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REPORT

ION-EXCHANGE SEPARATION OF KILOCURIE QUANTITIES
OF HIGH PURITY PROMETHIUM

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ION-EXCHANGE SEPARATION OF KILOCURIE QUANTITIES OF HIGH PURITY PROMETHIUM

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INTRODUCTION

The trivalent rare earth fission products can be removed from the concentrated fission product waste and separated from cerium by precipitation^(1,2) or by solvent extraction processes.^(3,4) Separation of the individual rare earths can be accomplished most easily by ion exchange. Recent work in this laboratory⁽⁵⁾ and at ORNL⁽⁶⁾ has clearly demonstrated the feasibility of producing highly purified promethium on a kilogram scale.

The objective of the research program described in this report was to provide critical experimental evaluation of the effects of changes in the various operating parameters on both the extent and the rate of separation, for the eluting agents ethylenediamine-tetraacetic acid (EDTA), hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA). Such an evaluation should aid in the design of minimum sized, maximum capacity equipment, the selection of the most appropriate eluting agent, and the optimum process conditions for that specific eluting agent. Pm^{147} has a half-life of 2.620 ± 0.005 yr, and a heat generation rate of 0.3330 ± 0.0005 W/g.⁽⁷⁾ Among the heat producing radioisotopes, Pm^{147} has unique value

because no intense primary gamma radiation is emitted and the soft beta radiation yields a maximum bremsstrahlung energy of only 0.225 MeV. Although isotopic heat-source shielding requirements are a function of several parameters, significantly less shielding is required for Pm^{147} sources than for many of the other isotopes being considered for thermal power sources, particularly for large sources.⁽⁸⁾

During the past 20 years, the technology for the separation of the individual rare earth elements from each other has advanced from classical fractional crystallization methods to modern ion exchange and solvent extraction processes. Because of the relatively small separation coefficients and the consequent large number of separation stages required to isolate any individual rare earth in high purity, ion exchange has been preferred over solvent extraction by the several processors who produce rare earths commercially. A rather large number of eluting agents have been proposed for both anion and cation exchange separation processes, and are reviewed elsewhere.⁽⁹⁾ EDTA, HEDTA, and DTPA have been used most successfully for the purification of the individual "light"* rare earths on a macro scale. These

*The rare earths, lanthanum through gadolinium

three eluting agents are used in the commercial rare earth separations plants. EDTA was used by Wheelwright and Roberts⁽⁵⁾ in 1963 to purify 13,000 Ci of promethium in the Hanford Laboratories' High Level Radiochemical Facility. The high chemical and radiochemical purity of this promethium was unprecedented. P. B. Orr at Oak Ridge⁽⁶⁾ has used DTPA successfully in similar macro-scale separations. A thermodynamic treatment of this type of system and the requirements of a so-called "barrier" or "retaining" ion are described in the literature.^(5,10)

In developing a process for separating promethium from the adjacent rare earths and from all other possible contaminants, it is essential to minimize exposure of the resin and the eluting agent to radiolysis by adjusting the process parameters to yield an optimum degree of purification in a minimum of exposure time. Both kinetic and thermodynamic properties must be considered. Some of the properties are unique to a given eluting agent or exchange resin. Parameters which can be adjusted are eluant concentration, pH, elution temperature and flow rate.

SUMMARY

Optimum conditions for the purification of the individual light rare earth elements by ion-exchange elution have been determined for the eluting agents EDTA, HEDTA, and DTPA. The conditions apply directly to the isolation of macro-quantities of pure promethium from the fission product rare earths. DTPA was demonstrated to be superior to both EDTA and HEDTA. Operating conditions are described

which allow a 4-fold reduction of both the elution time cycle and the volume of waste solution generated compared to previously reported work.

Seven 9-ft-high, water-thermostated ion-exchange columns, ranging from 8 to 1 in. ID, plus associated tanks, pumps and instrumentation, have been installed in one of Battelle-Northwest Laboratory's hot cells. The technology developed during the isolation of 1,000,000 Ci of Pm¹⁴⁷ in this equipment is summarized.

EXPERIMENTAL

THEORETICAL SEPARATION COEFFICIENTS

It can be shown that the separation coefficient for any two rare earths, R_1 and R_2 , can be approximated as a ratio of the stability constants of the complexes formed between the cations and the complexing agents^(5,10)

$$K_{\text{sep}} \approx \frac{K_{R_2 \text{Ch}}}{K_{R_1 \text{Ch}}},$$

with the symbol Ch representing the complexing agent anion. The stability constants of the complexes formed between the "light" rare earths and the three complexing agents have been determined.^(11,12,13) The promethium stability constants have not been determined, but since promethium is known to elute between samarium and neodymium in each of the three systems, stability constant values equidistant between samarium and neodymium are assumed for promethium. Because of experimental uncertainties in the values of the stability constants, the separation coefficients given in Table I are no more accurate than ± 0.15 . The data indicate that for

TABLE I. Promethium Separation Coefficients

Rare Earth Pair	K_{R_2Ch}/K_{R_1Ch}		
	EDTA	HEDTA	DTPA
Pm-La	41.7	30.9	380
Pm-Ce	8.9	7.4	34.7
Pm-Pr	3.9	3.6	4.9
Pm-Nd	1.8	1.7	2.0
Pm-Sm	1.7	1.7	2.0
Pm-Eu	2.2	1.8	2.3
Pm-Gd	2.3	1.8	3.0
Pm-Y	11.0	<1.7	<2.0
Nd-Sm	3.1	2.8	4.0
Nd-Pr	2.0	2.1	2.5

separating promethium from neodymium or samarium, DTPA is a slightly better eluting agent than EDTA or HEDTA. The superiority of DTPA for separating promethium from cerium and lanthanum is striking. Since the separation of neodymium from samarium and praseodymium by use of EDTA, HEDTA, and DTPA will be described in detail, the Nd-Sm and Nd-Pr separation coefficients are also given in Table I for comparison purposes.

ELUTION SEQUENCE

The sequences in which most of the cations of interest elute with EDTA,

TABLE II. Elution Sequences

EDTA
Zn ⁺² , Al ⁺³ , Y ⁺³ , Gd ⁺³ , Eu ⁺³ , Sm ⁺³ , (Fe ⁺² , UO ₂ ⁺² , Pm ⁺³), Nd ⁺³ , Pr ⁺³
HEDTA
Zn ⁺² , Pb ⁺² , Al ⁺³ , Gd ⁺³ , Eu ⁺³ , Sm ⁺³ , Y ⁺³ , (UO ₂ ⁺² , Pm ⁺³), Nd ⁺³ , Pr ⁺³
DTPA
Zn ⁺² , Pb ⁺² , (Er ⁺³ , Am ⁺³), Gd ⁺³ , Eu ⁺³ , Sm ⁺³ , Y ⁺³ , Pm ⁺³ , Nd ⁺³ , Pr ⁺³

HEDTA, and DTPA have been reported by James and Powell.⁽¹⁴⁾ Contrary to their disclosure, we have found that in the DTPA system, Pb⁺² elutes ahead of Er⁺³ rather than between Sm⁺³ and Nd⁺³. Pm⁺³ was found to elute between Y⁺³ and Nd⁺³. Table II reflects these observations.

EXPERIMENTAL EVALUATION OF ELUTION PARAMETERS

In addition to the thermodynamic properties unique to a given eluting agent, the following must be considered:

- Concentration of the eluting agent
- pH of the eluting solution
- Flow rate of the eluting solution
- Elution temperature
- The elution distance* required to effect the desired separation
- Resin porosity (crosslinkage)
- Resin particle size
- The ratio (on a mole equivalent basis) of the desired ion (Pm⁺³) to the impurities in the feed solution.

* Elution distance is defined as the distance an absorbed "band" of mixed ions must be eluted to separate the individual components of the mixture into individual adjacent bands of pure material. It is convenient to express this number as a function of the length (or volume) of the initially absorbed mixture.

Resin porosity and particle size are intrinsic to the specific resin chosen and cannot affect the choice of eluting agent. However, if a resin of low capacity and poor kinetics is used, the separation process is limited by the exchange kinetics of the resin phase, and a proper evaluation of eluting agents cannot be made. The Pm impurities ratio likewise cannot affect the choice of eluting agents or conditions.

A series of experiments was performed in identical three-column systems. The columns, in sequence, were

- An eluant degasser column
- A feed absorption column
- An elution column.

The degasser column was $5.06 \text{ cm}^2 \times 25 \text{ cm}$ long, and filled to a depth of 15 cm with NH_4^+ -cycle Dowex 50W, X-8 (50 to 100 mesh) resin. The column was water-jacketed and operated at 90°C , and except for an occasional venting of collected gas, required no attention. The absorption column was $2.38 \text{ cm}^2 \times 60 \text{ cm}$ long and contained 100 ml (in water) of H^+ -cycle Dowex 50W resin. The elution column was $1.31 \text{ cm}^2 \times 190 \text{ cm}$ long with variable volumes of H^+ -cycle Dowex 50W resin. With 100 ml of resin in the absorption column and 200 ml in the elution column, an absorbed band moved 2.0 band lengths during the elution. Both absorption and elution columns were water-jacketed for elevated temperature operation, and the temperature was controlled to $\pm 0.5^\circ\text{C}$.

In the experimental procedure followed, the resin in the absorption column was completely saturated with rare earth ions from a nitrate feed solution

containing equi-molar amounts of samarium, neodymium, and praseodymium, adjusted to pH 4. The resin was then water washed to remove unabsorbed ions, connected in series between the degasser and elution columns, and eluted at a controlled flow rate under a variety of experimental conditions. The column effluent solution was fractionated as it drained from the elution column, and the concentration of each rare earth in each fraction was determined by use of a Cary Model 14 spectrophotometer. Figure 1 illustrates a typical elution curve. A graphic integration of the various areas under the elution curve provided the data for comparing the separation effectiveness, and neodymium was used as the standard of reference. By keeping the ratio of neodymium to samarium and praseodymium constant in the feed, the effects of the other process variables were evaluated, and the "separation" was defined as the percent of the neodymium found in the "pure" center cut.

For any given set of elution conditions, the percent of neodymium in the center cut will increase as the total amount of neodymium in the feed increases. Because the quantity of neodymium was held constant for all experiments, the percent in the center cut was a valid measure of separation performance. Once equilibrium separation is achieved on a column of given size, the amount of neodymium in the zones of binary mixing is constant, and all of the rest is in the pure center cut. Since (within reasonable limits) the amount of material in the binary mixed zones is a function of the cross-sectional area of the absorbed

FIGURE 1. Typical Elution Curve

band, it is desirable to increase the length-to-area ratio of the band of desired material as the elution progresses. This ratio increase is accomplished by decreasing the column diameter consistent with the desired production rate.

The first six elution parameters listed on page 3 were examined in this study. Not all of the parameters were varied independently for each of the three eluting agents, but a sufficient number of permutations were made for a reasonable evaluation. In all of the experiments described, H^+ served as the barrier ion for elutions with HEDTA, Zn^{+2} as the barrier ion for EDTA elutions, and either H^+ or Zn^{+2} for DTPA elutions.

The desired pH was achieved by adding NH_4OH to the acid form of the chelating agent. The effect of each

variable is discussed in the following sections.

Concentration of the Eluting Agent

Figure 2 shows the separation achieved for several runs in which the eluant concentration was varied and

FIGURE 2. Effect of Concentration of Eluting Solution

the remaining parameters kept reasonably constant. With all three eluting agents, better separation is achieved at lower concentration, but at the cost of longer elution time cycles and lower product concentration. For example, in the pH range of 5 to 7, the maximum concentration of neodymium product increases from 0.006 to 0.047M as the DTPA concentration is increased from 0.012 to 0.052M. Dowex 50W, X-8 (50 to 100 mesh) resin was used for these experiments.

EDTA cannot be used much above a concentration of 0.012M at 60 °C because of the retrograde solubility limit of the light rare earth-EDTA complexes. Since the solubility of the NH_4MCh -complex is greater than the HMCh -complex, the eluant pH must not be lower than about 8.4 at 60 °C.

When an H^+ barrier ion is used, DTPA must be limited to a maximum concentration of about 0.03M because of the relatively low solubility of the acid form in the prebreakthrough effluent solution on cooling. The DTPA concentration can be increased to 0.075M when Zn^{+2} is used as the barrier. However, the separation efficiency limits the maximum concentration to about 0.05M.

pH of Eluting Solution

The data given in Figure 3 resulted from experimental separations in which the pH was varied and the flow rate, total elution distance, and temperature were held constant. The resin was Dowex 50W, X-8 (50 to 100 mesh).

HEDTA is most effective in the pH range of 5.0 to 5.5. The DTPA results show much less pH dependence than EDTA or HEDTA, and any pH between 5.5 and

FIGURE 3. Effect of pH of Eluting Solution

7.0 gives good results. As expected, DTPA is more pH-sensitive at higher concentrations than at lower values. EDTA is very pH-sensitive; below pH 8.0 the metal ion complexes precipitate, and above 8.8 the rare earths pass through the Zn^{+2} barrier.

Elution Flow Rate

Dowex 50W, X-8 (50 to 100 mesh) resin was used for elution flow rate experiments. The elution distance for the HEDTA and DTPA experiments was held at 2.3 band lengths, and at 1.8 band lengths in the EDTA experiments. The temperature in all cases was 60 °C. The flow rate results shown in Figure 4 indicate that DTPA and HEDTA are still efficient at rates up to 4 ml/min-cm². HEDTA shows less decrease in separation efficiency with increasing flow rate at pH 5.0 than at pH 5.5. The EDTA results cannot be compared directly with the others because of the shorter elution distance.

FIGURE 4. Effect of Flow Rate of Eluting Solution Flow Rate

At a flow rate of 4 ml/min-cm^2 , it would appear that 0.030M HEDTA at pH 5.00 gives the best results, but this is not true when consideration is given to the product concentration. With 0.025M DTPA at pH 6.50, the separation was completed in 32 hr and the product concentration was 0.015M ; whereas, with 0.030M HEDTA at pH 5.00, the separation required 67 hr and the product concentration was only 0.007M . Thus, a small increase in the amount of recycle is an advantageous "trade-off" for a 50% decrease in the time required for separation.

Elution Temperature

The results given in Figure 5 show that maximum separation is achieved at the highest practical temperature. A very pronounced increase in separation is achieved when the temperature is increased from 25°C to the 50 to 70°C range. Because of adverse on column gassing, the maximum practical temperature is probably in the 65 to 75°C range. Dowex 50W, X-8 (50 to 100 mesh) resin was used for these experiments, and the elution

FIGURE 5. Effect of Elution Temperature

distance was held at 2.3 band lengths. Elution Distance

In elution distance experiments, the amount of resin in the absorption column was held at a constant 100 ml while various amounts of resin were used in the elution column. Dowex 50W, X-8 (50 to 100 mesh) resin was used, and the flow rate and temperature were 3.1 ml/min-cm^2 and 60°C (Figure 6). DTPA yields identical results at 1.3 and 2.3 band lengths, while the other two eluting agents show a marked decrease in separation efficiency when

FIGURE 6. Effect of Elution Distance

the elution distance is decreased below 2.3 band displacements. This is probably a result of the larger DTPA separation coefficients.

Resin Porosity

Three experiments were performed with Dowex 50W, X-12 (50 to 100 mesh) resin to provide data for a comparison of resin kinetics. Perhaps the most meaningful way to present this type of information is to show the separation efficiency in terms of the rate at which the absorbed band advances down a column. This is important to the process engineer since it defines the process time cycle. For a given eluting agent, the rate of band advance is a function of concentration, pH, and flow rate. In these experiments with DTPA, all of these parameters were varied, while the temperature and total elution distance were held constant. As a result, the data are less accurate than if only one parameter had been varied (Figure 7). As expected, the curves diverge for the two resins as the rate increases.

FIGURE 7. Effect of Resin Crosslinkage

The lower crosslinked resin appears to be superior by about a factor of 2.

Recommended "Optimum" Operating Parameters

Recommended operating parameters for the three eluting agents are given in Table III. DTPA is superior to HEDTA for the separation of the light rare earths because less elution distance is required and the effective elution rate (as a result of 4-fold higher concentration of rare earth in the aqueous phase) is four times as high. Both DTPA and HEDTA are superior to EDTA with feed mixtures that do not contain Y^{+3} . If significant amounts of Y^{+3} are present in a feed solution processed for promethium recovery, one can first use DTPA for separation of promethium from lanthanum, cerium, praseodymium, and some of the neodymium, followed by EDTA for final purification from neodymium, yttrium, and samarium. The switch in eluting agents can be made directly without interposing a wash cycle between them. In promethium processing, a minimum time cycle is highly desirable because of resin radiolysis effects. It is the authors' opinion that, owing to the much longer time cycle involved when EDTA is used, a straight DTPA elution (at the cost of a higher recycle volume of binary

TABLE III. Recommended Operating Conditions

	DTPA	HEDTA	EDTA
Molar Concentration	0.050	0.03-0.04	0.012
Eluant pH	5.5 - 6.5	5.0-5.5	8.4-8.6
Maximum Eluant Flow Rate, ml/min-cm ²	4.0	4.0-5.0	3.0
Elution Temperature, °C	60-70	60-70	60-70
Resin	← Dowex 50W, X-8 →		

mixture material from the two ends of the promethium band) is preferable.

DEMONSTRATION OF "OPTIMUM" PROCESS WITH SYNTHETIC FEED

To test the optimum DTPA flowsheet under conditions closely simulating plant conditions, one 1-in. ID feed absorption column and two 1/2-in. ID elution columns were filled to a depth of 67 in. with H^+ cycle Dowex 50W, X-8 (50 to 100 mesh) resin. The columns were water-jacketed and operated at 60 °C. Three experiments were performed to determine the composition of the effluent solution from each of the three columns. In these experiments, the feed column was operated separately; the feed column was connected in series with one elution column; and the feed column was connected in series with two elution columns. Except for the addition of columns, the conditions were identical. A feed solution (Table IV) was prepared and spiked with tracer amounts of Pm^{147} and Ce^{144} . This solution contained the fission products in the ratios resulting from nuclear fission plus impurities expected to be present in a plant feed.

TABLE IV. Feed Solution

Y = 5.2 g/l	La = 11.9 g/l
Sm = 6.0 g/l	Pb = 0.6 g/l
Nd = 37.0 g/l	Fe = 0.1 g/l
Pr = 10.8 g/l	Na = 0.4 g/l
Ce = 23.5 g/l	HNO_3 = 0.4M

For Run No. 1, the resin in the absorption column was saturated with the feed, washed free of excess feed solution with water, and eluted at 3.8 ml/min-cm² with 0.052M DTPA adjusted to pH 6.50 with ammonium hydroxide. The effluent solution from the column was collected in 50 ml fractions and the compositions were determined. Promethium and cerium were determined radiochemically; samarium, neodymium, and praseodymium were determined optically by use of a Cary Model 14 spectrophotometer. The other feed constituents, including yttrium (which is colorless), were not determined. The results are shown in Figure 8.

After resin regeneration, the absorption column was again saturated with the same feed and connected in series

FIGURE 8. Effluent Solution Composition on Elution Directly from the Feed Absorption Column

with one of the elution columns (resin previously converted to Zn^{+2} cycle). Run No. 2 was initiated under identical elution conditions (Figure 9). The experiment was repeated using both elution columns for Run No. 3, and these results given in Figure 10.

FIGURE 9. Effluent Solution Composition at the Bottom of the First Elution Column

FIGURE 10. Effluent Solution Composition at the Bottom of the Second Elution Column

Figures 8, 9, and 10 thus show the increasing separation that is achieved by each column when all three are

connected together in series. Figure 9 shows that under these conditions, promethium is completely separated from cerium at the bottom of the first elution column (an elution distance of one-fourth the initial band length). At the bottom of the second elution column, promethium has been separated from cerium, praseodymium, and from two-thirds of the neodymium band.

LARGE SCALE PROMETHIUM PURIFICATION

To supply the Pm^{147} needed for both the AEC's isotopic heat source research and development program, and for prototype heat source fabrication during the interim period before the Isochem Fission Product Conversion Encapsulation plant goes on stream, an ion exchange facility was installed in one of the shielded cells of the High Level Radiochemistry Facility at Battelle-Northwest. Included were seven 9-ft high ion exchange columns ranging from 8 in. down to 1 in. ID. The 8 in. column is stainless steel and the others are glass. Each column is water-jacketed for controlled-temperature operation. Also in the cell are associated tanks, valves, and instrumentation. The instrumentation includes two particularly useful units: an in-cell gamma spectrometer,⁽¹⁵⁾ which can "read" both individual samples and in-line streams and an automated optical spectrometer for in-line monitoring.⁽¹⁶⁾ The sensing units of both instruments are in the shielded cell, and the instrumentation is in the operating gallery. The plumbing arrangement is such that one or more columns can be connected together in series by the use of flexible polyethylene jumpers, with the in-line

instrumentation sensing units interposed between them.

The process flowsheet and equipment schematic are shown in Figures 11 and 12, respectively. In operation, feed solution is pumped down-flow through the 8 in. absorption column and to waste at a rate of 1 to 2 liters/min until the in-line gamma spectrometer detector on the effluent line indicates an activity breakthrough. At this point the effluent is diverted back to the feed tank, and the absorption cycle is continued until the detector indicates a 10 to 20% breakthrough. The feed cycle is then terminated, and the loaded

resin is washed free of unabsorbed feed with distilled water. Promethium losses are eliminated by cycling the final portion of the feed effluent and the wash effluent back to the feed tank for subsequent use.

The elution cycle is initiated by connecting the loaded absorption column in series with the first 4 in. diam elution column and pumping 0.05M DTPA solution, buffered to pH 6.5 with ammonium hydroxide down-flow through the two columns at 3.5 to 4.0 m./min-cm². As the absorption band moves down the system, fresh Zn⁺² cycle resin beds are added ahead of the band, and the flow

Run Conditions:

Elution Temperature	65 C
Elution Flow Rate	4 ml/min-cm ²
Rate of Band Advance	16-18 cm/hr

Run Cycle Time

Absorption Cycle	4 hr
Elution Cycle	160 hr
Turn Around Time	72 hr

FIGURE 11. Promethium Purification Flowsheet

FIGURE 12. Promethium Purification Flow Diagram

FROM BASEMENT MAKE-UP
TANKS TO TANKS A & B

FROM ETHIUM PURIFICATION
FLOW DIAGRAM

DRAWN: JFJ/ROSCHE PHONE 3464
DATE: 7-16-65 352A BLDG

rate is adjusted to correspond to the smallest diameter column in service. Trailing columns are removed from the system and stripped free of remaining rare earths when the detection equipment indicates the promethium content in the effluent to be down to an acceptable level.

As the elution progresses and the promethium becomes progressively concentrated in a sub-band near the leading edge of the combined elution band (Figures 8 to 10), judicious elution to waste of the leading edge, combined with removal of loaded columns from the trailing edge, greatly reduces the quantity of material in process when the promethium moves onto progressively smaller columns. When the promethium band reaches the final column, it is 150 and 250 cm long, depending on batch size, with 20 to 40 cm on the leading edge contaminated with yttrium and about 25% that amount on the trailing edge contaminated with neodymium. As the promethium band is eluted from the column, the binary mixtures from each end are segregated for recycle and the pure center cut collected for product conversion. The in-line instrumentation guides this fractionation. The Y-Pm separation coefficient is much smaller than the Pm-Nd coefficient so the Y-Pm overlap is greater.

Within 24 hr, radiolytic decomposition of the DTPA results in a mixed carbonate-oxalate precipitation of the promethium in both the product and rework fractions. Acidification to 0.5M HNO_3 immediately after purification prevents the carbonate precipitation. After a few weeks the oxalate

is likewise decomposed, yielding a clear nitric acid solution of promethium.

Eleven production runs have been completed; they utilized feeds of compositions which differed primarily in the sodium, cerium, and promethium contents. Unfortunately, most of the feed solution processed contained rather large amounts of Ce^{144} (curie ratio $\text{Ce}^{144}/\text{Pm}^{147} \approx 1$). In a typical high-cerium run, $1.6 \times 10^4 \text{ Ci Pm}^{147}$, a similar amount of Ce^{144} , and the associated rare earth fission products were absorbed on the feed column. The 1300 W_t generated by the Ce^{144} decay caused severe gassing in the resin containing absorbed cerium. As a result of this bed disruption, the promethium elution band tailed into the Nd-Pr-Ce band. Unlike the three-column pilot separation (shown in Figures 8 through 10), 2 to 3% of the absorbed promethium remained on the absorption column when the front edge of the promethium band reached the bottom of the second 4 in. column. With the addition of a 2 in. column and attendant reduction in flow rate, the cerium heat load on the absorption column required that it be removed and immediately stripped to prevent boiling. Approximately 3/4 of the cerium remained on the feed column and left the system when that column was valved out. At this point the promethium band was predominately on the second 4 in. column, but it did tail across the first 4 in. column and resulted in failure of the final 5 to 8% to catch up before the promethium band reached the final column. To secure a high decontamination from europium, the

trailing promethium was left behind before the promethium band was eluted down the final column.

The tailing problem does not exist when the cerium content is low. In one production run, the end cuts from previous runs were added to the feed and caused the Pm^{147} content to increase from nominal 2.3% to approximately 20%; the Ce^{144} content decreased by a factor of 10. Only enough feed was available to saturate the top 2/3 of the absorption bed, resulting in a longer elution prior to the addition of the 2 in. column. In this run, little or no gassing was observed in the feed column, there was a complete separation of promethium from cerium at the bottom of the first 4 in. column, and the promethium band did not tail out. Of the 1.47×10^5 Ci Pm^{147} absorbed, 1.1×10^5 Ci were recovered in the pure center cut and 3.8×10^4 Ci were sent to recycle for a material balance recovery of 100%. In addition, europium content in the promethium product was less than 10^{-9} Ci $\text{Eu}^{154}/\text{Ci Pm}^{147}$. This low concentration of europium can be detected only by very sophisticated radiochemical counting techniques, and it is completely inconsequential from the standpoint of the radiation dose rate or shielding requirements of a promethium heat source.

The tailing problem with the high-cerium feed should be capable of correction by adding an additional large diameter column to give more elution distance; or by taking an enriched promethium crude product off the bottom of the second 4 in. column, collecting this low-cerium material from several enrichment runs, and then re-

cycling it back through the system. Steps are being taken to test these approaches.

During the course of the eleven production runs, 9.7×10^5 Ci (1041 g) of "product fraction" promethium have been recovered. The chemical purity of the promethium at the time of separation averaged 98 to 99%. The product was segregated from the binary end fractions in such a manner that the major impurities were neodymium and yttrium, each at an average composition of less than 1%, while other impurities were less than 0.1%. A summary of the production to date is given in Table V.

The principle radiochemical contaminants of interest are Ce^{144} and Eu^{154} , but two problems are encountered in obtaining and maintaining the ultra high purity desired from these contaminants. The first problem is the possibility of back contamination

TABLE V. Results of Promethium Purification Runs to Date

Purification Date	Curies	Grams	Curie Ratio $\text{Pm}^{148}/\text{Pm}^{147}$
10/21/65	62,500	67.3	$<1 \times 10^{-9}$
3/7/66	145,000	156.3	1.2×10^{-2}
4/4/66	75,200	81.0	$<1 \times 10^{-9}$
5/1/66	88,000	94.8	1.7×10^{-7}
5/21/66	63,200	68.1	1.7×10^{-7}
6/16/66	109,000	117.5	1.7×10^{-7}
6/23/66	67,700	73.0	$<1 \times 10^{-9}$
9/5/66	65,100	70.2	$<1 \times 10^{-9}$
9/14/66	80,600	86.9	$<1 \times 10^{-9}$
9/24/66	83,500	90.0	$<1 \times 10^{-9}$
10/16/66	126,200	136.0	$<1 \times 10^{-9}$

from the feed material kept in the same cell, and the other is separation from europium. In the elution sequence, both samarium and yttrium elute between europium and promethium, but the separation coefficients are small. With the high Ce^{144} runs, trace amounts of europium tail just like promethium, and to obtain ultra high decontamination factors from Eu^{154} , it is necessary to valve out the trailing columns sooner and to accept high promethium losses. The Eu^{154} contamination has varied from 10^{-7} Ci $\text{Eu}^{154}/\text{Ci Pm}^{147}$ to 10^{-8} Ci $\text{Eu}^{154}/\text{Ci Pm}^{147}$. In low- Ce^{144} runs, the ratios have been decreased to 1.5×10^{-9} Ci $\text{Eu}^{154}/\text{Ci Pm}^{147}$; in the worst instance, this represents a contaminant factor from Eu^{154} of 10^5 . This is very high for equipment subject in part at least, to continued recontamination with each new batch of feed solution. Even with a $\text{Eu}^{154}/\text{Pm}^{147}$ curie ratio of 10^{-7} , the shielding required by the Eu^{154} is less than that by the Pm^{146} for a 60 W source. In the run 3/7/66, "green" promethium feed was used, so the $\text{Pm}^{148}/\text{Pm}^{147}$ ratio for this product was very high. Even though the cell and equipment were decontaminated extensively following the 3/7/66 run, the feed used for runs 5/1/66, 5/21/66, and 6/16/66 was back-contaminated with a small amount of "green" promethium, resulting in a slightly high Pm^{148} content. Ce^{144} can be detected as low as 10^{-12} Ci $\text{Ce}^{144}/\text{Ci Pm}^{147}$, or lower if the Pm source is large, but has been detected in only one product fraction. The possibility of back contamination was known to exist with that fraction.

Production has been halted during the fourth quarter of CY 66 for equip-

ment modification. Following sufficient decontamination to permit cell entry, the 8 in. steel column will be replaced with a similar sized column of improved design. In addition, 10 in. ID and 14 in. ID stainless steel columns will be installed in the cell. At the same time, four 250 gal tanks are being installed in a vault below the cells. These modifications will increase the capacity by a factor of 3, and will permit a 2 cycle purification flowsheet wherein a number of runs will be made using only the three large columns and producing a cerium-free concentrate containing 25% promethium. This will give an initial Eu^{154} decontamination factor of 10^2 to 10^3 . Following an extensive cleanup of equipment, the promethium concentrate can then be processed as needed in batch sizes up to 10^6 Ci. Several advantages will be gained: the time required for a run will be reduced from 8 days to <5 days; the two-cycle process will permit substantially higher decontamination factors from Eu^{154} ; $<10^{-10}$ Ci $\text{Eu}^{154}/\text{Ci}^{147}$ should be achievable; the rate of production will be increased, and rather large quantities of pure promethium can be produced as needed.

AMERICIUM RECOVERY

In the DTPA elution sequence, Am^{+3} was found to elute between Zn^{+2} and Gd^{+3} . It proved convenient to elute an Am-Gd-Eu-Sm fraction into a separate tank from the bottom of the second 4 in. column and to monitor the americium by the in-line optical spectrometer. Americium recoveries were about 95 to 100%. The americium from a series of

promethium purification runs will be pooled, and purification will be eventually completed by means of a special americium purification run.

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