PURIFICATION OF PROMETHIUM BY

LIQUID-LIQUID EXTRACTION

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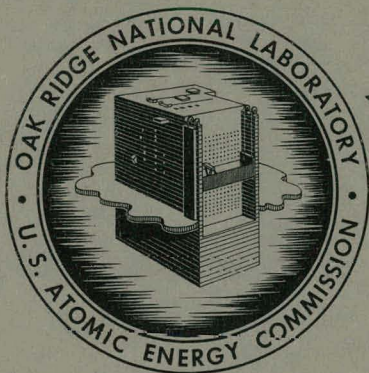
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Boyd Weaver and F. A. Kappelmann

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ABSTRACT

A process was developed for separating promethium from mixed fission product rare earths by continuous multistage countercurrent extraction with 100% tri-$\underline{n}$-butylphosphate from nitric acid of 12 $\underline{N}$ or higher concentration. Distribution coefficients at 12 $\underline{N}$ acidity for neodymium, promethium, and samarium are 0.43, 0.82, and 1.55, respectively. Single-stage separation factors of 1.9 between successive elements can be maintained throughout the system to give separations dependent only on the number of stages. Extracted values can be recovered from the organic solution by stripping with a smaller volume of dilute nitric acid.

A flowsheet for purification of promethium includes one cycle for separation of promethium from neodymium and lighter elements and a second cycle for removal of samarium and heavier elements. Each cycle consists of a series of countercurrent partitioning stages, followed by stripping stages and an evaporator. With 20 stages in the first cycle and 34 stages in the second, a 90% yield of promethium with a purity of 83% can be obtained from a typical mixture of fission product rare earths, assuming essentially perfect mechanical efficiency. An increase to 34 stages in the first cycle would permit a 93% yield of 99% promethium.

CONTENTS

1.0 INTRODUCTION

This report describes the development of a process for separating the synthetic element promethium from the other fission product rare earths. The process is to be applied on a production scale by the Isotopes Division of the Oak Ridge National Laboratory. The order and nature of experiments performed were affected considerably by changes in aims and needs indicated by those interested in application. Chronologically these aims were: removal of yttrium in order to obtain less radioactive feed material for ion exchange columns; removal of lanthanum, praseodymium and most of the neodymium in order to decrease the bulk and increase the promethium capacity of ion exchange columns; and, finally, production of promethium of required purity by a two-cycle extraction process alone. The process adopted for cerium recovery also removed most of the yttrium, and the feasibility of promethium purification by extraction became more obvious as this study progressed. The feasibility of purifying promethium on a large scale depends on the maintenance of theoretical separation factors throughout a long series of stages, the absence of a buildup of rare earths sufficient to noticeably decrease distribution coefficients in any part of the system, and the quantitative stripping of the extracted elements from the organic stream into a reasonable volume of dilute nitric acid.

The nature of the equipment used for multistage experiments and its location were such that processing of radioactive materials was not feasible. Therefore no promethium was present in any of these experiments. However, single-stage experiments established the relation between promethium and the neighboring elements well enough that accurate information for promethium can be obtained by interpolation in data obtained from mixtures of neodymium and samarium. The accuracy of multistage data was limited by the accuracy of spectrographic analysis.

This phase of the development was carried only to the point that feasibility of a suggested flowsheet appeared to have been established and assemblies of stainless steel Knowles-type mixer settlers became available in the Isotopes Division. At this point development was transferred there. Preliminary tests with individual tracer elements have confirmed predictions made from the results of experiments reported here.

Peppard et al.[1] first reported the separation of rare earths by extraction with tributyl phosphate from concentrated nitric and hydrochloric acids. Distribution coefficients, i.e., ratios of concentration in the organic phase to concentration in the aqueous phase, increased with acidity.

Separation factors, i.e., ratios of distribution coeffi-
cients, between successive rare-earth elements in the fission
product range were about 1.9 with acidities above 10 $\underline{N}$ HNO_3.
Much information concerning these extractions and separations
has been contributed by McKay et al.[2] Spedding et al.[3]
studied the separation of rare earths in concentrated solu-
tions of low acidity. In this laboratory natural rare earths
have been separated on a kilogram scale by Weaver et al.[4]
Brezhneva[5] et al. report a multistage distributive separation
of fission product rare earths.

The authors gratefully acknowledge the very careful
second-shift operation of the separation cascade by J. P.
Eubanks. R. E. McHenry was helpful in keeping the course of
the investigation related to the prospective needs of the
Isotopes Division. Spectrographic analyses were devised and
performed by J. A. Norris and associates in the Analytical
Chemistry Division. Tracer distribution data were obtained
by Janet Debnam and J. P. Eubanks.

2.0 FLOWSHEET

A two-cycle flowsheet was devised on the basis of data
obtained in a laboratory-scale study (Fig. 1). Indicated
flow rates for the first cycle are a 10-fold scaleup of those
suitable for the experimental equipment. The second cycle
fits the experimental equipment and is adequate to handle the
product of the first cycle. There are no chemical limita-
tions on scaleup to a production plant.

One conspicuous lack in the above flowsheet is the
number of stages in each separations cascade. The production
plant of the Isotopes Division has 20 stages in the first
cascade and 34 stages in the second. The first cascade is
limited to a separation factor of ~500 between promethium and
neodymium, while the 34 stages of the second cascade allow a
factor of ~35,000 between samarium and promethium. The yield
and/or purity of the promethium is severely limited by the
small number of stages in the first cascade. The first sec-
tion of Table 1 shows one calculated possible result of oper-
ation of this cascade. The yield of promethium was arbi-
trarily set at 90% in the first cycle and the samarium
removal at 99% in the second. Attainable separations are
calculated from a single stage separation factor of 1.85
between successive elements. Quantities are based on feed
containing 1000 g of mixed fission product rare earths. The
composition of the feed material is calculated from the
expected results of removing cerium from a mixture of arbi-
trary but possible composition. An increase to 25 stages in
the first cascade allows an increase in promethium purity
to 93% (Table 1, middle section). There is more need for
high separation power in the first cycle than in the second

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Feed – 25 g RE/liter 12.5 N HNO$_3$

0.5 liter/hr

TBP (equilibrated
with 12 N HNO$_3$)
25.4 liter/hr

Product in TBP
(Pm, Sm, Eu, Gd, Y)

1st Separations Cascade

12 N HNO$_3$
14.5 liter/hr

Waste (15 liter/hr)
(La–Nd)

2 N HNO$_3$,
8.5 liters/hr

10-Stage Stripper

Stripped TBP
to Recycle

HNO$_3$ Distillate

Evaporator

0.1 liter/hr, Adjusted to 12.5 N HNO$_3$

TBP (equilibrated
with 12 N HNO$_3$)
1.77 liter/hr

2nd Separations Cascade

Waste to Stripper
(Sm, Eu, Gd, Y)

12 N HNO$_3$
1.9 liter/hr

2.0 liter/hr
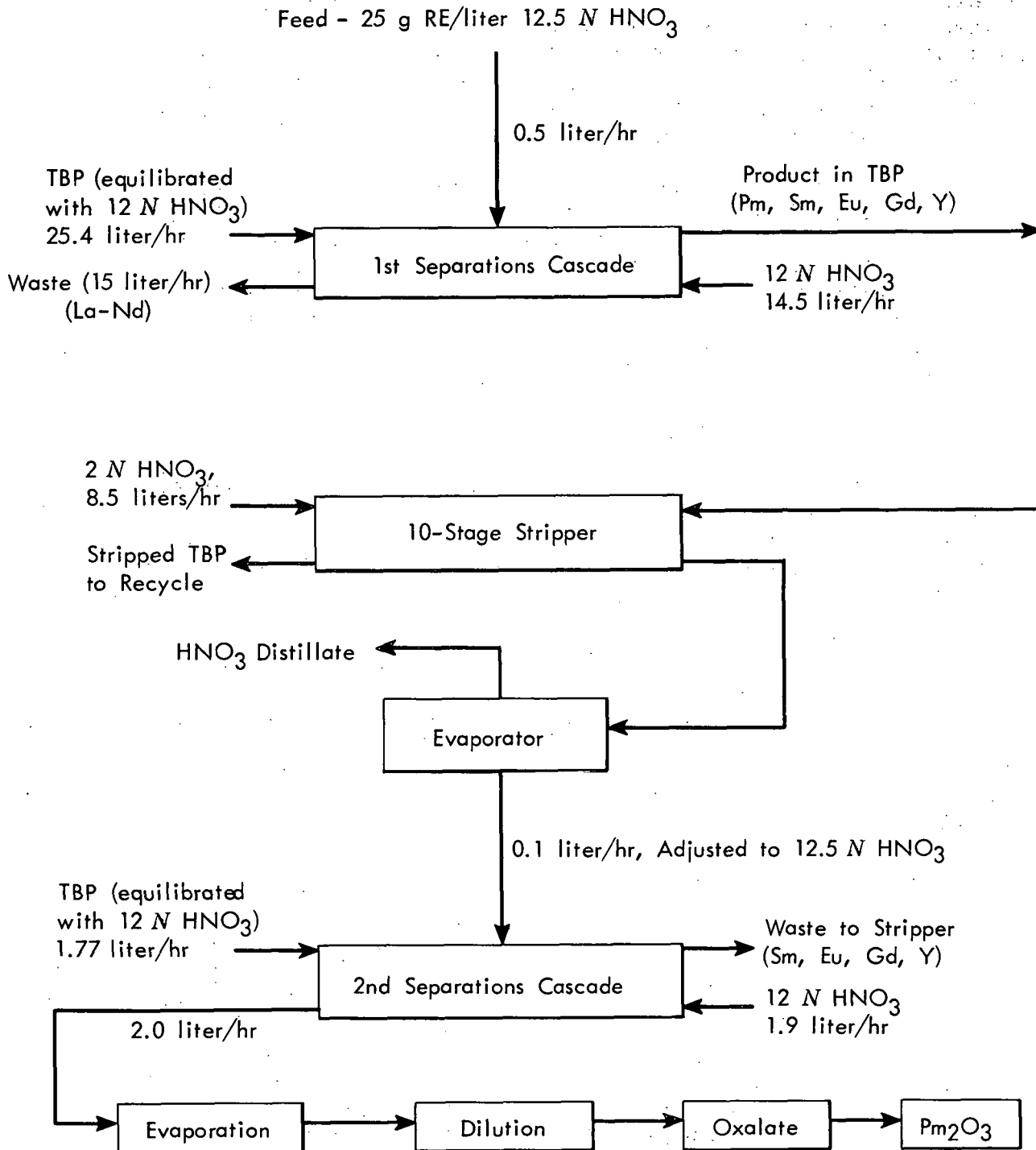
Evaporation → Dilution → Oxalate → Pm$_2$O$_3$

Fig. 1. Promethium purification flowsheet.

Table 1. Calculated Material Balance

in Promethium Purification

34 stages in 2nd cycle

Element	Feed, g	1st Cycle Waste, g	1st Cycle Product, g	2nd Cycle Waste, g	2nd Cycle Product, g
20 Stages in 1st cycle, Pm Yield 90%, Purity 83%					
La	142	142	–	–	
Pr	142	142	–	–	
Nd	537	527	10.1	–	10.1
Pm	63	6.3	56.7	0.16	56.5
Sm	108	0.025	108	107	1.1
Eu	3.6	–	3.6	3.6	1×10^{-6}
Gd	0.7	–	0.7	0.7	–
Y	3.3	–	3.3	3.3	–
	1000	817	182	115	68
25 Stages in 1st cycle, Pm Yield 90%, Purity 93%					
La	142	142	–	–	–
Pr	142	142	–	–	–
Nd	537	534	3.3	–	3.3
Pm	63	6.3	56.7	0.16	56.5
Sm	108	–	108	107	1.1
Eu	3.6	–	3.6	3.6	1×10^{-6}
Gd	0.7	–	0.7	0.7	–
Y	3.3	–	3.3	3.3	–
	1000	824	176	115	61
34 Stages is 1st Cycle, Pm Yield 93%, Purity 99%					
La	142	142	–	–	–
Pr	142	142	–	–	–
Nd	537	537	0.3	–	0.3
Pm	63	3	60	0.7	59
Sm	108	–	108	108	0.3
Eu	3.6	–	3.6	3.6	5×10^{-8}
Gd	0.7	–	0.7	0.7	–
Y	3.3	–	3.3	3.3	–
	1000	824	176	116	60

because neodymium is the major constituent of the original mixture. With 34 stages in each cascade it would be possible to obtain a 93% yield of 99% promethium (Table 1, bottom section).

While this flowsheet is based on 12 $\underline{N}$ HNO_3, operation at higher acidity is feasible. Relative flow rates would be different with a smaller organic flow, but separation factors would be only very slightly higher. Suitable flow rates for any acidity for which distribution coefficients are known can be calculated without further experiments.

3.0 EXPERIMENTAL

3.1 Apparatus and Techniques

Single-stage data were obtained by contacting prepared phases in separatory funnels, separating the phases, pipetting 2-ml samples of each phase into a culture tube with a cork stopper, and measuring the gamma activity in a well-type scintillation counter. Tracers used were Nd^{147}, Pm^{148}, and Sm^{153} obtained from Isotopes Division stocks. Nitric acid concentrations were determined by titrating the 2-ml samples in water with standard 1 $\underline{N}$ NaOH to a methyl orange end point. Distribution coefficients were ratios of counts per unit time in the two phases.

The basic unit of the multistage extraction system was a glass mixer-settler (Fig. 2). The desired number of these units were connected in series by Tygon tubing containing an adjustable gravity leg for control of the interface height in each stage. The central pumping impeller and mixing blades were powered by a 0.01-hp Bodine motor attached to each shaft by tubing. Since the impeller in this mixer-settler pumps whatever liquid becomes available to it, there was no internal control of the flow rates. The most frequent cause of interruption was the breakage of glass shafts. The process streams were supplied by Milton Roy proportioning pumps and microbellows pumps. The chief activity of the operator was the checking of flow rates by measuring feed or effluent volumes. Evaporators were continuous and were constructed of glass pipe with steam-heated tantalum fingers. There was sufficient difficulty in maintaining constant flow rates into the system and uninterrupted flow through all the mixer-settlers that attainment of equilibrium was far from routine. In several experiments the full efficiency of the chemical system was not obtained from the mechanical system. Moreover, lack of equilibrium was not always obvious and became evident only on later analysis. With the low concentrations used in most of these experiments, adequate sampling required termination of experiments and the use of large fractions of the total volumes as samples. In each experiment at least 25 hr of steady operation were allowed for attainment of equilibrium.

3.2 Single-stage Data

Extraction of both neodymium and promethium increased with acidity up to about 4 $\underline{N}$ HNO_3 and then decreased slowly
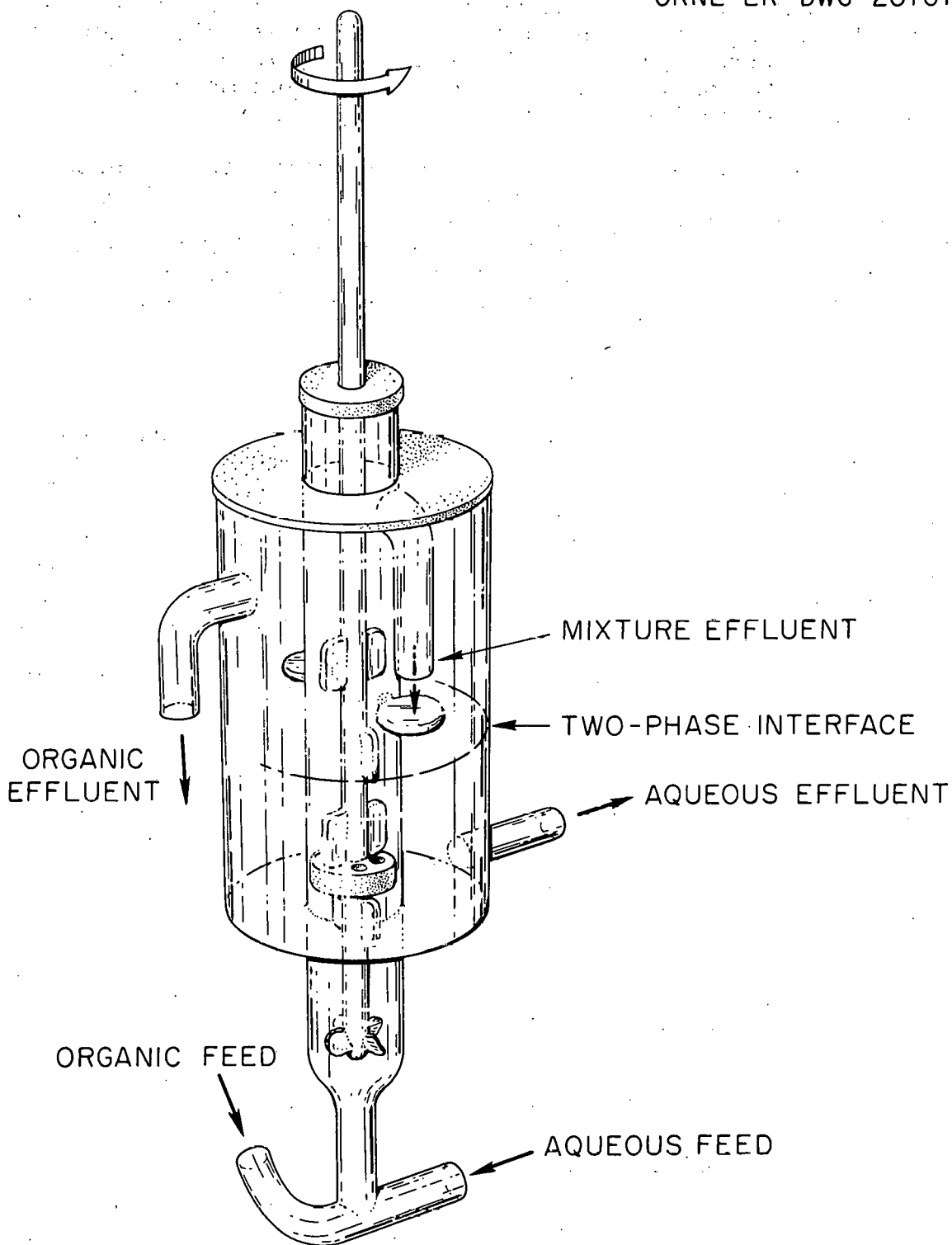
Fig. 2. Pump mixer-settler.

to nearly 8 $\underline{N}$ HNO$_3$, before increasing rapidly with higher acidity (Fig. 3). The extraction coefficient of samarium from about 12 $\underline{N}$ acid has been measured repeatedly. Readings from these curves give coefficients of 0.43, 0.82, and 1.55, respectively, for neodymium, promethium, and samarium. The calculated separation factor for both pairs is 1.9.

In the middle acid range, coefficients are low enough to permit stripping of the rare earths from the TBP by a volume of acid equal to or somewhat less than the volume of TBP. Since nitric acid distributes between TBP and water, its countercurrent stripping maintains the acidity in a suitable range for stripping the rare earths if the proper flow ratios are used.

3.3 Eleven-stage Experiments

In the first experiment, designed (Table 2, part a) to determine the separability of yttrium from neodymium, 99% of the yttrium was concentrated in the extract, which contained only 7% of the total feed. The apparent absence of neodymium in the extract prevented the calculation of separation factors between neodymium and other elements. Analysis of both phases in 6 of the 11 stages (Fig. 4) showed that the highest concentration in any stage was less than 2 g of RE$_2$O$_3$ per liter. This is less than 1% of the loading capacity of TBP. The highest concentration was at the feed point.

In a second experiment the organic/aqueous flow ratio was increased in order to measure the separation between samarium and neodymium (Table 2, part b). The indicated overall separation factor between samarium and neodymium is 880, or 3.42 per stage. The corresponding calculated Sm/Pm and Pm/Nd factors are 1.85. This is very near the experimental single-stage value of 1.9, indicating a high efficiency in the separation system.

When the feed point was at stage 9, the maximum concentration of total rare earths remained at this point (Fig. 5), but the concentration of neodymium was at a maximum nearer the middle of the cascade (Fig. 6). The neodymium concentration decreased rapidly above the feed point.

3.4 Twenty-stage Experiments and Data

When it became certain that the Isotopes Division would have equipment with 20 stages for separation of promethium from neodymium, experiments were performed with 20 glass mixer-settlers. Flow rates were chosen (Table 3) so as to split between promethium and neodymium, on the basis that their distribution coefficients from 12 $\underline{N}$ HNO$_3$ were 0.95 and 0.46, respectively. Though there is considerable uncertainty
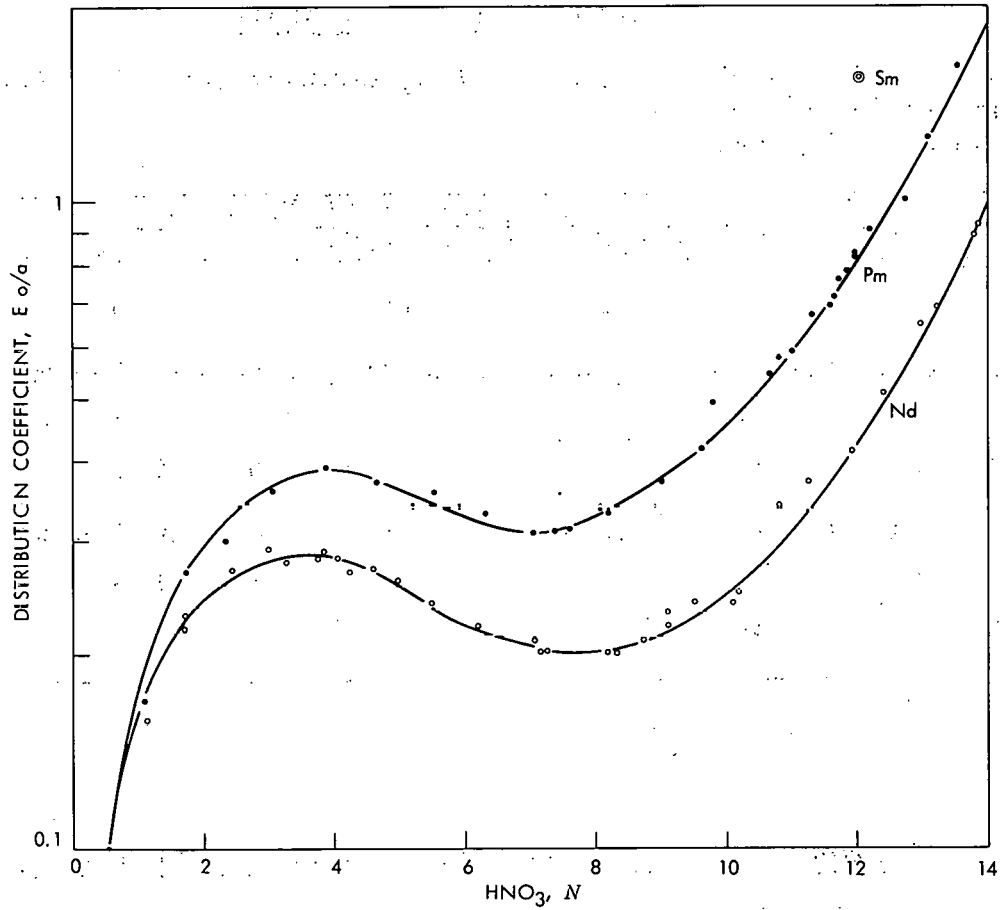
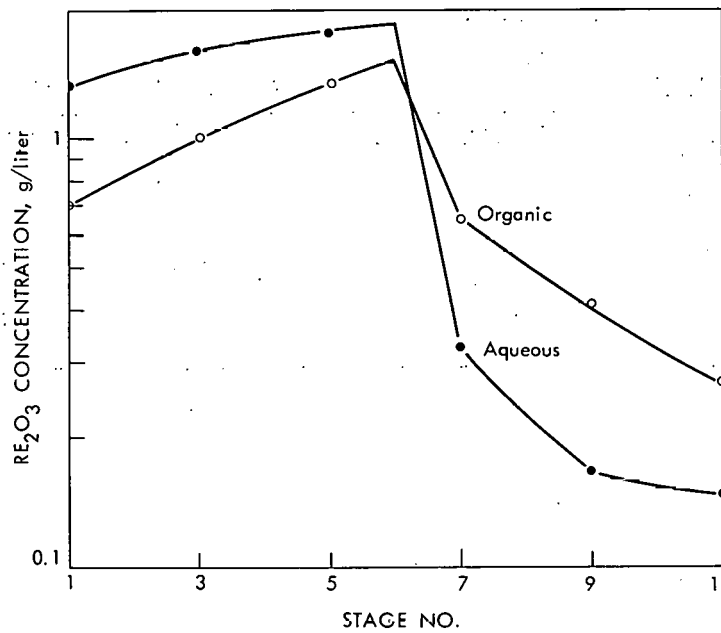Fig. 3 Extraction of neodymium, promethium, and samarium by pure TBP from HNO_3.

Fig. 4. Rare earth concentration profiles in 11-stage cascade feed in stage 6.

Table 2.   Eleven-stage Separation of Neodymium from
(a) Yttrium and (b) Samarium

Feed: 250 ml/hr of 12.5 $\underline{N}$ HNO$_3$ containing 2.5 g RE$_2$O$_3$
Organic: 100% TBP
Aqueous: 12 $\underline{N}$ HNO$_3$

Stream	RE$_2$O$_3$, g/hr	La$_2$O$_3$	Pr$_6$O$_{11}$	Nd$_2$O$_3$	Sm$_2$O$_3$	Eu$_2$O$_3$	Gd$_2$O$_3$	Dy$_2$O$_3$	Y$_2$O$_3$
				Analysis, % of Total RE$_2$O$_3$					
Feed	2.5	15	3.3	61	14	0.15	0.4	–	5.5
(a) Feed into Stage 6; organic 600 ml/hr, aqueous 1500 ml/hr									
Organic	0.178	–	–	–	8.8	0.3	5.2	0.3	86
Raffinate	2.24	15	4.4	67	12.8	0.05	0.1	–	<0.1
(b) Feed into Stage 8; organic 1100 ml/hr, aqueous 950 ml/hr									
Organic	0.5	–	–	8.7	59	0.14	1.8	–	30
Raffinate	2.0	20	5	74	0.57	–	–	–	–

Table 3.   Twenty-stage Separation of Samarium from Neodymium

Feed: 250 ml/hr of 12.5 $\underline{N}$ HNO$_3$ containing 2.5 g RE$_2$O$_3$
Organic: 1000 ml/hr TBP pre-equilibrated with 3 $\underline{N}$ HNO$_3$
Aqueous: 850 ml/hr 12 $\underline{N}$ HNO$_3$

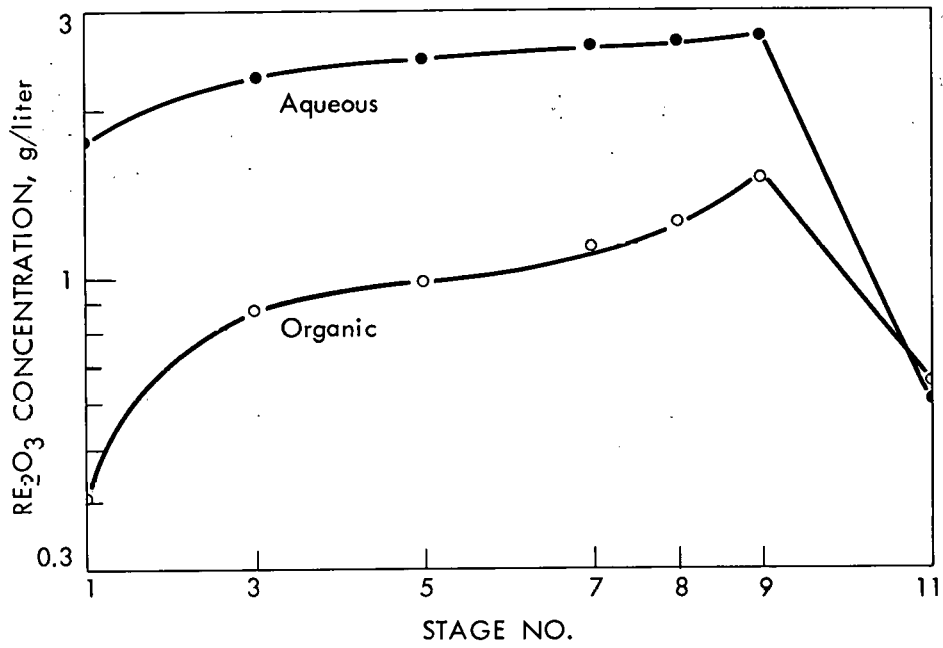| Stream	RE$_2$O$_3$, g/hr	La$_2$O$_3$	Pr$_6$O$_4$	Nd$_2$O$_3$	Sm$_2$O$_3$	Y$_2$O$_3$
			Analysis, % of Total RE$_2$O$_3$			
Feed	2.5	17	4	60	15	5.5
Organic	0.48	–	–	2	71	27
Aqueous	2.02	20	3	77	0.02	–

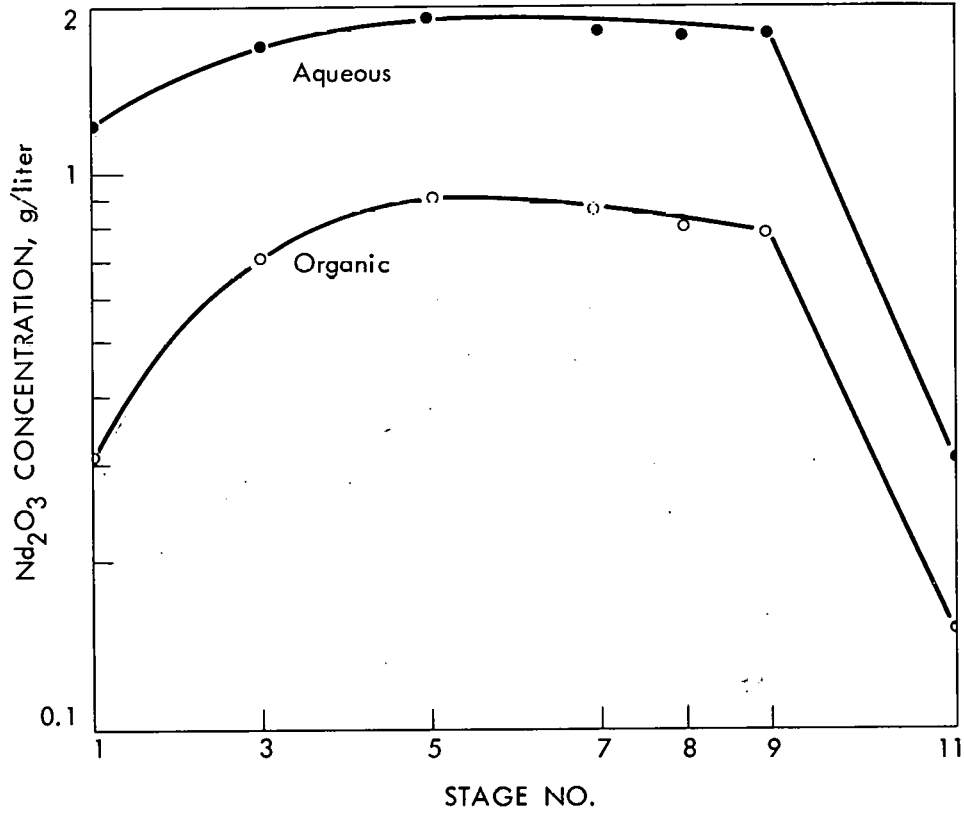Fig. 5. Rare earth concentration profiles in 11-stage cascade, feed in stage 9.

Fig. 6. Neodymium concentration profiles in 11-stage cascade, feed in stage 9.

in the small value of 0.02% Sm_2O_3 in the raffinate, the indicated overall Sm/Nd separation factor is ~100,000, or nearly 3.2 per stage. This approaches the experimental single-stage value. Analysis of both phases of 13 of the 20 stages (Fig. 7) showed that the highest concentration in the solvent was only 0.8 g of RE_2O_3 per liter.

Experiments were performed to obtain data to be used as a guide in determining the proper feed points for specific yields and purities. In most of these experiments imperfect performance of one or more of the mixer-settlers prevented attainment of equilibrium and full efficiency of the system and decreased usefulness of the data. However, this information can be calculated as accurately as it can be determined with perfectly efficient apparatus.

3.5 Thirty-four-stage Experiment and Data

The Isotopes Division has 34 stages available for the separation of samarium from promethium. Two experiments were performed in the glass apparatus with 34 stages, though the separation expected was too high for measurement. A small difference in the organic flow rate (Table 4) made a marked difference in the amount of samarium extracted. In neither case was enough neodymium extracted to make possible a calculation of a separation factor.

3.6 Stripping

Stripping from the organic phase was studied. Extraction data indicate that stripping should be maximum with aqueous acidities between 5 and 8 N and that in 10 stages stripping should be essentially complete with organic/aqueous flow ratios up to 4. The acidity of the stripping solution will increase toward the stage from which it leaves the system, with the acid level depending somewhat on the acidity of the original strip solution but more on the flow ratio. When the organic effluent from a 20-stage separation experiment was stripped in 10 stages with 1/4 volume of 4 N HNO_3, the final acidity of the strip solution was nearly 10 N (Fig. 8). Stripping with 2 N HNO_3 gave a slightly less acid effluent. It appears advisable to maintain an aqueous/organic ratio of at least 1/3, though the spectrographic laboratory reported that no rare earths were detectable in the TBP from the stripping experiment.

4.0 DISCUSSION

The separation of natural rare earths is limited by concentration effects. Rare earths are extracted by formation of complexes with TBP of the form $RE(NO_3)_3 \cdot 3TBP$. Pure TBP is approximately equivalent to a 1 M rare earth solution. Distribution coefficients are constant only at low concentrations
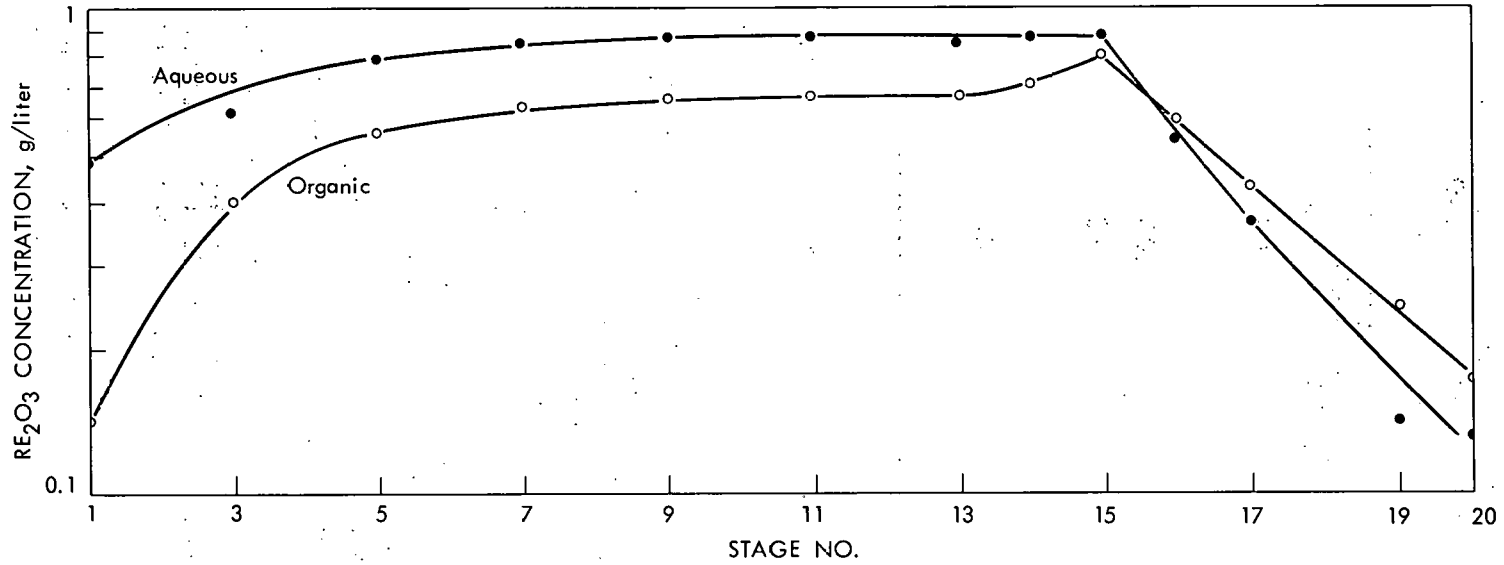
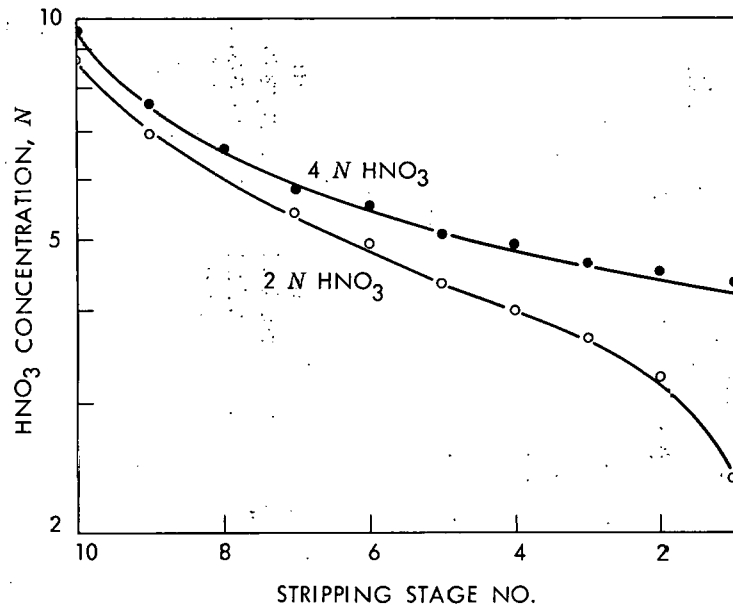Fig. 7. Rare earth concentration profiles in 20-stage cascade.

Fig. 8. Profile of stripping acidity.

Table 4. Thirty-four-stage Separation
of Samarium from Neodymium

Feed: 100 ml/hr 12.5 $\underline{N}$ HNO$_3$ containing 4.0 g RE$_2$O$_3$
Organic: 100% TBP pre-equilibrated with 12 $\underline{N}$ HNO$_3$
Aqueous: 1900 ml/hr 12 $\underline{N}$ HNO$_3$

Stream	RE$_2$O$_3$, g/hr	Analysis, % of Total RE$_2$O$_3$	
		Nd$_2$O$_3$	Sm$_2$O$_3$
Feed	4.0	6	94
(a) Organic 1520 ml/hr			
Organic	2.28	–	100
Aqueous	1.64	22	78
(b) Organic 1770 ml/hr			
Organic	4.03	–	100
Aqueous	0.22	96	4

and decrease as loading of the solvent increases (Fig. 9) In
extractions from as little as 0.1 $\underline{M}$ rare earth nitrate, the
effective free reagent concentration is decreased by 10%. With
a third-power dependency of extraction coefficients on reagent
concentration, there is considerable variation in coefficients
throughout a multistage system, greatly decreasing its effi-
ciency. This effect increases with atomic number and the con-
sequently greater extractability. Therefore, the lighter and
more abundant elements are more easily separated than are the
heavier and rarer ones.

In the separation of fission product rare earths, the
disadvantages of liquid extraction are greatly diminished.
The value of the material is measured in curies of activity
rather than in weight units. Highly active solutions can be
obtained without excessive loading of the extractant. Only
the lighter rare earths and yttrium are present. There is no
great localization of activity as in the case of ion exchange,
but effluent concentrations and flow rates may be higher.
Extracted values may be stripped from the TBP by dilute nitric
acid, and all aqueous nitrate solutions may be concentrated to
any desired degree by evaporation.

The purpose of this investigation was not to demonstrate
the efficiency of any given contacting device but to determine
whether the separation factors indicated by single-stage dis-
tribution data can be extended to a multistage system, and to
obtain some information on the limitations on concentrations,
and consequently on throughput capacity, and on necessary
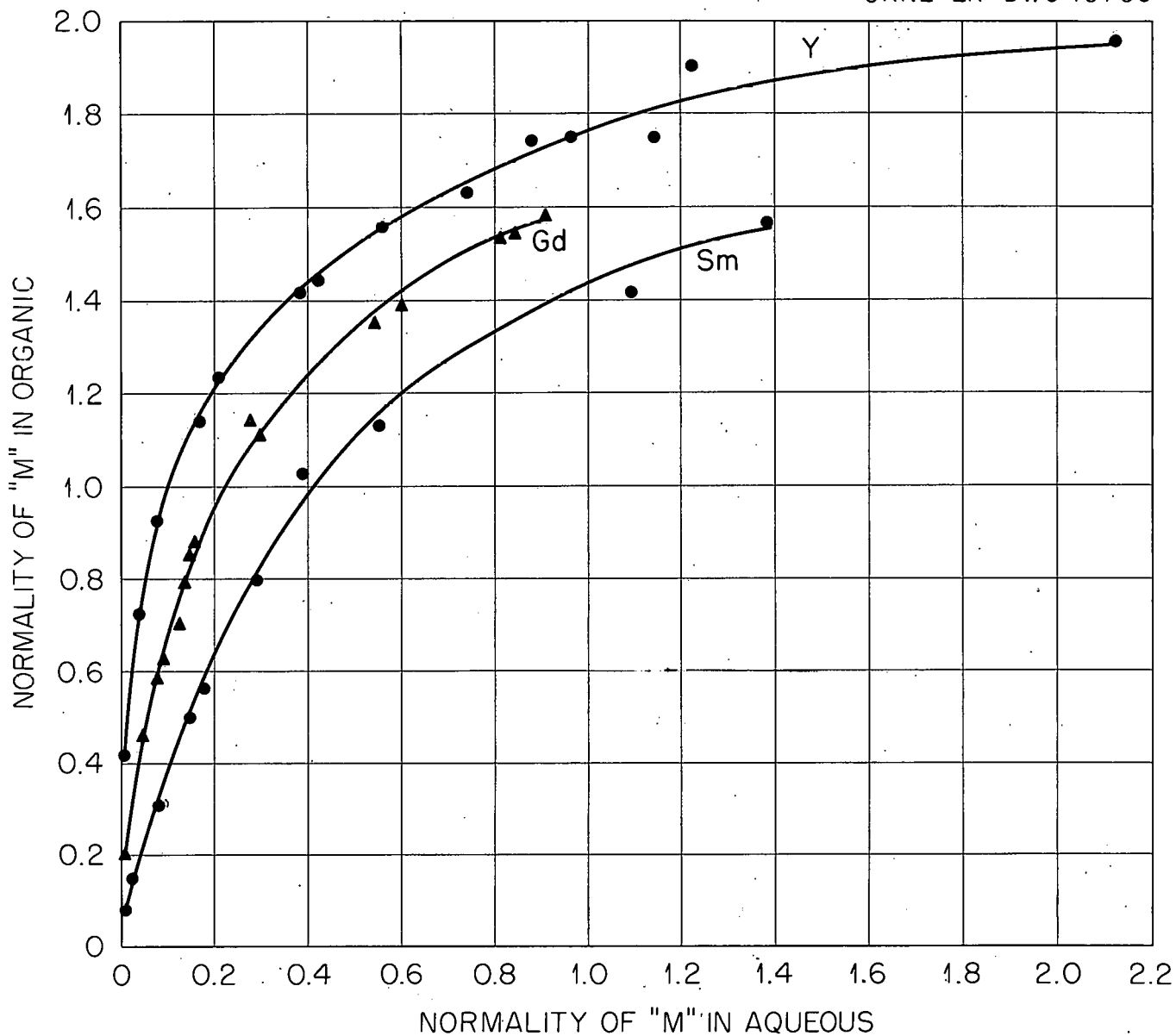
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Fig. 9. Distribution of elements between TBP and 14.2 N HNO$_3$.

ratios of stripping solutions to organic flow. The most
likely hindrance to full efficiency in the separation cascade
would be excessive buildup of concentration around the feed
point from internal reflux. The attainment of theoretical
separation in an experiment would indicate complete effi-
ciency of all stages in the separation device and confirm the
soundness of the predictions from single-stage data. These
aims were realized or closely approached in several experi-
ments. Though effective separations were accomplished with
feed flows up to one-fifth of the total aqueous flow and with
concentrations up to 2.5 g/liter, the slight buildup of con-
centration around the feed point indicates the advisability
of limiting feed flows to 5% of the total aqueous flow and
aqueous concentrations in the cascade to 1 g/liter. This is
adequate for separation of large quantities of promethium in
reasonably small equipment.

Distribution of elements and separation between them in
a liquid-liquid extraction system are governed by simple
arithmetical relations. The distribution coefficient, E_a^O, of
a given element is the ratio of its concentration in the
organic phase to that in the aqueous phase at equilibrium.
The separation factor between two elements, α, in a given
system is the ratio of their distribution coefficients; i.e.,
$\alpha_{1,2} = E_1/E_2$. In a single-stage distribution of an element,
the ratio of quantities in the two phases is the product of
the distribution coefficient and the ratio of organic and
aqueous volumes; i.e., $E_a^O \times V_o/V_a$. In a multistage counter-
current system with continuous feed at an intermediate stage
and takeoff at both ends, an element tends to appear prefer-
entially in the organic effluent when $E_a^O V_o/V_a$ is greater
than unity, but in the aqueous effluent, or raffinate, when
this product is less than unity. In a continuous system the
V's represent flow rates rather than volumes. Separation
between a pair of elements can be obtained by adjusting V_o/V_a
so that $E_a^O V_o/V_a$ is greater than unity for one element and
less than unity for the other. The elements will be distribu-
ted symmetrically in the cascade and their ratios in the
effluents will be reciprocals if $V_a/V_o = (E_1/E_2)^{1/2}$ and the
feed point is in the center stage.

In devising a flowsheet for this system, the aim has
been to maintain this arithmetical relation regardless of the
position of the feed point. The distribution of the two
elements at equilibrium will tend to be symmetrical about the
feed point, but the ratios of the two elements in each
terminal stage will depend on the number of stages from the
feed point to this stage. The introduction of a feed results
in different flow ratios, or operating lines, in the two parts
of the cascade. In the present case, compensation can be pro-
vided by increasing the acidity of the larger aqueous flow by
introducing the feed at a higher acidity. This also results

in slightly different equilibrium lines on either side of the feed point. This small effect is neglected in the calculations which follow.

In a continuously producing cascade with no external reflux, a total separative power of n stages is $\alpha^{n/2}$. With total reflux it would be α^n, but there would be no production. This separative power may be distributed to the advantage of purity or yield of either element by shifting the feed point.

One method of determining the location of a feed point that will give a specified yield of one element with a specified limit on contamination by another is the use of McCabe-Thiele diagrams. It is necessary to have sufficient separative power in the cascade and to know the extraction coefficients of the two elements.

Figures 10 and 11 are McCabe-Thiele diagrams by which the proper feed point is determined for a 90% yield of promethium with decontamination from neodymium by a factor of 50. With a single-stage separation factor of 1.85, this separation can barely be accomplished with 20 stages. Figure 10 is the diagram for the promethium yield. The slope of the promethium equilibrium line (E.L.) is 0.82. Since the distribution coefficient of neodymium is 0.43, the ideal operating line (O.L.) is $(0.82\text{x}0.43)^{1/2} = 0.59$. Assuming a feed flow of 0.05 times the total aqueous flow below the feed point, the slope of the operating line above the feed point is 0.56. The ratio of promethium in the extract to that in the raffinate is 9/1. The graphical solution shows that 8 stages or slightly more below the feed point are required for 90% promethium recovery.

Figure 11 is a graphical determination of the number of stages required to reduce the neodymium content by a factor of 50. The slope of the neodymium equilibrium line is 0.43 and the operating lines are the same as above. The graph shows that 11 stages are required above the feed point. The required feed point for a yield of 90% promethium with a 50/1 decontamination from neodymium is in the ninth stage. There are barely 11 stages left out of a total of 20. This agrees with the fact that an overall separation factor of 450 is required and 20 stages give 1.9^{10} or ~600.

When the required overall separation factor is very large, one or both of the diagrams will be difficult to read unless drawn on a large scale. Then a second method of determining the feed point may be more convenient. The point may be calculated as it has been done by Benedict and Pigford[7] for hafnium-zirconium separations. For 95% yield of promethium, with decontamination from samarium by a factor of 200, from a promethium-samarium mixture containing 34% promethium and 61.5% samarium, the solution is as follows:
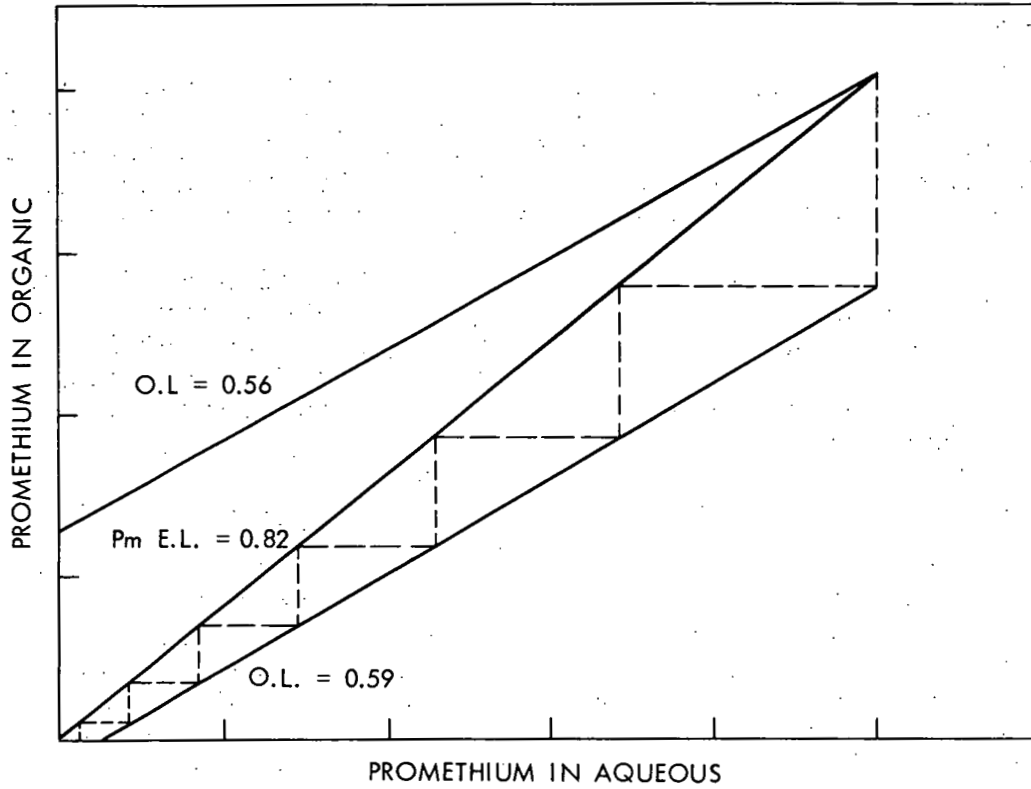
Fig. 10. Determination of feed point for 90% yield of promethium. Arbitrary concentration units.
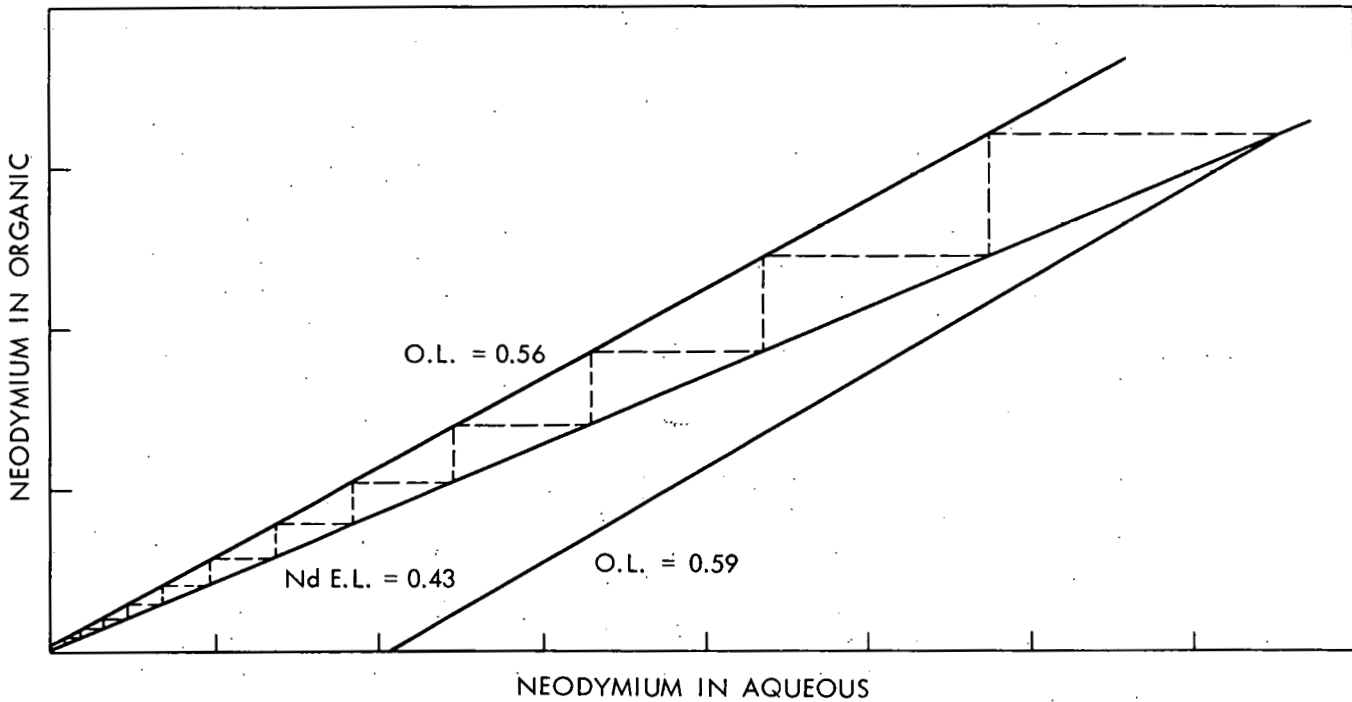

Fig. 11. Determination of feed point for 98% removal of neodymium from promethium. Arbitrary concentration units.

The promethium and samarium extraction coefficients are 0.82 and 1.55. With a feed volume equal to 5% of the total aqueous flow, the operating lines are 1.07 and 1.13 above and below the feed point. For the calculation, the more extractable element, samarium, is regarded as the element to be recovered. While all the stages behave essentially the same in accomplishing separations, the stages from the feed point to the aqueous exit are designated as the extraction section, and those between the feed point and the organic exit as the scrubbing section. Given and derived:

$D_{Sm} = E_a^o$ for Sm = 1.55

$D_{Pm} = E_a^o$ for Pm = 0.82

Aqueous flow, s = 1.9 liters/hr

Feed flow, F = 0.1 liter/hr, containing 4.0 g RE's

Organic flow, E = 1.77 liters/hr

Aqueous feed concentration:

Samarium, x_{Sm}^F = 40x0.615 = 24.6

Promethium, x_{Pm}^F = 40x0.34 = 13.6

Solvent feed concentration:

Samarium, $y_{Sm,o}^E$ = 0

Promethium, $y_{Pm,o}^E$ = 0

Samarium recovery, $\rho = E y_{Sm,1}^S / F x_{Sm}^F$ = 0.995

Promethium decontamination factor, $f = \dfrac{y_{Sm,1}^S / y_{Pm,1}^S}{x_{Sm}^F / x_{Pm}^F} = 19$

Flow ratios, S/E = 1.07

E/(F + S) = 0.885

F/E = 0.056

Number of stages: Extracting, N

Scrubbing, M

Concentrations in organic extract:

Samarium: $y_{Sm,1}^S = \dfrac{\rho F x_{Sm}^F}{E} = 0.995 \times 0.056 \times 24.6 = 1.38$

Promethium: $y_{Pm,1}^S = \dfrac{y_{Sm,1}^S / f}{x_{Sm}^F / x_{Pm}^F} = \dfrac{1.38/19}{24.6/13.6} = 0.40$

Concentrations in aqueous residue (by material balance):

Samarium: $x_{Sm,1}^{E} = \dfrac{(1-\rho)Fx_{Zr}^{F}}{S + F} = \dfrac{0.005 \times 0.1 \times 24.6}{2.0} = 0.00615$

Promethium: $x_{Pm,1}^{E} = \dfrac{Fx_{Pm}^{F} - Ey_{Pm,1}^{S}}{S + F} = \dfrac{0.1 \times 13.6 - 1.77 \times 0.40}{2.0} = 0.65$

Extraction Factors:

Samarium:

Extracting: $\dfrac{D_{Sm}E}{S+F} = \dfrac{1.55 \times 1.77}{2.0} = 1.38$

Scrubbing: $\dfrac{D_{Sm}E}{S} = \dfrac{1.55 \times 1.77}{1.9} = 1.45$

Promethium:

Extracting: $\dfrac{D_{Pm}E}{S+F} = \dfrac{0.82 \times 1.77}{2.0} = 0.73$

Scrubbing: $\dfrac{D_{Pm}E}{S} = \dfrac{0.82 \times 1.77}{1.9} = 0.77$

Solving for samarium in the equation,

$$\frac{(S/ED)^{M+1}-1}{S/ED - 1} \, y_1^S = \frac{[DE/(S+F)]^{N}-1}{[DE/(S+F)]-1} \, (Dx_1^E - y_o^E) + y_o^E$$

$$\frac{(0.69)^{M+1}}{0.69 - 1} \times 1.38 = \frac{(1.38)^{N}-1}{1.38 - 1} \times 1.55 \times 0.00615$$

$$- 4.45(0.69)^{M+1} + 4.45 = 0.0263(1.38)^{N} - 0.0263$$

Neglecting $(0.69)^{M+1}$, a small value,

$$(1.38)^{N} = 170$$

$$N = \frac{\ln 170}{\ln 1.38} = 15.9 \text{ stages}$$

Solving for promethium,

$$\frac{(1.30)^{M+1}-1}{1.30 - 1} \times 0.04 = \frac{(0.73)^{N}-1}{0.73 - 1} \times 0.82 \times 0.65$$

$$0.133(1.30)^{M+1} - 0.133 = -1.97(0.73)^{N} + 1.97$$

Neglecting $(0.73)^{N}$,

$$(1.30)^{M+1} = 15.8$$

$$M+1 = \frac{\ln 15.8}{\ln 1.30} = 10.5$$

$$M = 9.5$$

The calculation indicates that 16 extracting stages and 10 scrubbing stages are required. The calculated separation factor for 26 stages is $1.9^{26/2} = 4200$. The calculated factor from yield and decontamination factors is $19 \times 200 = 3800$. This is a close check. In a separations cascade with 34 stages there are several stages left for obtaining a higher yield of promethium and/or a higher degree of separation from samarium.

The promethium content of a mixture of cerium-free fission product rare earths will be not more than about 6%, decreasing on aging with a 2.5-year half-life. Any extraction process for its purification consists of two cycles, the first of which reduces the bulk by a factor of about 10. However, the volume of the organic stream carrying the promethium may approach 50 times the feed volume, or 500 times the feed volume of a second cycle with the same feed concentration. Reduction of volume for feed to the second cycle is accomplished mostly by evaporation, but the necessary capacity of the evaporator is determined by the volume reduction obtainable in stripping the promethium from the first-cycle organic stream. Successful stripping was obtained with a volume reduction of 4, but the approach to 10 N HNO_3 in the final stage of the stripping section (Fig. 8) indicates the advisability of limiting the organic/aqueous flow ratio to 3 in the stripping section of a production flowsheet. This would maintain the acidity in all stripping stages in the most favorable range. Stripping solutions of at least 2 N HNO_3 are preferred to water because of their higher density and higher stripping coefficients.

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