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LARGE-SCALE SEPARATION OF TRANSPLUTONIUM
ACTINIDES BY PRESSURIZED CATION EXCHANGE

by

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1. ABSTRACT

A brief history of pressurized ion exchange separations is presented, and the advantages of pressurized cation exchange compared to conventional cation exchange are discussed. In reviewing present applications of pressurized cation exchange, a 100-g-scale separation of ^{244}Cm , a multigram-scale separation of transplutonium elements, and a milligram-scale separation of transcurium elements are discussed in detail. Other applications of pressurized cation and anion exchange are also presented.

2. INTRODUCTION

Conventional low pressure cation exchange has been an effective method for separating transplutonium actinides from lanthanides as well as for separating adjacent transplutonium elements. This method was used for chemical identification in the discovery of berkelium, californium, einsteinium, fermium, and mendelevium¹. Transplutonium actinides were separated as a group from lanthanides by preferential sorption on cation exchange resin of lanthanides, which form weaker anionic, chloro, and thiocyanato complexes than do the actinides^{2,3}. For separation of neighboring transplutonium elements, cation exchange chromatography with a variety of chelating organic acid anions has been a successful technique. Anions of citric^{4,5}, glycolic⁶, tartaric^{7,8}, lactic^{5,7-9}, α -hydroxyisobutyric (AHIB)¹⁰⁻¹², ethylenediaminetetraacetic (EDTA)^{13,14}, nitrilotriacetic (NTA)¹⁵, N-hydroxyethylethlenediamine triacetic (HEDTA)¹³, and diethylenetriamine pentaacetic (DTPA)^{15,16} acids have been used as eluting agents. These applications include elution development chromatographic separations, which are normally small scale, and displacement development chromatographic separations, which are usually large scale. Review material on conventional cation exchange separation of transplutonium actinides is included in references by Seaborg and Katz¹, Penneman and Keenan¹⁷, Higgins¹⁸, Stary¹⁹, Ulstrup²⁰, and Baybarz²¹.

2.1 History of Pressurized Ion Exchange Systems

In high pressure ion exchange, finely divided resin particles (5 to 10 μ or 30 to 60 μ) are used instead of the 100 to 200 μ or larger resin particles used in conventional low pressure or gravity fed columns. Flow rates from \sim 1 to \sim 50 ml/min cm² have

been obtained with positive displacement pumps at pressures up to 2500 psig. A pressure limit is finally reached where a further increase in pressure does not result in increased flow due to resin compaction. The exact conditions of resin particle size, elutriant flow rate, column pressure drop, and column temperature depend on the particular application.

The first high pressure ion exchange system was developed by Scott²² for separating biochemical constituents in urine. The system consisted of *Dowex** 1 resin (5 to 10 μ) in a 0.28 cm² by 200-cm-long heated column. The sodium acetate-acetic acid buffer solution (pH = 4.4) was pumped at 1.7 ml/min cm² with a pressure drop of \sim 2000 psig. More than 140 chromatographic peaks were resolved from a 2.0 ml urine sample.

Campbell and Buxton^{23,24} demonstrated high pressure cation exchange for the quantitative and rapid separation of adjacent lanthanide elements by elution development chromatography with 0.43M AHIB (pH = 4.4). Lanthanides were purified on a 100-mg scale with 0.34 cm² by 150-cm-long heated columns containing *Dowex* 50W-X12 (10 to 20 μ) resin. Satisfactory separations were obtained at flow rates from \sim 0.5 to \sim 25 ml/min cm² at pressures up to 2500 psig.

Lowe²⁵ developed a pressurized cation exchange system to separate ¹⁴⁷Pm from other fission product lanthanides on a gram scale by displacement development chromatography with 0.05M DTPA (pH = 6.0). A series of four 150-cm heated columns with inner diameters of 4.75, 2.21, 1.09, and 0.79 cm were loaded with 30 to 60 μ *Dowex* 50W-X8 resin. The columns were operated at flow

* Trademark of Dow Chemical Co.

rates up to 15 ml/min cm² at pressures up to 800 psig. A similar DTPA displacement development system was developed on a gram scale for purifying transplutonium actinides by Hale and Lowe²⁶ and on a 100 g-scale by Lowe *et al.*²⁷ (see Section 4.1).

Campbell²⁸ demonstrated on a laboratory scale that the high pressure cation exchange system of Campbell and Buxton²⁴ successfully used to separate the lanthanides would also separate the transplutonium actinides. Baybarz²⁹ scaled up the process to the milligram level for purification of transcurium elements (see Section 4.3). Burney and Harbour³⁰ developed a similar large-scale high pressure cation exchange system with AHIB to separate milligram quantities of ²⁵²Cf from multigram quantities of ²⁴⁴Cm and ²⁴³Am (see Section 4.2).

3. ADVANTAGES OF PRESSURIZED CATION EXCHANGE

With small particle resin, equilibration between solution and resin is rapidly attained and results in potentially better separations than in conventional ion exchange. Rapid equilibrium for small particle resin results from decreased diffusion distances in both the resin particles and in the aqueous film surrounding the particle. The use of small particle resin improves kinetics and gives a more uniform flow, which allows fast flow rates for the loading and elution steps. These high flow rates drastically reduce time necessary to attain a given separation. The decreased residence time of highly radioactive feed materials on the resin reduces radiation damage to the resin, especially during the loading step. Also, localized heating due to radioactive decay energy being deposited in the system is reduced.

To achieve the fast flow rates possible with small particle resin, the elutriant and feed solutions are pressurized. Pressur-

izing these solutions has the advantages of dissolving the radiolytic gases produced. In highly radioactive solutions, radiolytic gases are generated by radiolysis of the solution primarily by alpha particles and fission fragments from decay of transplutonium actinides. Radiolytic gases can cause bed disruptions, which may result in irregular flow and channeling. Some gassing may occur at the bottom of the column, but the high pressure keeps bubble size small and removes the gas immediately. When the columns are operated at elevated temperatures, solution viscosity is reduced, and the pressure drop is lower for a given flow rate.

High pressure ion exchange permits greater freedom than conventional ion exchange in selection of operating parameters, such as resin particle size, flow rates, and column length. The effluent stream from high pressure systems is easily monitored in-line³¹.

A thorough safety analysis of any high pressure system for handling radioactive materials should be made prior to use. Pressurized systems with positive displacement pumps to feed non-radioactive solutions to ion exchange columns directly have been operated safely with the use of pressure relief valves, check valves, surge tanks, and radioactivity monitors (see Sections 4.1 and 4.2).

4. PRESENT APPLICATIONS

4.1 Displacement Development: 100 g-Scale Separation of ²⁴⁴Cm

After gram-scale tests demonstrated that californium, curium, and americium could be separated from each other and from lanthanides by pressurized cation exchange with DTPA²⁶ elutriant, equipment was designed at Savannah River Laboratory (SRL) to separate two moles of actinides and lanthanides per production run.

Feed for the larger-scale separations came from a ^{244}Cm production program at the Savannah River Plant³², with ^{239}Pu as the starting material. ^{239}Pu is converted to ^{244}Cm by successive neutron captures and beta decays. For most efficient production, the irradiation was conducted in two stages: ^{239}Pu was converted to a mixture of higher plutonium isotopes in the first stage, and the higher isotopes were irradiated in the second stage to produce ^{242}Pu , ^{243}Am , and ^{244}Cm . After each stage, the targets were dissolved and plutonium was recovered in two cycles of countercurrent solvent extraction with tri-n-butyl phosphate (TBP) in n-dodecane. After the second irradiation stage, americium, curium, californium, and lanthanide fission products were recovered from the aqueous waste of the first plutonium solvent extraction cycle by batch extraction with 50% TBP in n-dodecane, back extraction into dilute nitric acid, and concentration by evaporation. This solution provided the raw feed for cation exchange separation. For a typical cation exchange run with two moles of actinides and lanthanides, the feed contained 60 g of ^{244}Cm , 27 g of ^{243}Am , 180 μg of ^{252}Cf , and 240 g of lanthanides.

Dilute nitric acid feed was loaded onto fine-particle resin. The elution process was controlled with in-line radiation monitors. Product fractions were processed by several techniques; overlap fractions containing curium or americium were recycled. Approximately 3 kg of ^{244}Cm were purified by this process.

4.1.1 Cation exchange system

The production equipment (Figure 1) consists principally of four columns, a feed tank, and a resin transfer tank. The columns were constructed of 304L stainless steel, schedule 80 pipe, and are 122 cm long with nominal diameters of 10.2, 7.6, 5.1, and 2.5 cm. Resin is held in the column by a 10 μ stainless steel frit.

The columns are jacketed for temperature control with a steam-water mixture, and are rated for continuous operation at 1000 psig and 93°C. A positive displacement pump is used to feed solution to the columns. The system is designed so that the pump can feed the cation exchange columns directly (with nonradioactive solutions), or by water displacement through a pressurized feed tank (for delivery of resin slurries or radioactive feed). Radioactive solution is never transferred through the pump. Each line leading from the pump passes through a relief valve to prevent over-pressurization of the system. Each column is also provided with a pressure relief valve. To prevent backup of radioactive solution, each feed line passes through a spring-loaded check valve, a surge tank, and another check valve. Gamma monitors are placed near the feed lines where the lines enter the shielded cell wall. A warning horn would be sounded in the event of any activity backup.

Two sizes of *Dowex* 50W-X8 resin are used. 200 to 400 mesh resin is hydraulically graded to 40 to 110 μ by deionized water flowing upward at various rates through a 25.4-cm-diameter, 366-cm-long steel pipe with a 183-cm-conical bottom. The -400 mesh resin is first graded in the steel pipe and further graded to 20 to 40 μ in a glass system described by Scott³³.

In the early production runs, -400 mesh resin was used in all four columns. However, the design flow of 16 ml/min cm² could seldom be obtained at the 1000 psig limit on the 10.2 and 7.6 cm columns. The decrease in pressure drop with decreasing column diameter at constant linear flow was explained by the wall effects observed by Eastwood *et al.*³⁴. The resin bed porosity increased from \sim 0.23 on the 10.2 cm column to \sim 0.30 on the 2.5 cm column.

During the production campaign, adequate curium-ameridium resolution could be obtained with 200 to 400 mesh resin in the 10.2, 7.6, and 5.1 cm columns and -400 mesh resin in the 2.5 cm column. Resolution was not adequate when 200 to 400 mesh resin was used in the 2.5 cm column. Approximate maximum pressure drops at 16 ml/min cm² are 250 psig on the 10.2 cm, 200 psig on the 7.6 cm, 175 psig on the 5.1 cm, and 1000 psig on the 2.5 cm column. Resin in the 10.2 and 7.6 cm columns is used twice before discharge; new resin is used in the 5.1 and 2.5 cm columns for each run. When resin was used for more than two runs, pressure drops were extremely high and curium could not be eluted in a compact band.

4.1.2 In-line analysis system

All column effluent flows through a doubly contained 0.64-cm stainless steel line which passes through the cell wall, forms a loop, and passes back into the cell. Three radiation detection systems are positioned around the loop: a BF₃ neutron monitor, a NaI scintillation detector for high energy gamma rays, and a Ge(Li) low energy photon detector³¹.

Spontaneous fission neutrons from ²⁵²Cf and ²⁴⁴Cm are detected with the BF₃ probe. Although ²⁵²Cf and ²⁴⁴Cm are not differentiated with the neutron counting system, they are easily distinguished by monitoring the 42.9 keV ²⁴⁴Cm photopeak with the Ge(Li) detector. The BF₃ tube is shielded from background radiation with ~13 cm of paraffin and *Benelex** to thermalize fast neutrons and 0.64 cm of cadmium to stop the thermal neutrons. The system has shown no gamma sensitivity for radiation levels up to 10³ R/hr.

* Registered trademark of Masonite Corporation.

The NaI scintillation detector consists of a single-channel analyzer set on the 1274 keV peak of ^{154}Eu . The system also responds to Compton gamma rays from $^{106}\text{Ru-Rh}$ and $^{144}\text{Ce-Pr}$, and to the prompt fission gamma rays of ^{252}Cf and ^{244}Cm . The NaI system is used to confirm results from the other two systems and to detect breakthrough of ^{154}Eu in the curium-ameridium fraction. In the absence of terbium, europium is the first element to elute after ameridium.

The Ge(Li) detector gives specific quantitative analyses for ^{244}Cm , ^{243}Am , ^{154}Eu , $^{144}\text{Ce-Pr}$, ^{237}Np , and $^{106}\text{Ru-Rh}$. The lower limit of detection for each nuclide is determined by the background, primarily Compton events from higher energy gammas, and is a factor of 10^3 below the maximum elution level of each nuclide. The Ge(Li) detector is calibrated before each run by flowing standard solutions through the steel loop.

Initially, the BF_3 and NaI systems were connected to scalars and recorders, and the Ge(Li) system was coupled to a 4096-channel pulse height analyzer equipped with a high speed printer. Activity data were reduced to nuclide concentrations with a programmable electronic calculator. However, it was difficult to monitor more than one isotope and to make calculations every 60 seconds or less. As described by Peterson and Wakat³¹, a computerized system was designed and developed around a PDP-9* computer and a 200 MHz analog-to-digital converter. The concentration of all nuclides of interest and activity data from the BF_3 and NaI detectors are printed as often as every 30 seconds. Ge(Li) spectra are displayed on an oscilloscope.

* Digital Equipment Corp.

4.1.3 Process chemistry

Targets of irradiated $^{242}\text{PuO}_2\text{-Al}$ are dissolved in Hg^{2+} -catalyzed HNO_3 , the ^{242}Pu is removed by solvent extraction (see Section 4.1), and the residual actinide-lanthanide solution is converted by either precipitation or solvent extraction to feed suitable for cation exchange. Composition of this actinide-lanthanide solution is shown in Table I.

TABLE I
Composition of Actinide-Lanthanide Solution
After ^{242}Pu Solvent Extraction

Component	Concentration
^{244}Cm	2.7 g/l
^{243}Am	1.2 g/l
^{252}Cf	11 $\mu\text{g/l}$
Lanthanides	~ 11 g/l
$\text{Al}(\text{NO}_3)_3$	1.8 M (from irradiated slugs)
$\text{Fe}(\text{NO}_3)_3$	0.22 M (from equipment corrosion)
$\text{Hg}(\text{NO}_3)_2$	0.16 M (catalyst in slug dissolution)
HNO_3	~ 1 M
$^{144}\text{Ce-Pr}$	675 Ci/l
$^{106}\text{Ru-Rh}$	300 Ci/l
$^{95}\text{Zr-Nb}$	2.2 Ci/l
Heat	11.9 watt/l

In the precipitation method, curium solution is added to excess 8 M NaOH to precipitate actinide, lanthanide, and iron hydroxides, and HgO . Aluminum (as aluminate anion) and most of the $^{106}\text{Ru-Rh}$ (as amphoteric nitrosylruthenium hydroxide) are removed in the filtrate. The hydroxides are dissolved in dilute nitric acid, just enough ammonium chloride is added to complex

Hg^{2+} , and solid ammonium oxalate is added to precipitate the lanthanide and actinide oxalates. Mercury (as HgCl_2), iron, niobium, and zirconium (as oxalato complexes) are removed in the filtrate. The dry cake is allowed to stand for 16 hours while alpha radiolysis converts oxalate to carbonate. The carbonates are then dissolved in dilute nitric acid to give a suitable feed for cation exchange. Total curium loss through both steps is typically <0.5%. Decontamination obtained in the precipitation process is shown in Table II.

The flowsheet for feed preparation by solvent extraction is shown in Figure 2. The actinide-lanthanide solution is diluted to 1.5M Al and the TBP-dodecane stream is acidified to prevent precipitation of $\text{Fe}(\text{OH})_3$ in the first bank of mixer-settlers (A bank). In the A bank, actinides and lanthanides (and nitric acid) are extracted from the $\text{Al}(\text{NO}_3)_3$ solution. The curium extract in stages 1 to 10 is scrubbed with 6M NaNO_3 to remove traces of iron, aluminum, and mercury. At a scrub-to-extract ratio of 0.28 in the A bank, 99.0% of the curium is recovered.

In the second bank of mixer-settlers (B bank), actinides and lanthanides are back-extracted with dilute nitric acid. During normal operation, <0.1% of the curium remains in the raffinate and spent solvent waste streams. Decontamination obtained in the solvent extraction process is shown in Table II.

Cation exchange feed solution containing 2 moles of actinides and lanthanides is diluted to 20 liters in a pressurized feed tank, loaded onto the 10.2 cm column (30 to 40% capacity), and separated with 0.05M DTPA at pH 6.0 and at 70°C.

A typical run was described by Lowe, Hale, and Hallman²⁷. In normal operation, DTPA is pumped through the 10.2 cm column

at 1.2 l/min (16 ml/min cm²) immediately after loading the feed and the dilute Zn(NO₃)₂ rinse. When the BF₃ probe indicates neutron breakthrough (²⁵²Cf), the 7.6 cm column is valved in, and flow is reduced to 16 ml/min cm² on the 7.6 cm column. Similarly, the 5.1 cm column is valved in and the flow is reduced when ²⁵²Cf breakthrough occurs from the 7.6 cm column.

TABLE II
Preparation of Feed for Cation Exchange

	<u>Actinide- Lanthanide Solution</u>	<u>Precipitation Product</u>	<u>DF^b</u>	<u>Solvent Extraction Product</u>	<u>DF</u>
V, l ^a	21.1	4.24	-----	17.7	-----
²⁴⁴ Cm, g/l	2.7	13.1	-----	3.22	-----
HNO ₃ , M	~1	1.3	-----	1.0	-----
Al, M	1.8	0.016	560	0.0034	633
Fe, M	0.22	0.043	254	0.009	292
Hg, M	0.16	6.1 x 10 ⁻⁴	1310	<4 x 10 ⁻⁵	>4770
¹⁰⁶ Ru-Rh, Ci/l	300	12.6	119	41.4	8.6
⁹⁵ Zr-Nb, Ci/l	2.2	<0.13	>84	<0.061	>45

a. Data normalized to same initial amount of actinide-lanthanide solution

b. DF = decontamination factor

The ^{252}Cf fraction is collected off the 5.1 cm column, and elution continues until ^{244}Cm breakthrough (shown by BF_3 probe and $\text{Ge}(\text{Li})$ detector). The 2.5 cm column is then valved in, and the flow is reduced. The ^{244}Cm product fraction is collected off the 2.5 cm column until the $\text{Ge}(\text{Li})$ detector indicates breakthrough of ^{243}Am . Mixed ^{244}Cm - ^{243}Am and pure ^{243}Am fractions are collected until the NaI and $\text{Ge}(\text{Li})$ detectors indicate ^{154}Eu breakthrough. A ^{243}Am - ^{154}Eu fraction is collected until ^{243}Am is no longer detectable. Lanthanides remaining on the columns are flushed to the drain with 0.30M DTPA at pH 8.0. A typical elution diagram is shown in Figure 3.

Under these conditions, the elution sequence is: Cu^{2+} , Ni^{2+} , Cf^{3+} , Zn^{2+} , Pb^{2+} , Cm^{3+} , Am^{3+} , Eu^{3+} , Nd^{3+} , Pr^{3+} , and Ce^{3+} . In early tests, Cu^{2+} or Ni^{2+} was used as the barrier ion in all four columns. In each case, californium was collected in a small volume but contained an undesirably large amount of curium. With Zn^{2+} barrier ion in all four columns, californium moves ahead of the curium-ameridium-lanthanide band and is collected in a larger volume (20 to 30 liters) with 0.1 g of curium.

High acidity ($>0.5\text{M}$) can adversely affect the separation of californium and curium when Zn^{2+} is the barrier ion. H^+ absorbed on the 10.2 cm column during feed loading lowers the pH of the DTPA elutriant. At low pH, Zn^{2+} is a barrier to Cf^{3+} (because the protonated Zn^{2+} -DTPA complex is formed in preference to that of Cf^{3+}), and californium cannot move ahead of the curium-ameridium band. When most of the acid has been eluted, californium begins to advance into the zinc barrier ion, and resolution is incomplete. This effect of excess acidity can be eliminated by pumping ten column volumes (90 liters) of 0.05M $\text{Zn}(\text{NO}_3)_2$ through the 10.2 cm column after feed loading. H^+ is washed from the column without spreading the actinide-lanthanide band. When

DTPA elution begins, californium moves immediately into the zinc barrier ion.

During the ^{244}Cm production campaign, several batches of cation exchange feed were contaminated with lead from dissolved tank and clamp solder. In DTPA elution, Pb^{2+} elutes just slightly ahead of Cm^{3+} , but there is an overlap and resolution is incomplete. Lead is eliminated prior to DTPA elution by pumping 0.20M $\text{Zn}(\text{NO}_3)_2$ through the 10.2 cm column after feed loading. The high concentration of Zn^{2+} moves the actinide-lanthanide band (3^+ ions), but moves Pb^{2+} faster. This method is useful for removing any monovalent or divalent cation that cannot be separated with the complexing agent.

When the in-line detectors indicate radiation breakthrough from the 10.2 cm column, the 7.6 cm column is valved in, and normal DTPA elution begins. ~96% of the lead is removed from the 10.2 cm column before radiation breakthrough.

In early cation exchange runs with feed prepared by solvent extraction, ^{106}Ru -Rh contaminated the product fractions and interfered with in-line analyses. At 1M HNO_3 , four ruthenium species are present³⁵: $\text{RuNO}(\text{H}_2\text{O})_5^{3+}$ (48%), $\text{RuNO}(\text{NO}_3)(\text{H}_2\text{O})_4^{2+}$ (21%), $\text{RuNO}(\text{NO}_3)_2(\text{H}_2\text{O})_3^+$ (19%), and $\text{RuNO}(\text{NO}_3)_3(\text{H}_2\text{O})_2$ (2%). The 3^+ and 2^+ species are absorbed on the 10.2 cm column and are only slowly eluted with DTPA. Adjusting the feed to 0.15M HNO_2 (by addition of NaNO_2) at $>70^\circ\text{C}$ converts $>90\%$ of the total ruthenium to $\text{RuNO}(\text{NO}_2)_2(\text{H}_2\text{O})_3^+$ (90%) and $\text{RuNO}(\text{NO}_2)(\text{H}_2\text{O})_4^{2+}$ (10%)³⁶. The monovalent species is not absorbed on the 10.2 cm column, and the divalent ion is eluted before product collection.

In early production runs, the curium-ameridium overlap fraction contained 30 to 50 g of curium (out of 80 to 110 g in the feed). As resin grading techniques improved, the normal

amount of curium in the overlap zone was 15 to 25 g, even with 200 to 400 mesh resin in the 10.2, 7.6, and 5.1 cm columns.

The ^{244}Cm product met the purity requirements that: (a) the gamma dose rate from fission product impurities be <10% of the dose rate from ^{244}Cm ; (b) that no single impurity (except americium) exceed 0.2 wt %; (c) that the total impurity (except americium) be <1.0 wt %; and (d) that the total impurities (including americium) be <3.0 wt %. A careful material balance on eight consecutive cation exchange production runs gave 99 \pm 3% for ^{244}Cm and 94 \pm 5% for ^{252}Cf .

Product solutions are purified from DTPA and zinc by both chemical and radiation procedures³⁷:

- ^{252}Cf product fraction: Actinides in the ^{252}Cf product must be separated from zinc and DTPA before elution development purification with AHIB. The ^{252}Cf product solution is adjusted to 0.25M HNO_3 and passed through a column containing *Dowex* 50W-X8, 50 to 100 mesh resin. Resin volume is 1/50th of the solution volume. At this acidity, >99% of the californium is absorbed. DTPA and its degradation products are washed from the column with 10 bed volumes of 0.25 M HNO_3 . Then >99% of the californium is eluted with five bed volumes of 5 M HNO_3 . The product is adjusted to \sim 1 g of lanthanum per liter, and the actinides are separated from Zn^{2+} by carrier precipitation of lanthanum-actinide hydroxide in 3 M excess NaOH . The hydroxides are filtered and dissolved in dilute HNO_3 . The product contains <2% of the zinc from the feed. NH_4OH cannot be used as the

precipitant in the presence of strong complexing agents, such as DTPA, because the low free OH^- concentration is not sufficient for quantitative precipitation of the lanthanum-californium hydroxides.

- ^{244}Cm product: DTPA is removed from the curium product by autoradiolysis. The curium product is acidified to 4M HNO_3 and allowed to stand for 16 hours. DTPA is destroyed by both $\text{H}\cdot$ and $\text{OH}\cdot$ produced by alpha radiolysis of water. Destruction is complete in ~ 13 hours. At $< 2\text{M}$ HNO_3 , precipitates (such as oxalates) are formed, which inhibit radiolysis. Curium is purified from small amounts of zinc and DTPA degradation products by precipitation with 6M NaOH or 6M NH_4OH . The hydroxide is dissolved in dilute HNO_3 , and the oxalate is precipitated and calcined to $^{244}\text{CmO}_2$. Curium can also be recovered from cation exchange product solution by precipitation with ammonium oxalate or precipitation in 5M excess NaOH . However, solids formed in the ^{244}Cm cation exchange product solution in ~ 6 hours make quantitative transfer to a filter difficult. The autoradiolysis process is preferred.
- ^{244}Cm - ^{243}Am binary product: DTPA is removed from the curium-ameridium binary product by autoradiolysis as with the pure curium product. The curium-ameridium mixture is precipitated in 2M excess NaOH , dissolved in dilute HNO_3 , and recycled to the next cation exchange production run.

- ^{243}Am - ^{154}Eu binary product: Initially, DTPA was destroyed in the americium-europium binary product by external irradiation with ^{60}Co at $\sim 10^6$ R/hr for one day. The americium-europium mixture was precipitated in 4M excess NaOH, dissolved, and recycled. However, on occasion some of the hydroxide precipitate would not dissolve completely in dilute HNO_3 . Presumably, some oxalate from degraded DTPA remained in the irradiated solution. In later production runs, the americium-europium mixture was precipitated in 5M excess NaOH shortly after collection, dissolved, and recycled.
- Pure ^{243}Am product: In some cation exchange production runs, the feed contained sufficient americium for collection of a pure americium product. The product was acidified to 4M HNO_3 and stored until the end of the production campaign. Americium was then precipitated in 2M excess NaOH, dissolved in dilute HNO_3 , precipitated as the oxalate, and calcined to $^{243}\text{AmO}_2$.

In 50 production runs, ~ 3 kg of ^{244}Cm , 1.3 kg of ^{243}Am , and 8 mg of ^{252}Cf were separated by the displacement development process. After the ^{252}Cf elution, Pb and ^{106}Ru -Rh contamination, and high pressure drop problems were solved, production runs were made every 2 to 3 days when a large amount of feed was available from solvent extraction. Each run required ~ 16 hours. Beginning in 1972, this process will be used to separate ^{252}Cf in ~ 150 mg batches from curium-americium.

4.2 Elution Development: Multigram-Scale Separation of Transplutonium Elements

At SRL^{30,31}, ^{252}Cf has been purified by pressurized cation exchange elution development from two types of process feed material. For an outline of chemical processing steps for recovery of transuranium elements from targets irradiated in a high flux reactor, see Section 4.1. For one feed material, a solvent wash solution from a Tramex³⁸ cycle (solvent extraction with a mixture of tertiary amines) and containing ~ 10 g of ^{244}Cm and ~ 15 g of ^{243}Am per milligram of ^{252}Cf was used. The other feed material which was the californium fraction collected from a DTPA cation exchange system to separate transplutonium actinides contained less than 0.3 g of ^{244}Cm per milligram of ^{252}Cf .

Because some of these feed materials contained gram quantities of actinides, a large-scale process was necessary. The ^{252}Cf was purified by pressurized cation exchange elution chromatography with AHIB as the elutriant in a pH gradient elution. The ^{252}Cf product was separated from AHIB on a small cation exchange column, and the resin was calcined to give a final product of californium oxysulfate or californium oxide.

4.2.1 Cation exchange system

A schematic drawing of the pressurized cation exchange system for the purification of ^{252}Cf is shown in Figure 3. The column was a 122-cm length of 5.1-cm stainless steel pipe with a stainless steel frit to support the resin. The jacketed column was maintained at 75°C with a steam-water mixture. A positive displacement pump was used to feed radioactive solutions by water displacement from the feed tank. A system of check valves,

pressure relief valves, and a surge tank allowed safe operation up to 1000 psig. Operations were performed with manipulators in shielded cave facilities.

The column contained about 2.4 liters of 20 to 40 μ -diameter *Dowex* 50W-X8 resin in NH_4^+ form. This resin was obtained by hydraulically grading -400 mesh resin³³.

The control measurements for collecting enriched product fractions were made with in-line gamma and neutron detectors, which continuously monitored the effluent as it came through the column. Inside the shielded cell, a highly directional fast-neutron detector followed the ^{252}Cf on the column, and an in-line silicon surface barrier detector sensitive to alpha activity from ^{252}Cf and ^{244}Cm and to beta activity from ^{144}Ce gave preliminary indications of these nuclides³⁸. The effluent stream flowed through the cell wall in a closed loop of stainless steel tubing and was analyzed continually by BF_3 , NaI, and Ge(Li) detectors (described in Section 4.1.2) for ^{252}Cf , ^{244}Cm , ^{243}Am , ^{154}Eu , and ^{144}Ce ³¹.

4.2.2 Process chemistry

Two types of feed material have been processed with the cation exchange system. The first was a solvent wash solution from the *Tramex* process which contained 0.4 M LiCl, 0.5 M HCl, and significant quantities of ^{254}Es , ^{252}Cf , ^{249}Bk , ^{244}Cm , ^{243}Am , ^{154}Eu , and ^{144}Ce . After the solvent wash solution was concentrated, the actinides and lanthanides were precipitated by adding NH_4OH . The precipitate was washed with 0.1M NH_4OH -0.1M NH_4NO_3 and then dissolved in a liter of dilute nitric acid, and the cycle was repeated. This treatment removed most of the lithium and chloride and concentrated the actinides for efficient absorption on the resin.

The second type of feed was the californium-DTPA fraction from DTPA pressurized displacement chromatography (see Section 4.1); this feed solution also contained ^{254}Es , ^{249}Bk , and residual ^{244}Cm . The feed for the AHIB ion exchange cycle was prepared as described in Section 4.1.3.

The resin was conditioned with a 0.2 M NH_4NO_3 -0.02 M HNO_3 solution (pH = 1.8) after loading the feed to stabilize the pH of the elutriant in the early stages of the separation. When the solution is passed through *Dowex* 50W-X8 resin, the ratio of hydrogen to ammonium ion on the resin is the same as when 0.4 M AHIB at pH = 3.4 is passed through the resin.

The concentrated actinide solution is displaced from the feed tank to the column with 0.1 M NH_4NO_3 solution at a flow of 8 ml/min cm^2 while the column is maintained at 75°C. A 0.2 M NH_4NO_3 -0.02 M HNO_3 solution was pumped through the column to assure that the resin was completely converted to NH_4^+ before elution with AHIB.

The elutriant was 0.4 M AHIB partially neutralized with ammonium hydroxide to a pH of 3.4. The pH of the AHIB solution was increased stepwise during the elution as shown in Figures 5 and 6. Flow rate was maintained at 8 ml/min cm^2 at a pressure of 500 to 700 psig. The elution diagram in Figure 5 is for Traxem feed material containing 14 g of ^{244}Cm , 21 g of ^{243}Am , and 1 mg of ^{252}Cf . Figure 6 is an elution diagram for a separation with californium-DTPA feed material containing 1.5 g of ^{244}Cm and 1.5 mg of ^{252}Cf . In this separation, ^{254}Fm , ^{253}Es , and ^{250}Bk tracers were added to the feed. Four product fractions may be collected: a transcalifornium fraction containing fermium and einsteinium, a californium fraction, a berkelium fraction, and a fraction containing residual curium and americium. A typical separation

required about five hours from loading of the feed to elution of ^{252}Cf . The subnanogram amounts of ^{254}Es and submilligram amounts of ^{249}Bk were recovered only in selected production runs to demonstrate the process.

After testing several alternative processes, the accepted procedure for bulk processing the californium-AHIB solution was to adjust the solution to 0.25 M HNO_3 , absorb the californium on 10 ml of *Dowex* 50W-X8, 50 to 100 mesh resin in a platinum-lined column, and wash with water to remove HNO_3 . The column was heated in air to either 800°C for 8 hours to produce $(\text{CfO})_2\text{SO}_4$ or to 1250°C for 8 hours to produce $\text{Cf}_2\text{O}_3^{39}$. The column was then sealed and placed in a secondary container. The $(\text{CfO})_2\text{SO}_4$ or Cf_2O_3 is the starting material for preparing ^{252}Cf sources⁴⁰. Fermium-einsteinium and berkelium product fractions can be similarly processed.

In a two year period, ~3.5 mg of ^{252}Cf have been purified in five separations from Tramex feed material and ~5.5 mg of ^{252}Cf have been purified in six separations from DTPA feed material. The ^{252}Cf batch size from Tramex material was limited by curium-ameridium content.

Decontamination factors from ^{244}Cm for ^{252}Cf product were 10^5 to 10^6 . The conditioning of the column with 0.2 M NH_4NO_3 -0.02 M HNO_3 and the wash of the column with this solution after loading had a pronounced effect on the resolution of ^{252}Cf peak by eliminating pH gradients on the column in the early phases of the separation. Recovery of californium was greater than 98 percent. Back-flushing all lines to the feed tank before elution with AHIB prevented the small amounts of feed material held up on the equipment lines from leaking onto the column during elution. Major radioactive impurities in the feed included ^{239}Np (decay

product of ^{243}Am), ^{240}Pu (decay product of ^{244}Cm), ^{106}Ru , ^{154}Eu , ^{144}Ce - ^{144}Pr , and ^{95}Zr - ^{95}Nb . Most of the neptunium, plutonium (IV), ruthenium, zirconium, and niobium eluted during loading or in the column wash. Europium eluted just after berkelium and cerium eluted after the curium-ameridium (Figure 6). For the ^{252}Cf product from DTPA feed material, spark source mass spectrometric analyses showed major nonradioactive impurities zinc, iron, calcium, and sulfur to be at about the same concentration as ^{252}Cf . The mass ratios of impurity elements to ^{252}Cf will decrease in future processing because the ^{252}Cf batch size will be increased from 1 mg to approximately one hundred milligrams while the impurity level remains constant.

Thirty cation exchange production runs to remove DTPA from californium-DTPA fraction were made with an average of <0.25% nonabsorbed californium. Thirty hydroxide precipitations with lanthanum carrier were made successfully with NaOH. For the absorption of milligram quantities of ^{252}Cf on a 10 cm³ bed of cation resin from several liters of AHIB solution, the losses were less than 0.1 percent.

The process described here has been successful at the milligram scale for purification of ^{252}Cf from multigram quantities of curium and ameridium and will be used in the near future to purify ^{252}Cf in batches of hundreds of milligrams. In this processing, the feed will be from the DTPA cation exchange cycle (see Section 4.1) and will contain less than 0.3 g of ^{244}Cm per batch. Other products to be recovered in this processing by the pressurized AHIB system are ^{257}Fm , ^{254}Es , and ^{249}Bk .

4.3 Elution Development: Milligram-Scale Separation of Transcurium Elements

At ORNL⁴¹⁻⁴⁴, the processing steps for transcurium element product are: (1) dissolution of target materials irradiated in the High Flux Isotope Reactor (HFIR), (2) recovery of plutonium, (3) decontamination of transplutonium elements by Tramex, (4) separation of americium and curium from transcurium elements by LiCl based anion exchange, and (5) separation and purification of berkelium, californium, einsteinium, and fermium by pressurized cation exchange elution chromatography with AHIB.

In processing experience to date, ²⁵²Cf, ²⁵³Es, and ²⁴⁹Bk have been purified by pressurized cation exchange elution development from two types of process feed material. Some feed was Tramex product solution; in most cases, feed was the transcurium fraction from LiCl-based anion exchange. The LiCl system separates transplutonium elements that have been decontaminated from fission products by Tramex extraction into a curium-amerium fraction and a transcurium fraction.

4.3.1 Cation exchange system

A typical column is a 122-cm-long by 0.76-cm-diameter stainless steel tube, water jacketed for temperature control at 80°C. A positive displacement pump feeds process solutions directly to the column. Radioactive feed solutions were displaced onto the column.

The column contained about 40 ml of 20 to 40 μ *Dowex* 50W-X8 graded³³ resin in the ammonium form. The movement of the californium elution band down the column was monitored by in-cell

neutron detectors; an in-line alpha detector monitored the eluate stream.

4.3.2 Process chemistry

Both the Tramex and LiCl-anion exchange feed materials were prepared for cation exchange by hydroxide precipitation with NH_4OH . The Tramex product solutions contained impurities in concentrations sufficient to precipitate with ammonia and carry the actinides. For the LiCl solutions, iron was added as a carrier. In each case the metal hydroxide was filtered, washed, dissolved in concentrated nitric acid, and diluted to 0.1 M HNO_3 .

Feed was pumped to the column at 25 ml/min cm^2 with a 1000 psig pressure drop. The column was then washed with 20 ml of water. A solution of 0.3 M NH_4NO_3 was pumped through the column to replace NH_4^+ that had been displaced by excess acid in the feed.

The transcurium elements were eluted at 20 ml/min cm^2 with 0.25M AHIB that had been partially neutralized with ammonium hydroxide to a pH of 4.25. Three product fractions were collected: a transcalifornium fraction containing einsteinium and fermium, a pure californium fraction, and a berkelium fraction. Subsequent small-scale separations on an AHIB column yielded pure einsteinium and fermium product.

The AHIB-containing product fractions were converted to acid solutions by cation exchange. The pH of product fractions was adjusted to 1.0, and the solutions were passed through small columns of *Dowex* 50W-X4 resin to load the actinides. The columns were washed with 0.2 M acid to remove AHIB, and the actinides

were eluted with 6 to 8 M acid.

In three recent campaigns to process targets irradiated in HFIR, a total of about 7 mg of ^{249}Bk , 54 mg of ^{252}Cf , 380 μg of ^{253}Es , and 5×10^8 atoms of ^{257}Fm have been recovered. Feed to the pressurized AHIB column typically contained californium-einsteinium with a mass ratio of 500:1, and product fractions contained greater than 99% of the respective elements with less than 1% cross-contamination. This compares with 80 to 90% yields in the product fraction and 10% cross contamination for conventional cation exchange column operation. The largest quantity of material processed in a single production run was about 200 mg of ^{244}Cm , 3 mg of ^{252}Cf , and 6 μg of ^{253}Es . A typical elution diagram is shown in Figure 7.

In small-scale development work prior to operation of the above system, Campbell²⁸ found that after loading the actinides, a wash with an ammonium formate solution of the same pH as the elutriant (pH = 4.4) prevented excess acid introduced in the feed from causing a pH gradient on the column. Peak positions were more reproducible, and resolution was improved with this wash step. Campbell also demonstrated that loading may be accomplished at a very high flow rate with a short column containing very fine resin. After loading, the small column may be coupled to another column where separation occurs. His studies of band tailing showed the concentration in the tails could be reduced to 3 to 5 orders of magnitude less than in the peaks.

In the future, feed to the pressurized AHIB ion exchange cycle will be exclusively the transcurium fraction from LiCl-based anion exchange. It is anticipated that this system can be used to process 100 mg batches of ^{252}Cf at ORNL.

5. OTHER APPLICATIONS OF PRESSURIZED ION EXCHANGE

Since its inception in the field of biochemistry, pressurized ion exchange has been a powerful technique for the separation of molecular constituents of complex human body fluids. The successes of pressurized ion exchange (see Section 2.1) in transplutonium actinide separations suggests that the general technique should be considered for any separations of highly radioactive materials. A few possible applications of pressurized anion exchange as well as pressurized cation exchange systems are discussed below.

5.1 Cation Exchange

In the programs⁴⁵ for using radioisotopes produced in power reactors, production and recovery of ²⁴⁴Cm for heat source fabrication has been proposed. Chemical processing to purify curium would require a large-scale curium-ameridium separation. This separation could be achieved with pressurized cation exchange displacement development chromatography with DTPA as discussed in Section 4.1.

Pressurized cation exchange has been successfully applied to analytical separations. Farrar *et al.*⁴⁶ have employed a small pressurized cation exchange system to rapidly separate berkelium from californium and curium by elution development chromatography with 0.25 M AHIB (pH = 4.2). The stainless steel column (63.5 cm long; 0.18 cm in diameter) was jacketed so that temperature of 80 ±4°C were maintained by recirculating hot water. Flow rates of 18 ml/min cm² were normally attained at pressures from 1000 psig to 2500 psig. The application of pressurized ion

exchange to other analytical ion exchange separations problems could greatly reduce operating time and provide improved separations.

The technique of pressurized cation exchange has been used to obtain rapid chemical separations for research purposes. To study short-lived radioactive rare earth nuclides produced in accelerators or reactors, fast chemical separations of adjacent rare earth elements are necessary. Campbell and Ketelle³² studied rapid chromatographic elutions of trace concentrations of praseodymium(III) on a small pressurized AHIB column. A typical column was 12.5 cm by 0.08 cm² loaded with 10 to 20 μ Dowex 50-X12 resin. The eluting solution was 0.57M AHIB (pH = 4.4). They concluded that adequate separation for adjacent lanthanides should be obtained at flow rates of 6.2 ml/min cm², which corresponds to an elution in five minutes. When greater band overlap can be tolerated, a flow rate of 50 ml/min cm², which corresponds to an elution in about one minute, would be satisfactory. Figure 8 shows the effect of flow rate on band width. This type of separation could also be used to separate quickly adjacent transplutonium elements.

5.2 Anion Exchange

The advantages of pressurized cation exchange (see Section 3) apply equally well to anion exchange. In laboratory-scale tests, ORNL⁴⁷ has pressurized the LiCl-based anion exchange system for preliminary separation of americium and curium from californium (see Section 4.3). When compared with results obtained in conventional equipment, results from the first pressurized tests showed significantly improved actinide separations. Large

volumes of feed solution were pumped through the column without adverse effects. Flow rates were 10 ml/min cm². An elution curve is shown in Figure 9. Americium eluted with the curium, and einsteinium eluted with californium. The californium fraction contained 98.6% of the californium and 0.03% of the curium.

The technique of pressurized ion exchange could be applied to the separation of plutonium and neptunium by HNO₃-based anion exchange⁴⁸, and to the separation of americium and curium by LiNO₃-based anion exchange⁴⁹. However, because of hazards observed with HNO₃-anion exchange systems under certain conditions⁵⁰, a careful safety analysis should be made of any pressurized anion exchange system involving nitrates.

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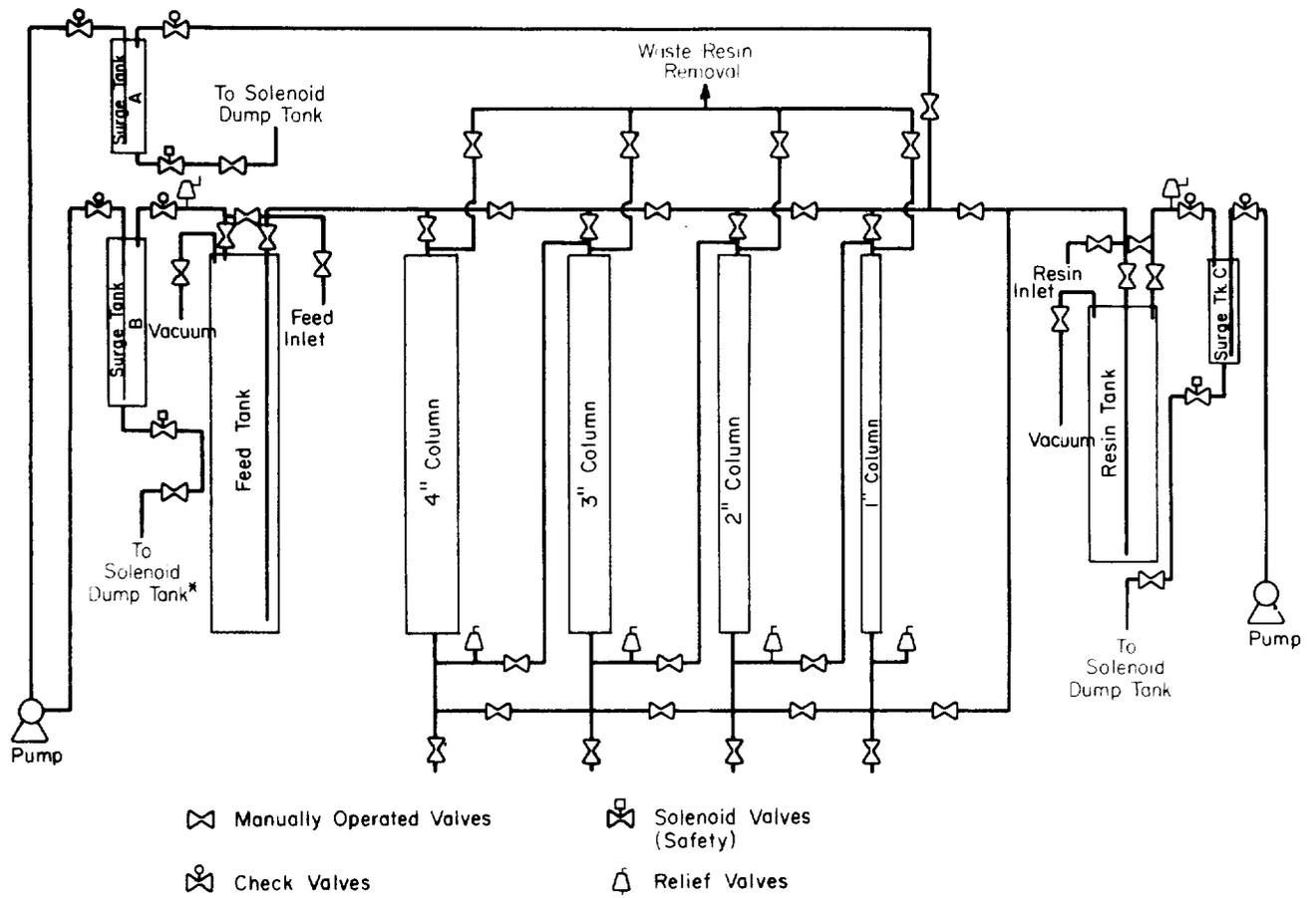


FIG. 1 FLOW DIAGRAM FOR COLUMNS

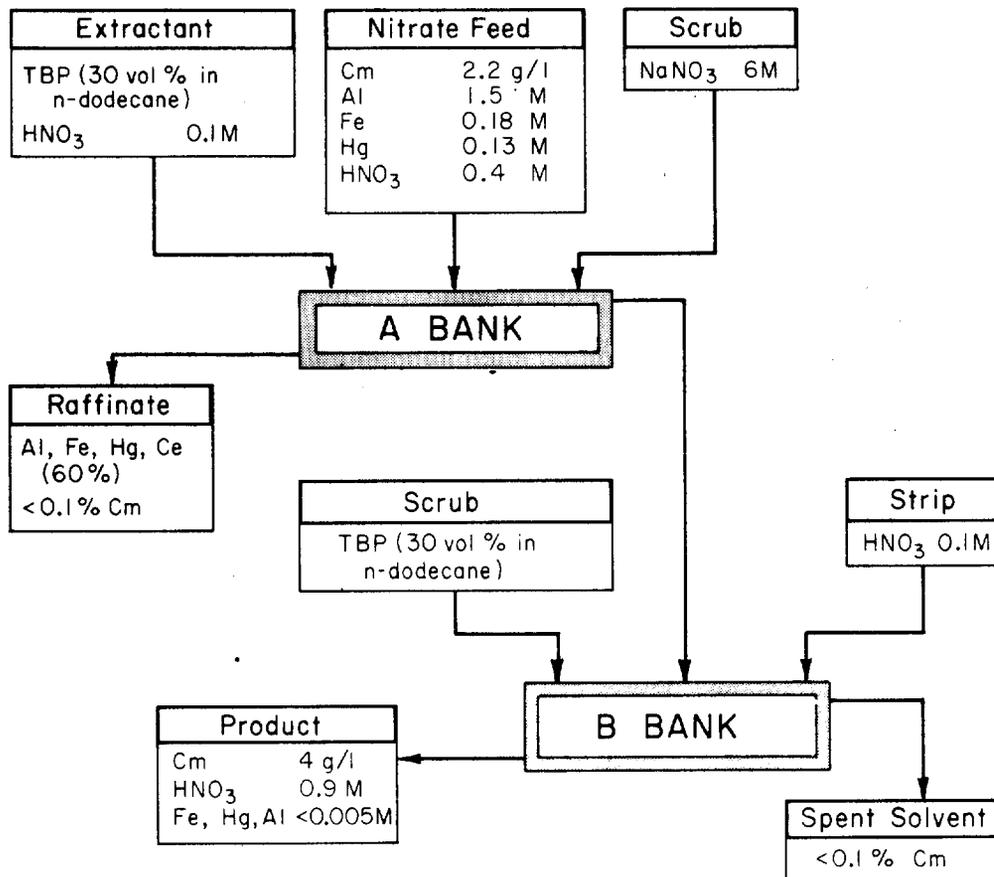


FIG. 2 PREPARATION OF CATION EXCHANGE FEED BY SOLVENT EXTRACTION

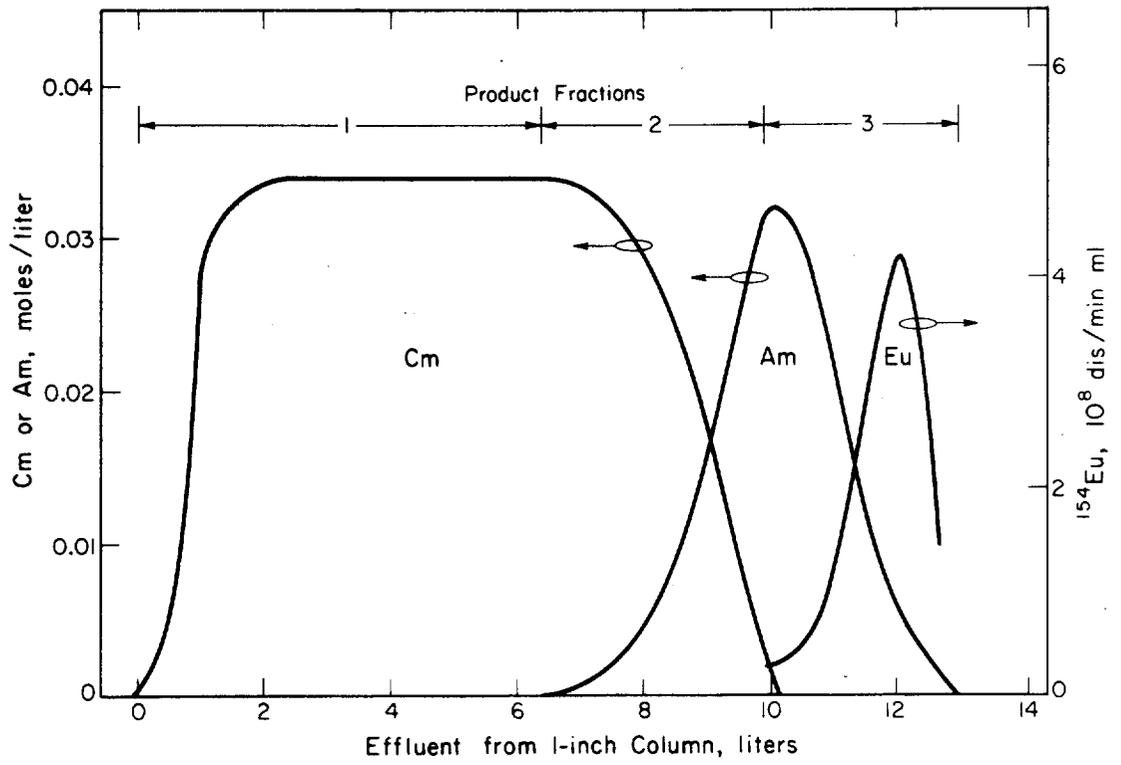


FIG. 3 TYPICAL ELUTION DIAGRAM

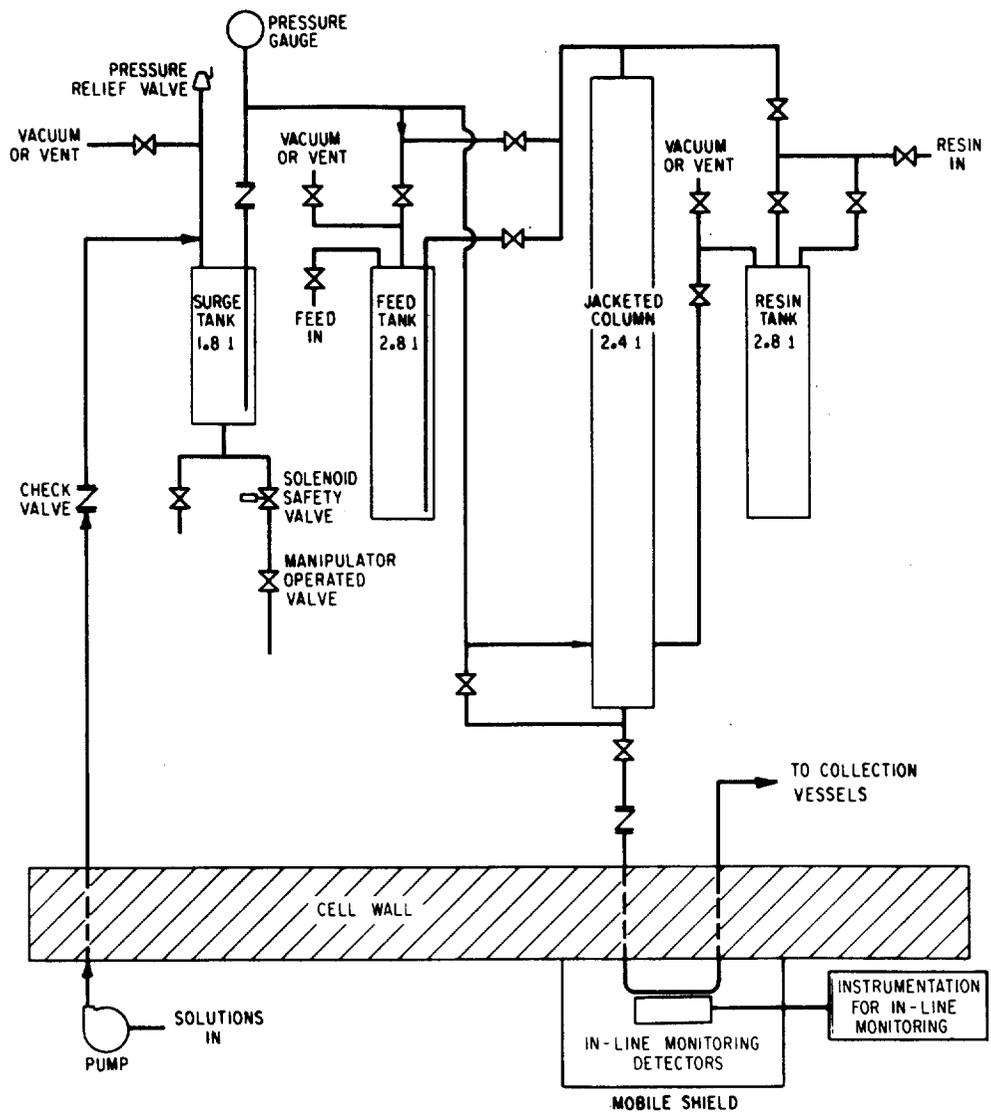


FIG. 4 SCHEMATIC DRAWING OF PRESSURIZED CATION EXCHANGE SYSTEM FOR THE PURIFICATION OF ^{252}Cf

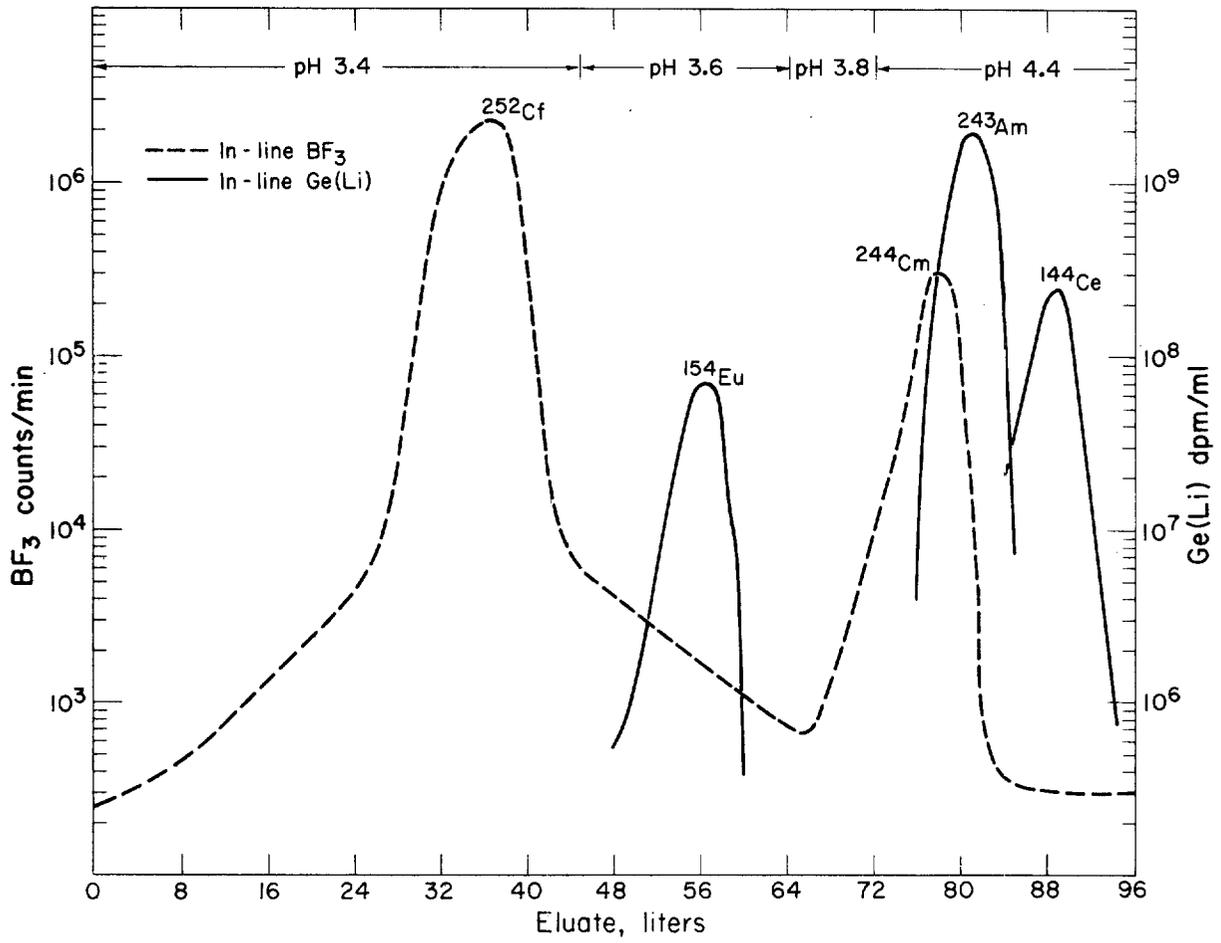


FIG. 5 ELUTION DIAGRAM FOR TRAMEX FEED MATERIAL

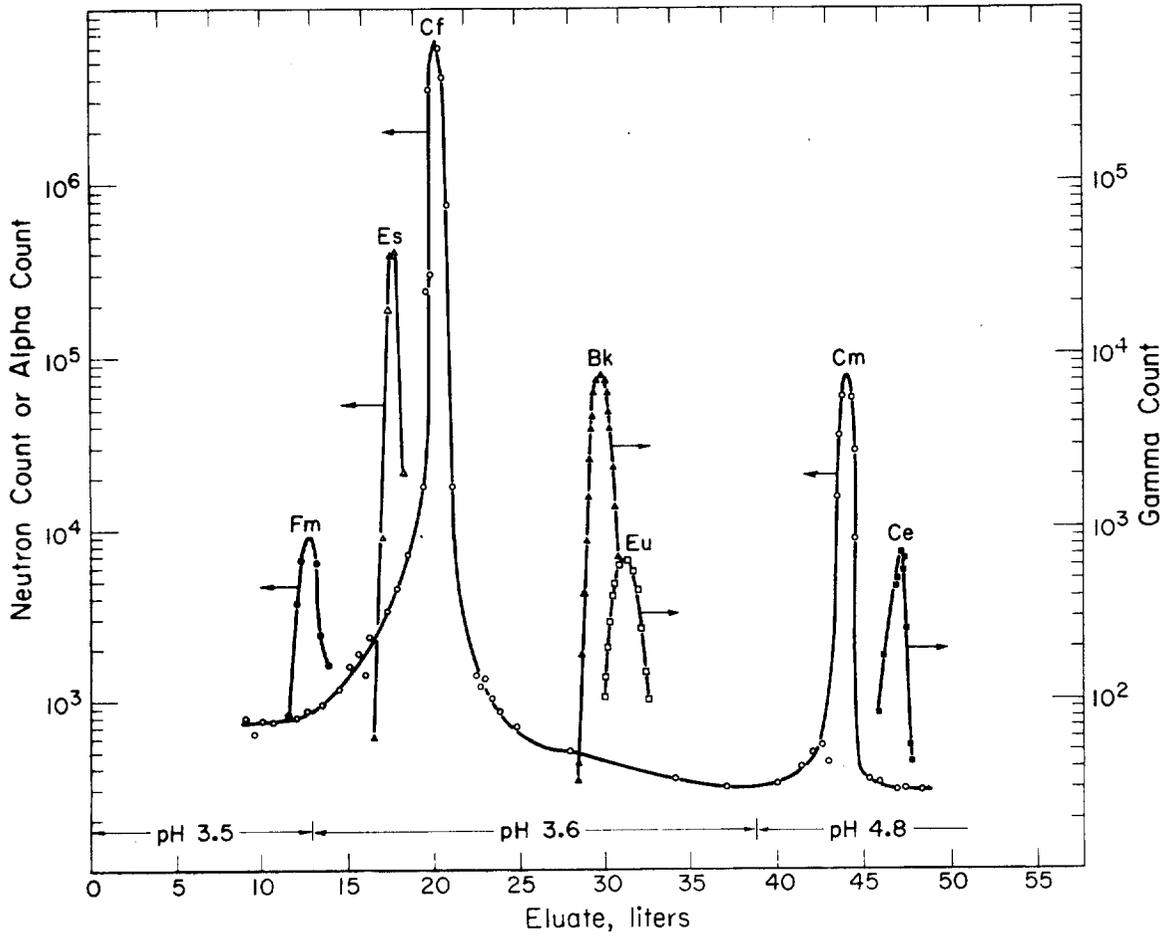


FIG. 6 ELUTION DIAGRAM FOR ^{254}Fm , ^{253}Es , AND ^{250}Bk SEPARATION OF DTPA FEED MATERIAL

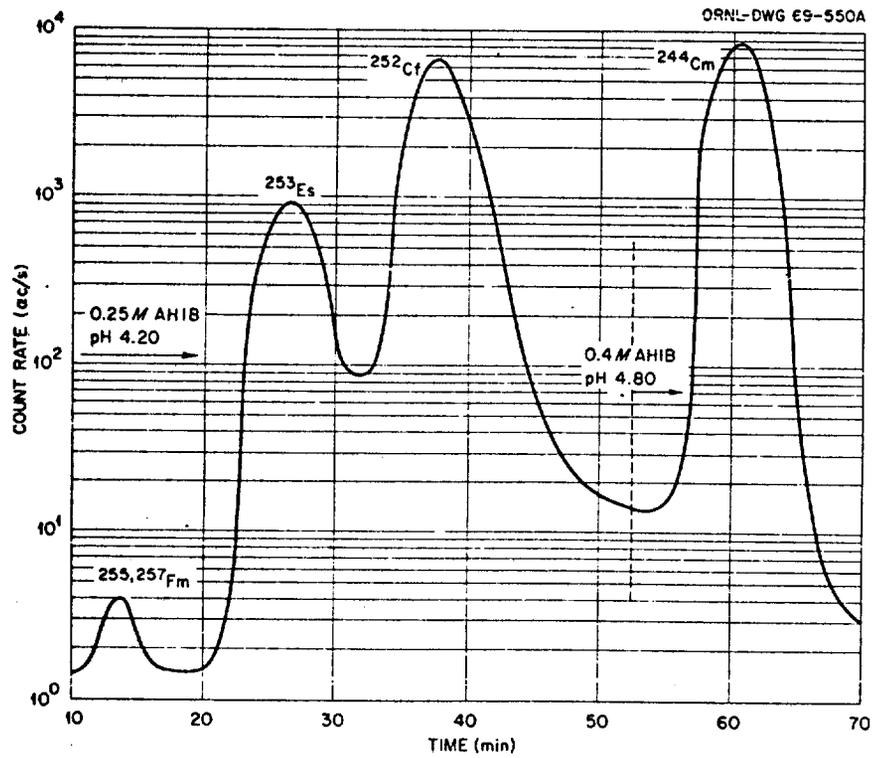


FIG. 7 TYPICAL SEPARATION OF ACTINIDE ELEMENTS ON A HIGH-PRESSURE COLUMN AS INDICATED BY AN IN-LINE ALPHA DETECTOR

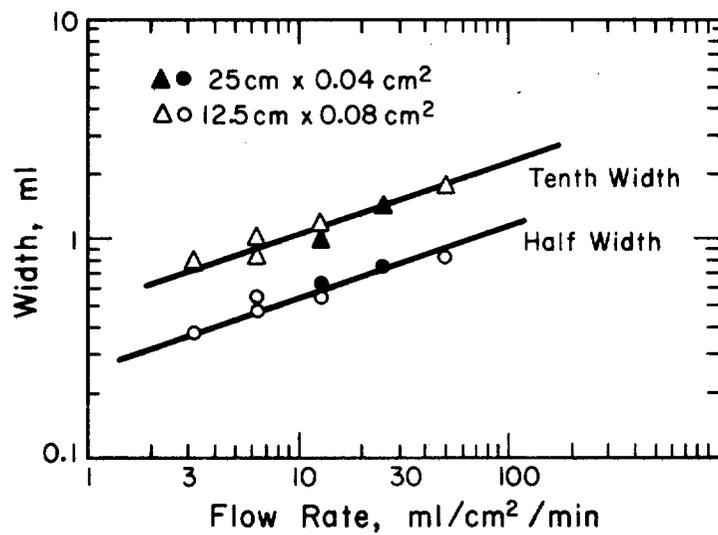


FIG. 8 EFFECT OF FLOW RATE ON BAND WIDTH

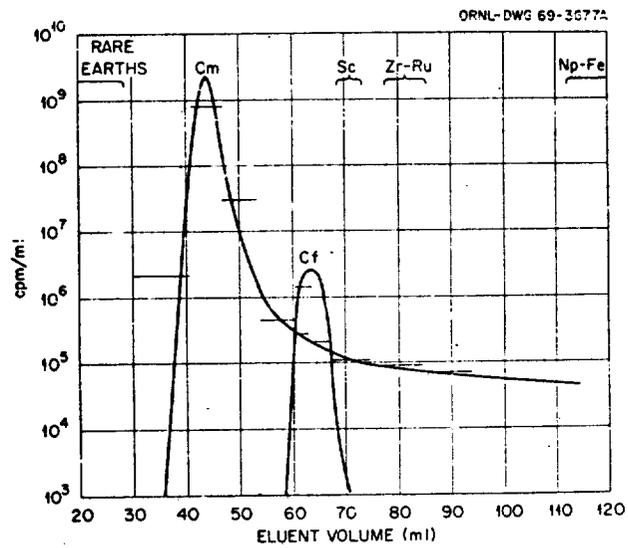


FIG. 9 ACTINIDE ELUTION CURVES FOR LiCl-BASED ANION EXCHANGE HIGH-PRESSURE COLUMN RUN.