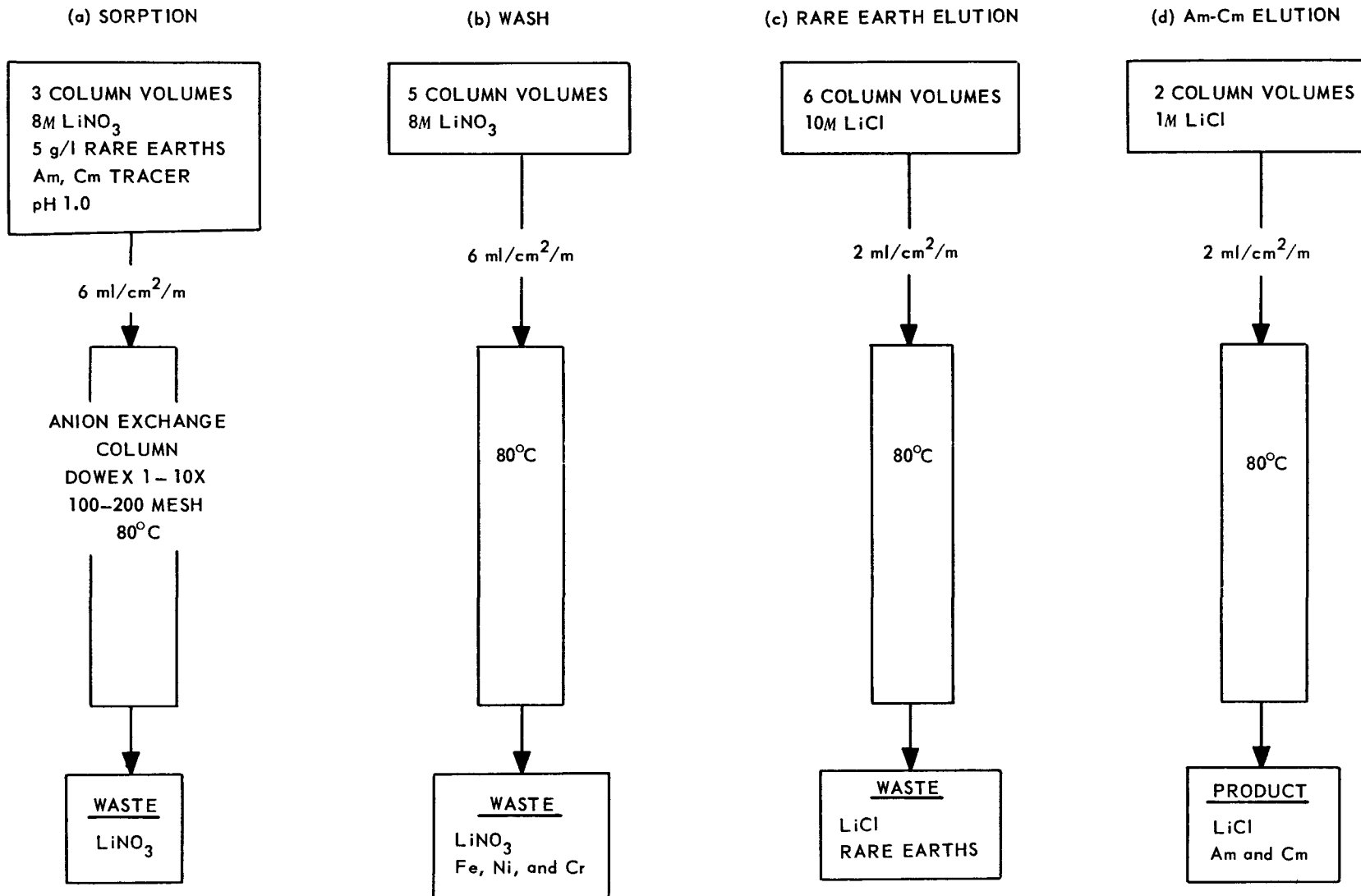
FIG. 1. TRANSURANIUM ELEMENT RECOVERY PROCESS.

2.0 PROCESS DESCRIPTION

The anion exchange process shown in Fig. 2 for separating actinides and lanthanides is a modification of the methods used at the University of California Radiation Laboratory² and at Argonne National Laboratory.³ The principal difference is that sorption onto the anion resin is from lithium nitrate solution instead of from lithium chloride solution, a method based on data reported by Marcus and Nelson.⁴ It offers several advantages over sorption from chloride solution: (1) nitrate solutions from solvent extraction processes can be readily adjusted to feed conditions, (2) feed with lower rare earth concentrations can be used because of the greater distribution coefficients from nitrate solutions, and (3) moderate quantities of iron in the feed do not interfere with actinide and lanthanide sorption.

Conditions of the anion exchange process for separating rare earths from americium and curium are given in Fig. 2. During the sorption cycle, 8 M LiNO₃ at pH 1.0 containing 5 g/liter rare earths and tracer americium and curium is passed through a column of Dowex 1-10X (100-200 mesh) resin at 80°C. To load the column with 7.5 g of rare earths per liter of resin, 3 column displacement volumes* are pumped through the resin at a flow rate of 6 ml/cm²/min. A wash at 80°C with 5 column volumes of 8 M LiNO₃ at 6 ml/cm²/min is used to remove weakly sorbed materials such as iron, chromium, and nickel. Essentially all the rare earths are then eluted at 80°C in 6 column displacement volumes of 10 M LiCl at a flow rate of 2 ml/cm²/min. During this elution, americium and curium gradually migrate

* A column displacement volume is the volume of voids in the resin column and is approximately equal to one-half the bulk resin volume.



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FIG. 2. ANION EXCHANGE FLOWSHEET FOR SEPARATING Am AND Cm FROM RARE EARTHS.

down the column, but if the column length is sufficient the rare earths are eluted before an appreciable amount of americium or curium is removed. Americium and curium are completely removed by elution at 80°C in 2 column displacement volumes of 1 M LiCl at a flow rate of 2 ml/cm²/min.

In laboratory demonstrations of this flowsheet in a glass column 2.5 cm dia packed with 40 cm of Dowex 1-10X resin (100-200 mesh) recovery of americium and curium was >99.5%. The product contained no rare earths detectable by oxalate precipitation. This represents a rare earth decontamination factor of greater than 100.

3.0 DISCUSSION OF PROCESS VARIABLES

Since the initial objective of this work was to develop an acceptable flowsheet for separating actinides and lanthanides, a complete study of all process variables was not made. The variables investigated were evaluated in terms of the percentage of americium and/or curium recovered in a product cut free of rare earths. In order to ensure absence of rare earths in the product, the rare earth cut was considered to be all eluate containing rare earths detectable by oxalate precipitation plus 1 additional column displacement volume. All subsequent eluate containing americium and/or curium was considered the product.

Contaminants in the feed can vary considerably without appreciably affecting the separation of americium and curium from rare earths. Feeds containing 1 g of iron, 1 g of chromium, and 1 g of nickel per liter have been satisfactorily processed, producing products completely free of these contaminants. Although iron is weakly sorbed, it is readily displaced by actinides and lanthanides. Chromium sorption is weaker than iron sorption,

and nickel sorption is very weak if it occurs at all. In order to prevent iron precipitation, the feed must be kept at pH below 2.0. Since sorption of rare earths⁴ and actinides decreases rapidly even with small increments of free acid, careful adjustment of the acidity is required. Satisfactory runs at pH 0.9 have been demonstrated, and probably even more free acid can be tolerated. Aluminum nitrate in the feed does not interfere. In fact, the lithium nitrate can be partly replaced with aluminum nitrate. Successful separations were made from a feed containing 6 M LiNO₃ and 1 M Al(NO₃)₃. Preliminary data indicate that it may be possible to completely replace the lithium with aluminum.

Lanthanide and actinide distribution coefficients between Dowex 1-10X resin and concentrated lithium nitrate solutions are high (Fig. 3). Because of the favorable distribution coefficients, it is feasible to use feed containing low concentrations of lanthanides and actinides. Satisfactory loadings and subsequent separations have been made in which 7.5 g of rare earths and americium were loaded per liter of resin from 8 M LiNO₃ containing 0.5 g of rare earths per liter and tracer americium. Increasing the lithium nitrate concentration from 8 to 10 M increases the distribution coefficients (Fig. 3). As a result, a larger volume of 10 M LiCl is required to completely elute the rare earths, and americium recovery in the rare earth-free product cut is slightly less. A 20-cm column of Dowex 1-8X (100-200 mesh) resin loaded from 10 M LiNO₃ required 8 column displacement volumes for complete rare earth elution and gave 92% americium recovery in the product. When the same resin column was loaded from 8 M LiNO₃, 7 column volumes were required for rare earth elution and americium recovery was 95%.

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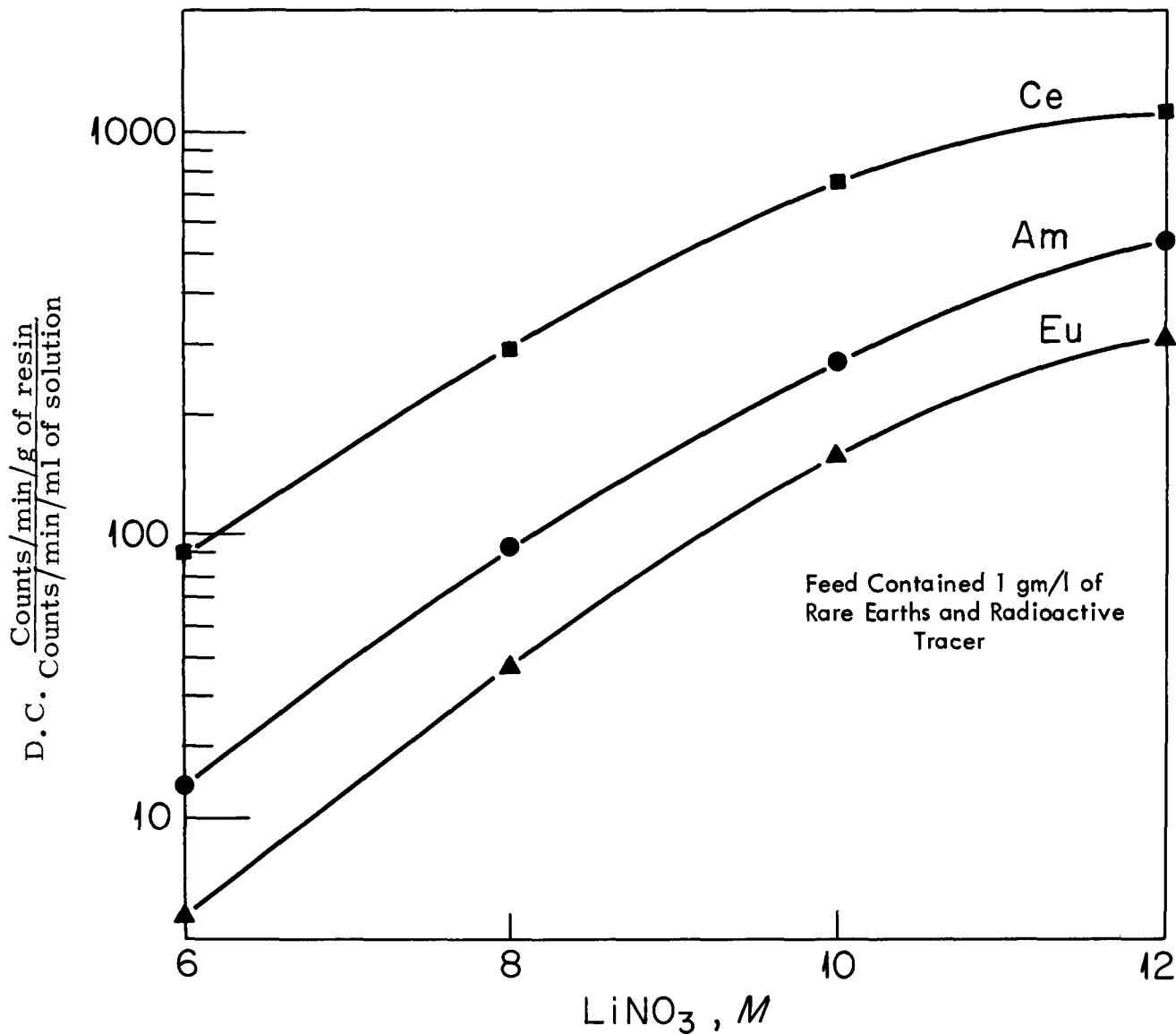


Fig. 3. Distribution Coefficients Between Dowex 1-10X and LiNO₃ Solutions at 80° C

Variation in feed flow rates up to 6 ml/cm²/min has little effect on the separation (Table 1). It may be possible to use higher feed flow rates.

Table 1. Effect of Feed Flow Rate

Feed: 8 M LiNO₃
Rare earth eluant: 10 M LiCl at 2.1 ml/cm²/min
Column: 2.5 x 20 cm of Dowex 1-8X, 100-200 mesh
Temp: 80°C

Feed Flow Rate, ml/cm ² /min	Column Volumes to Elute Rare Earths	Am in Product, %
2.1	7	95
3.2	7	95
6.0	7	94

The flow rate of 10 M LiCl to elute rare earths is much more critical (Table 2). Increasing the flow rate increases the volume of eluant needed to remove rare earths and results in a sharp decrease in americium in the product. Flow rates even lower than 2 ml/cm²/min may be desirable.

Column loadings up to 12 g of rare earths per liter of resin were tested and found acceptable. Good separations at higher loadings may be possible. The length of the resin column and the available free resin after loading are important, as shown by similar runs with resin loadings of 6 g/liter on 2.5 cm-dia columns 20 and 40 cm long. With optimum conditions for the 20-cm column, only 88% of the americium was collected in a product cut free of rare earths, but the 40-cm column gave a product free

Table 2. Effect of Rare Earth Eluant Flow Rate

Feed: 8 M LiNO₃ at 6 ml/cm²/min
 Rare earth eluant: 10 M LiCl
 Column: 2.5 x 20 cm of Dowex 1-8X, 100-200 mesh
 Temp: 80°C

Eluant Flow Rate, ml/cm ² /min	Column Volumes to Elute Rare Earths	Am in Product, %
2.1	7	94
3.2	8	82
6.0	10	60
12.0	10	62
18.0	10	56

of rare earths containing 99.9% of the americium.

In scouting tests with Dowex 1 resin, separations of americium and rare earths were better with finer mesh resin (Table 3). In identical

Table 3. Effect of Resin Type and Size

Feed: 8 M LiNO₃ at 2.1 ml/cm²/min
 Rare earth eluant: 10 M LiCl at 2.1 ml/cm²/min
 Column: 2.5 x 20 cm
 Temp: 80°C

Resin	Mesh	Am in Product, %
Dowex 1-8X	50-100	88
Dowex 1-8X	100-200	95
Dowex 21K	20-60	64
Permutit SK	20-60	61

runs, 100-200 mesh resin gave a product containing 95% of the americium, and 50-100 mesh resin gave a product containing only 88% of the americium. With Permutit SK and Dowex 21K resins, which are more stable to radiation, separation was poor; but only 20-60 mesh resin was available when those runs were made. Assuming the same effect of resin size as noted with Dowex 1, it may be feasible to use fine-mesh Permutit SK or Dowex 21K. This would be desirable since radiation levels will be high when actually processing americium, curium, and rare earths from highly irradiated plutonium.

4.0 CONCLUSIONS

Laboratory demonstrations of the flowsheet presented in Fig. 2 using gram quantities of mixed rare earths and tracer amounts of americium and curium gave products containing more than 99.5% of the americium and curium with no rare earths detectable by oxalate precipitation tests. The flowsheet is capable of handling considerable quantities of iron, chromium, nickel, and aluminum impurities in the feed. In fact, lithium can be at least partly replaced with aluminum.

A great deal of additional investigation is desirable to thoroughly evaluate the variables in a systematic manner. In order to make this process acceptable for large-scale processing, testing is needed to determine the effect of volume scaleup and the effect of high-level radiation. Such tests are being planned. Not only will they provide the opportunity to investigate these variables, but they will also make it possible to determine rare earth decontamination factors more precisely.

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