Basic Principles Involved in the Macro-Separation of Adjacent Rare Earths from Each Other by Means of Ion Exchange*

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Abstract

The separation of rare earth mixtures by ion exchange using ammonium ethylenediaminetetraacetate and ammonium N-hydroxyethylethylenediaminetriacetate as eluting agents has been discussed in detail. Simple counter-current separation theory has been used to predict the minimum number of displacements of an adsorbed band that are necessary in order to separate the components of binary mixtures. It has been shown how the theory can be applied to even more complex systems and experimental data have been presented for some of the more difficultly separable groups of rare-earth species. Experimental results agree very well with the theoretical predictions.

I. Introduction

In an earlier paper (1) a general theory concerning the use of dilute ammonium citrate solutions for eluting the rare earths

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was presented in some detail. It is the purpose of this article to extend the original theory to cover the use of ethylenediaminetetraacetate (EDTA) and N-hydroxyethylethylenediaminetriacetate (HEDTA) solutions for separating rare earths on cation-exchange columns. Wheelwright, Spedding and Schwarzenbach (2) and Schwarzenbach, Gut and Anderegg (3) have measured the stability constants of the individual rare earth-EDTA complexes of the form RCh^- in 0.1 M KCl and KNO_3 solutions. Spedding, Powell and Wheelwright (4) have also reported the stability constants for the rare earth-HEDTA complexes of the form RCh. The symbol Ch is used to denote the chelating agent whether it be EDTA or HEDTA. The relatively large differences between the stability constants of adjacent rare earth-EDTA complexes made EDTA attractive as an eluting agent and it was shown, subsequently, by Spedding, Powell and Wheelwright (5,6) that EDTA solutions could be used to separate adjacent rare earths by the ion-exchange technique, provided a suitable retaining ion was adsorbed on the resin bed ahead of the rare-earth band.

In the case of elutions with dilute citrate and HEDTA solutions, H^+ ion can be used as the retaining ion, i.e., H^+ ion adsorbed ahead of the rare-earth band causes the rare earths to redeposit on the resin bed by combining with the chelating anion to form H_3Ch. Removal of the chelating species, $Ch^{\equiv}$, causes the metal chelates to decompose yielding R^{+3} ions which reabsorb on the resin bed. Hydrogen ion cannot be used efficiently as the retaining ion when rare earths are being eluted with EDTA, because the free-acid form of EDTA, H_4Ch is insoluble in water and precipitates in the interstices of the hydrogen-form resin bed.

In general, any cation which forms a soluble, more stable complex with EDTA than the rare earths do can be used as a retaining ion. Likewise, a cation which forms a soluble complex which is slightly less stable than the rare-earth complexes, but which is less tightly held by the resin than the rare earths, can also be used as a retaining ion, provided that the combined effects cause the ion to precede the rare earths down the column. Both Fe^{+3} (5) and Cu^{+2} (6) have been used successfully, but Cu^{+2} appears to be superior to Fe^{+3}. It was found that the pH range was limited when Fe^{+3} was used, since H_4Y tended to form and precipitate when the eluant was too acidic and $Fe(OH)_3$ when the eluant was too basic. There is also some evidence that a small amount of cyclic ferrous-ferric oxidation-reduction occurs and leads to trailing of the iron through the rare earth bands. Due to the greater solubility of $Cu(OH)_2$, Cu^{+2} can be used over a considerably greater pH range than Fe^{+3}. At eluant pH values above 8.4, however, some of the heavier rare earths, such as Lu, Yb, Tm and Er, are not completely retained by a Cu^{+2} bed. This may result in a partial or total loss of these elements unless precautions are taken. High EDTA concentrations coupled with high pH values promote the formation of a deep-blue insoluble substance, having the empirical composition Cu_2Ch, which may clog the column. Generally, it appears to be desirable to keep the EDTA concentration below 0.015 M and the pH of the eluant between 8.2 and 8.5.

In preliminary experiments with Cu^{+2} as the retaining ion, difficultly separable groups of rare earths were used and the adsorbed bands were eluted for distances just equal to their original lengths. Nevertheless, the separations achieved were considerably better than those obtained by eluting far greater distances with citrate as the eluant. Since the original experiments were performed, further studies have been undertaken and it seems desirable that the results of these investigations be presented.

II. Theoretical Considerations

A. Separation Factors for the EDTA System

When a rare earth is eluted down a cupric-state resin bed with an ammonium salt of EDTA, the following equilibria take place in the column.

$$\overline{R}^{+3} + 3NH_4^{+} \rightleftharpoons R^{+3} + 3\overline{NH_4}^{+} \qquad (1)$$

$$R^{+3} + Ch^{\equiv} \rightleftharpoons RCh^{-} \qquad (2)$$

The barred symbols refer to the resin phase and the unbarred symbols to the aqueous phase. The over-all reaction can be written as follows:

$$\overline{R}^{+3} + 3NH_4^+ + Ch^{\equiv} \rightleftharpoons 3\overline{NH}_4^+ + RCh^- . \qquad (3)$$

The equilibrium constant for this reaction is given by equation (4).

$$K_R = \frac{a^3_{(\overline{NH}_4^+)} \cdot a_{(RCh^-)}}{a^3_{(NH_4^+)} \cdot a_{(\overline{R}^{+3})} \cdot a_{(Ch^{\equiv})}} \qquad (4)$$

Due to the very large formation constant of the rare-earth chelate, K_R for this reaction is also very large. As will be shown later, the large constant in equation (4) results in ammonium ion displacing rare earth from the resin in one theoretical plate. Correspondingly, at the front edge of the band, the very large formation constants of the $CuCh^=$ and $CuHCh^-$ species, combined with the fact that the resin has a greater affinity for trivalent rare-earth ions than for divalent copper ion, result in a large equilibrium constant for the reaction by which the chelated rare earths displace the copper retaining ion. This again maintains a sharp boundary between the adsorbed rare-earth band and the retaining bed by causing the chelated rare earths to redeposit within the distance of one or two theoretical plates as the rare-earth eluate comes in contact with the adsorbed cupric ion. In the case of citrate and HEDTA, the formation constants of H_3Cit and H_3Ch are sufficiently larger than the stability constants of the rare-earth chelates that hydrogen ion serves as an adequate retaining ion when salts of these soluble acids are used as the eluant.

The imposition of these sharp constraints at the front and rear boundaries keeps the band compact as it progresses down the resin bed. Equilibrium is reached wherein the front and rear boundaries move at the same rate and 90-95% of the active sites on the resin within the confines of the band are occupied with rare-earth ions.

A plane of reference perpendicular to the resin bed can be envisioned which always maintains a fixed position with respect to the ends of the band as it moves down the bed. When the system is viewed from this plane it can be seen that ion-exchange elution of this sort is a countercurrent process in which rare earths are being transported upward in the resin phase and downward in the aqueous phase. It is logical, therefore, to use the concept of a theoretical plate or stage which is defined as an increment of the band of such size that the ratios of two components leaving it in opposite directions in the counter-current streams are related by the first power of the separation factor.

When two rare earths, designated by the symbols R_1 and R_2, are present as a mixture in a column, the following equilibrium occurs,

$$\bar{R}_1^{+3} + R_2Ch^- \rightleftharpoons \bar{R}_2^{+3} + R_1Ch^- \qquad (5)$$

and

$$K_{R_2}^{R_1} = \frac{K_{R_1}}{K_{R_2}} = \frac{a_{(\bar{R}_2^{+3})} \cdot a_{(R_1Ch^-)}}{a_{(\bar{R}_1^{+3})} \cdot a_{(R_2Ch^-)}} .$$

As long as conditions are such that R_1Ch^- and R_2Ch^- are the only rare earth-containing ions which are present in appreciable amounts in the aqueous phase, K_{R2}^{R1} represents the separation factor which is defined as the ratio of R_1 to R_2 in solution divided by the ratio of R_1 to R_2 in the resin phase.

Since the resin itself is not highly selective as far as two adjacent rare earths are concerned, then

$$\frac{a_{(\bar{R}_1^{+3})} \cdot a_{(R_2^{+3})}}{a_{(\bar{R}_2^{+3})} \cdot a_{(R_1^{+3})}} = K_a \cong 1. \qquad (7)$$

Actually the value of K_a for Er = R_1 and Nd = R_2 has been found to be about 1.8 in perchlorate solution (μ = 0.015 and 0.15). These elements are eight apart in the rare-earth sequence. Therefore, for adjacent pairs, K_a would be less than 1.08. If K_a is assumed to be unity, as is done hereafter, it only introduces a maximum error of about eight per cent. If more accurate results are desired, K_a can be measured and taken into account. Multiplying equation 6 by equation 7 gives

$$K^{R_1}_{R_2} \cong \frac{a_{(R_2{+3})} \cdot a_{(R_1Ch^-)}}{a_{(R_1{+3})} \cdot a_{(R_2Ch^-)}} = \frac{\gamma_{(R_2{+3})} \cdot m_{(R_2{+3})} \cdot \gamma_{(R_1Ch^-)} \cdot m_{(R_1Ch^-)}}{\gamma_{(R_1{+3})} \cdot m_{(R_1{+3})} \cdot \gamma_{(R_2Ch^-)} \cdot m_{(R_2Ch^-)}} . \tag{8}$$

This means that one should be able to use data obtained from aqueous solutions alone to predict the behavior of two rare earths when they are eluted down a non-selective ion-exchange bed with EDTA. For the rare earths, the activity coefficients are so nearly identical that they virtually cancel one another in the expanded form of equation (8) to give

$$K^{R_1}_{R_2} \cong \frac{m_{(R_2{+3})} \cdot m_{(R_1Ch^-)}}{m_{(R_1{+3})} \cdot m_{(R_2Ch^-)}} , \tag{9}$$

where m refers to the molal concentration rather than the activity.

The stability constants of Wheelwright, Spedding and Schwarzenbach (2) for the EDTA complexes of the rare earths were defined as follows:

$$K'_{R_1Ch^-} = \frac{m_{(R_1Ch^-)}}{m_{(R_1^{+3})} \cdot m_{(Ch^{\equiv})}} \qquad (10)$$

and

$$K'_{R_2Ch^-} = \frac{m_{(R_2Ch^-)}}{m_{(R_2^{+3})} \cdot m_{(Ch^{\equiv})}} . \qquad (11)$$

Consequently,

$$\frac{K'_{R_1Ch^-}}{K'_{R_2Ch^-}} = \frac{m_{(R_2^{+3})} \cdot m_{(R_1Ch^-)}}{m_{(R_1^{+3})} \cdot m_{(R_2Ch^-)}} \cong K^{R_1}_{R_2} . \qquad (12)$$

It is possible, therefore, to use the stability constants of the EDTA-rare earth complexes in aqueous solutions to predict the separation factors and the behavior of rare earths when they are eluted down ion-exchange columns with EDTA. It is unfortunate that 0.1 m solutions, for which the apparent stability constants have been measured, are too concentrated to be used conveniently for eluting rare earths, but within the accuracy claimed above these data can still be used as a guide for predicting what will occur. $K_{R_2}^{R_1}$ would be expected to be nearly independent of ionic strength, since nothing but rare earth species are involved and changes in activity coefficients would probably compensate each other.

In Table I the data of Wheelwright, Spedding and Schwarzenbach (2) have been used to calculate values of K_{Y}^{R}. R refers to a particular rare-earth species and Y stands for yttrium in this notation. From the values of K_{Y}^{R} it is apparent that all the rare earths, with the exception of dysprosium and terbium, will separate from yttrium very readily when eluted with EDTA down a cation-exchange column.

Values of $K_{R'}^{R}$ for adjacent elements, where R refers to one rare earth and R' to the next less tightly complexed member of the series, are also given in Table 1. From these values it is apparent that all adjacent pairs of rare earths, except gadolinium and europium, can be separated fairly easily from each other. Four pairs of rare earths, which separated poorly with citrate as the eluant, namely lutetium and ytterbium, dysprosium and yttrium, yttrium and terbium, and gadolinium and samarium, should separate fairly readily using EDTA, since the values of $K_{R'}^{R}$ for these groups are 1.8, 1.5, 1.5 and 1.4, respectively. With separation factors of this magnitude, almost complete separation is accomplished

Table 1

Values of K^{R}_{Y} and $K^{R}_{R'}$ Calculated from EDTA Stability Constants

[from data of Wheelwright, Spedding and Schwartzenbach (2)]

Rare Earth (R)	$\log K^{R}_{Y}$	K^{R}_{Y}	$K^{R}_{R'}$
Lu	2.09	123	1.8
Yb	1.83	68	2.1
Tm	1.51	32	3.3
Er	0.99	9.8	1.8
Ho	0.75	5.6	3.6
Dy	0.19	1.5	1.5
Y	0.00	1.00	1.5
Tb	-0.18	0.66	4.8
Gd	-0.86	0.138	1.02
Eu	-0.87	0.135	1.4
Sm	-0.01	0.098	3.1
Nd	-1.50	0.032	2.0
Pr	-1.81	0.016	2.3
Ce	-2.17	0.0068	4.7
La	-2.84	0.0014	

by eluting a distance equal to two or three times the length of the adsorbed band as will be shown in a later section.

B. Exchange Constants for the HEDTA System

When an ammonium salt of N-hydroxyethylethylenediaminetriacetic acid is used to elute rare earths, hydrogen ion can be used as the retaining ion, since the acid is soluble in water to the extent of at least seventy grams per liter. Cupric ion can also be used if desired. Regardless of the retaining ion used, equations (1) through (12) apply to the use of HEDTA, as well as EDTA, provided that one reduces the negative charges of the chelating anion and the rare-earth chelate by one. HEDTA has only 3 ionizable hydrogen ions, whereas EDTA has 4.

Separation factors for adjacent rare earths have been computed for the HEDTA system from the data of Spedding, Powell and Wheelwright (4) and are given in Table 2. The stability constants of the chelates formed with elements holmium through samarium are so similar in magnitude that separation factors cannot be calculated with any degree of certainty, but the stability constants of the other rare-earth chelates suggest some interesting possibilities. For the light rare-earth elements, lanthanum to samarium, the separation factors for adjacent pairs compare favorably with those given in Table 1 for the EDTA system. For the heavy

Table 2

Values of $K^{R}_{R'}$ Calculated from HEDTA Stability Constants

Rare Earth (R)	$\log K_{RCh}$	$\log K^{R}_{R'}$	$K^{R}_{R'}$
Lu	15.79	0.15	1.4
Yb	15.64	0.26	1.8
Tm	15.38	0.21	1.6
Er	15.17	0.11	1.3
Ho	15.06	-	-
Dy	15.08	-	-
Tb	15.10	-	-
Gd	15.10	-	-
Eu	15.21	-	-
Sm	15.15	0.44	2.8
Nd	14.71	0.32	2.1
Pr	14.39	0.31	2.0
Ce	14.08	0.86	7.3
La	13.22		

rare earths, holmium through lutetium, the separation factors are smaller for HEDTA than for EDTA; nevertheless, it appears that the kinetics for the exchange of ions is better for HEDTA than for EDTA in the case of these rare earths. This gives a more favorable steady-state equilibrium at faster flow rates. In addition, common impurities, such as Pb, Zn, Cd and Co which elute along with the heavy rare earths with EDTA, do not contaminate the group when HEDTA is used as the eluant.

C. Displacement Required to Separate a Pair of Rare Earths

The minimum distance of elution required to attain virtually complete separation of a pair of rare earths under idealized conditions can be calculated from the exchange constant $K^{R_1}_{R_2}$ (K^{R}_{Y} and $K^{R}_{R'}$ of Table 1 are special cases of this more general constant). Spedding, Powell and Svec have shown previously how the equilibrium constant can be used to calculate the number of displacements required to separate the isotopes of nitrogen by an ion-exchange method (7).

The conditions required in the development which follows are: (1) that the height equivalent to a theoretical plate (HETP) of the ion-exchange bed used must be sufficiently small, and (2) that the value of $\epsilon = K^{R_1}_{R_2} - 1$ must be sufficiently large that the region of overlap between adjacent rare earths in the fully developed band is small compared to the lengths of the individual adsorbed bands. By adjusting the diameter of the column used to the amount of rare earths to be separated, it is possible to apply this treatment with some accuracy even though the HETP is fairly large or the value of ϵ is fairly small.

Consider an adsorbed band containing a mole of mixed rare earths in which the mole fractions, N_0 and $(1-N_0)$, of the rare earths, R_1 and R_2, respectively, are initially constant throughout as in Fig. 1. This condition is obtained when a pair of rare earths is adsorbed on the resin from a dilute acid solution containing no complexing agent. Experience has shown that any selectivity that occurs during loading is so small that it can be neglected.

When a complexing eluant such as EDTA percolates through the resin bed, the band is displaced progressively down the resin bed. In this model, using units of distance occupied by a mole of adsorbed rare earth, the initial spread-out, which may be considerable in citrate elutions but which is less than ten per cent of the original band length in elutions with EDTA and HEDTA, can be ignored. As the band is displaced, the mixture desorbed at the rear edge of the band must pass through a region of the adsorbed mixture where the mole ratio of R_1 to R_2 in the resin phase is equal to

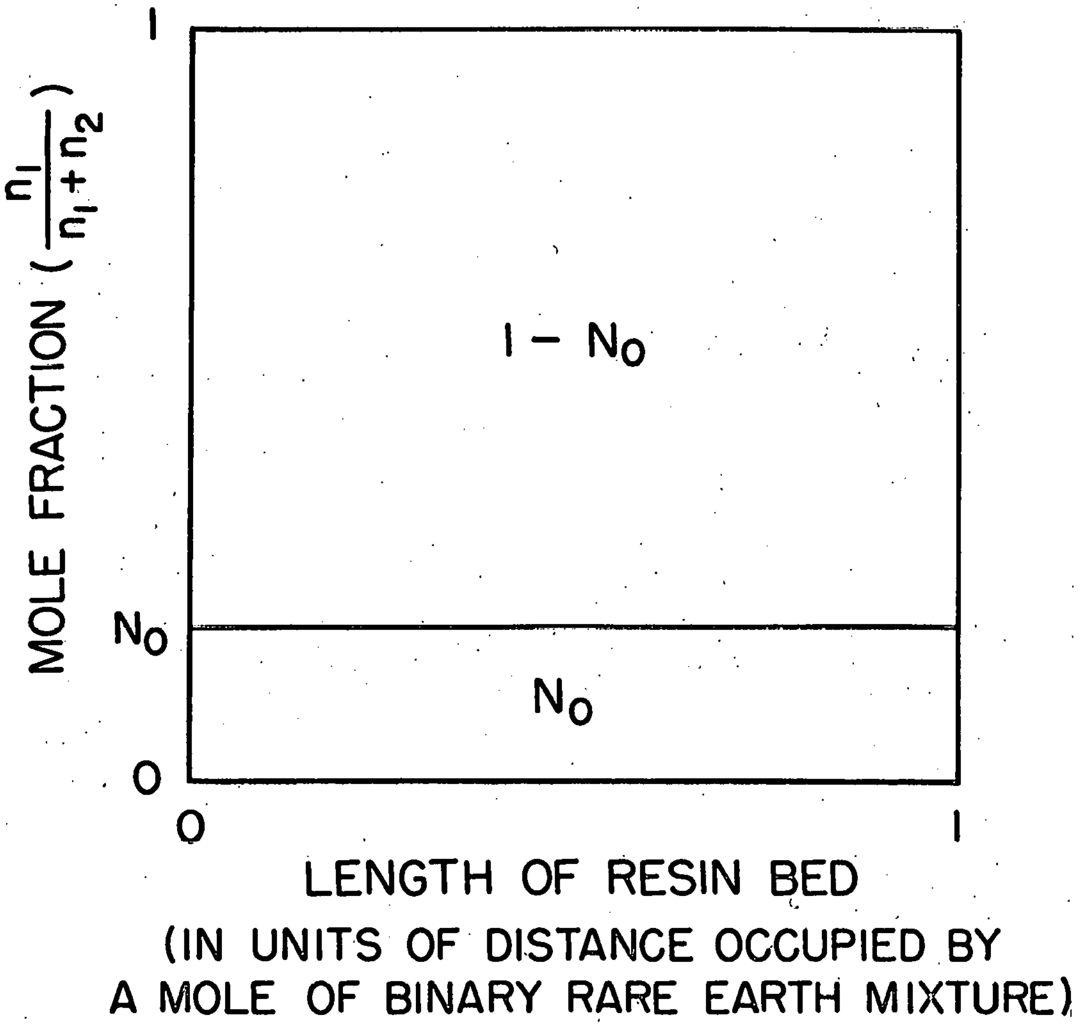

Fig. 1. Model of an adsorbed band of one mole of homogeneous rare-earth mixture composed of N_o moles of R_1 and $(1-N_o)$ moles of R_2.

$\frac{N_o}{1-N_o}$. As long as any of this region of normal abundance remains in the adsorbed band, the eluate passing through the region will be forced to approach an equilibrium in which the mole ratio of R_1 to R_2 in the eluate will be

$$\frac{N}{1-N} = K^{R_1}_{R_2} \frac{N_o}{1-N_o} = (1 + \epsilon) \frac{N_o}{1-N_o} . \qquad (13)$$

Therefore, as long as any appreciable amount of the normal region remains in the band, the net number of moles of R_1 transported from the rear of the band to the front of the band, through this normal region, per mole of rare-earth mixture displaced by the eluant is

$$\Delta n = N - N_o . \qquad (14)$$

Substituting the value of N, obtained by solving equation (13), into equation (14),

$$\Delta n = \frac{N_o(1 + \quad)}{1 + \quad N_o} - N_o = \frac{N_o(1 - N_o)}{1 + \quad N_o} . \qquad (15)$$

Referring to Fig. 2, it can be seen that the net total number of moles of R_1 which must be transported to obtain complete separation of the species R_1 and R_2 is $N_o(1 - N_o)$.

Consequently, the minimum number of band displacements required to effect separation of the bulk of the mixture into pure components, leaving only a relatively small region of

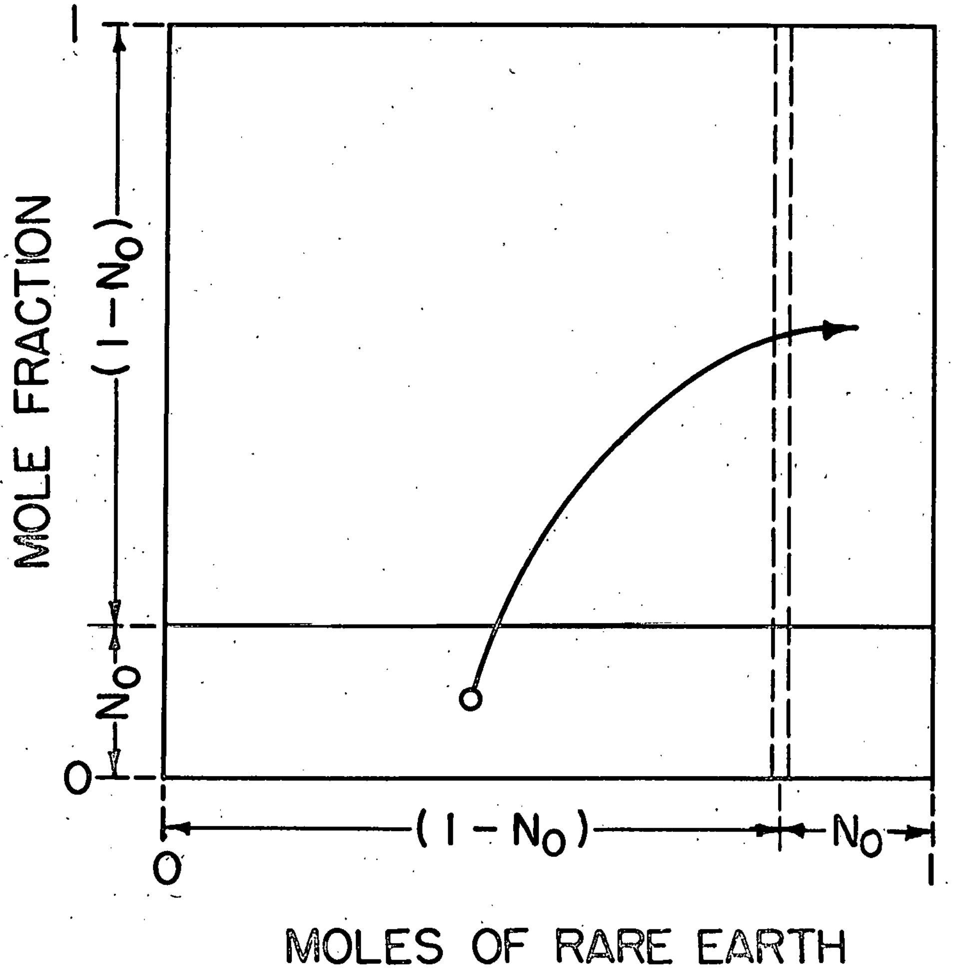

Fig. 2. Model of an adsorbed band demonstrating conditions before and after separation of a mole of binary mixture. The area $N_o(1-N_o)$ represents the net total number of moles of R_1 that must be transported forward and of R_2 that must be transported rearward to achieve complete separation. The area between the dashed lines represents the region in which the transition from pure R_1 to pure R_2 occurs in the fully developed band. This region is of finite length and is determined by the separation factor and the HETP for the system.

mixed rare earths, under these idealized conditions is

$$\nu = \frac{N_o(1 - N_o)}{\Delta n} = \frac{1 + \epsilon N_o}{\epsilon} . \qquad (16)$$

When ϵ is very small compared to one, the number of displacements required is

$$\nu = 1/\epsilon \quad ; \; \epsilon \ll 1. \qquad (17)$$

For large values of ϵN_o, the number of displacements required is

$$\nu = N_o ; \quad \epsilon N_o \gg 1. \qquad (18)$$

D. The Steady State

When a binary mixture of rare earths has been eluted ν times the length of the adsorbed band, the last residue of the normal region vanishes and a state is approached beyond which no further separation takes place. Since ion-exchange elution is actually a counter-current process, one can introduce the concept of theoretical stages or plates which move with the band as it is eluted. The height of a theoretical stage, h, is primarily a function of the time of contact and the rate of interchange of the species; hence it must depend upon flow rate, particle size, concentration, pH, temperature and even the stability constants of the chelates of the rare earths being considered. Nevertheless, HETP can be evaluated for any set of conditions from data obtained after the steady state has been reached.

The ratio of the two components leaving a given stage in the aqueous phase will be related to the ratio leaving that stage in the resin phase by the separation factor $K^{R_1}_{R_2}$. Furthermore, due to the steady state conditions and the fact that the band is in total reflux during elution, there can be no net change in the amount of either component in the stage. That is

$$\frac{N_n}{1-N_n} = K^{R_1}_{R_2} \frac{\overline{N}_n}{1-\overline{N}_n} \quad \text{(definition of a theoretical plate)} \tag{19}$$

and

$$N_{n+1} + \overline{N}_{n-1} = N_n + \overline{N}_n \quad \text{(steady state)}, \tag{20}$$

where N_n, and N_{n+1} are the mole fractions of R_1 leaving the _n_th and (_n+1_)th stages in the aqueous phase and $\overline{N}_{n-1}$ and $\overline{N}_n$ are the mole fractions of R_1 leaving the (_n-1_)th and _n_th stages via resin phase.

Since the system is in a state of total reflux, the rare earths issuing from the front edge of the rare-earth band in the aqueous phase deposit on the resin and re-enter the first stage of the band continually with no change in ratio.

Therefore,

$$N_1 = \overline{N}_0 \quad \text{(total reflux)}. \tag{21}$$

Applying equation (20) to the first stage

$$N_2 + \bar{N}_0 = N_1 + \bar{N}_1 \qquad (22)$$

and substituting the condition of total reflux

$$N_2 = \bar{N}_1, \qquad (23)$$

it follows that

$$N_{n+1} = \bar{N}_n. \qquad (24)$$

Substitution of this steady state condition in equation (19) gives

$$\frac{N_n}{1-N_n} = K^{R_1}_{R_2} \frac{N_{n+1}}{1-N_{n+1}}\,. \qquad (25)$$

It can be seen that the ratio of R_1 to R_2 in the aqueous phase leaving the nth plate is related to the ratio entering the nth plate via the aqueous phase by the separation factor. If one next considers the ratios of R_1 to R_2 at any two points which are m plates appart and defines the ratio of R_1 to R_2 entering the hindmost plate as n_o and the ratio of R_1 to R_2 leaving the foremost plate as r_m, then

$$r_m = (K^{R_1}_{R_2})^m\, r_o \qquad (26)$$

or

$$\log r_m = m \log K^{R_1}_{R_2} + \log r_o. \qquad (27)$$

If *L* is the distance from the rear edge of the hindmost plate to the front edge of the foremost plate being considered and if the heights of the stages are equal as they will be when a steady state is reached with the band in total reflux

$$h = \frac{L}{m} \tag{28}$$

and equation (27) becomes

$$\log r_m = \frac{\log K^{R_1}_{R_2}}{h} L + \log r_o . \tag{29}$$

When *log r* is plotted versus *L*, a straight line with a slope equal to $\log K^{R_1}_{R_2}/h$ is obtained and the height equivalent to a theoretical plate can be calculated from the slope of *log r* vs. *L*.

$$h = \log K^{R_1}_{R_2} \frac{\Delta L}{\Delta \log r} . \tag{30}$$

Suppose now that a rare earth which is greater than 99.9% pure is acceptable for most purposes. Then the overlap between adjacent rare-earth bands at the steady state will be the region in which R_1 decreases from 99.9% to 0.1% and R_2 increases from 0.1% to 99.9%. The ratio of R_1 to R_2 increases approximately a million-fold in this distance. The number of theoretical plates required to produce such a change in ratio can be calculated from equation (27), that is

$$m = \frac{6}{\log K^{R_1}_{R_2}} \tag{31}$$

and the length of the portion of the band which is involved in the overlap is

$$L = \frac{6h}{\log K^{R_1}_{R_2}} . \qquad (32)$$

It is obvious that the total length of the band must be greater than L in order to obtain any pure rare earths from an elution.

III. Experimental

Considerable quantities of rare earths have been separated by the methods discussed above. Certain examples have been selected from accumulated data to illustrate the theory just presented.

A. Rapid Concentration of the Heavy-Rare-Earth and Light-Rare-Earth Groups from Gadolinite Ore Concentrate

It is not as simple to predict the behavior of a complicated mixture of rare earths as it is to calculate the behavior of a simple binary mixture. In general, however, it is safe to assume that the distance of elution required to separate the constituents of a simple binary mixture of adjacent rare earths, such as 80% yttrium and 20% dysprosium, would be more than sufficient to separate the main constituent from a more complicated mixture, such as 80% Y and 20% total of Dy, Ho, Er, Tm, Yb and Lu. For computing ν one would use the mole fraction 0.2, in this case, because the elements Ho, Er, Tm, Yb and Lu separate from yttrium even more readily than does Dy. A rough analysis of a previous batch of gadolinite ore concentrate was presented in an earlier paper (8). Assuming that the present source has the same composition as this earlier lot of ore, one can calculate the approximate number of band displacements required to free the bulk of the yttrium from each of the other components, i.e., to concentrate this other constituent either at the front or at the rear of the adsorbed band. The values of $\underline{\nu}$ have been calculated and are given in Table 3.

Fifteen kilograms of crude R_2O_3 concentrate, dissolved in 30 liters of 15 $\underline{N}$ HCl and 100 gallons of water were adsorbed on the first seven of a series of -20+30 mesh, ammonium-form, Nalcite HCR resin beds, each 48-52 inches long. The last of the 100 gallons of solution was flushed on through the beds with distilled water and, when the first trace of rare earth appeared in the effluent solution from the seventh column, column number 8 was connected into the series. Column 8 was originally in the cupric state and about 5 inches of the cupric bed was converted to the rare-earth cycle during this rinsing operation. The entire rare-earth band was 362 inches long at this time. The adsorbed band was then eluted down the series of beds with 0.0153 $\underline{M}$ EDTA at a pH of 8.4 and a flow rate of 800 ml. per min.

Table 3

The Minimum Distance of Elution Required to Separate the Major Constituent Yttrium from Other Rare Earths Present in Gadolinite Ore Concentrate with EDTA as the Eluant

Component	Actual N_0	N_0 Used	ϵ	ν
Lu	0.003	0.003	122	0.011
Yb	0.027	0.030	67	0.05
Tm	0.003	0.033	31	0.06
Er	0.027	0.060	8.8	0.18
Ho	0.008	0.068	4.6	0.28
Dy	0.044	0.112	0.5	2.11
Tb	0.003	0.840*	0.5	2.84
Gd	0.038	0.840	6.2	1.00
Eu	0.000	0.840	6.4	1.00
Sm	0.038	0.840	9.2	0.95
Nd	0.041	0.840	31	0.87
Pr	0.016	0.840	64	0.86
Ce	0.016	0.840	147	0.85
La	0.008	0.840	690	0.84
Y	0.728			

*From this point on the assumption is made that the problem is equivalent to separating a mixture of 0.84 mole per cent Y and 0.16 mole per cent Tb, Gd, Eu, Sm, Nd, Pr, Ce or La.

Table 3 shows that under ideal conditions all the Lu, Yb and Tm and most of the Er in the mixture would have concentrated near the front of the band by the time the band front reached the bottom of the eighth column, having been driven 47 inches or about an eighth of a band length by the eluant. Therefore, the first foot of the adsorbed band was allowed to pass off the eighth column onto a 4-inch diameter bed of 100-200 mesh, Dowex 50-X12 in the cupric state, upon which it formed a band 27 inches long. This band was rapidly eluted off the short column in order to ascertain how much separation had been accomplished by eluting one-eighth of a band length.

From Table 3 it was also predicted that the remainder of the erbium, the holmium and a part of the dysprosium would have concentrated at the front of the band by the time the front edge reached the bottom of the tenth column. Therefore, another foot of the adsorbed band was diverted onto an auxiliary resin bed when the band reached the bottom of column 10 and was handled in the same manner as the material diverted from the eighth column.

The material diverted and recovered from the eighth column weighed 871.3 grams and was composed as follows: 68.1 grams of Lu_2O_3 and/or ThO_2; 453.0 grams of Yb_2O_3;

56.7 grams of Tm_2O_3; 278.3 grams of Er_2O_3; 15.0 grams of Ho_2O_3; and 0.2 grams of Dy_2O_3. The material diverted from the tenth column weighed 704.8 grams and contained 15.5 grams of Yb_2O_3, 7.7 grams of Tm_2O_3, 243.3 grams of Er_2O_3, 169.1 grams of Ho_2O_3, 179.7 grams of Dy_2O_3 and 89.5 grams of Y_2O_3. It can be seen that virtually all of the lutetium, ytterbium and thulium, as well as about half the erbium, were contained in the first fraction diverted. The remainder of the erbium and most of the holmium were contained in the second fraction. Some holmium and dysprosium appeared in the first fraction and some ytterbium and thulium appeared in the second fraction; nevertheless, the theoretical predictions are well substantiated by these results. One would not expect a clean-cut separation of adjacent elements at this point.

Column 10 was attached next to column 11 of the 6-inch series and elution was continued at 800 ml per min. When the band front reached the bottom of column 15, the elements gadolinium through lanthanum should have concentrated at the rear of the band according to Table 3. As a matter of fact, the Nd band which is visible appeared to be fairly well formed and was passing between columns 8 and 9 at this point. Consequently, the band was divided between columns 9 and 10 to give one band six columns long (294 inches), consisting primarily of adsorbed yttrium with traces of dysprosium and terbium and a second band somewhat more than a column long (more than 52 inches) containing the light rare earths, lanthanum through gadolinium, and perhaps some terbium and yttrium.

It will be noted that the entire adsorbed band, counting the two feet of material diverted previously, was slightly longer than the original 362 inches at this point. In coming to equilibrium with the EDTA eluant, an adsorbed band expands by 5-10% of its original length due to the deposition of some NH_4^+ and H^+ ions within the confines of the band.

B. Resolution of the Dysprosium, Yttrium and Terbium Group

As the yttrium-rich portion of the adsorbed band started down the 16th column, samples of the solution in contact with the band were withdrawn at the bottoms of all columns 9 through 15. As the band moved on down column 16, additional samples were withdrawn from time to time. In this manner, it was possible to obtain a complete profile of the adsorbed yttrium band within a 24 hour period. Six days later, after the yttrium had progressed down six additional columns or one more band length, a second profile was taken in the same manner. The data are plotted in Fig. 3.

Due to the coarse particle size of the resin and the rapid rate of elution used, the HETP was fairly large in this experiment. It can be seen that the plateau of the

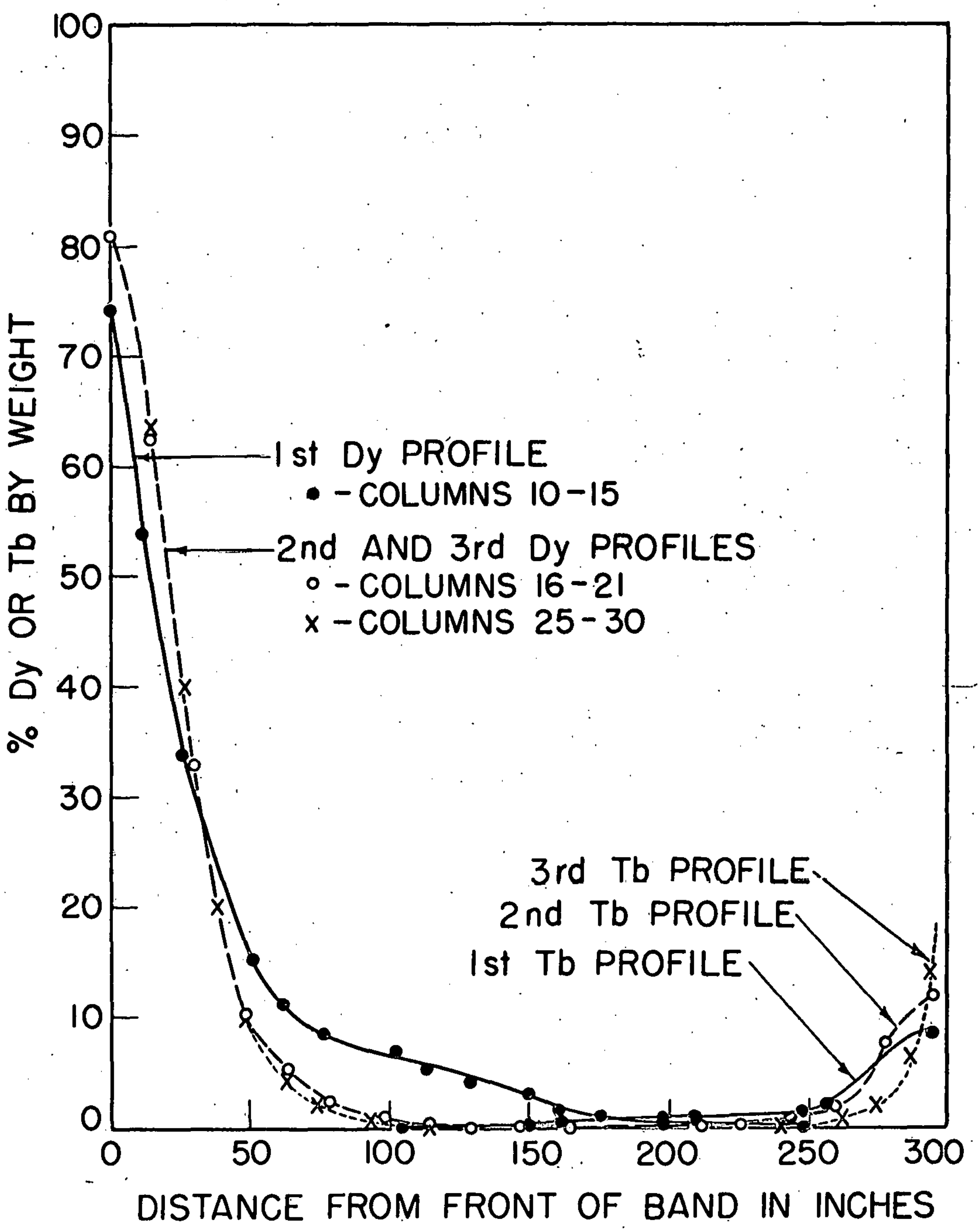

Fig. 3. Profiles taken at intervals during the elution of a Dy-Y-Tb mixture with EDTA.

dysprosium elution curve was disappearing rapidly at the time the first profile was taken. The terbium plateau, however, was still fairly pronounced. By the time the second profile was taken both plateaus had been pretty nearly consumed. A final profile was taken as the band front moved down the 30th column and is compared to the earlier profiles in Fig. 3. As might be expected, the separation of dysprosium and yttrium did not improve significantly with continued elution at this flow rate, but the yttrium-terbium separation increased somewhat.

It is apparent that, after eluting the band just slightly more than twice its length, a steady state condition was approached as far as the dysprosium-yttrium separation was concerned. If one desires to achieve a more complete resolution of the dysprosium-yttrium-terbium mixture, it is necessary to use conditions which produce more favorable values of the HETP, and hence a narrower region of overlap at the steady state. It is necessary according to theory to elute nearly three band lengths in order to resolve the yttrium and terbium in the mixture, but the resolution of the dysprosium and yttrium requires only about two band lengths. Consequently, if one loads x feet of resin bed with such a Dy-Y-Tb mixture and elutes the band down 2x additional feet of bed, the dysprosium and yttrium will be resolved by the time the front of the band reaches the end of the resin bed system. Furthermore, the terbium which concentrates at the rear edge of the band will receive the benefit of an additional band length of elution as the dysprosium and yttrium are being collected. Therefore, the terbium and yttrium will be resolved by the time the band is eluted completely off the resin bed.

C. The Isolation of Yttrium from a Crude Concentrate Obtained from Xenotime.

The composition of the rare-earth mixture obtained from xenotime is approximately the same as that obtained from gadolinite. Xenotime, however, is more readily available in the United States, contains half again as much R_2O_3 as gadolinite, and is simpler to process.

For large scale operations the following procedure for obtaining feed material from xenotime worked very well. Four hundred pounds of 93% sulfuric acid were heated to about 190°C in a 50-gallon, glass-lined, steam-jacketed, reaction vessel. Two hundred and fifty pounds of finely pulverized xenotime, preheated to about 170°C were then added to the reactor and the sulfuric acid-xenotime mixture was stirred by an anchor type agitator running at 100 rpm. The heat of reaction caused the temperature to rise to 240-250°C and the reaction was nearly complete after 10-12 hours. The digested sludge was then flushed into a 300-gallon, glass-lined, dilution tank with cold water.

An ion-exchange unit was constructed which was capable of processing the equivalent of 1000 lbs. of R_2O_3 concentrate from gadolinite or xenotime per cycle. The unit consisted of 12 columns, each one 30 inches in diameter and 10 feet high. Each column was filled to the 9 1/2-foot level with -40+50 mesh, Amberlite IR-120 in the H^+ state and the resin bed was carefully backwashed by bolting a spare 30-in. x 10-ft. cylinder to the top flange of the column and flowing water in from the bottom. The columns were constructed of type 316 ELC stainless steel. If only rare earths are to be separated on the column system, rubber-lined or plastic-lined columns and tanks could be used.

In order to load the first four columns of this unit with rare-earth mixture, it was necessary to digest seven, 250-pound batches of xenotime in the manner described above. Each batch was diluted to 300 gallons and the strongly acidic initial solutions of rare earth sulfates from all seven batches were filtered and passed through a small bed of anion-exchanger into the first and second columns of the cation-exchange unit. The undissolved rare-earth sulfates from each batch were allowed to accumulate in the dilution tank and the combined material was finally leached repeatedly with water. The successive leachates became less and less acidic and were passed through the first and second columns as the third and fourth columns were loaded. In this way, an adsorbed band of nearly neutral rare earths was obtained eventually which completely filled the first four resin beds. The excess rare earths were flushed out and recovered. It was calculated that the load was equivalent to about 1000 pounds of crude R_2O_3. The remaining eight columns of the system were converted to the Cu^{+2} state by passing a solution of technical grade cupric sulfate through them.

It was apparent from previous experiments that fast flow rates gave rather poor HETP values. Consequently, the rare-earth band was eluted at 5 liters per minute, which is equivalent to 200 ml per minute on six-inch columns or one-fourth the linear flow rate used in experiments A and B. The eluant was 0.0153 M EDTA at a pH of 8.4.

When the front of the adsorbed band reached the bottom of the fifth column, having traveled one-fourth its length, the equivalent of 3.2 feet of the 30-inch diameter band was diverted onto a group of six-inch diameter columns to give a band 80 feet long. Elution was continued down the 30-inch series until it was determined that the terbium peak was passing from column 6 to column 7. At this point, the light rare earths, lanthanum through gadolinium, were concentrated on column 6. This light rare earth portion of the band was eluted off and the eluate was collected in 100-gallon portions. It was found that the light-rare-earth bands were not completely resolved from each other by elution on the 30-inch columns. Nevertheless, some gadolinium-rich fractions were obtained 98% pure and a number of neodymium-rich fractions were greater than 95% pure. Some samarium fractions exceeded 85% and praseodymium reached a peak purity of 75%. Since most of this material was obtained as simple binary mixtures, it was obvious that collection on six-inch columns followed by further elution would have resulted in high yields of the individual rare earths.

When the main yttrium-bearing portion of the band reached the bottom of the twelfth column, an additional 3.2 feet of the front edge was collected on six-inch columns to give a dysprosium-rich band 80 feet long.

The remainder of the material, consisting of a large amount of pure yttrium and some yttrium-terbium mixture, was eluted directly off the 30-inch series of columns and the eluate was collected in 100-gallon fractions. Eighty-nine per cent of the originally adsorbed yttrium was recovered greater than 99.9% pure by this procedure.

D. The Resolution of Some Enriched Rare-Earth Mixtures

Our best estimate of the abundances of the individual rare earths in xenotime concentrate is given in Table 4.

Table 4

The Composition of Crude R_2O_3 Obtained from Xenotime

Constituent	% by weight
Lu_2O_3	0.3
Yb_2O_3	5.0
Tm_2O_3	0.8
Er_2O_3	5.7
Ho_2O_3	1.7
Dy_2O_3	7.3
Y_2O_3	60.0
Tb_2O_3	0.9
Gd_2O_3	2.7
Eu_2O_3	0.1
Sm_2O_3	1.2
Nd_2O_3	2.8
Pr_2O_3	0.8
Ce_2O_3	4.3
La_2O_3	3.1

When the 30-inch diameter system of ion-exchange columns was loaded with a thousand pounds of concentrate from xenotime, the adsorbed band was thirty-six feet long. Although sufficient yttrium was present to give a resolved band twenty-seven or eight feet long, only eighty-nine per cent of the yttrium was recovered in pure form. The remaining eleven per cent was involved in overlaps with the neighboring elements, dysprosium and terbium. The separation factors are somewhat larger for most pairs of adjacent rare earths than for dysprosium and yttrium and yttrium and terbium, but the overlapping regions in most cases would be of the order of six inches or a foot in length, based upon the extent to which yttrium overlaps with its neighbors after the steady state has been reached. It can be seen from the data in Table 4 that the abundances of the other components of xenotime are too small to permit resolution of these minor constituents under the conditions which were used to obtain pure yttrium. It is expedient, therefore, to readsorb the partially resolved rare earths that concentrate either at the front or the rear edge of the band, as it is eluted a short distance down a 30-inch system, on columns of smaller diameter. For example, if one calculates the composition of the heavy-rare-earth mixture one might recover by eluting a band composed of xenotime concentrate a quarter band length, one obtains the percentages given in Table 5.

Table 5

Percentages of Individual Heavy Rare Earths Anticipated in the Mixture Diverted from the Main Band

Constituent	% by weight
Lu_2O_3	2.2
Yb_2O_3	37.0
Tm_2O_3	5.9
Er_2O_3	42.2
Ho_2O_3	12.6

The heavy rare earth material from a thousand pounds of xenotime concentrate is sufficient to fill about 80 feet of bed on a six-inch diameter ion-exchange system. Consequently, if the mixture contains the percentages of rare earths given in Table 5, the resolved bands would be nearly 2 feet long in the case of lutetium, 30 feet long for ytterbium, 5 feet long for thulium, 34 feet for erbium and 10 feet for holmium. A flow rate of 200 ml per minute on six-inch columns produces results comparable to 5 liters per minute on 30-inch columns so that an excellent yield of erbium can be obtained by elution to the steady state on six-inch columns. Although the ytterbium band is nearly as long as the erbium band, the yield of pure ytterbium is generally poor when EDTA is used as the eluant. The resolution of lutetium and ytterbium is less than would be expected from the size of the separation factor alone. The difficulty seems to be due to a decrease in the rate of exchange of the two rare earths as the stabilities of their EDTA complexes increase. This effect has been noticed in the case of ytterbium-thulium and thulium-erbium separations but is most apparent in the case of lutetium and ytterbium.

In addition to the poor kinetics of exchange between the heavier rare earths, the lutetium- , ytterbium- , and thulium-rich fractions are generally found to be contaminated with lead, thorium, zinc and cobalt. These observations have lead to the investigation of an alternate chelating agent for use in resolving heavy-rare-earth mixtures.

An inspection of the EDTA and HEDTA stability constants given in Table 6 reveals the fact that HEDTA-rare earth complexes are more than five thousand-fold less stable than the corresponding EDTA complexes for lutetium, ytterbium and thulium.

The separation factors for adjacent pairs of these rare earths are smaller for HEDTA than for EDTA, but since the overlap of rare earth bands depends as much on the HETP as on the separation factor, resolution may be improved greatly by the substitution of HEDTA for EDTA.

A heavy-rare-earth mixture, which was diverted from the fifth column of the 30-inch series to give 80 feet of adsorbed band on a six-inch series of columns, was used in the following experiment. In order to preserve as much of the EDTA-induced separation as possible while maintaining a flow rate of five liters per minute on the 30-inch series, twenty-one six-inch columns were arranged in three parallel rows of seven columns during the collection step. The columns were all filled to a height of four feet with -40+50 mesh Amberlite IR-120 in the cupric state and the flow rate through each row of columns was adjusted to

Table 6

Comparison of the Stabilities of the Heavy Rare Earth Chelates Formed with EDTA and HEDTA

Rare Earth	$\log K_{RCh^-}$ (EDTA)	$\log K_{RCh}$ (HEDTA)
Lu	19.65	15.79
Yb	19.39	15.64
Tm	19.07	15.38
Er	18.55	15.17
Ho	18.31	15.06
Dy	17.75	15.08

1.67 liters per minute (much too fast for good resolution). When the front edges of the three parallel rare-earth bands approached the ends of the beds provided and the colored rare earths, erbium and holmium, stopped issuing from the 30-inch series of columns, the six-inch system was detached from the larger column series. At this point about one foot of cupric-cycle resin remained at the bottom of each seven-column series and the colored rare earths were concentrated on the last four columns of each set. Lutetium was pretty generally distributed throughout the ytterbium-rich portion of each series.

The three parallel series of columns were connected so as to feed into a single series of six-inch columns. These additional columns were filled to a height of 4 1/2 feet with -40+50 Amberlite IR-120 in the H^+ state and were added as required by the advance of the band during subsequent elution with HEDTA.

The eluant contained five grams of HEDTA per liter and enough ammonia to give a pH of 7.5 This pH corresponds roughly to that produced by the compound $(NH_4)_2HCh$ dissolved in water. At the beginning the flow rate was maintained at 500 ml per minute, but after 20 columns had been added the flow rate dropped to about 400 ml per minute.

Since the two main constituents of this mixture, ytterbium and erbium, are two elements apart in the rare-earth series and were at least partly resolved by the EDTA solution, the problems at this point were to separate the less abundant rare earths, lutetium and thulium, from ytterbium and to separate the thulium, holmium and dysprosium from erbium. It was assumed, therefore, that all the lutetium and half of the thulium were contained in the ytterbium which was already separated from the erbium. This ternary mixture constituted about 42% or 34 feet of the total length of the band. It was calculated that it would require elution down an additional 88 feet of resin bed (22 columns) in order to resolve the lutetium contained in the ytterbium-rich part of the band. The separation of the thulium from the ytterbium would take place simultaneously since an elution of only 75 feet would be required.

Assuming that erbium contaminated with thulium and holmium made up 58% or 46 feet of the total band length, it was determined that a displacement of 76 feet by HEDTA would suffice to separate the thulium from the erbium. The resolution of erbium and holmium would require 193 feet if the erbium and holmium were completely mixed at the beginning. Actually, erbium and holmium were pretty nearly separated by elution with EDTA before the HEDTA elution was begun.

Profiles were taken periodically as the band was eluted down 22 additional six-inch columns. By the time the front of the band was passing from the bottom of the 21st column to the top of the 22nd, the lutetium had accumulated at the head of the band behind a short band of lead. The HETP determined for the Lu-Yb overlap on six-inch columns at a flow rate of 400 ml per minute was 3.3 cm. Since 40 theoretical plates are required for the transition from 99.9% lutetium to 99.9% ytterbium, the Lu-Yb overlap was calculated to be 132 cm or 4 1/3 feet long and no really pure lutetium could be isolated from a band that would only be two feet long if completely resolved. The flow rate, therefore, was reduced to 200 ml per minute while the band was eluted down two additional columns (23 and 24) and then the lead, lutetium and some of the ytterbium were allowed to pass off the six-inch series onto a series of four-inch columns at 100 ml per minute. The band adsorbed on the four-inch series was about nine feet long, representing four feet of adsorbed band from the six-inch diameter bed. The lead-lutetium-ytterbium mixture was recovered after eluting down a total of seven four-inch beds, each four feet long. The lead was removed from the first few samples as the sulfide, prior to precipitation of lutetium as the oxalate. Nine hundred grams of better than 99.9% Lu_2O_3 were obtained. An additional 400 grams of Lu_2O_3 were obtained mixed with Yb_2O_3.

The regions of the six-inch columns which contained pure ytterbium and pure erbium at this point were stripped with HEDTA while the regions containing the Yb-Tm-Er and Er-Ho overlaps were collected at 100 ml per minute and analyzed. When Ho appeared in the effluent, the Ho-Dy separation was not yet complete and separation of this mixture was continued on down a series of four-inch columns. Actually, one would not expect holmium and dysprosium to separate from each other at all, due to the similarity of the stability constants of HoCh and DyCh. Some separation with HEDTA is apparent, but EDTA is undoubtedly a more efficient eluant than HEDTA for the final resolution of holmium and dysprosium. The treatment described above resulted in the isolation of 900 grams of Lu_2O_3, 24,050 grams of Yb_2O_3, 3,520 grams of Tm_2O_3, 26.900 grams of Er_2O_3 and 4,380 grams of Ho_2O_3 in purities greater than 99.9 per cent.

E. Recovery of HEDTA from Elution Wastes

Since HEDTA is an amino acid, it forms cationic species by associating with either one or two protons. Therefore, if H_3Ch is passed through a bed of cation-exchanger in the hydrogen cycle, it attaches itself to the resin presumably in the form H_5Ch^{+2}. When rare earths are eluted with an ammonium salt of HEDTA the species RCh is formed first. When this species comes in contact with the hydrogen retaining ion it decomposes, due to the formation of the more stable H_3Ch and the rare earth is deposited on the resin. The H_3Ch then deposits on the resin forming a band of H_5Ch^{+2} ahead of the rare-earth band. As a result of this behavior, nothing but water issues from the bottom end of a column until the band of chelating agent breaks through. The effluent then contains approximately twice the original concentration of HEDTA in the form of H_3Ch if the eluant composition is $(NH_4)_2HCh$. The supposition is that, when two ammonium ions are deposited behind the rare-earth band, two hydrogen ions attached to a molecule of H_3Ch are driven off at the front edge of the band. The combination of the $HCh^=$ anion with H_5Ch^{+2} results in an eluate containing H_3Ch at double the original $(NH_4)_2HCh$ concentration. If the adsorbed species were H_4Ch^+, the H_3Ch concentration in the eluate would be three times the $(NH_4)_2HCh$ concentration. The ratio of HEDTA in the eluate to HEDTA in the eluant exceeds two only at high concentrations so the adsorbed ions must generally consist of H_5V^{+2}.

The water which issues from the column first can be saved and used to dilute the concentrated H_3V solution. After adjusting to a pH of 7.5 with NH_4OH, the solution can be recycled as eluant.

A large percentage of the HEDTA used in each run is found in the rare-earth bearing eluate in the form of RCh, H_3Ch and NH_4H_2Ch. When the rare earths are recovered as their oxalates, all this HEDTA remains in the filtrate along with the excess oxalic acid used as the precipitant. If this filtrate is passed through a series of hydrogen-cycle resin beds, the oxalic acid passes through, and can be concentrated and reused. The HEDTA deposits, of course, as does any unprecipitated rare earth. The rare earths can be salvaged from the first column of the series by eluting with $(NH_4)_2HCh$ and the HEDTA can be recovered from the remaining resin beds by eluting with 0.5 $\underline{M}$ NH_4OH. Ammonium hydroxide neutralizes the hydrogen ions to which the H_3Ch is attached and the resulting eluate is about 0.25 $\underline{M}$ in H_3Ch.

IV. Summary

Since rare earths are not scarce in nature, but have been hard to obtain in the past due to the difficulty encountered in separating them, the ion-exchange method makes it possible to obtain large quantities of the individual rare earths at moderate cost. Experience at Ames has shown that no difficulties are encountered in maintaining level band fronts in columns up to thirty inches in diameter. There appears to be no reason why tank-like columns six to twenty feet in diameter could not be used. Doubling the diameter of the column, of course, doubles the output.

If a number of tanks are arranged in series, it is possible to operate with adsorbed bands one hundred or more feet long, and since the overlap region between adjacent elements varies from a few inches to a few feet depending on the flow rate, the bulk of the rare earths in a long band can be obtained pure in a single pass. The longer the adsorbed band, the higher the percentage of pure material that can be obtained at a given flow rate and the faster the flow rate that can be used without increasing appreciably the fraction of the material which must be recycled.

With rows of columns it is possible to elute one band behind another with only small gaps between bands where the retaining ion is being replenished. Plant efficiency increases when the gaps between bands are small compared to the lengths of the adsorbed bands.

Operating the columns at elevated temperatures should also increase efficiency, since faster flow rates would be permissible due to the more rapid rate of exchange.

Actually, the process requires very little labor and attention and most of the chemicals and water can undoubtedly be recycled in commercial scale operations.

Contrary to popular belief, the properties of the pure rare-earth metals and salts are not all alike, instead they differ considerably. When it is realized that these elements, which comprise nearly one-sixth of the naturally occuring members of the periodic table, are no longer rare but are becoming commercially available at reasonable prices, it will be surprising if a considerable number of important industrial uses do not develop.

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