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PREPARATION OF FISSION RARE-EARTH ISOTOPES

R. S. Pressly

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R. S. Pressly

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PRODUCTION OF FISSION RARE-EARTH ISOTOPES

R. S. Pressly

INTRODUCTION

The early investigations of ion exchange separations of fission-product rare earths were made by Cohn, Tompkins, and Khym,[1] Swartout *et al.*,[2] and Boyd and a group of co-workers.[3] Marinsky[4] and Khym[1] performed the first order-of-elution experiments, and later Marinsky separated by ion exchange the fraction of rare earths between yttrium and cerium and thus made possible the positive identification of Pm^{147} and Nd^{147}.

Parker and Lantz[5] separated milligram to gram quantities of Pm^{147}, Eu^{155}, and Sm^{151} and observed their radiation characteristics.

During the years 1948 and 1949, the production of rare-earth radioisotopes was principally by ion exchange. The process developed from tracer level to a more expanded level of handling curie quantities of gross fission products. The method is described in the following paragraphs.

Uranium slugs, which had been irradiated in the ORNL Graphite Reactor from 30 to 60 days, were dissolved in nitric acid, and the I^{131} was removed by volatilization. This uranyl nitrate solution [approximately 50% uranyl nitrate hexahydrate (UNH) and 1–2 *N* in HNO_3] was diluted to five times its volume and added to a cation resin bed. This ion exchange column was 6 in. in diameter and 3 ft long. All the cations were adsorbed on the resin. The effluent contained Ru^{103} and other activities existing as anions.

Zirconium and niobium were adsorbed at the top of the resin column because they exist as colloids. The uranium was removed as a complex anion from the resin by washing with 0.25 *M* H_2SO_4. The top ½ in. of the resin column was washed with 5% oxalic acid, and the solution was removed from the column without disturbing the bulk of the adsorbed fission products.

The rare-earth group was removed from the large column with 0.2 *M* citrate solution adjusted to a pH of 3.5 with ammonium hydroxide. These rare earths were then readsorbed on another ion exchange column by reducing the pH to 2.5 with nitric acid. This adjustment of the pH was by dilution with the use of flowmeters. From this rare-earth separation column, the rare earths were removed by elution with 0.2 *M* citrate solution at pH 3.0.

Barium and strontium were eluted from the first large ion exchange column by elution with 0.2 *M* citrate solution adjusted to a pH of 7.5 and readsorbed on a smaller column in the same manner as were the rare earths.

Separations on such equipment were not very good. Group separations were made, and, by concentration on smaller columns and with repeated elutions, suitable products could be obtained.

Ketelle and Boyd[6] demonstrated, on a tracer level, that sharper separations could be made if the ion exchange bed were heated to 90 to 95°C.

Baldwin[7] used silica gel to adsorb Zr^{95} and Nb^{95} from Redox solutions. This method was developed and used to adsorb zirconium and niobium from uranyl nitrate solutions.

This report is written for the purpose of describing the methods now used for the separation of the short-lived rare earths. The separation techniques have been improved to the point that a single ion exchange column can be used to separate the short-lived rare earths from each other and from the actinide elements which are present in the solution.

This report also describes the process of separating the long-lived rare-earth group and the development work which has led to this process. Ion exchange has been used effectively in separating the individual long-lived rare earths from each other and from the actinide elements in small quantities. The Pm^{147} is now separated from Am^{241} by precipitating PmF_3 from 3.0 *M* hydrofluosilicic acid, leaving americium complexed in solution. Americium and promethium are recovered, and larger quantities are handled.

[1] E. R. Tompkins, J. X. Khym, and W. E. Cohn, *J. Am. Chem. Soc.* **69**, 2769–2777 (1947).

[2] J. A. Swartout and D. N. Hume *et al.*, CN-1839 (July 1944) (Classified).

[3] G. E. Boyd, *Heavy Isotopes and Chemistry of the Heavy Elements: Lecture 29*, "Adsorption as a Separations Technique and Possible Applications to the Actinides," M-3964, 1947.

[4] J. A. Marinsky and L. E. Glendenin, CN-2809, p 9 (April 1945) (Classified).

[5] G. W. Parker and P. M. Lantz, *The Separation of Milligram Quantities of Element 61 from Fission*, ORNL-75, 1948.

[6] B. H. Ketelle and G. E. Boyd, *J. Am. Chem. Soc.* **69**, 2800 (1947).

[7] W. H. Baldwin, ORNL CF-49-9-178 (Sept. 28, 1949) (Classified).

PROCEDURE

Purification of Short-Lived Rare Earths

The procedure for the production of short-lived rare earths is shown in Fig. 1. Uranyl nitrate solution is taken from the I^{131} production facility as soon as the iodine has been removed. This solution is 40 to 50% uranyl nitrate and 1–2 *N* in HNO_3. There are also contaminants of iron, chromium, and nickel from the processing in stainless steel.

The total gross beta activity is as follows:

Isotope	Amount (%)
Ru^{103}	0.5
Sr^{89}	9.6
Ba^{140}	14.6
Zr^{95}	3.6
Trivalent rare earths	57.6

Removal of Zr^{95} and Nb^{95}. – The uranyl nitrate solution is added to a silica gel (20–40 mesh) column to adsorb Zr^{95} and Nb^{95}. The capacity of silica gel for zirconium is 187 curies/g (8.0 mg/g, or 0.8%). The flow rate is three column volumes per hour to ensure an 80% adsorption of zirconium.

Extraction of Uranyl Nitrate. – Nitric acid is added to increase the concentration to 5.2 *N*.[8] An equal volume of 30% tributyl phosphate in carbon tetrachloride, which has been previously equilibrated with 5.2 *N* HNO_3, is added to the solution, and uranyl nitrate is extracted into the tributyl phosphate.

This extraction, which is repeated five times, removes all but a trace of uranium and plutonium. Such elements as Zr^{95}, Nb^{95}, and Ru^{103} are extracted. Recovery of rare earths and alkaline earths through this extraction process is 80%. At higher nitric acid concentrations, more of the rare earths are extracted, but only a small amount of the alkaline earths is extracted even at 16 *N* nitric acid concentration[9] (see Fig. 1).

[8] D. E. Ferguson and T. C. Runion, ORNL-260 (Oct. 7, 1949) (Classified).

[9] A. C. Topp and Boyd Weaver, *Distribution of Rare-Earth Nitrates Between Tributyl Phosphate and Nitric Acid*, ORNL-1811 (Oct. 15, 1954).

Precipitation of Rare-Earth Oxalate. – Carrier lanthanum is added to the fission-product solution, and the solution is boiled to near dryness and diluted to 1–2 *N* in HNO_3. Saturated oxalic acid is added to precipitate lanthanum oxalate which carries the rare earths. This precipitate is dissolved in a small amount of 16 *N* HNO_3, and the solution is diluted to 0.4 *N* in HNO_3 or lower.

Separation of Rare Earths by Ion Exchange. – Nalcite HCR, 100–200 mesh, is washed thoroughly with distilled water to remove all the fine resin. It is then equilibrated with a 6 *M* solution of ammonium chloride for 3 to 4 hr and again washed with distilled water to remove the excess ammonium chloride. The resin is added to the ion exchange column (0.10 cm ID by 40 cm long).

The rare earths are adsorbed at room temperature on the top portion of the resin bed from the weak nitric acid solution.

The elutriant is 0.2 *M* citrate solution adjusted to a pH of 3.2 with ammonium hydroxide and degassed by refluxing. This solution is then added to the rare-earth-containing resin bed, which has previously been raised to 95°C. The Cs^{137} and Ru^{103} are removed in two separated peaks of activity before Y^{91} is eluted from the column. The Nd^{147}, Pr^{143}, and Ce^{141} are removed in that order after the yttrium peak. For a typical elution curve of the short-lived rare earths, see Fig. 2.

The bands of activity move down the ion exchange bed and separate from each other upon elution with 0.2 *M* citrate at pH 3.2. Sharper separations of adjacent activities are made by eluting at a temperature of 95°C. Bands of activity remain on the column for a longer time, and this has the same effect as increasing the length of the column. The effect of increased temperature can also be expressed as an increase in the distribution coefficient, where the coefficient is defined as the ratio

$$\frac{\text{activity per gram of resin}}{\text{activity per milliliter of solution}} .$$

There is a second effect which has been used to purify Y^{91} from uranium and plutonium. At higher temperatures, there is a shifting of the uranium and plutonium peaks so that these elements are removed before yttrium; thus yttrium is produced in one column separation.

Each peak of activity is identified by absorption curves or by determination of the characteristic energy of the gamma radiation, such as the 1.22-Mev gamma ray (intensity, 0.3%) of Y^{91}.

Isotopes determined as 99.9% pure are adsorbed from the citrate solution on small cation columns. After reduction of the pH of the solution to 1.5, these activities are removed from the small concentrating columns as chlorides or nitrates.

Production Yields. – Calculations have been made of the yield of certain rare-earth isotopes from uranium metal which has been processed within 30 days after discharge of the uranium from

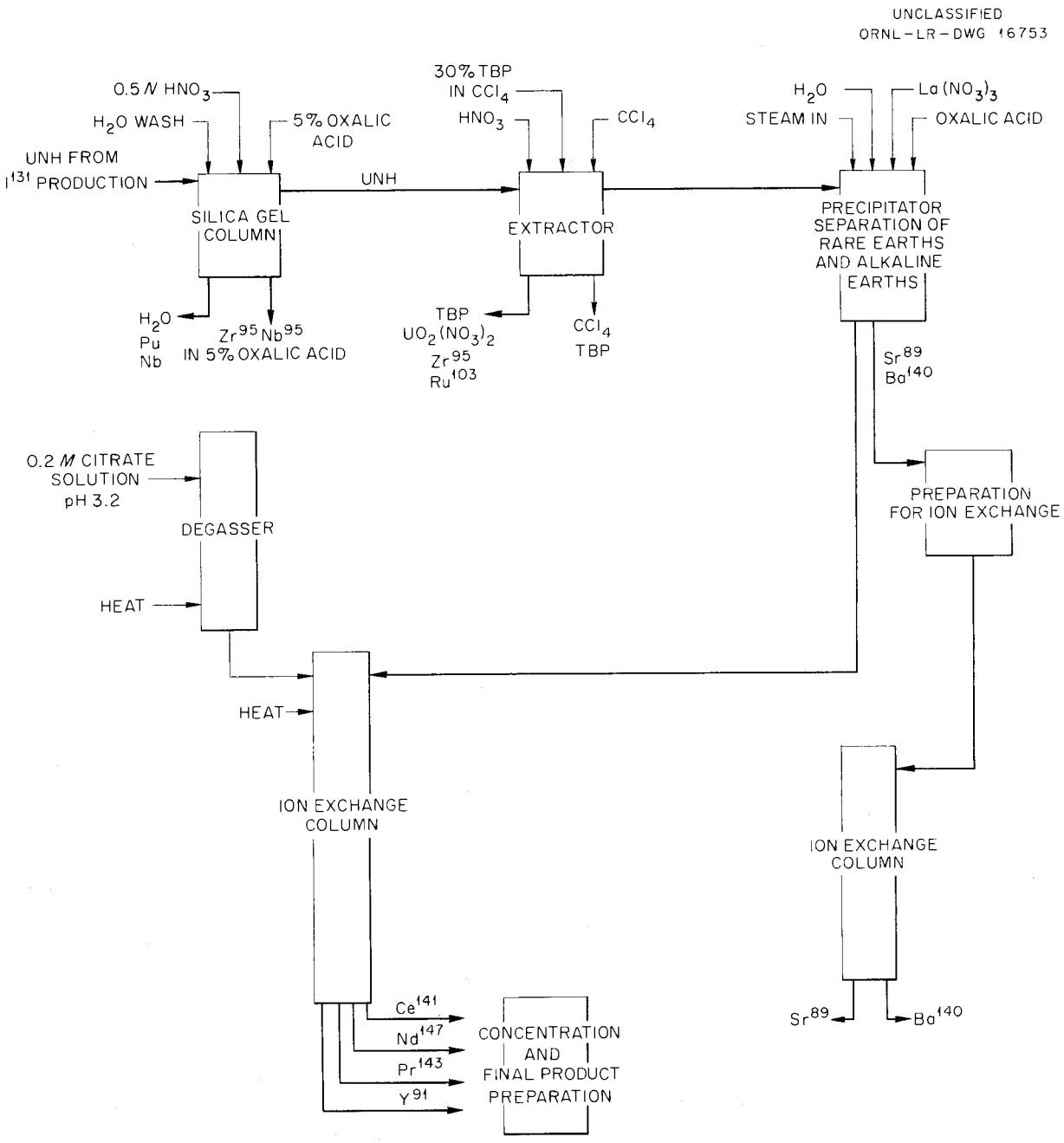

Fig. 1. Flow Diagram for Production of Short-lived Fission Rare Earths.

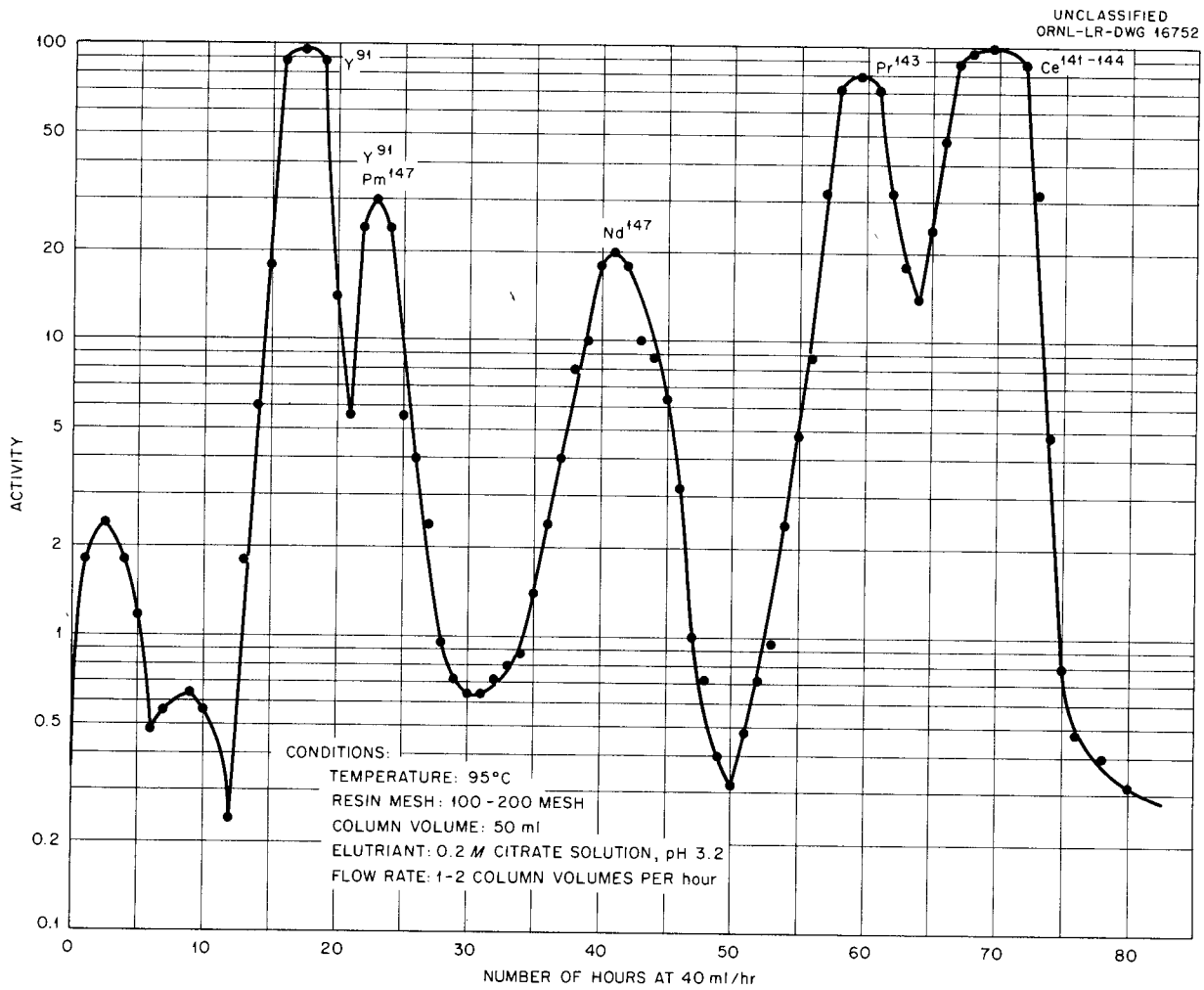

Fig. 2. Elution of Rare Earths from Nalcite HCR.

a reactor. The standard ratios of yields are as follows:

Isotope	Relative Yield
Y^{91}	11
Nd^{147}	1
Pr^{143}	4
$Ce^{141,144}$	13

Purification of Long-Lived Rare Earths

The procedure for the separation of long-lived rare earths is shown in Fig. 3. A concentrated solution of the long-lived rare earths is received from the Cs^{137} production facilities at ORNL. The pilot plant, from which 150–200 curies of mixed rare earths per year has been obtained, is being made obsolete by the Multikilocurie Fission Product Plant now in construction at Oak Ridge.

This plant is being built to produce Cs^{137} and Sr^{90}. The Cs^{137} production will be 100,000 to 200,000 curies per year at the time of processing (4- to 4½-year decay of slugs). There is present in the equivalent starting solution one-half million to one million curies of Ce^{144} and 50,000 to 100,000 curies of Pm^{147}.

The isotopes Pm^{147}, Ce^{144}, Eu^{155}, and Sm^{151}, as well as the actinide elements curium, plutonium, and americium, are in the crude rare-earth fraction. The specific activity of Ce^{144} is 20 to 30 curies per gram of cerium.

The Ce^{144} is separated from the trivalent rare earths by precipitation as ceric iodate. The re-

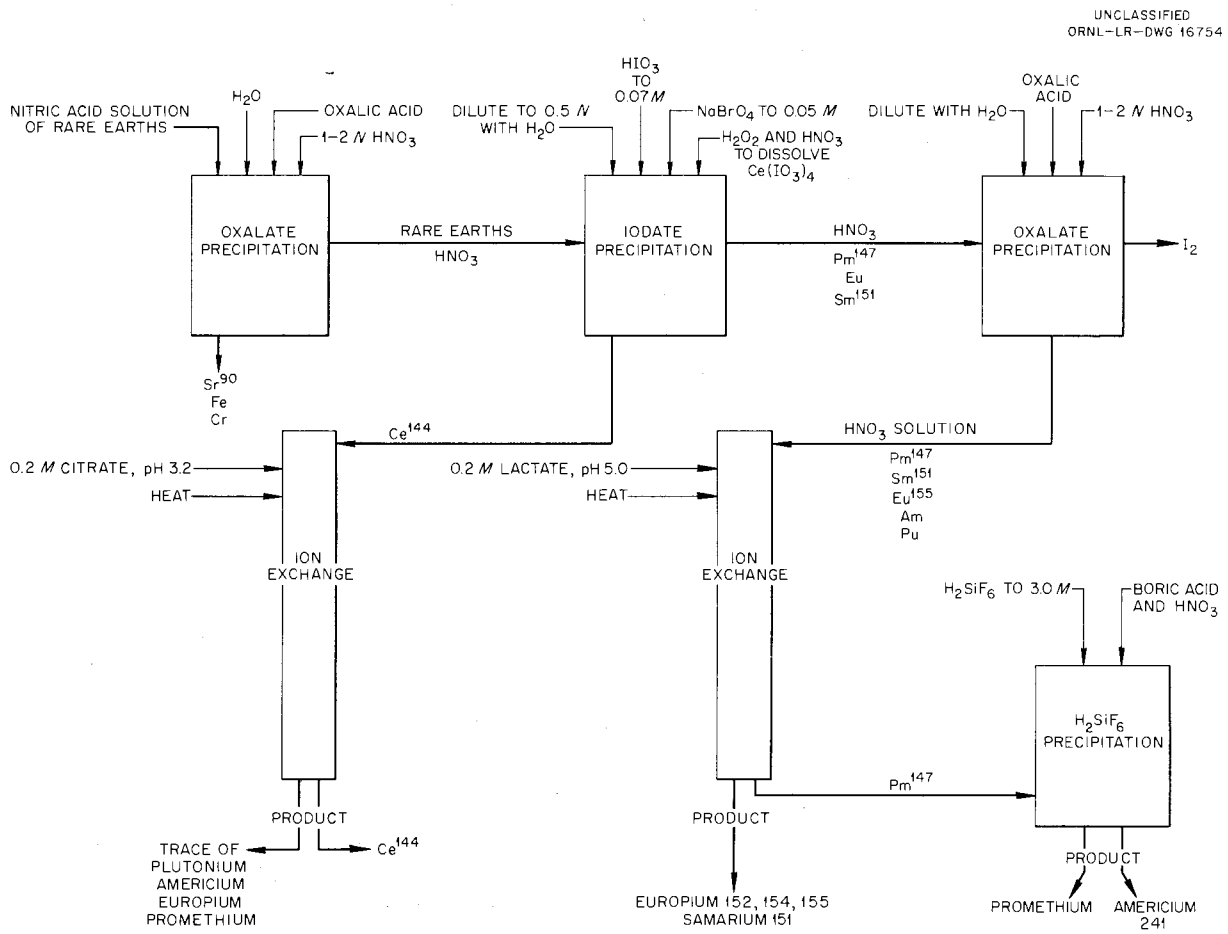

Fig. 3. Flow Diagram for Separation of Long-lived Fission Rare Earths.

maining rare earths are best separated by ion exchange.

Separation of Contaminants. – The solution containing mixed rare earths is diluted to 1–2 *N* in nitric acid. Saturated oxalic acid is added to precipitate the mixed rare-earth oxalate. The supernatant liquid contains iron, chromium, Sr^{90}, and 2 to 4% of the total Ce^{144} (see Table 1). The cerium oxalate precipitate, containing the other rare earths, is dissolved in a small volume of 16 *N* nitric acid. This solution is heated to 100°C to destroy oxalates and is then diluted to 1500 ml.

Separation of Ce^{144} by Ceric Iodate Precipitation. – A typical analysis of a solution of long-lived rare earths is as follows:

Isotope	Amount (mc)	Per Cent
Ce^{144}	20,438	75.0
Eu^{155}	101.4	0.37
Pm^{147}	6,637	24.4

The solution is made 0.07 *M* in HIO_3 and 0.05 *M* in $NaBrO_3$ to oxidize Ce^{3+} to Ce^{4+} and to precipitate $Ce(IO_3)_4$. The ceric iodate precipitate is dissolved in 4 *N* HNO_3 after the Ce^{4+} is reduced to Ce^{3+} with H_2O_2. Loss of Ce^{144} into the supernatant liquid from the ceric iodate precipitate is less than 1% (Table 1).

Purification of Ce^{144} by Ion Exchange. – Cerium-144 is sometimes separated from the other rare earths by ion exchange. This method has been used to purify 40 to 50 curies of Ce^{144}. The Ce^{144} is adsorbed on a Nalcite HCR (100–200 mesh) column from a 0.1 *N* HCl solution and eluted from the column with 0.2 *M* citrate solution adjusted to pH 3.2 with ammonium hydroxide. The temperature during elution is approximately 94°C.

Traces of plutonium and americium and quantities of europium and promethium are removed before the cerium. The time necessary for purification is approximately 100 to 200 hr of continuous

Table 1. Separation of Ce^{144}

Sample	Trivalent Rare Earths (mc)	Ce^{144} (mc)	Ce^{144} (%)	Remarks
RE-I-P-2		16,200	100	Starting solution
Ce-3-2		58		
Ce-3-3		120		
Ce-3-4		273		
Ce-3-5		145		
Ce-3-6		160		
Ce-3-7		150	10.4	Loss in oxalate supernatant liquid in ten precipitations
Ce-3-8		182		
Ce-3-9		415		
Ce-3-10		150		
Ce-3-12		35		
Ce-3-11		14,500	89.5	$Ce(IO_3)_4$
Ce-3-13	3180	57.6	0.4	Loss into supernatant from $Ce(IO_3)_4$
		Total Ce^{144}, mc	16,245	
		Ce^{144} accounted for, %	100.3	

operation. The cerium is recovered from the citrate solution by oxalate precipitation within two weeks after removal from the ion exchange column to prevent decomposition of the citrate by radiation.

Separation of the Long-Lived Trivalent Rare Earths. – There remains a rare-earth mixture, after Ce^{144} is separated, with analysis as follows:

Isotope	Per Cent
Y^{91}	0.094
Eu^{155}	0.10 to 0.20 (not extrapolated to zero absorber)
Sm^{151}	(Identified but not analyzed for)
Ce^{144}	3.15
Pm^{147}	96.67

An absorption curve of a sample of this rare-earth mixture mounted on polystyrene is shown in Fig. 4. Promethium is present in such quantities that its beta activity of 4 mg per square centimeter half-thickness obscures the softer radiations of Eu^{155} and Sm^{151}.

This mixture is best separated by ion exchange. A column 1.0 cm ID, 64 cm long, and filled with Nalcite HCR, 100–200 mesh, is used. For a preliminary separation of europium from promethium, 0.25 *M* lactic acid is preferred (Fig. 5). Separation by this method takes 15 hr. The separation factor, defined as the ratio of the elution volumes at the peaks of the activities, is 1.3 for promethium/europium and 1.16 for promethium/americium. The americium peak extends into the europium peak.

Europium is recovered from the lactate solution by reducing the pH to 1.0 and adsorbing on a small concentrating cation column. From the small column, europium is removed with 6.0 *N* HCl, boiled to a low volume, and diluted to 0.1 *N* in HCl.

Europium from the first separation with lactate at pH 5.0 may be contaminated with more than 200 alpha counts of americium per millicurie. The last traces of americium can be removed to below 200 alpha counts per millicurie by a second ion exchange separation similar to the first except that the pH of the elutriant is 4.75 (see Fig. 6).

An analysis of the beta spectrum of separated fission europium showed that the Eu^{155} contributed 93.6% of the total beta and that $Eu^{152,154}$ contributed not more than 6.6%. A study of the gamma spectrum (gamma-ray spectrometer) was made to ascertain whether this fission europium

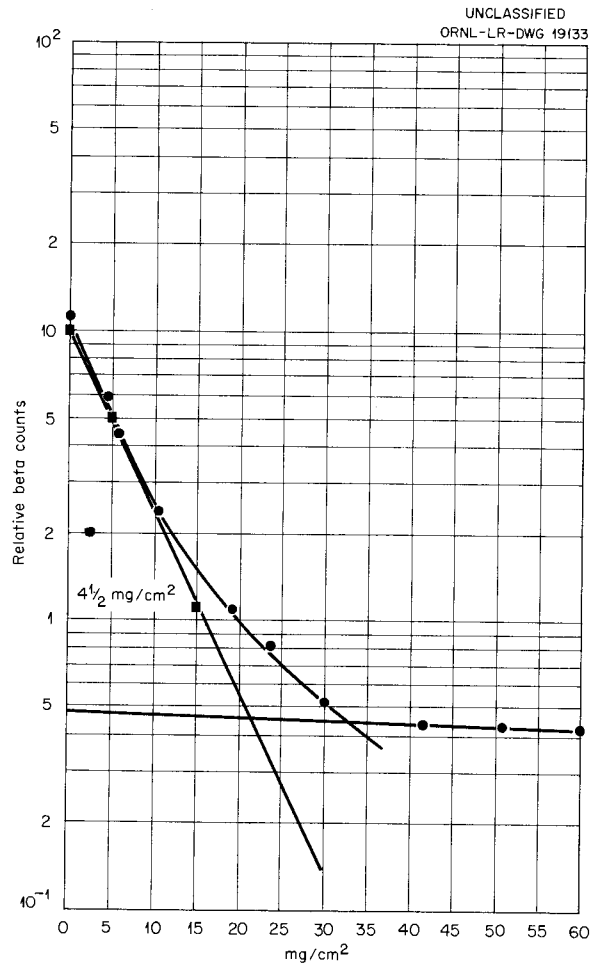

Fig. 4. Gross-Beta Absorption Curve of Rare-Earth Activity After Separation of Ce^{144}.

could be used to fabricate a useful source of low-energy x rays (energy of Eu^{155} gamma is 0.085 Mev). Gamma energies of 0.085, 0.760, 1.06, and 1.37 Mev were found. The gamma energies of 0.760, 1.06, and 1.37 Mev are contributed by the Eu^{152} and Eu^{154} present. Of the total gamma spectrum, 59.2% was contributed by $Eu^{152,154}$, and 40.8% was contributed by Eu^{155}. This information indicates that europium from fission is not a very good source of x rays of low energy unless it is separated soon after removal from the reactor.

Samarium-151 is contained in the effluent between the europium and promethium peaks of activity. This isotope (73-year half life) has a 0.019-Mev gamma activity and a 0.076-Mev beta activity and is difficult to detect with a G-M

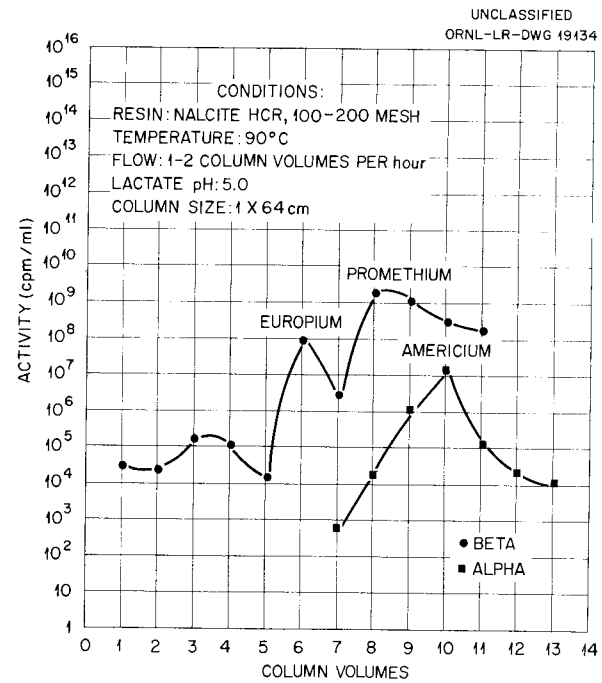

Fig. 5. Ion Exchange Separation of Europium, Americium, and Promethium.

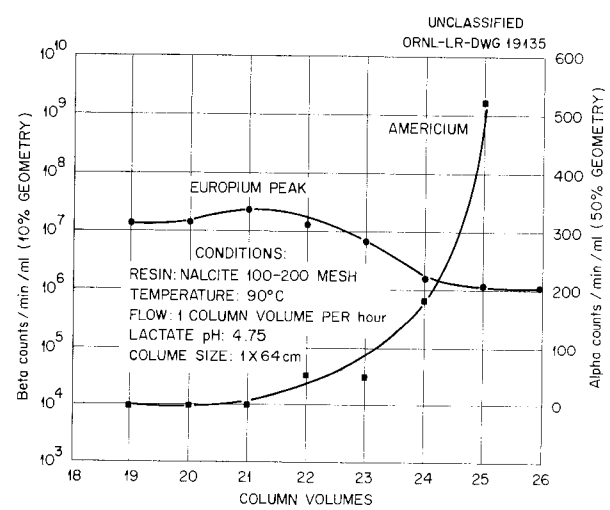

Fig. 6. Ion Exchange Separation of Americium and Europium.

counter. By analyzing the europium and promethium with absorption curves counted on a G-M counter and by taking the effluent between europium and promethium, a solution enriched in Sm^{151} was obtained. Beta proportional counting on the same samples indicated the presence of Sm^{151} (Fig. 7).

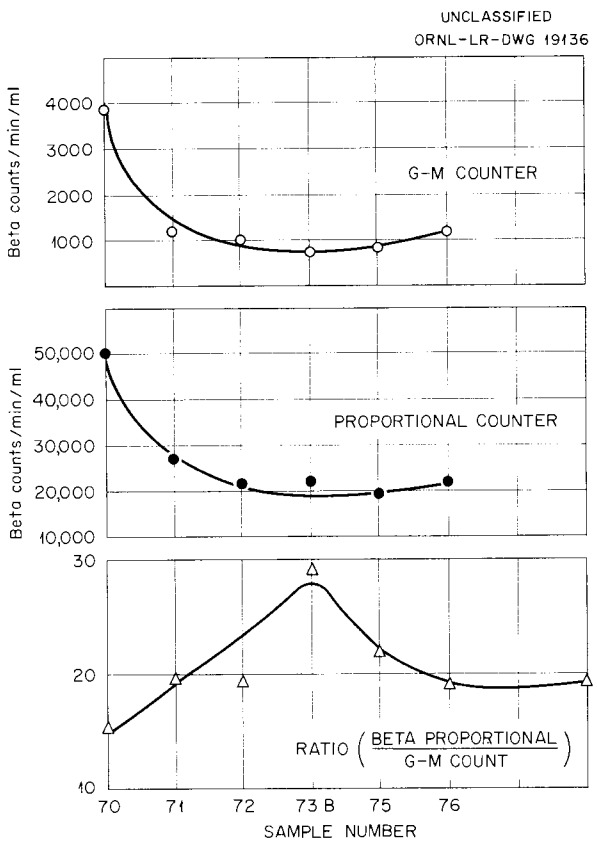

Fig. 7. Elution Curves Between Europium and Promethium.

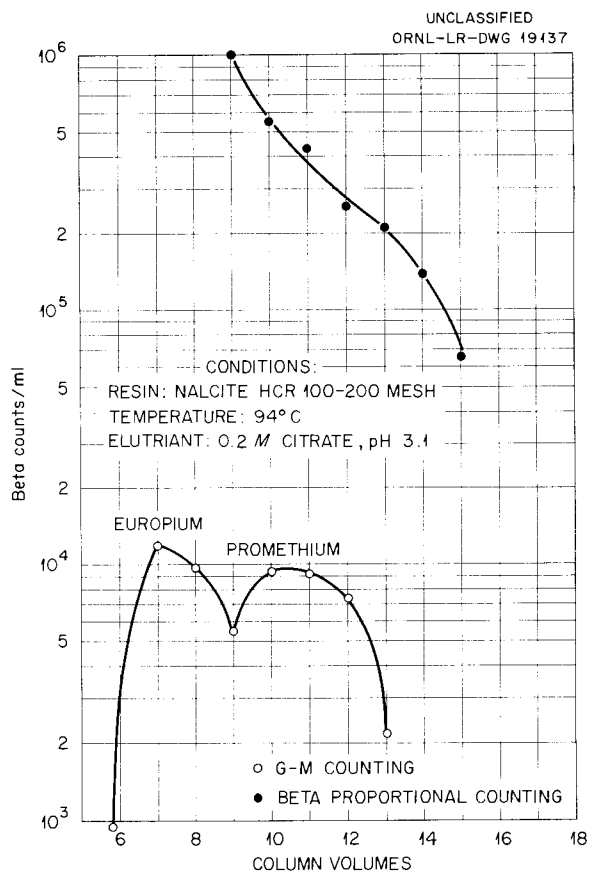

Fig. 8. Elution Curve – Column Volume vs Activity, G-M and Beta Proportional Counts.

This solution was prepared for another ion exchange separation by burning out the organic matter in a furnace, dissolving $Sm^{151}{}_2O_3$ in 70% HNO_3, and diluting to 0.1 *N*.

The activity was adsorbed on a 100- to 200-mesh Nalcite HCR column and eluted from the column with 0.2 *M* citrate at pH 3.1. (Figure 8 shows the elution curve.) Europium and promethium were separated as indicated, and the presence of the soft activity was shown by the analysis of the same elution fractions by beta proportional counting. A spectrographic analysis of a portion of the effluent between europium and promethium indicated samarium.

An analysis of the gamma spectrum indicated a 19-kev gamma which is characteristic of Sm^{151} (Fig. 9). This samarium was also contaminated with europium (Fig. 10).

Separation of Am^{241} and Cm^{242}. – During the process of isolating Sm^{151}, two peaks of alpha were detected in the citrate effluent. The first was Cm^{242} associated with samarium, as determined by an alpha pulse-height analysis, and the second peak was americium associated with Pm^{147}. The elutriant was 0.2 *M* citrate solution at pH 3.15. The temperature was 90°C, and the resin was Nalcite HCR, 100–200 mesh.

Separation and Purification of Promethium from Americium. – Several methods have been used to separate promethium from americium.

Separation by Ion Exchange. – Elution of promethium from Nalcite HCR with 0.25 *M* lactate solution separates promethium from inactive neodymium, europium, and samarium. As shown by Fig. 11, this process does not separate americium from promethium effectively.

Equilibrium studies were made to determine the distribution of promethium and americium between Nalcite HCR, 100–200 mesh, and different complexing solutions. The distribution coefficient

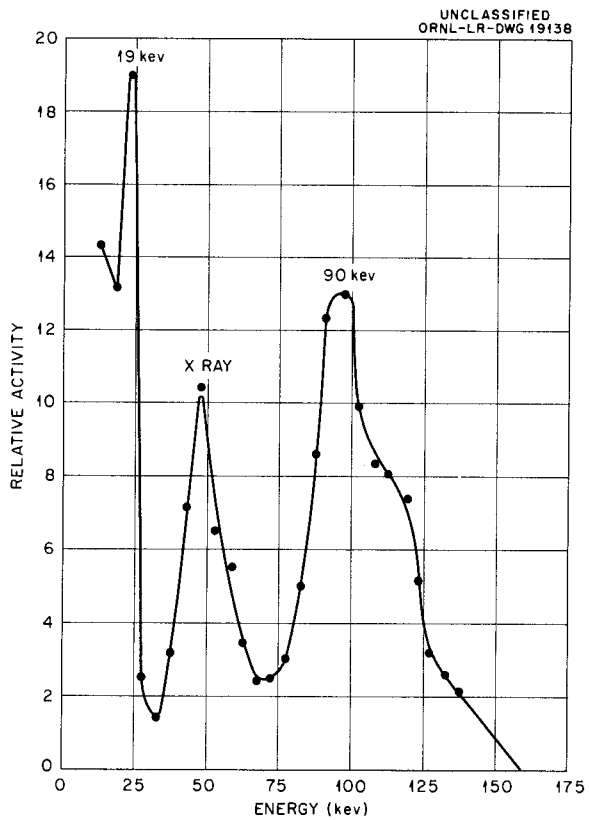

Fig. 9. Analysis of Gamma Spectrum of Fission Samarium Products.

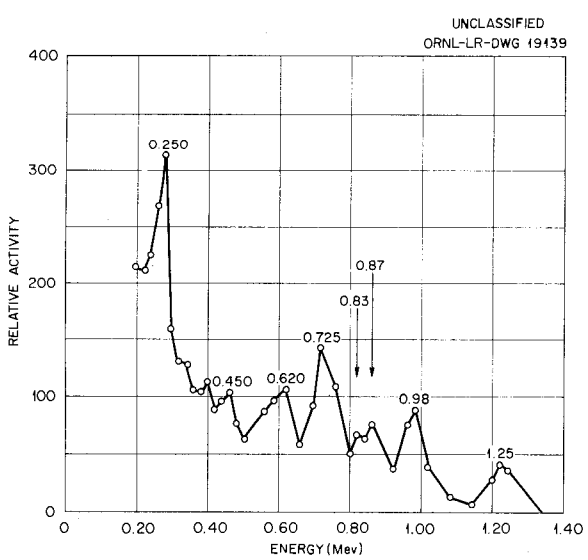

Fig. 10. Analysis of Gamma Spectrum of Fission Samarium Product Showing Presence of Europium.

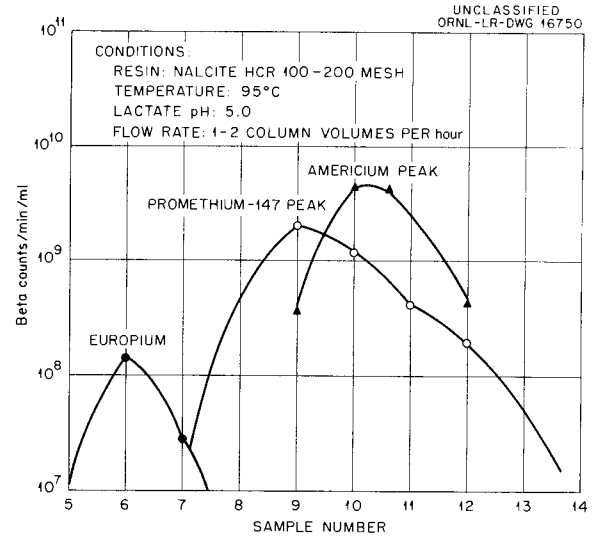

Fig. 11. Separation of Americium and Promethium by Ion Exchange.

is defined as

$$\frac{\text{counts/minute/gram of resin}}{\text{counts/minute/milliliter of solution}},$$

and separation factors are calculated as ratios of the distribution coefficients. If C represents the number of free column volumes of effluent at the peak of the activity,[10] the ratio of two C values can be shown to be equal to the separation factor. Equilibrium conditions which give distribution coefficients of 350–400 do not establish conditions for economical separation where the flow through the column is 1 to 2 column volumes per hour.

The variation of the distribution coefficient of americium and promethium with changes in pH of 0.25 M pentanedione is shown in Fig. 12. This solution was agitated with 100–200 mesh Nalcite HCR resin.

Studies of the distribution of Pm^{147} and Am^{241} between H_2SiF_6 and Nalcite HCR at different concentrations of acid showed that the two activities could be separated by elution from a resin bed with 2.0 M H_2SiF_6. (See Fig. 13.) By this method, promethium was effectively separated from americium, at first when small amounts of activity were used and then later when 30-curie amounts were used. Promethium was removed first from the

[10] S. W. Mayer and E. R. Tompkins, *J. Am. Chem. Soc.* **69**, 2866 (1947).

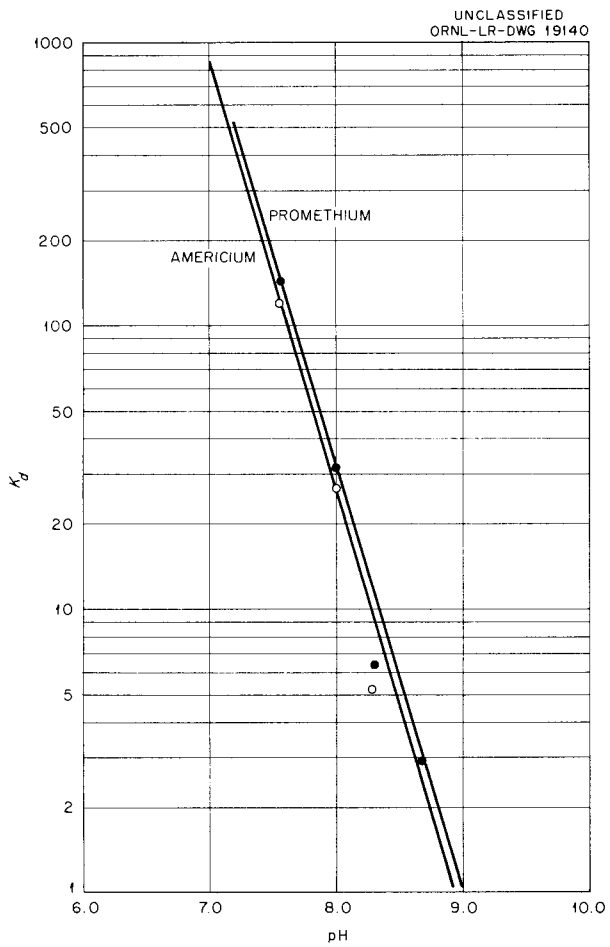

Fig. 12. Variation of K_d of Promethium and Americium with Change of pH of 0.25 *M* Pentanedione Agitated with Nalcite HCR, 100–200 Mesh.

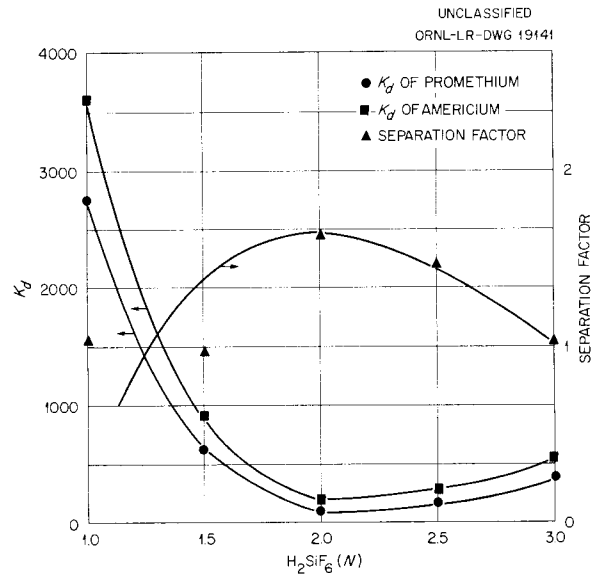

Fig. 13. Equilibrium Studies of Promethium and Americium in H_2SiF_6 Solution Agitated with Nalcite HCR, 100–200 Mesh.

resin bed, which shows that the distribution coefficient is less than that of americium (Fig. 14).

The 2.0 *M* H_2SiF_6 is diluted to 1.0 *M*, and promethium is adsorbed on a small cation column. From this resin bed, promethium is removed with 6.0 *N* HCl.

Precipitation of PmF_3 from Hydrofluosilicic Acid. – Promethium and americium are contained in the lactate effluent from the ion exchange columns in high enough concentration to be precipitated as oxalates with little loss of activity. The oxalate precipitation is a concentration step prior to final purification. The solutions should contain Pm^{147} that is 99.9% pure except for americium.

A report by the Chemistry Division at the University of Chicago[11] states that americium was purified by adding Ce(III) to an H_2SiF_6 solution containing americium and precipitating cerium as a fluoride or fluosilicate. The problem was to obtain americium separated from fission rare earths. The beta/alpha of their final product was 100/1.

The problem at ORNL Operations Division was to obtain promethium separated from americium. The beta/alpha ratio of the starting solution was 3.2×10^4 and the calculated purity of the final product was to be a beta/alpha ratio of 1.2×10^7. Briefly, the procedure is as follows:

1. make up americium and promethium in a 1–2 *N* HNO_3 solution,
2. add H_2SiF_6 until the solution is 3.0 *M*,
3. heat to approximately 80°C to precipitate PmF_3,
4. centrifuge PmF_3 from solution,
5. wash precipitate with distilled water,
6. dissolve PmF_3 in a minimum amount of boric acid and 16 *N* HNO_3,
7. dilute to 1–2 *N* in HNO_3,
8. repeat steps 1 through 7 as another cycle.

A decontamination factor of 3.7 can be expected for each cycle (Fig. 15).

[11] *Chemistry Division Report*, University of Chicago, CS-3359 (Dec. 1945) (Classified).

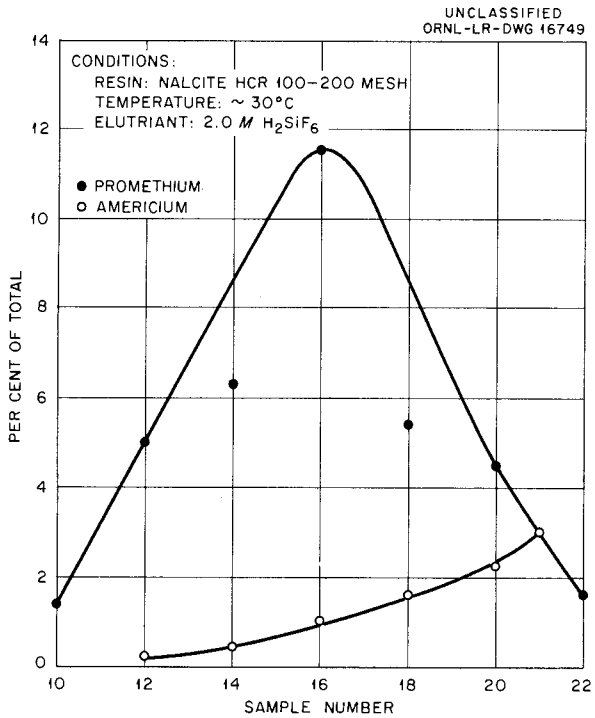

Fig. 14. Elution of Promethium and Americium from Nalcite HCR, 100–200 Mesh, with 2.0 *M* H_2SiF_6.

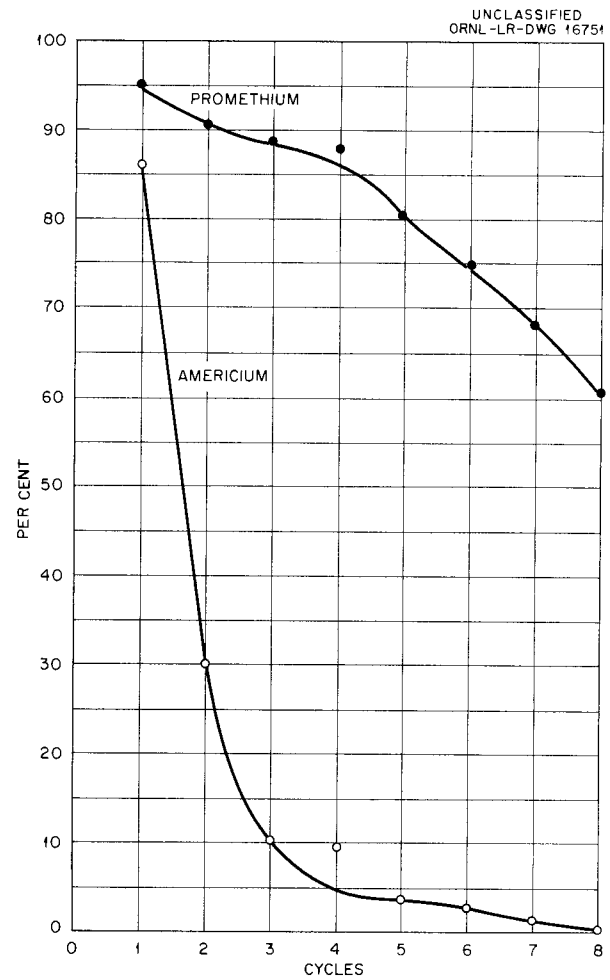

Fig. 15. Amount of Promethium and Americium Left in PmF_3 Precipitate Formed in 3.0 *M* H_2SiF_6 Solution.

CONCLUSION

Because of increased demand for short-lived rare earths and also for other short-lived activities such as Ba^{140}, Sr^{89}, and Ru^{103}, a new Short-Lived Fission Product Plant has been built. It is now planned to extract rare earths into tributyl phosphate from 16 *N* HNO_3 solution. Some extraction studies for this process are summarized in Table 2.

Problems are anticipated, as 100 liters of mixed fission products must be boiled down to 1.0 liter or less. Nitration reactions on traces of tributyl phosphate at high temperatures will produce organic materials which must be destroyed or perhaps removed by solvent extraction.

The ion exchange column for separating long-lived trivalent rare earths will necessarily be increased in size.

Facilities for purifying large quantities of Pm^{147} and Ce^{144} will be adequate in the new Multikilocurie Fission Product Plant, which is now under construction.

ACKNOWLEDGMENT

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Table 2. Extraction Studies with 100% Tributyl Phosphate

	8.7 mg/ml $Fe^{+++} + Fe^{59}$ (%)	57 mg/ml $La^{+++} + Y^{91}$ (%)	Y^{91} Tracer (%)	Fe^{+++} with Y^{91} Tracer		Zr^{95} Tracer (%)	Sr^{89} Tracer (%)	Pm^{147} Tracer (%)
				Fe^{+++} (%)	Y^{91} (%)			
Extraction into TBP from 16 *N* HNO_3								
First extraction	60	67	77	96	94	94	0.35	36.0
Second extraction	29	22	5	4	5.2	4.8	0.31	17.3
Third extraction	3	0.4	1					
Fourth extraction	0.3	0.0	0					
Left in 16 *N* HNO_3	8.0	11.0	17.0					
Stripping from TBP								
HNO_3 Washes of First Extraction Solution								
14 *N*	10.0	0.0		24.0	11.0	1.5		
12 *N*	16.0	18.0		13.0	15.0	1.5		
10 *N*	14.0	31.0		23.0	26.0	1.7		
8 *N*	3.0	19.0		3.0	35.0	3.0		
HNO_3 Washes of Second Extraction Solution								
14 *N*	16.0	1						
12 *N*	7.0	1						
10 *N*	8.0	2						
8 *N*	6.0	1						
HNO_3 Washes of Third Extraction Solution								
14 *N*	1.0	0						
12 *N*	2.0	0						
10 *N*	1.0	0						
8 *N*	1.0	0						
Total left in TBP	7	16						