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PARAMETRIC EVALUATION OF DTPA, EDTA, AND HEDTA
FOR ION EXCHANGE PURIFICATION OF PROMETHIUM

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FOR ION EXCHANGE PURIFICATION OF PROMETHIUM

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September, 1965

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PARAMETRIC EVALUATION OF DTPA, EDTA, AND HEDTA FOR ION EXCHANGE PURIFICATION OF PROMETHIUM

INTRODUCTION

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. Much lighter shielding is required for multikilocurie sources of Pm^{147} than for many of the other isotopes being considered for power sources.⁽¹⁾

A correct evaluation of the relative merits of promethium has been delayed by erroneous extrapolations of availability and of obtainable purity (from some early laboratory work). Recent work in this laboratory⁽²⁾ and by P.B. Orr at ORNL⁽³⁾ has clearly demonstrated the feasibility of producing highly purified promethium on a kilogram scale.

The trivalent rare earth fission products can be removed from the concentrated fission product waste and separated from cerium, if necessary, by precipitation^(4,5) or by solvent extraction processes.^(6,7)

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 companies who produce pure rare earths on a commercial basis.

A rather large number of eluting agents have been proposed for both anion and cation exchange separation processes and are reviewed elsewhere.⁽⁸⁾ The three eluting agents which have been used most successfully for the purification of the individual "light" rare earths, on a macro scale, are the aminopolyacetic acids—ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA). All three eluting agents are used in the commercial rare earth separations plants. EDTA was used by Wheelwright and Roberts⁽²⁾ 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 (Table XI) was unprecedented. P.B. Orr at Oak Ridge⁽³⁾ has since 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.^(2,9)

In developing a process for separating promethium from the adjacent rare earths and from all other possible contaminants, it is expedient to minimize exposure of resin and 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 parameters must be considered. Some of the parameters are

*The rare earths, lanthanum through gadolinium.

**Ci is the recently adopted abbreviation for curie.

unique to a given eluting agent or exchange resin. Parameters which can be adjusted are eluant concentration, pH elution temperature and flow rate.

The objective of the research program described in this report was to provide a critical experimental evaluation of the effect of changes in the various operating parameters both on the magnitude and the rate of separation for the eluting agents EDTA, HEDTA, and DTPA. Such an evaluation then should aid in the design of minimum-sized, maximum-capacity equipment; the selection of the most appropriate eluting agent; and the optimum process variables for that specific eluting agent.

SUMMARY

Optimum conditions for the purification of the individual light rare earth elements by ion exchange elution have been determined for the eluting agents DTPA, EDTA, and HEDTA. The conditions apply directly to the production of macro amounts of pure promethium. DTPA was demonstrated to be superior to both EDTA and HEDTA with feed solutions which do not contain significant amounts of Pb^{+2} or Y^{+3} . In the event that Pb^{+2} or Y^{+3} are present, EDTA or a sequence of first DTPA and then EDTA gives better results than DTPA alone. Because of the much higher separation coefficient of promethium from cerium in the DTPA system and its use of a H^+ retaining ion, an initial fast "rough" separation would be made with DTPA to reduce radiolysis from Ce^{144} and to permit a reduction in column size for subsequent columns. All three eluting agents can be used in the same equipment.

The column equipment is described and a flowsheet proposed for a separation plant capable of producing 6×10^6 Ci of high purity promethium per year on a 10 months per year operational basis.

DISCUSSION

THEORETICAL SEPARATION COEFFICIENTS

It can be shown that the separation coefficient for any two rare earths R_1 and R_2 can be expressed as a ratio of the stability constants of the complexes formed between the cations and the complexing agent^(2,9)

$$K_{sep} = \frac{K_{R_2Ch}}{K_{R_1Ch}}$$

The stability constants of the complexes formed between the "light" rare earths and the three complexing agents have been determined.⁽¹⁰⁻¹²⁾ 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. Due to 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 DTPA is a slightly better eluting agent than EDTA or HEDTA for separating promethium from neodymium or samarium. 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 is described in detail in a later section of this report, the Nd-Sm and Nd-Pr separation coefficients are given in Table I for comparison.

ELUTION SEQUENCE

The sequence in which various cations of interest elute with EDTA, HEDTA, and DTPA have been determined⁽¹³⁾ and are given in Table II. The elution of Pm^{+3} between Sm^{+3} and Nd^{+3} has been experimentally verified.⁽²⁾ It is significant to note that the presence of Y^{+3} ,

Co^{+2} , or Pb^{+2} between Sm^{+3} and Nd^{+3} in the DTPA elution sequence does not make it easier to separate Sm^{+3} from Nd^{+3} by acting as a wedge because their presence has no effect upon the thermodynamic separation coefficient. The impurities make the isolation of pure Sm^{+3} or pure Nd^{+3} more difficult; because, for example, it is easier to separate Sm^{+3} from Nd^{+3} than it is to separate Pb^{+2} from Nd^{+3} or Sm^{+3} . By analogy, if any cation impurity which elutes between Sm^{+3} and Nd^{+3} with a given eluting agent is present in a promethium feed solution, the separation of promethium from that impurity will be more difficult than the separation of promethium from the next rare earth in the sequence.

Before selection of an eluting agent, the presence or absence of Fe^{+2} , UO_2^{+2} , Y^{+3} , Co^{+2} , and Pb^{+2} in the promethium feed solution must be considered. In any fission product feed solution there will be more inactive Y^{89} than Pm^{147} unless it is removed by a prior extraction step. Both lead and iron may be added as process chemicals and may be present as impurities in the fission product solutions. If they are not removed by prior processing, then they must be con-

sidered in the choice of an eluting agent. It is rather unlikely that Co^{+2} , Cd^{+2} , Fe^{+2} , or UO_2^{+2} would be present in a mixed rare earth feed in significant amounts. From the point of view of elution sequence only, EDTA is the preferred eluting agent.

EXPERIMENTAL EVALUATION OF ELUTION PARAMETERS

In addition to the thermodynamic properties which are 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 particle size
- Resin porosity (crosslinkage)
- The ratio (on a mole equivalent basis) of the desired ion (Pm^{+3}) to the impurities in the feed solution.

Items (f) and (g) are intrinsic to the specific resin chosen and cannot affect the choice of eluting agents. 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 can not be made. Item (h) likewise cannot affect the choice of eluting agents or conditions.

Each experiment described in this report was performed in an identical three column system. The columns, in sequence, were an eluant degasser column, a feed absorption column, and an elution column. The degasser column was 5.06 cm² by 25 cm long, filled to a depth of 15 cm with NH_4^+ cycle Dowex 50W,

* 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.

TABLE I

PROMETHIUM SEPARATION COEFFICIENTS

RARE EARTH PAIR	$K_{\text{RCH}}/K_{\text{R}^+\text{Ch}}$		
	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

TABLE II

ELUTION SEQUENCE

EDTA	
Co ⁺³ , Bi ⁺³ , Fe ⁺³ , Ni ⁺² , Th ⁺⁴ , Pb ⁺² , Zn ⁺² , Co ⁺² , Cd ⁺² , Al ⁺³ , Y ⁺³	
Gd ⁺³ , Sm ⁺³ , Fe ⁺² , UO ₂ ⁺² , Nd ⁺³ , Pr ⁺³ , Mn ⁺² , Ce ⁺³ , La ⁺³ , Ca ⁺² , Mg ⁺²	
	Pm ⁺³
HEDTA	
Co ⁺³ , Bi ⁺³ , H ⁺ , Ni ⁺² , H ₅ CH ⁺² , Fe ⁺³ , Cr ⁺³ , Zn ⁺² , Pb ⁺² , Co ⁺²	
Cd ⁺² , Th ⁺⁴ , Al ⁺³ , Gd ⁺³ , Eu ⁺³ , Sm ⁺³ , UO ₂ ⁺² , Y ⁺³ , Nd ⁺³	
	Pm ⁺³
Pr ⁺³ , Ce ⁺³ , Mn ⁺² , La ⁺³ , Ca ⁺²	
DTPA	
Th ⁺⁴ , Ni ⁺² , UO ₂ ⁺² , Zn ⁺² , Gd ⁺³ , Eu ⁺³ , Sm ⁺³ , Y ⁺³ , Co ⁺² , Cd ⁺² , Pb ⁺²	
	Pm ⁺³
Nd ⁺³ , Pr ⁺³ , Ce ⁺³ , La ⁺³ , Mn ⁺² , Al ⁺³ , Ca ⁺² , Sr ⁺²	

X-8 (50 to 100 mesh) resin. The column was water-jacketed and operated at 90 C. Except for an occasional venting of collected gas, this column required no attention. In a hot-cell installation, the degasser column would be installed outside the cell. The absorption column was 2.38 cm² by 60 cm long and contained 100 ml (in water) of H⁺ cycle Dowex 50W, X-8 (50 to 100 mesh) resin. The elution column was 1.31 cm² by 190 cm long and, initially, contained 230 ml (in water) of H⁺ cycle Dowex 50W, X-8 (50 to 100 mesh) resin.

With these relative amounts of resin in the absorption and elutions columns, an absorbed band was defined as moving 2.3 band lengths during the elution. Both absorption and elution columns were water-jacketed for elevated temperature operation. The temperature was controlled within ± 0.5 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 equal molar amounts of samarium, neodymium, and praseodymium, adjusted to pH 4. The resin was then water washed to remove unabsorbed ions, connected in series with the elution column, 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 the fractions 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 curves provided the data for comparing the effectiveness of the separation achieved. Neodymium was used as the standard

FIGURE 1

Typical Elution Curve

of reference. By keeping the ratio of neodymium to samarium and praseodymium constant in the feed, the effects of the other process variables could be evaluated.

For any given set of elution conditions, the percent of pure neodymium in the "center cut" will increase directly as the total amount of neodymium in the feed increases. In other words, once an equilibrium separation is achieved on a column of given size, the amount of neodymium in the zones of binary mixing is constant; all of the rest, be it a great amount or a small amount, 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 band, it is desirable to increase the length to area ratio of the band of desired material as the elution progresses by decreasing the column diameter.

The parameters examined are items (a) through (e) given previously. Not all of the parameters were independently varied for each of the three eluting agents, but a sufficient number of permutations were made to give a reasonable evaluation. The three experiments shown in Table III illustrate the degree of reproducibility. The shorter total elution time and higher neodymium product concentration in Run 3 result from the slightly higher concentration of the eluting solution and a slightly faster flow rate. The percent purity of neodymium in Zone A and the percent

of total neodymium recovered in Zone A are each quite reproducible and are probably accurate to $\pm 2\%$. They are not, however, strikingly responsive to changes in separation efficiency. Values below 88 to 90 reflect rather poor separation. Since the curves are symmetrical—a result of equal amounts of samarium, neodymium, and praseodymium in the feed—these two values are also equal to each other within $\pm 2\%$. The percent of neodymium recovered 100% pure is a little less reliable because of dependence on where the samarium and praseodymium elution curves are drawn at the 1 to 5% impurity level, but is a more sensitive indication of the separation achieved than the percent purity or recovery in Zone A. In all of the experiments described in this report, H^+ is used as the barrier ion for elutions with DTPA and HEDTA. Zn^{+2} is used for all EDTA elutions. NH_4OH was used to adjust the eluant pH for all runs except the four shown in Table VI. For those runs NaOH was used.

Concentration of the Eluting Agent

Table IV contains the data for the several runs in which the eluant concentration was changed and other variables kept reasonably constant. 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 type complexes is greater than the $HMCh$ type complexes, the eluant pH

TABLE III

EXPERIMENTAL REPRODUCIBILITY

Run	<u>ELUTING SOLUTION DATA</u>				Total Elution Time, hr	Neodymium Product Concentration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temperature, C
	Eluting Agent	Molar Concentration	pH	Flow Rate ml/min-cm							
1	HEDTA	0.030	5.00	2.87	96	0.89	96	96	80	2.3	60
2	"	0.029	5.00	3.00	98	0.90	97	96	76	2.3	60
3	"	0.032	4.99	3.11	84	1.01	96	96	78	2.3	60

TABLE IV

EFFECT OF ELUTING SOLUTION CONCENTRATION

ELUTING SOLUTION DATA					Total Elution Time, hr	Neodymium Product Concen- tration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temper- ature, C
Run	Eluting Agent	Molar Concen- tration	pH	Flow Rate, ml/min- cm ²							
1	HEDTA	0.029	5.00	3.00	98	0.90	97	96	76	2.3	60
2	"	0.045	5.01	3.09	58	1.72	95	95	71	2.3	60
3	"	0.015	5.53	2.95	106	0.72	97	96	80	1.52	60
4	"	0.029	5.50	2.99	66	1.64	94	94	65	2.3	60
5	"	0.044	5.49	3.09	44	2.58	90	90	45	2.3	60
6	"	0.060	5.55	2.91	33	3.64	< 80	< 80	0	2.3	60
7	DTPA	0.012	5.50	2.8	72	0.89	94	94	74	1.52	60
8	"	0.026	5.96	2.9	44	2.12	96	95	69	2.3	60
9	EDTA	0.012	8.40	3.07	72	1.50	93	93	61	1.8	60

must not be lower than about 8.0 at 60 C. DTPA must be limited to a maximum concentration of about 0.03M because of the relatively low solubility of the acid form in the pre-breakthrough effluent solution. With all three eluting agents, low concentration yields better separation but results in longer elution time and low product con-

centration. Best results with HEDTA are obtained in the concentration of 0.03 to 0.045M.

pH of Eluting Solution

The results in Table V show that HEDTA is most effective at pH 5.0 to 5.5. The DTPA results show much less dependence upon

TABLE V

EFFECT OF ELUTING SOLUTION pH

ELUTING SOLUTION DATA					Total Elution Time, hr	Neodymium Product Concen- tration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temper- ature, C
Run	Eluting Agent	Molar Concen- tration	pH	Flow Rate, ml/min- cm ²							
1	HEDTA	0.032	4.99	3.11	84	1.01	96	96	78	2.3	60
2	"	0.029	5.00	3.00	98	0.90	97	96	76	2.3	60
3	"	0.029	5.50	2.99	66	1.64	94	94	65	2.3	60
4	"	0.029	6.01	3.09	54	2.14	90	89	43	2.3	60
5	"	0.031	6.50	3.06	48	2.59	82	82	0	2.3	60
6	HEDTA	0.045	5.01	3.09	58	1.72	95	95	71	2.3	60
7	"	0.045	5.49	3.09	44	2.58	90	90	45	2.3	60
8	DTPA	0.023	5.49	2.84	53	1.82	96	96	70	2.3	60
9	"	0.026	5.96	2.90	44	2.12	96	95	69	2.3	60
10	"	0.024	6.51	3.02	44	2.07	95	95	68	2.3	60
11	"	0.027	7.00	2.90	42	2.33	95	95	69	2.3	60
12	EDTA	0.012	8.40	3.07	72	1.50	93	93	61	1.8	60
13	"	0.012	8.71	2.90	68	1.78	85	85	33	1.8	60
14	"	0.013	8.90	3.13	52	zinc barrier did not retain Rare Earths				1.8	60

solution pH than EDTA or HEDTA, and any pH between 5.5 and 7.0 gives good results. EDTA is quite pH sensitive. Below pH 8.0, the metal ion complexes precipitate, and above 8.8 the rare earths pass through the zinc barrier. Four EDTA runs were made in which NaOH was used to adjust the eluant pH. These are shown in Table VI. These results may indicate less pH sensitivity with NaOH than with NH_4OH . The useful pH range appears to be broader. Run 2 of Table VI shows about the same results as Run 2 of Table V, so it must be concluded that the use of NaOH does

not give a better separation. However, the substitution of NaOH for NH_4OH may be desirable for other reasons (restrictions on waste disposal).

Elution Temperature

The results given in Table VII show that the best separation is achieved at the highest practical temperature. A very pronounced increase in separation is achieved on increasing the temperature from 25 to 60 C. In spite of a substantial increase in flow rate (Runs 4 and 5) DTPA yielded much better separation at

TABLE VI
VARIATION OF ELUTING SOLUTION pH
EDTA BUFFERED WITH NaOH

Run	ELUTING SOLUTION DATA				Flow Rate, ml/min-cm ²	Total Elution Time, hr	Neodymium Product Concentration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temperature, C
	Eluting Agent	Molar Concentration	pH									
1	EDTA	0.012	8.00		3.00	87	1.25	93	94	70	1.8	60
2	"	0.012	8.40		2.90	83	1.37	92	92	62	1.8	60
3	"	0.012	8.60		2.98	80	1.34	93	94	64	1.8	60
4	"		8.80		3.02	76	1.38	94	95	67	1.8	60

TABLE VII
EFFECT OF ELUTION TEMPERATURE

Run	ELUTING SOLUTION DATA				Flow Rate, ml/min-cm ²	Total Elution Time, hr	Neodymium Product Concentration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temperature, C
	Eluting Agent	Molar Concentration	pH									
1	EDTA	0.012	8.40		3.2	80	1.45	80	82	0	2.3	25
2	"	0.012	8.40		3.1	72	1.50	93	93	61	1.8	60
3	DTPA	0.025	6.50		3.4	48	1.90	90	90	35	2.3	25
4	"	0.027	6.50		4.9	25	2.16	93	93	57	2.3	60
5	"	0.025	6.51		4.9	27	2.10	94	94	67	2.3	76
6	HEDTA	0.031	5.50		5.05	38	1.70	91	91	45	2.3	60
7	"	0.030	5.50		4.95	38	1.73	91	91	51	2.3	76

60 C than at 25 C. Because of column gassing, the maximum practical temperature range is probably 65 to 75 C.

Elution Flow Rate

The flow rate results shown in Table VIII indicate that DTPA and HEDTA are still efficient at rates up to 4 ml/min-cm².

HEDTA shows less decrease in separation efficiency with an increased flow rate at

pH 5.0 than at pH 5.5. The EDTA results cannot be compared directly with the others because the elution distance is shorter. However, there seems to be little loss in separation in operating at a rate up to 3 ml/min-cm².

Elution Distance

Table IX gives the data on elution distance. DTPA yields identical results at 1.3 and 2.3

TABLE VIII

EFFECT OF ELUTING SOLUTION FLOW RATE

<u>ELUTING SOLUTION DATA</u>											
Run	Eluting Agent	Molar Concentration	pH	Flow Rate, ml/min-cm ²	Total Elution Time, hr	Neodymium Product Concentration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temperature, C
1	DTPA	0.024	6.51	3.02	44	2.07	95	95	68	2.3	60
2	"	0.026	6.51	3.90	31.5	2.11	94	94	66	2.3	60
3	"	0.027	6.50	4.90	25	2.16	93	93	57	2.3	60
4	HEDTA	0.029	5.00	3.00	98	0.90	97	96	76	2.3	60
5	"	0.033	5.01	3.91	67	1.05	95	95	74	2.3	60
6	"	0.031	5.00	5.06	53	0.99	96	96	74	2.3	60
7	"	0.030	5.55	1.41	145	1.59	96	96	76	2.3	60
8	"	0.029	5.50	2.99	66	1.64	94	94	65	2.3	60
9	"	0.032	5.49	3.98	50	1.66	92	92	52	2.3	60
10	"	0.031	5.50	5.05	38	1.70	91	91	45	2.3	60
11	EDTA	0.013	8.40	0.95	203	1.62	92	93	68	1.8	60
12	"	0.013	8.40	1.99	92	1.66	92	92	59	1.8	60
13	"	0.012	8.40	3.07	72	1.50	93	93	61	1.8	60

TABLE IX

EFFECT OF ELUTION DISTANCE

<u>ELUTING SOLUTION DATA</u>											
Run	Eluting Agent	Molar Concentration	pH	Flow Rate, ml/min-cm ²	Total Elution Time, hr	Neodymium Product Concentration, g/liter	% of Total Neodymium Recovered in Zone A	% Purity of the Neodymium Recovered in Zone A	% of the Total Neodymium Recovered 100% Pure	Elution Distance, band lengths	Elution Temperature, C
1	DTPA	0.025	6.49	3.08	33	2.07	94	94	67	1.3	60
2	"	0.026	6.51	3.05	39	2.10	94	95	70	1.8	60
3	"	0.024	6.51	3.02	44	2.07	95	95	68	2.3	60
4	HEDTA	0.031	5.49	3.09	45	1.71	88	89	22	1.3	60
5	"	0.031	5.51	3.12	54	1.68	92	93	56	1.8	60
6	"	0.032	5.51	3.05	65	1.66	94	94	70	2.3	60
7	EDTA	0.012	8.40	3.07	48	1.60	89	90	42	1.0	60
8	"	0.012	8.40	3.07	54	1.52	91	91	56	1.3	60
9	"	0.012	8.40	3.07	72	1.50	93	93	61	1.8	60

band lengths while the other two eluting agents show a marked decrease in separation efficiency when the elution distance is decreased below 2.3 band displacements. This is probably a result of the higher DTPA separation coefficients.

Evaluation of Results

Recommended operating parameters for the three eluting agents are given in Table X. DTPA is slightly superior to HEDTA for separation of the light rare earths because less elution distance is required and the product concentration is 25% higher. As a result, the elution time cycle is shorter. Both DTPA and HEDTA are superior to EDTA, mainly because of shorter time cycles to achieve comparable results. In addition, H^+ can be used as the barrier ion with both DTPA and HEDTA; whereas, a metal ion, such as Zn^{+2} , must be used with EDTA.

TABLE X

RECOMMENDED OPERATING PROCEDURES

	DTPA	HEDTA	EDTA
Molar Concentration	0.026	0.03 to 0.04	0.012
Eluant pH	5.5 to 6.5	5.0 to 5.5	8.4 to 8.6
Eluant Flow Rate, ml/min-cm ²	4.0	4.0 to 5.0	3.0
Elution Temperature, C	60 to 70	60 to 70	60 to 70

If significant amounts of Y^{+3} or Pb^{+2} are present in the feed solution, either EDTA alone or a sequence of DTPA and then EDTA is recommended. There are several specific advantages to using DTPA during the first part of any elution. If EDTA is used first, the feed solution acid concentration must be in the range of pH 1.5 to 5.

If the acid concentration is higher, some H^+ will load on the absorption column and result in the precipitation of the acid form of EDTA in the resin bed on elution. Since acid forms of both HEDTA and DTPA are reasonably soluble, H^+ can be used as the barrier ion and the con-

sequence of H^+ loading on the absorption bed, because of high feed solution acid conditions, is only a loss of capacity. Since the Ce-Pm separation coefficient is much larger with DTPA than with EDTA or HEDTA, an initial "rough" separation from cerium can be achieved much faster with DTPA than with the other eluting agents. After the initial discard of the La-Ce-Pr end of the feed spectrum, the loaded resin can be water washed and eluted down a Zn^{+2} cycle resin bed with EDTA to bring about a complete separation from Y^{+3} or Pb^{+2} , if they are present. If Y^{+3} or Pb^{+2} are absent, there is no incentive for switching eluting agents.

Chemical Costs

In the type of process described by this report, the chemical costs will be small compared to general operating costs. From an operating point of view, it is unimportant whether the resin is preconditioned with HNO_3 and washed with water or with $Zn(NO_3)_2$ and washed with water. Any significant difference is, therefore, in the direct chemical costs.

They are approximately as follows:

	<u>Cost/mole, \$</u>
DTPA	1.29
EDTA-Zn	1.07
HEDTA	0.92

The EDTA- Zn^{+2} system is actually a little less expensive than the DTPA- H^+ system because DTPA costs more per pound and has a higher molecular weight.

SUGGESTED FLOW SHEET AND EQUIPMENT FOR A PROMETHIUM PURIFICATION PLANT

A suggested column arrangement and flow sheet for a modest sized purification plant (currently being installed in a hot cell at Battelle-Northwest) are shown in Figure 2. The columns would each be jacketed and thermostated for operation at 65 C. The height of the columns would need to be 10 to 11 ft to

allow some space above the resin bed. In-line detection equipment on the effluent line from each column and suitable valving are needed but are not shown. Dowex 50W, X-8 (50 to 100 mesh) resin has reasonable properties and would be in the H^+ cycle before start of the run. If it does not prove to be kinetically limiting, Dowex 50W, X-12 (50 to 100 mesh) resin would be better because of its superior resistance to radiolysis. Similar resins by other manufacturers should also be considered. The final choice of the resin should be based not only on cost and availability but also upon its capacity, exchange kinetics

and resistance to radiolysis. Such a study has not, as yet, been completed.

In operation, feed solution would be pumped down-flow through the 8 in. absorption column and to waste at a rate of 4 to 5 liters/min until the effluent detector indicated activity. At that point, the effluent would be diverted back to the feed tank and absorption cycle continued until the detector indicated complete breakthrough. The feed cycle is then terminated and the loaded resin washed free of unabsorbed feed with distilled water. Promethium losses are eliminated by

Run Conditions:

Elution Temperature	65 C
Elution Flow Rate	4 ml/min-cm ²
Rate of Band Advance	10 cm/hr

Run Cycle Time

Absorption Cycle	4 hr
Elution Cycle	180 hr
Turn Around Time	72 hr

Length of Promethium Band on 1 in. Column, 400 cm
Pure Promethium Product per Run, 200 g (186,000 Ci)

FIGURE 2

Promethium Purification Flowsheet

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 absorption column in series with the first 4 in. diam elution column and pumping the DTPA solution down-flow through the two columns at a rate of 4 ml/min-cm². The effluent from Column 2 is sent to waste until the detection equipment indicates the presence of Eu¹⁵⁴ in the effluent. Column 3 is then added to the system. Column 1 (the absorption column) is disconnected from the system when the effluent line detection equipment indicates that the promethium content in the effluent has decreased to an acceptable waste level. The column is then stripped free of the remaining rare earths. This sequence of adding columns ahead of the band and removing them from behind the band is continued. At least half of the Ce-La will be left behind on Column 1 and sent to waste. The remaining Ce-La and a large fraction of Pr-Nd would go to waste at the bottom of column 2. As the promethium collects into a compact band, the unwanted material is cut off the rear end of the band by appropriate valve manipulations. It would be wise to elute most or all of the Eu¹⁵⁴ and some samarium to waste at the bottom of Column 3. By this time Eu¹⁵⁴ is not needed as a guide to detect the front edge of the absorbed band.

On continued elution, promethium solution will flow from the bottom of Column 6 in a manner similar to the elution curve shown for neodymium in Figure 1. The promethium concentration will be 2.3 g/liter and can be recovered from the pure "center cut" by an oxalate precipitation. After acidification, the impure promethium contained in the ends of the promethium band can be pumped back to the absorption column during the first part of the subsequent run.

With the type of flow sheet described, essentially all of the polyvalent ions in the feed solution absorb on the resin in the absorption column. The capacity of the equipment, per run, is therefore determined by the ratio of promethium to other polyvalent ions in the feed solution and the volume of resin in the absorption column. The absorption capacity of Dowex 50W, X-8 (50 to 100 mesh) resin is approximately 1.9 g equivalents per liter of H⁺ cycle resin, measured in water. In a feed solution aged 2.6 yr to allow for the removal of Pm¹⁴⁸ by decay, promethium represents 2.3 wt% of the fission product rare earths. If a cerium removal step is used prior to ion exchange, the percent promethium is increased to 3.2 wt%. Any non rare earth polyvalent cation impurities present in the feed reduce the amount of promethium that can be absorbed per run. The capacity of the equipment shown in Figure 2 of 200 g promethium per run assumes a feed low in polyvalent ionic impurities but without a prior cerium removal step. Promethium solutions meeting these qualifications have been prepared by the Chemical Processing Department of the General Electric Company at Hanford.

Promethium of 99.99% chemical purity from all elements is attainable. However, since Pm¹⁴⁷ decays to stable Sm¹⁴⁷ at a rate of 2.2% per month, there is little practical advantage in preparing promethium of a purity greater than about 99.5%. Table XI

TABLE XI

DEMONSTRATED PROMETHIUM PURITYChemical Purity

99% at time of separation
(Pm¹⁴⁷ decays to stable Sm¹⁴⁷
at a rate of 2.2%/month)

Radiochemical Purity

< 1000 disintegrations/min total α/Ci Pm¹⁴⁷
10⁻¹¹ Ci Eu¹⁵⁴/Ci Pm¹⁴⁷
No other activities detectable

shows the chemical and radiochemical purities that were achieved for the 13,000 Ci of promethium purified in this laboratory in 1963. The vanishingly small amounts of alpha emitters and of Eu^{154} conclusively demonstrate that users of promethium need not be concerned with Eu^{154} in their planning.

FUTURE WORK

An ion-exchange separation facility of the size shown in Figure 2 is being installed at the present time in one of the manipulator cells of the Battelle-Northwest High Level Radiochemical Facility. Fabrication of the individual components is complete. Installation in the cell will be complete and the first promethium run initiated during the first part of F. Y., 1965. Fully aged promethium feed is being prepared and set aside by the General Electric Company's Chemical Processing Department for final purification.

The promethium facility will be used to extend the results of this report to full-level feed. In particular, the optimum elution distance consistent with early discard of the bulk of the unwanted rare earth to waste will be determined. Optimum elution time cycles will be determined. An evaluation of the effect of radiation on several candidate resins will allow both the choice of a "best" resin and determination of the number of run cycles the resin can be used before discard. Several types of in-line instrumentation will be used and evaluated.

During the above described experimental work, kilogram quantities of pure promethium will be made available. In a glove box facility which is under construction, the technology will be developed for converting the pure promethium product solution to encapsulated heat sources of candidate heat source materials such as metal and oxide. The technology for large-scale preparation of pure

promethium metal will be perfected. The technology for preparation of high density Pm_2O_3 sources by pneumatic impaction⁽¹⁴⁾ will be tested. Welding techniques and the compatibility of promethium and Pm_2O_3 with potential capsule materials will be determined.

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