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SEPARATION OF MACRO-QUANTITIES OF ACTINIDE ELEMENTS AT SAVANNAH RIVER BY HIGH-PRESSURE CATION EXCHANGE

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ABSTRACT

Large-scale separation of actinides from fission products and from each other by pressurized cation exchange chromatography at Savannah River is reviewed. Several kilograms of ^{244}Cm have been separated, with each run containing as much as 150 g of ^{244}Cm.

Dowex® 50W-X8 (Dow Chemical Co.) cation resin, graded to 30-70 micron size range, is used, and separation is made by eluting with 0.05M diethylenetriamine pentaacetic acid (DTPA) at a pH of 3. The effluent from the column is continuously monitored by a BF_3 detector, a NaI detector, and a lithium-drifted germanium detector and gamma spectrometer to guide collection of product fractions.

Operating the columns at 300 to 1000 psi pressure eliminates resin bed disruption caused by radiolytically produced gases, and operating at increased flow rates decreases the radiolytic degradation of the resin per unit of product processed.

A portion of the hot canyon of a production radiochemical separation plant was converted from a remote crane-operated facility to a master-slave manipulator-operated facility for separation and purification of actinide elements by pressurized cation exchange. It also contains an evaporator, furnaces, a calorimeter, and several precipitators and associated tanks. Actinide processing from target dissolution to packaging of purified product is planned in this facility.

INTRODUCTION

Several kilograms of ^{244}Cm and ^{243}Am and several milligrams of ^{252}Cf were produced at Savannah River by irradiation of a mixture of plutonium isotopes (1). The plutonium was separated by solvent extraction, and the other actinides were separated from each other and from large quantities of fission-product rare earths by displacement-development chromatography in a system of pressurized steel columns in the high level caves at the Savannah River Laboratory (2). The elutriant was 0.05 M diethylenetriamine pentaacetic acid (DTPA) buffered with ammonium hydroxide. As much as 100 grams of ^{244}Cm was separated from several moles of mixed rare earths and other fission products in a single batch. A unique computer-controlled on-line monitoring system directs the separations in the ion exchange system (3).

A portion of one of the large radiochemical separation plants at SRP has been converted to a heavily shielded eight cell master slave manipulator operated facility (MPPF) for separation and purification of actinide elements by a pressurized cation-exchange system (4). The system, presently being tested for startup in 1980, also includes a dissolver, two evaporators, several precipitators, furnaces, a calorimeter, and associated tanks. Actinides will be processed in the MPPF from dissolution of irradiated targets to packaging of purified products. The size of the cation exchange columns will be varied as required for different programs. Neutron shielding will permit processing as much as 250 mg of ^{252}Cf per batch.

DISCUSSION

Advantages of Pressurized Cation Exchange

With small particle resin, equilibration between solution and resin is attained rapidly because diffusion distances are short in both the resin particles and in the aqueous film surrounding the particle. The use of small-particle resin improves the kinetics and gives a more uniform flow, which allows fast flows for the loading and elution steps. The high flows reduce the time necessary for separation and thus radiation and thermal damage to the resins from highly radioactive products.

To increase flows with small-particle resin, the feed and elutriant solutions are pressurized. Pressurizing these solutions has the advantage of dissolving the radiolytic gases generated by radiolysis of solution primarily by alpha particles and fission fragments. Radiolytic gases can cause bed disruptions, which may result in irregular flow and chaneling. When the columns are operated at elevated temperatures, solution viscosity is reduced and the pressure drop is lower for a given flow.

A thorough safety analysis of any high-pressure system should precede handling of radioactive material. Pressurized systems with positive displacement pumps to feed nonradioactive solutions to ion exchange columns directly have been operated safely with the use of pressure relief valves, check valves, surge tanks, and radioactive monitors.

Systems for Processing Macro Quantities of Actinides

Cation Exchange

The system consists principally of four columns, a feed tank, and a resin transfer tank (Fig. 1). The columns were constructed of Type 304L stainless steel, Schedule 80 pipe and are 122 cm long. Generally four columns with nominal diameters of 10.2, 7.6, 5.1, and 2.5 cm have been used but columns with diameters 20.3, 15.2, 10.2, and 5.1 cm will be used in MPPF when the mole ratio of lanthanides to actinides is 15 to 1 and quantities of americium and curium are approximately equal. Resin is held in the column by a 10 μm 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

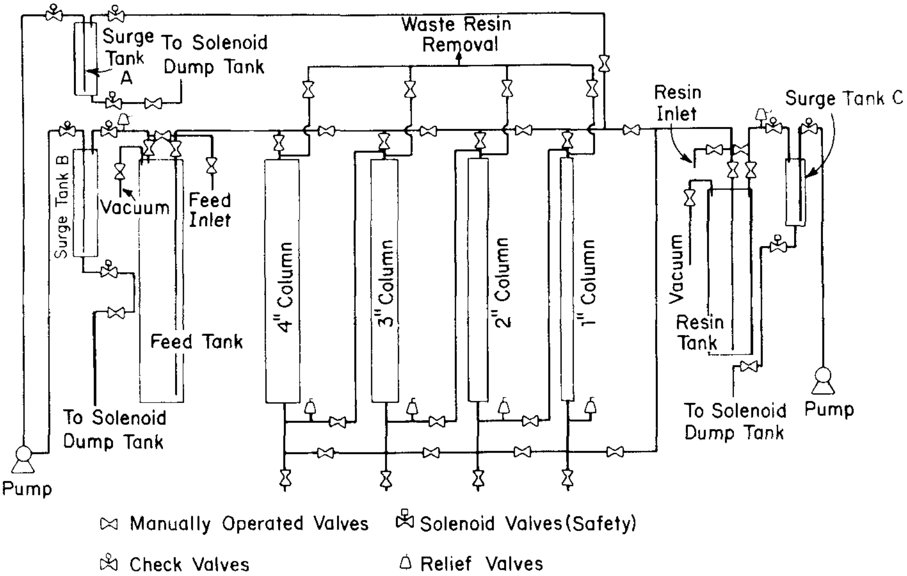

FIGURE 1. Pressurized Cation Exchange System

the cation-exchange columns either directly (for nonradioactive solutions), or by water displacement through a pressurized feed tank (for resin slurries or radioactive feed). Radioactive solutions are never transferred through the pump. Each line leading from the pump passes through a relief valve to prevent overpressurization of the system. Each column is also provided with a pressure relief valve. To prevent back-up 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.

Dowex® 50W-X8 resin (Dow Chemical) is hydraulically graded to approximately a 20 μm range; particles may be 40 to 110 μm. The narrow range (20 μm) is necessary to maintain the pressure drop below 1000 psig at flows of 16 mL/(min)(cm^2). Based on operating experience, resin exposure is limited to 4 kilowatt hours per liter. At higher exposures, the pressure drop was higher and curium was not eluted in a sharp band.

In-Line Analysis System

All column effluent flows through a doubly contained 0.64 cm stainless steel line that passes through the cell wall, forms a loop and passes back into the cell (Fig. 2). Three radiation detection systems are positioned around the loop: a BF_3 neutron monitor, a NaI scintillation detector for high energy gamma rays and a Ge(Li) low-energy photon detector (3).

Spontaneous fission neutrons from ^{252}Cf and ^{244}Cm are detected with a BF_3 probe. ^{252}Cf and ^{244}Cm are not differentiated with the neutron counting system, but are easily distinguished by monitoring the 42.9-keV ^{244}Cm photopeak with the Ge(Li) detector. The BF_3 tube is shielded for background radiation with 13 cm of paraffin and Benelex® (Masonite Corp.) to thermalize fast neutrons and 0.64 cm of cadmium to stop thermal neutrons. The system has shown no gamma sensitivity for radiation levels up to 1000 R/hr.

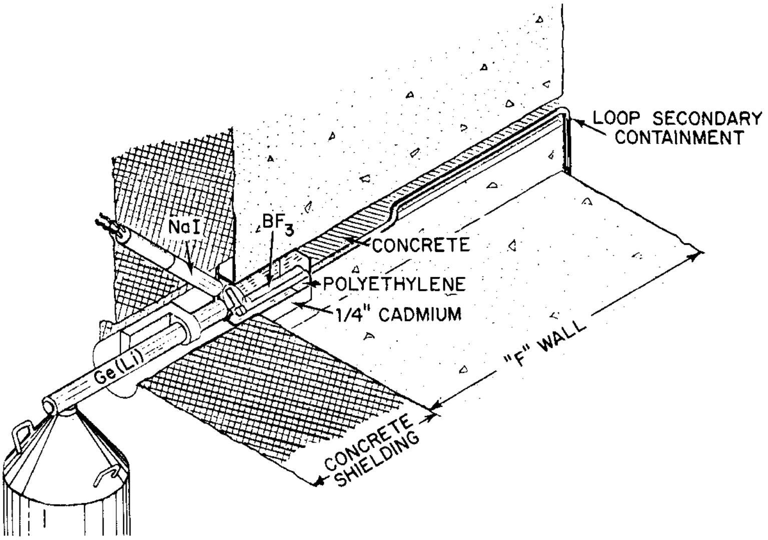

FIGURE 2. Monitor and Instrument Port Arrangement

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}Ru-Rh and ^{144}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 the breakthrough of ^{154}Eu in the curium and americium region. In the absence of terbium, europium is the first element to elute after americium.

The Ge(Li) detector gives specific quantitative analyses for ^{244}Cm, ^{243}Am, ^{154}Eu, ^{144}Ce-Pr, ^{237}Np, and ^{106}Ru-Rh. The lower limit of detection for each element 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 batch by flowing standard solutions through the steel loop.

A computerized system was designed and developed around a PDP-9 computer and a 200-mHz analog to digital converter (2). 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.

Process Chemistry

Because cation exchange resins show little selectivity among lanthanides and actinides, a chelating agent is used to separate the elements into separate bands. Displacement development chromatography with DTPA is used. The resin is loaded with zinc (as barrier ion) that has less affinity for the resin than the ions to be separated. Then a mixture of lanthanides and actinides is sorbed on the cation resin and DTPA flowed through the resin bed. Because the stability of the complex ion formed by each element is different, the elements form separate bands and are eluted from the column in order of decreasing stability constants of the complex. A binary zone, or overlap region is between each band of pure component because the column is not at equilibrium at finite flows.

Tests determined the number of moles of lanthanide plus actinide that can be loaded per liter of cation resin from solutions of various HNO_3, $NaNO_3$, and $Ln+An(NO_3)_3$ concentrations. Published data did not include the concentration ranges of interest. A general equilibrium treatment for sorption is given in Reference 5. To test the calculated curve, solutions of varying concentrations of nitric acid, sodium nitrate, and praseodymium nitrate were passed through cation-exchange resin loaded with zinc. The praseodymium was stripped with 2 M HNO_3 and determined by EDTA titration. Experimental and calculated data are compared in Fig. 3, which plots the fraction of resin in the actinide-lanthanide form and $\sigma = 0.125\ [Na^+] + 0.057\ [H^+]/[An\text{-}Ln]^{1/3}$.

Helfferich and James (6) described a method for calculating the band lengths of resin required to separate a multicomponent mixture by displacement development chromatography. Data required for the calculation are separation factors of the components relative to the last element eluting from the column and mole fraction composition of the mixture to be separated. A more

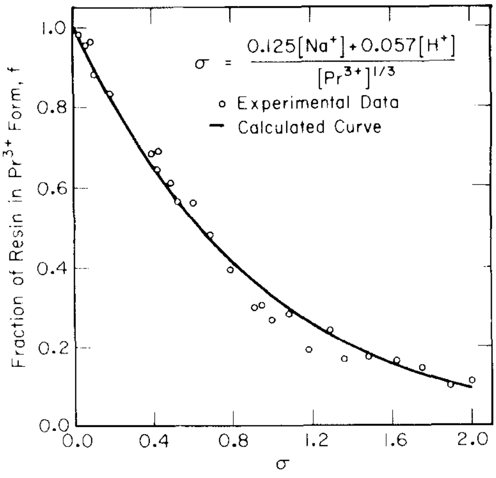

FIGURE 3. Sorption of Pr by Dowex® 50W-X8 at 70°C

detailed discussion of this method and a computer code to perform the calculation for mixtures of actinides and lanthanides is given in Reference 5.

The studies of Wheelwright (7) and Lowe (8) were extended to determine the effects of several variables on the separation of nonradioactive lanthanides. Equimolar mixtures of neodymium, praseodymium and samarium were sorbed in Dowex® 50W-X8, zinc-form resin, and separated by eluting with 0.05 M DTPA. The theoretical plate height (TPH) for each test was calculated by the method of Wheelwright(7) and Lowe (8).

The effect of temperature on theoretical plate height is shown in Fig. 4; the TPH decreases from 1.5 cm at 50°C to 0.9 cm at 70°C with other conditions constant. Fig. 5 shows results of

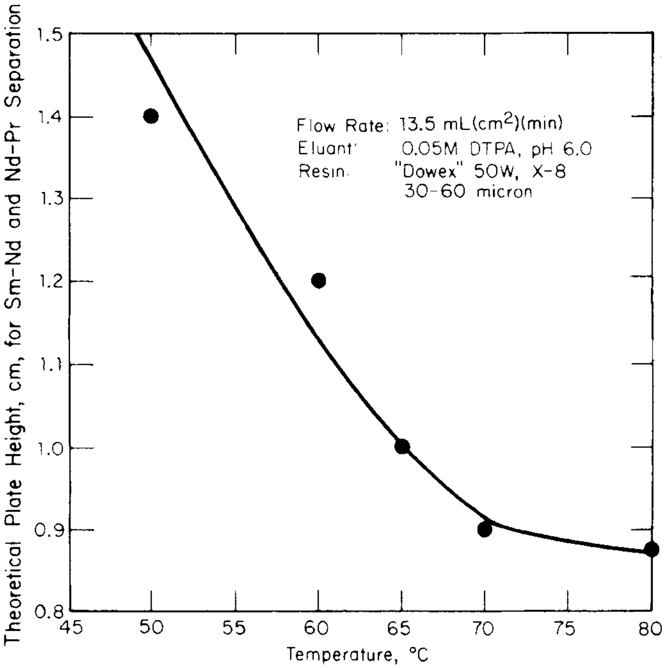

FIGURE 4. Effect of Temperature on Theoretical Plate Height

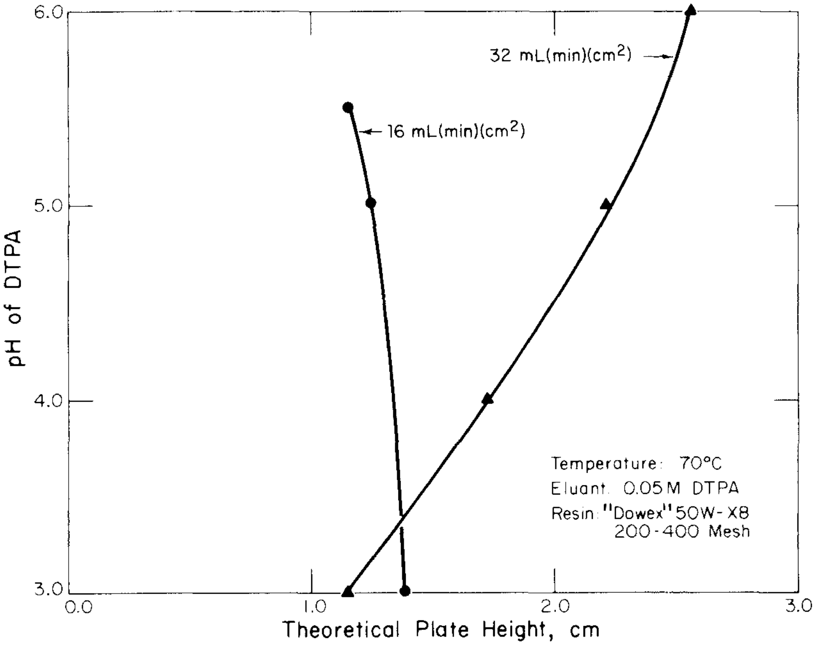

FIGURE 5. Effect of pH on Theoretical Plate Height

tests with 0.05 M DTPA at 16 and 32 mL/(min)(cm^2) and pH 3 and 6. The lower pH limit was set at 3 because DTPA crystallizes from 0.05 M solution at pH 2.8. The TPH for the test at pH 3 and 32 mL/(min)(cm^2) is approximately equal to that for the test at pH 6 and 16 mL/(min)(cm^2). These data indicate that separation of americium and curium is excellent with 0.05 M DTPA at any pH from 3 to 6 with a flow of 16 mL/(min)(cm^2). With 0.05 M DTPA at 32 mL/(min)(cm^2), pH 3 is required for a low TPH and good separation of americium and curium. In another test, the effect of flow between 10 and 20 mL/(min)(cm^2) on TPH is shown in Fig. 6.

The variation of pressure (ΔP) with particle diameter for different temperatures and at a constant void fraction (ε) of 0.26 is shown in Fig. 7. For the desired pressure drop limit of

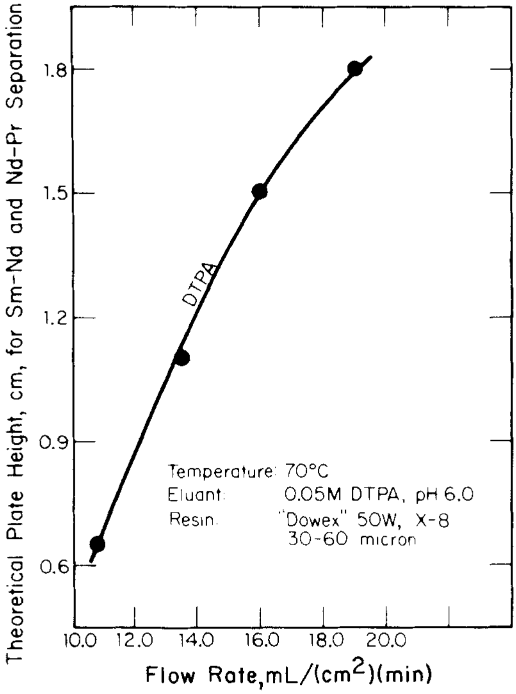

FIGURE 6. Effect of Flow Rate on Theoretical Plate Height

1000 psig, 35 μm resin can be used if the elutriant temperature is 50°C. In every test, ΔP was higher than calculated from the Ergun equation (9) because of the relatively wide range in diameter of the resin particles used.

Hale and Hammer (10) determined the cation exchange elution sequence of 42 cations, including all the lanthanides, eight actinides and most of the common divalent and trivalent ions. The elements were eluted with 0.05 M DTPA at pH 6 (Table 1). Prior data for the DTPA system (11, 12) was either limited to a few elements or the DTPA concentration and pH were different. These data were necessary for process design calculations, selection of a barrier ion, and control of product purity. The ion exchange elution sequences cannot be predicted accurately

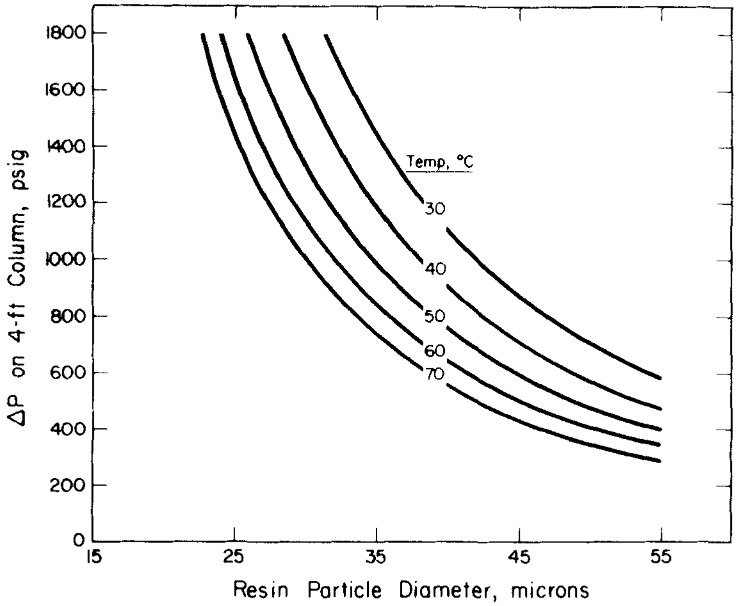

FIGURE 7. ΔP vs. Resin Particle Diameter at Various Temperatures

with the limited thermodynamic data available. Elution sequences are not correlated with metal-DTPA stability constants (Table 1).

Process Operation

Feed adjustment steps prior to sorption of Ln + An on Dowex® 50W-X8 resin include:

- Volume reduction by evaporation.
- Formic acid denitration to reduce the nitric acid concentration to <1M.
- Addition of $NaNO_2$ and heating to >70°C to convert the ruthenium nitrato-complexes to ruthenium nitro-complexes.

The nitric acid must be <1M to attain the desired loading of Ln + An on the resin; the ruthenium is adjusted to species that pass through the resin bed during loading so that the actinide products are not contaminated during elution with DTPA.

TABLE 1

Cation Exchange Elution Sequence with 0.05 M DTPA(pH 6.0) at 70°C

Ion	log K (M-DTPA)[a]	Ion	log K (M-DTPA)[a]
Pu^{4+}	29.49(20°C)	Tm^{3+}	21.95
Ga^{3+}	25.54(20°C)	Er^{3+}	21.99
Bi^{3+}	29.7(20°C)	Ho^{3+}	22.00
(Fe^{3+}		Dy^{3+}	22.00
In^{3+}	29.3(20°C)	Lu^{3+}	21.85
Cr^{3+})	27.65(?)	Am^{3+}	22.06
Cu^{2+}	20.07	Tb^{3+}	21.93
Ni^{2+}	19.00	(Gd^{3+}-Eu^{3+})	21.75-21.76
Fm^{3+}		Sm^{3+}	21.58
Es^{3+}	23.07	Y^{3+}	21.29
Cf^{3+}	23.02	Pm^{3+}	
Th^{4+}	28.78(20°C)	Nd^{3+}	20.92
Sc^{3+}	23.65	Pr^{3+}	20.45
Co^{2+}	18.24	Ce^{3+}	19.85
Bk^{3+}	22.70	La^{3+}	18.98
Zn^{2+}	17.40	Mn^{2+}	14.78
Cd^{2+}	17.96	Be^{2+}	
Pb^{2+}	16.83	Mg^{2+}	9.31
Cm^{3+}	22.12	Ca^{2+}	10.02
Al^{3+}	19.32	Sr^{2+}	8.95
Yb^{3+}	21.89	Ba^{2+}	7.88

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[a] All values at 70°C unless otherwise noted.

For one flowsheet, a system of four 122-cm-long columns is used: 10.2, 7.6, 5.1, and 2.5 cm in diameter. The columns are all water jacketed and operated between 70 and 80°C. The resin in each column is saturated with zinc barrier ion before each batch. The eluting agent is 0.05 M DTPA adjusted to either pH 6 or 3 with ammonium hydroxide.

In a typical test, feed is loaded onto resin in the 10.2-cm-diameter column by displacement from the feed tank with water. No separation is attained in this step. The Ln + An band is spread because the feed contains hydrogen and sodium ions. The resin is washed with dilute zinc nitrate to displace sodium and hydrogen with zinc, and DTPA flow is started. The bands are eluted successively through the four columns. Successively smaller diameter columns are used because the length of the overlap zone is independent of the column diameter but the amount of material in the zone increases as the square of the diameter.

The order of elution for the actinides and major lanthanide fission products is Cf, Cm, Am, Eu, Sm, Pm, Nd, Pr, and Ce. Es and Fm appear just ahead of Cf (and are eluted with Cf) and Bk is between Cf and Cm. Bk, Cf, Es, and Fm move into the zinc barrier and are well separated from Cm.

DTPA is pumped through the 10.2-cm column at 1.2 L/min [16 mL/(min)(cm^2)]. When the BF_3 detector indicates neutron breakthrough (∿50 μg Cf/L), the 7.6-cm column is valved in and the flow reduced to 16 mL/(min)(cm^2) on the 7.6-cm column. Similarly, the 5.1-cm column is valved in and the flow reduced when the ^{252}Cf exiting the 7.6-cm column is ∿50 μg/L. The ^{252}Cf is collected from the 5.1-cm column when the concentration reaches ∿50 μg/L until it drops to ∿50 μg/L. ^{249}Bk elutes between ^{252}Cf and ^{244}Cm, and a 50-liter berkelium fraction is collected following the ^{252}Cf fraction. The 2.5-cm column is added as soon as ^{244}Cm breaks through at 0.03 g/L. This column provides additional resolution of the products. ^{244}Cm is collected until the Ge(Li) detector indicates breakthrough of ^{243}Am, then a mixed Cm - Am fraction is collected until ^{244}Cm decreases to 0.03 g/L. A pure americium fraction is then collected until the NaI and Ge(Li) detectors indicate ^{154}Eu breakthrough; then a mixed Am - Eu fraction is collected until americium is no longer detectable. Lanthanides remaining on the columns are eluted to waste with 0.3 M DTPA at pH 8. The overlap fractions are recycled to a subsequent batch. A typical elution is shown in Fig. 8 for effluent from the 2.5-cm column (small amount of americium) and an idealized elution diagram for all products is shown in Fig. 9. The detection limits required are given in Table 2.

Another flowsheet was tested to demonstrate the separation and purification of curium and americium when the quantities of Cm and

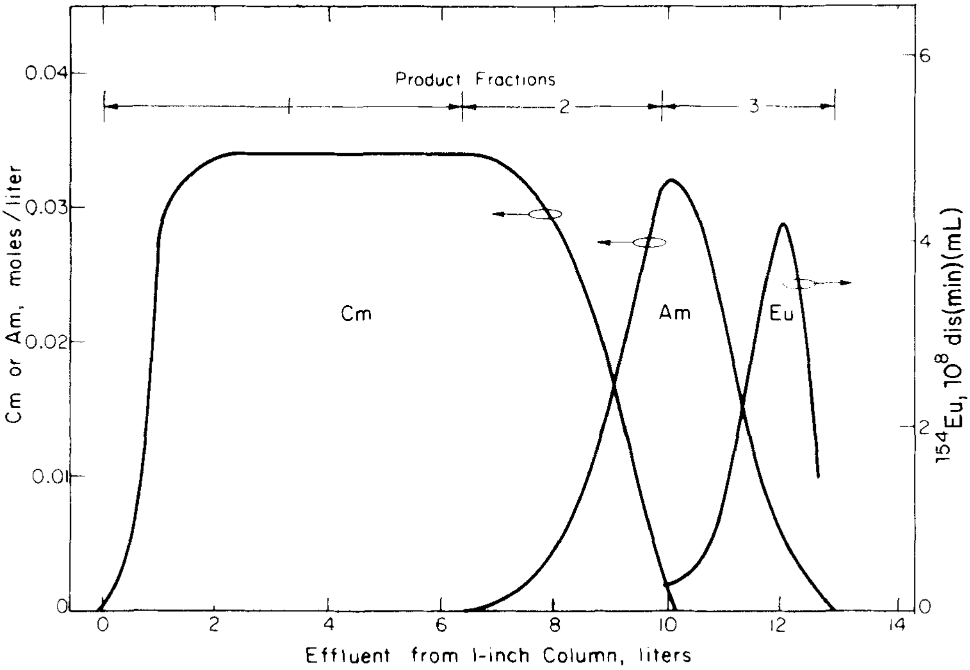
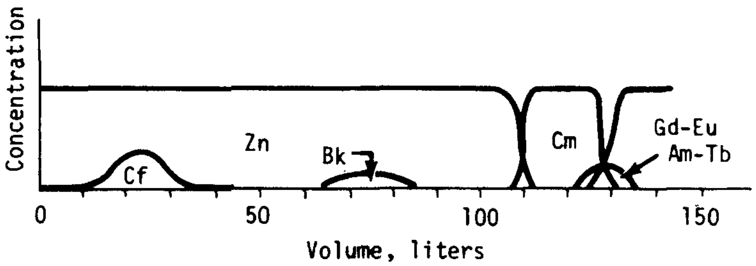


FIGURE 8. Typical Elution Diagram

Am were about equal and the mole ratio of lanthanides to actinides was about ten. The feed contained 81 g of Cm, 76 g of Am, 162 g of Ce, 60 g of Pr, 250 g of Nd, 65 g of Sm, 10 g of Eu, and 22 g of Gd. Three 122-cm-long columns were used: 10.2, 7.6, and 5.1 cm diameter. The 10.2-cm column was 80% loaded, and products were eluted with 0.05 M DTPA at pH 3. The flow was 16 mL/(min)(cm^2) through the 10.2- and 7.6-cm columns and 32 mL/(min)(cm^2) through the 5.1-cm column. The data are given in Fig. 10. Approximately 60 g of pure Cm and 30 g of pure Am were eluted from the 5.1-cm column. With a flow of 32 mL/(min)(cm^2) through the 5.1-cm column, the resin did not overheat.



- The effluent from the 4" col. is monitored for Cf; when Cf is detected at a level of 0.05 mg/L the effluent is diverted to the 3" column.
- The effluent from 3" col. is diverted to 2" col. at level of 0.05 mg Cf/L.
- Cf is collected from 2" col., starting when Cf is detected and continued until Cf concentration has dropped to 0.05 mg/L.
- Bk is collected from the 2" col. until Cm is detected at 0.03 g/L. At this time the effluent is diverted to the 1" col.
- The effluent from the 1" col. is diverted to waste until Cm is detected at 0.03 g/L. At this time Cm product is collected until ^{154}Eu breakthrough occurs at a level of 2 x 10^8 d/m/ml.
- Then the Cm-Am-Eu recycle fraction is collected until the Cm concentration has dropped to 0.03 g/L.
- Then the column effluent is diverted to waste until the fission products have been flushed from the 2 and 1" columns.

FIGURE 9. Idealized Elution Diagram

TABLE 2

Detection Limits Required for Cation Exchange Separation

Nuclide	Sensitivity
^{244}Cm	0.03 g/L
^{252}Cf	1 μg/L
^{243}Am	0.06 g/L
^{154}Eu	$2\text{x}10^8$ dpm/mL
^{144}Ce	$3\text{x}10^9$ dpm/mL
^{160}Tb	$2\text{x}20^8$ dpm/mL

The dose rate from gamma fission products impurities in the ^{244}Cm product was <10% of that from pure ^{244}Cm. No single impurity (except Am) exceeded 0.2 wt %. Total impurities (except Am) were <1 wt %; total impurities (with Am) were <3 wt %. The

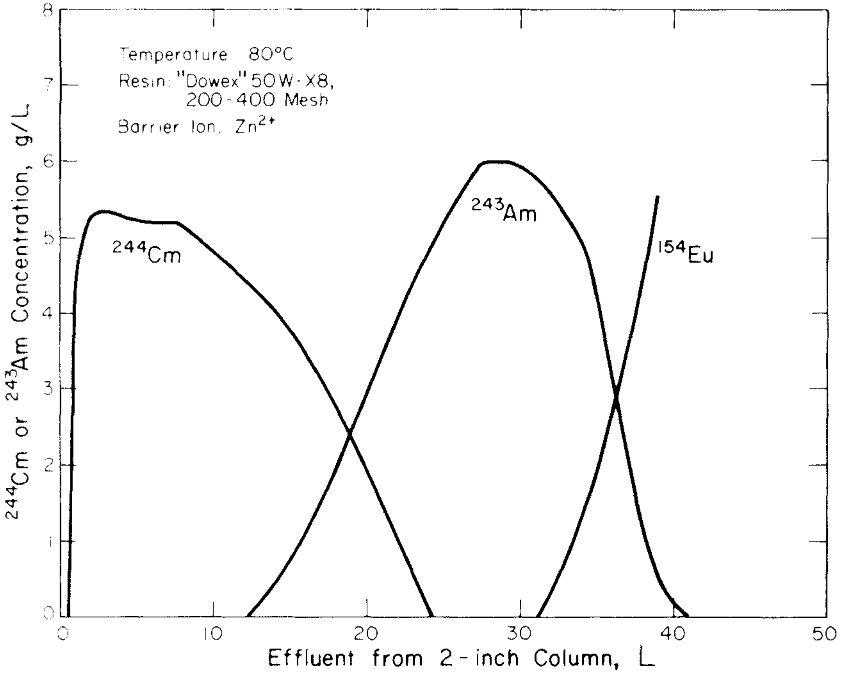


FIGURE 10. Separation of Am and Cm with DTPA

material balance for eight consecutive tests (>75 g Cm in each test) was 99 ±3%.

Multipurpose Processing Facility (MPPF)

The MPPF is a versatile processing facility for separation and purification of actinide elements (4). Some parts of the system are now used to precipitate ^{241}Am; the remainder will be used in 1980. The facility occupies eight heavily shielded cells in a large radiochemical separations plant (Fig. 11). The MPPF facility contains 80 tanks (1 to 500 liters capacity), ∿250 valves, and ∿7 miles of 3/8-inch tubing. Six cells are for chemical processing; two cells are for close-coupled analytical

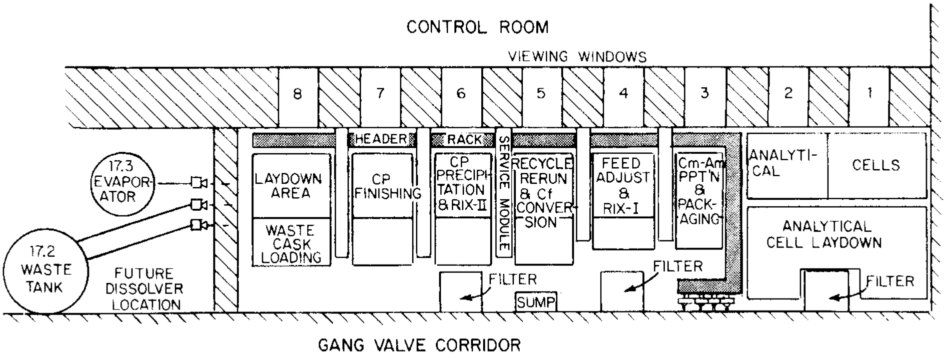


FIGURE 11. Plan View Multi-Purpose Processing Facility

support. Each cell has a viewing window of eight panes of high-density lead glass separated by six oil reservoirs. A 1-inch glass containment barrier on the hot side keeps the window from becoming contaminated and maintains containment when the shielding window is removed for repair. Each cell contains a pair of master-slave-manipulators to operate the process equipment. Process and service equipment is of a remotely replaceable modular type and service systems can be replaced without disturbing process equipment. Equipment and tanks are mounted on removable frames (Fig. 12). Systems are provided for removing products and solid waste in clean containers without spreading contamination. The in-line monitoring system has been described previously.

A flowsheet is given in Fig. 13. The feed may come from prior solvent extraction or from dissolution of irradiated targets and will probably require clarification and formic acid denitration. The actinides are separated from each other and from the lanthanides and other fission products by displacement chromatography. Transcurium elements, if present, will be separated and further purified by elution chromatography on a single cation exchange column using alphahydroxyisobutyrate (AHIB) (13). The

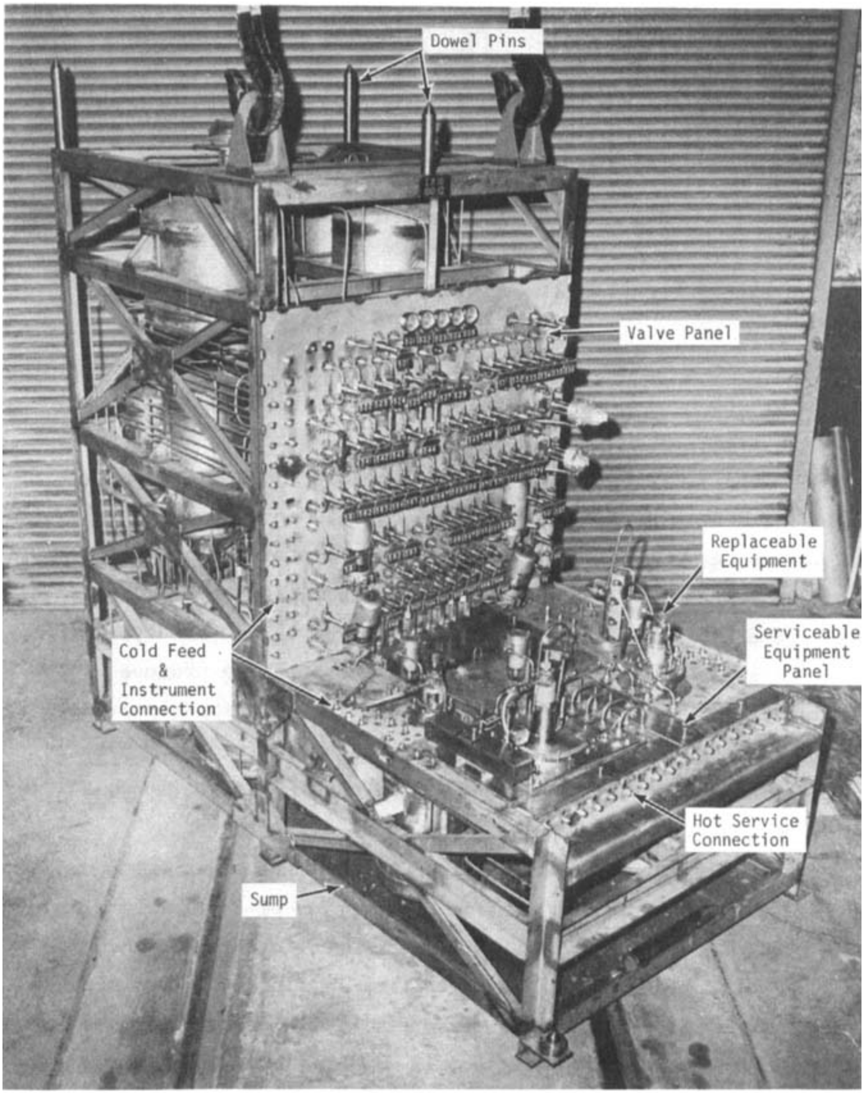


FIGURE 12. MPPF Frame Features

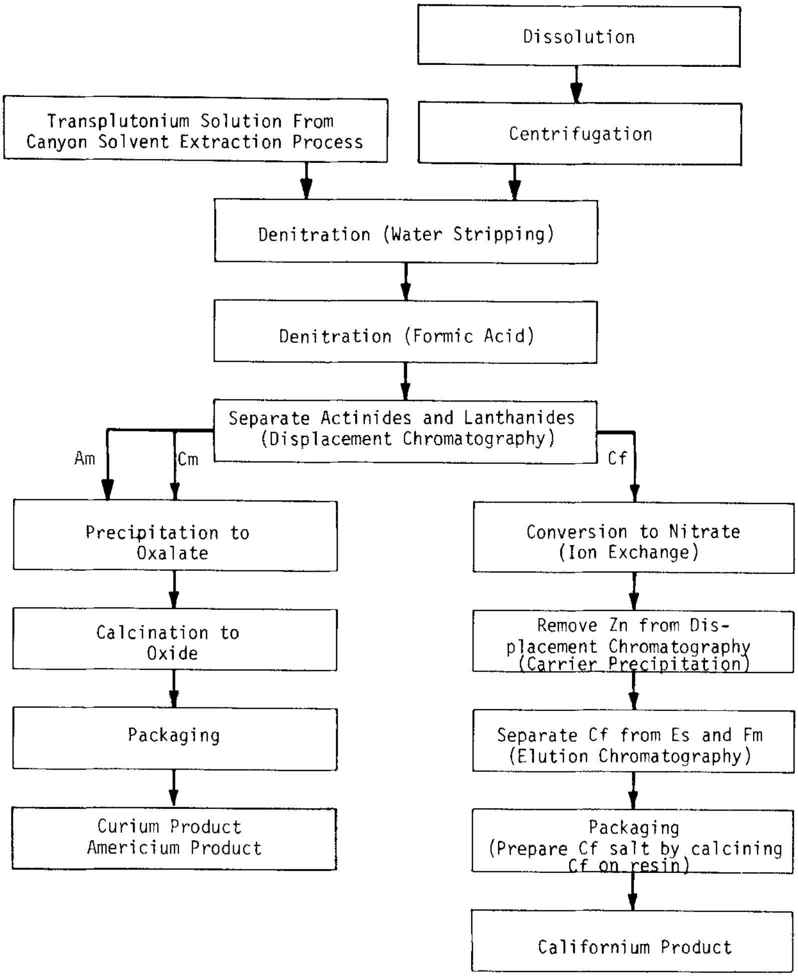


FIGURE 13. Schematic Flowsheet for MPPF Processing

transcurium products after separation are recovered on 25 to 50 mL of cation resin in a platinum column; the resin is combusted and the product oxides or oxysulfates are produced. The curium and americium products from displacement chromatography are precipitated as oxalates and calcined to the oxide. A calorimeter is used to measure the ^{244}Cm product. Other tanks and equipment are available to process any solutions to be recycled for product recovery.

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