

Jan. 11, 1966

R. E. LINDSTROM ETAL

3,228,750

PROCESS FOR SEPARATING RARE-EARTH ELEMENTS BY ION EXCHANGE

Filed June 7, 1962

5 Sheets-Sheet 1

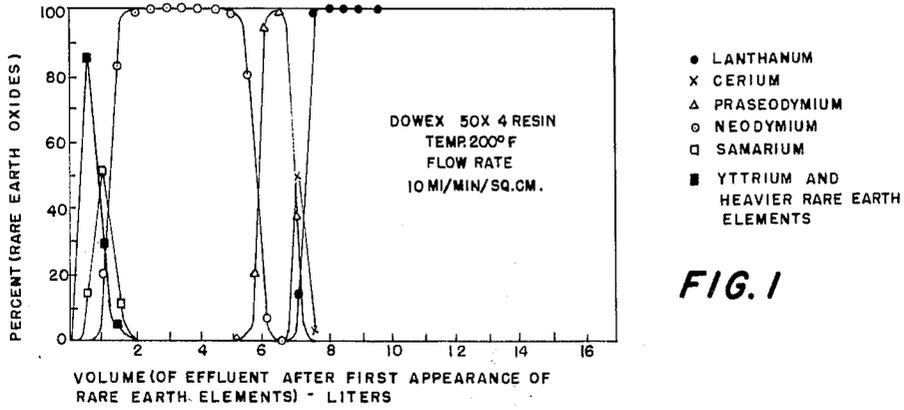


FIG. 1

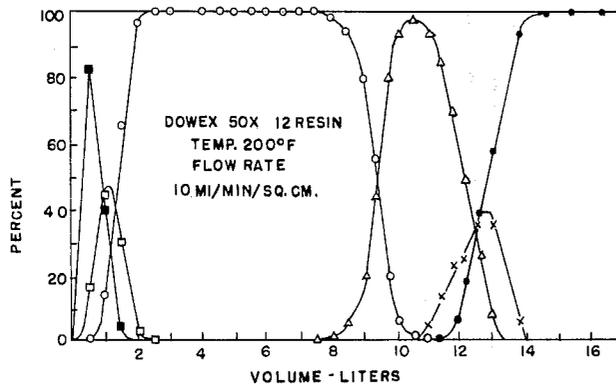


FIG. 2

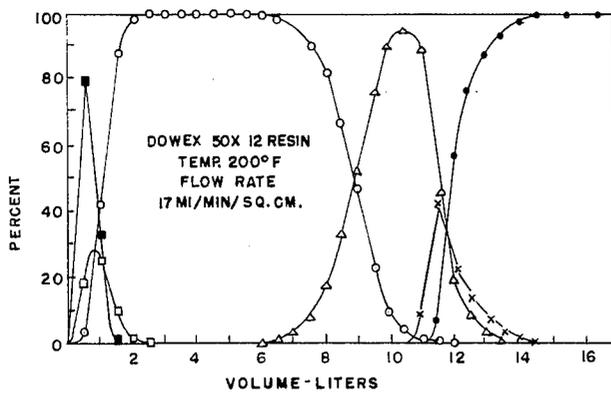


FIG. 3

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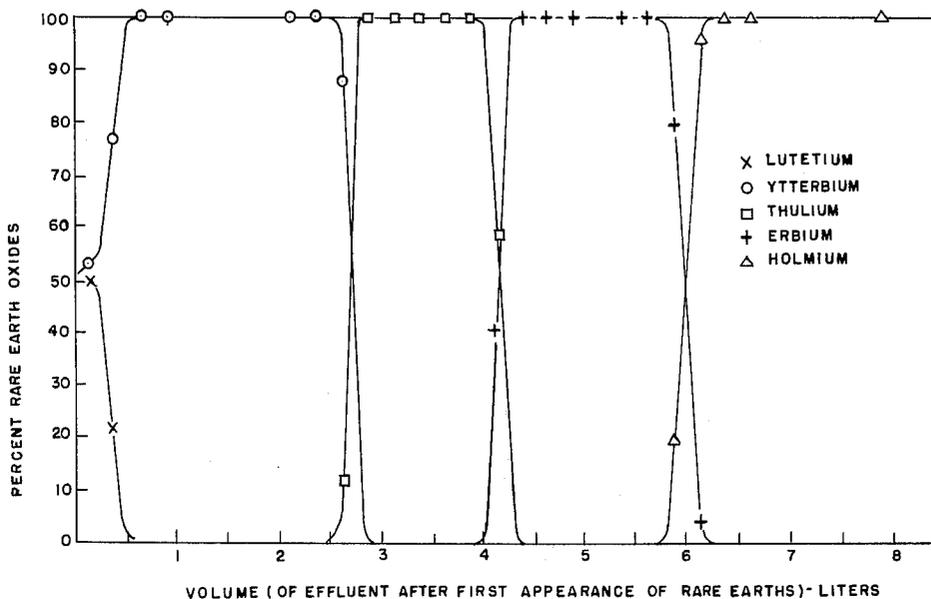


FIG. 4

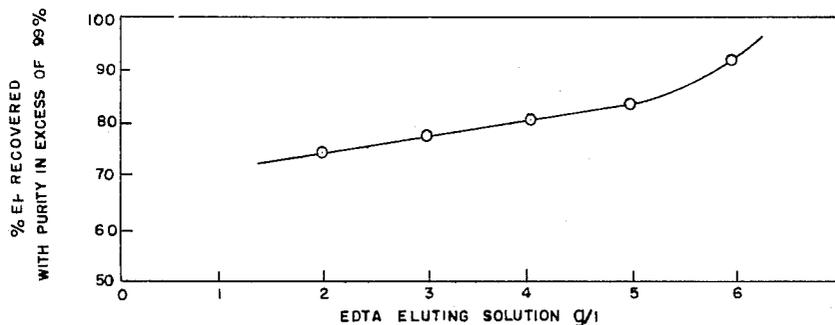


FIG. 5

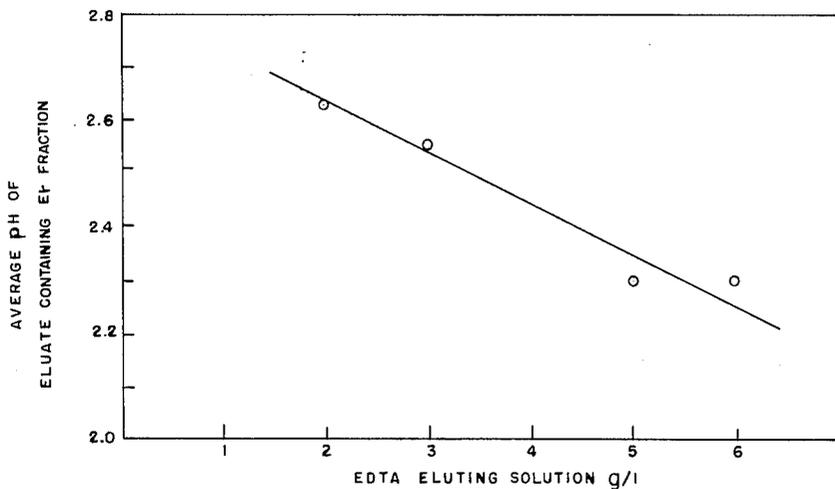


FIG. 6

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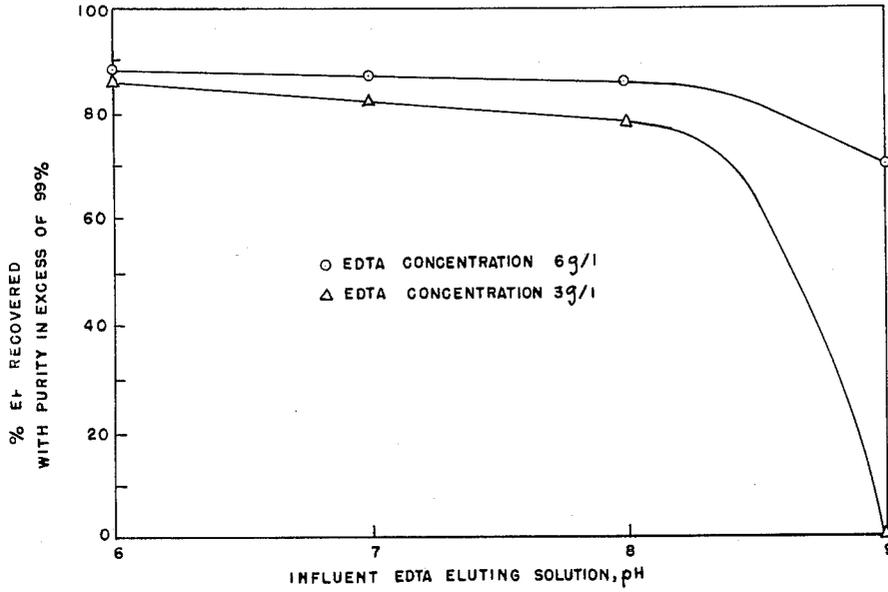


FIG. 7

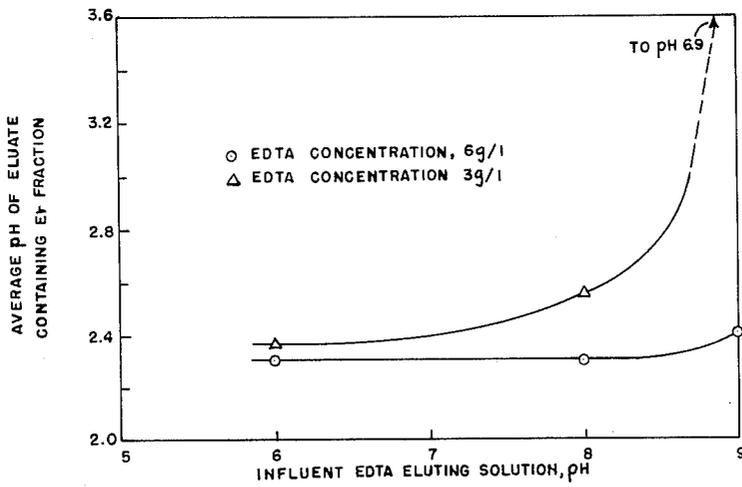


FIG. 8

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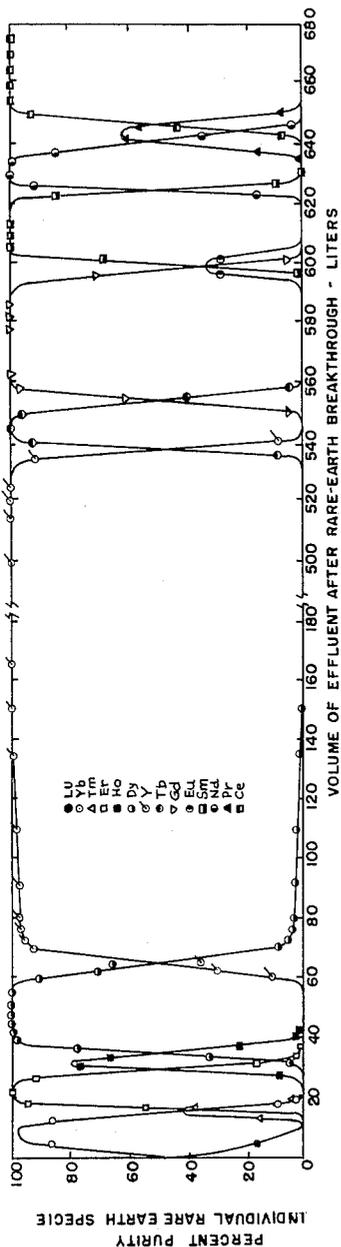


FIG. 9

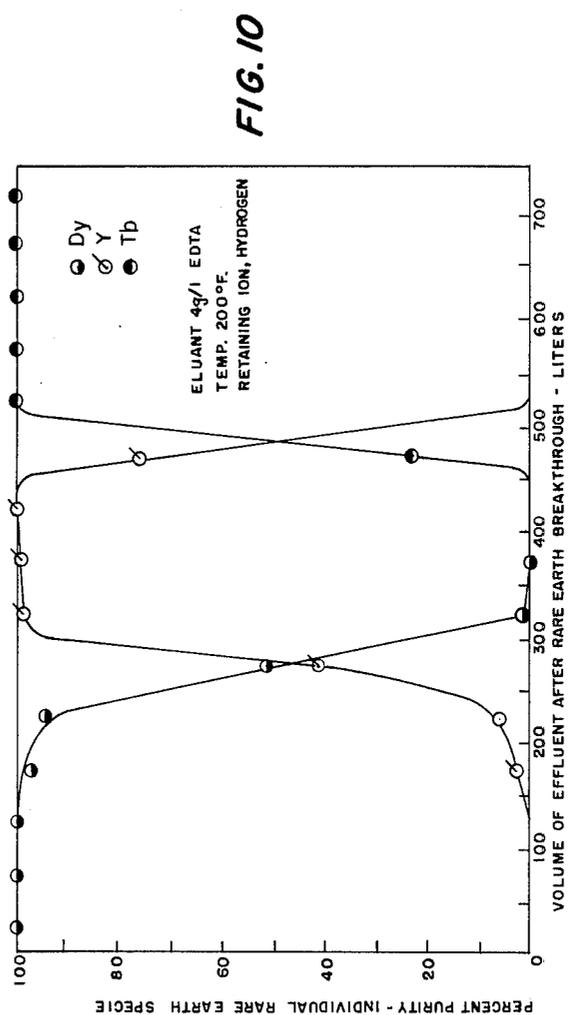


FIG. 10

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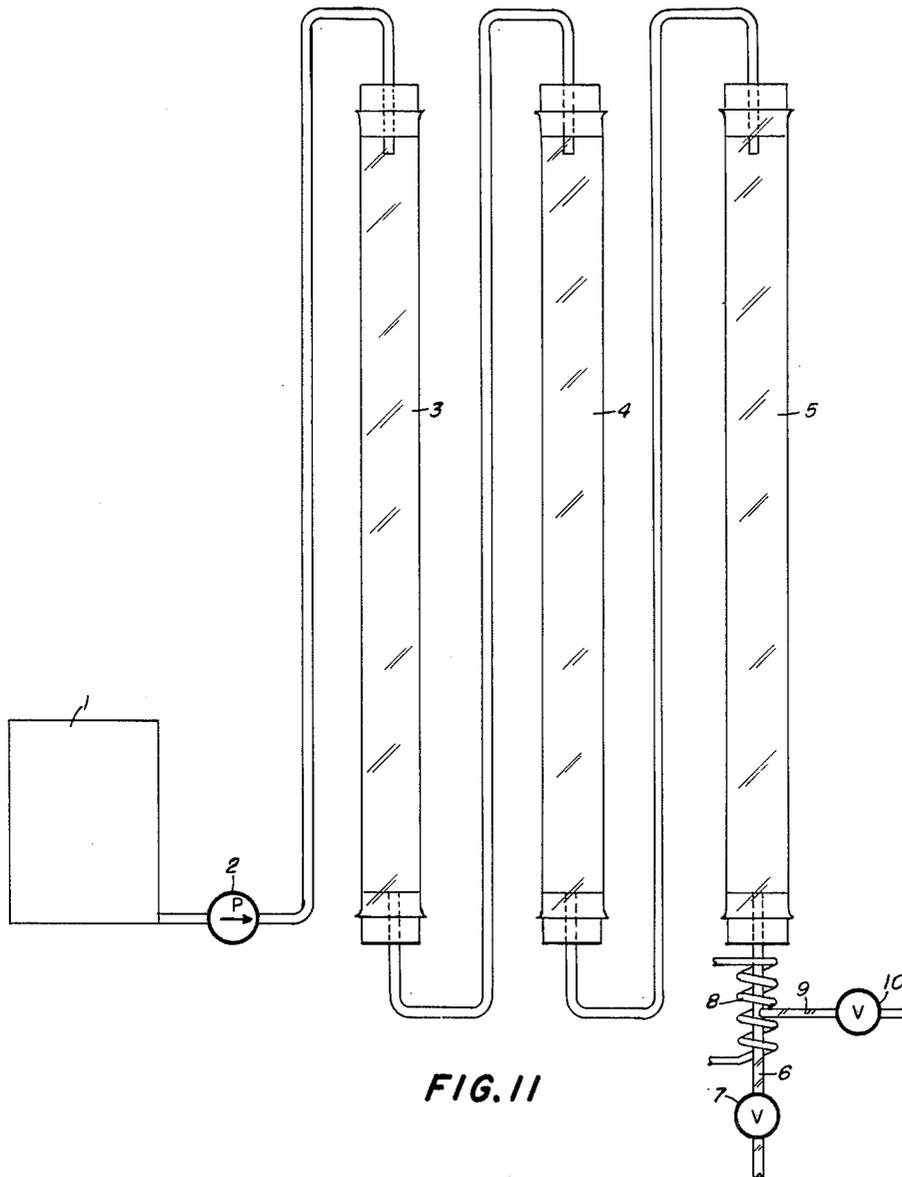


FIG. 11

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PROCESS FOR SEPARATING RARE-EARTH ELEMENTS BY ION EXCHANGE

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 Filed June 7, 1962, Ser. No. 200,894
 7 Claims. (Cl. 23-22)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention is concerned with a method for the fractionation of rare earth mixtures and the recovery of rare earth metals.

The term "rare earths" as used in the present specification includes the lanthanide rare earth elements having atomic numbers from 57 to 71, inclusive, and the element yttrium, atomic number 39, which is ordinarily found in rare earth concentrates and acts similarly to the rare earths in chemical separations.

The rare earths are usually obtained from ore concentrates of the oxides and are difficult to separate due to their great chemical similarity. Fractional crystallization has been employed to separate the rare earth oxide concentrates into their individual components. However, this procedure is a very laborious task and preparation of even comparatively pure individual rare earth species by this method is very difficult. More recently, a major advance occurred in separation of the rare earths with the discovery of the ion exchange method of obtaining individual rare earth species.

According to this method, a solution of the ions to be separated is contacted with an ion exchange resin resulting in an equilibrium between resin and solution. Separation of the different ions is made possible by differences in distribution of the various ions between the solid and liquid phases (values of equilibrium constants differ for different ions). These differences are enhanced by selectively complexing the ions in solution and repeating the ion exchange reaction many times. In practice, a mixture of the elements to be separated are adsorbed from an aqueous solution on a cation-exchange resin and are then washed down the column (eluted) by passing a solution of a complexing agent through the column until separation is achieved. The ion exchange reaction for each ion is repeated many times by this operation and in combination with the effect of the complexing agent results in separation of the individual elements into bands in the columns. Separated elements are then eluted from the column and collected as successive portions of eluate.

The use of citric acid as the elutriant is described in Spedding et al. Patent No. 2,539,282. Various complexing agents other than citric acid have also been employed such as acetic, malic and tartaric acids. It has been found, however, that ethylene diamine tetracetic acid (hereinafter referred to as EDTA), the use of which is described in Spedding et al. Patent No. 2,798,789, is particularly effective in obtaining efficient separation of the rare earths, particularly at high flow rates of the elutriant (aqueous solution of EDTA). Due to the great stability of the rare earth-EDTA complexes, the process of Spedding et al. requires the use of a cation exchange resin having adsorbed thereon a retaining metal ion such as copper^{II} since this ion forms a complex with the EDTA which is more stable than the rare earth-EDTA complexes. In accordance with this procedure the rare earths are first adsorbed on a cation exchange resin bed which is then physically connected with a second cation exchange resin bed having

the copper adsorbed thereon (in the cupric cycle). An aqueous solution of EDTA is then passed in sequence through the first bed containing the adsorbed rare earths and then through the second bed containing the resin in the cupric cycle (copper adsorbed on resin). Rare earths are eluted from the first resin bed in the form of the EDTA complexes and these complexes then exchange with the retaining ions (cupric ions) in the second resin bed. Water-soluble cupric-EDTA complexes are formed and are swept out of the column. The rare earth species form individual bands in the second column and these bands pass through the column, resulting in a very effective separation of the rare earths into the individual species as elution takes place in the column.

The process employing a resin in the copper cycle, however, has the disadvantage that recovery of copper and EDTA from the copper-EDTA complex obtained from the column is very troublesome and discarding the complex without recovery of copper and EDTA represents a considerable increase in operating costs. It would therefore obviously be very advantageous to employ a process in which the EDTA could be recycled directly or recovered easily. Another disadvantage of EDTA in prior art processes has been the insolubility of the acid form of the compound at ambient temperature and pH.

It is therefore an object of the present invention to provide an efficient and rapid method for separating mixtures of rare earth elements and yttrium into individual elements by means of an ion exchange process.

It is a further object of the present invention to provide such a method in which the ion exchange elutriant is EDTA.

It is a further object of the invention to provide such a method in which the EDTA is recovered from the ion exchange column as such and may be recycled directly.

Other objects and advantages will be apparent from the rest of the disclosure.

It has now been found that these objectives may be accomplished by means of an EDTA-ion-exchange process in which hydrogen is employed as the retaining ion and the ion-exchange column in the hydrogen cycle is maintained at an elevated temperature sufficient to insure solubility of the EDTA. In accordance with this process, the rare earths are first adsorbed on a cation exchange resin column in the conventional manner, and this column is then physically connected with a second cation exchange resin column having the resin in the hydrogen cycle and maintained at elevated temperature. An aqueous EDTA solution is then passed in sequence through the first bed containing the adsorbed rare earths and through the second bed containing the resin in the hydrogen cycle. The rare earths are eluted from the first resin bed in the form of rare earth-EDTA complexes and these complexes then exchange with the hydrogen ions on the second resin column resulting in separation of the rare earths into individual bands on the second column.

The acid form of EDTA is first eluted from the columns where it is collected ready for reuse on the addition of ammonia. Subsequently, the rare earths in bands on the second column pass down the column and are collected as separate portions of the eluate resulting in both in a very effective separation of the rare earths and recovery of EDTA as such without need for separation or purification of the EDTA.

Applicant does not wish to be bound by the theory of operation of the separation process, the chemistry of which is rather complex and not fully understood; however, the following reactions are believed to take place on the hydrogen cycle resin:

As the rare-earth-EDTA chelate solution flows from rare-earth-saturated resin through the hydrogen-cycle

resin, the rare-earth ion (from the chelate) is deposited on the resin, displacing (exchanging) three hydrogen ions which go to the EDTA previously holding the rare-earth ion chelated. This EDTA which, on addition of the three hydrogen ions, became a neutral molecule, subsequently associates with two more hydrogen ions from the hydrogen-cycle resin and becomes a divalent cation H_6EDTA^{+2} which is then adsorbed on the resin. The free-acid form of EDTA, which is formed as more rare-earths displace hydrogen, continues to associate with additional hydrogen and adsorb on the resin until, in effect, the adsorbed cationic EDTA has saturated the hydrogen-cycle bed and become the retaining ion. As the rare-earth elements displace the adsorbed EDTA, the EDTA proceeds down the column until it encounters more hydrogen ion, or until it passes from the column. Inasmuch as the EDTA is adsorbed on the resin, only water issues from the column until all the hydrogen-cycle resin is adsorbed with EDTA. After its appearance in the eluate, the EDTA concentration is approximately 1.5 times its original concentration in the eluent. The rare-earth elements continue to displace the adsorbed EDTA until they appear in the eluate. The foregoing discussion indicates that the theoretical concentration of EDTA in the eluate should be 2.5 times its concentration in the column influent. One must conclude (from the data in which the effluent was 1.5 times the influent concentration) that cationic EDTA species is not adsorbed on all the active sites in the resin but just a portion of them, resulting in a retaining column consisting of a mixture of cationic EDTA and hydrogen.

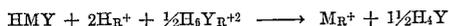
The exact equilibria involved are difficult to determine; however, our results indicate the following as a possibility (equation balances are approximate): During the initial phase of an elution cycle, the exchange reaction at the interface between rare-earth-cycle resin and hydrogen-cycle resin should be:



The H_4Y (free-acid form of EDTA), on contacting additional hydrogen-cycle resin, then enters into this reaction:



After the H_6Y comes to equilibrium with the entire column of hydrogen-cycle resin and the system has reached a steady state, the following over-all reaction apparently predominates:



where M is trivalent rare-earth element, Y is EDTA and the subscript R indicates that the ion is in the resin phase or combined with the resin. Similar phenomena were observed with diethylenetriaminepentaacetic acid by D. R. Asher et al., *Industrial and Engineering Chemical Process Design and Development*, January 1962, page 52, and with hydroxyethylethylenediaminetriacetic acid by J. E. Powell and F. H. Spedding, *Chemical Engineering Progress Symposium Series*, vol. 55, No. 24, 1959, page 111.

The cationic exchange resins employed in the present process are the conventional resins used for adsorbing rare earths such as those of the nuclear sulfonic type. These resins are made up of three dimensional organic networks, including charged or potentially charged groups which are neutralized by mobile ions of opposite charge. Freedom of these mobile ions to move in and out of the resin is provided by water imbibed by the resin on immersion in an aqueous solution which opens up the resin structure, permitting diffusion of ions into and out of the resin-water phase during ion-exchange. The most satisfactory and preferred resins have been found to be the sulfonic acid type resins, such as Dowex 50, which are formed from linear polystyrene chains cross-linked by divinylbenzene (DVB) to form a network structure. Sulfuric acid groups are then attached to this network by sulfonating with concentrated sulfuric acid. The

resins may be obtained in a variety of bead sizes (mesh sizes) and with different porosity or cross-linking. In the case of Dowex 50 the percentage of cross-linking (percentage of DVB) is indicated by an additional number, as Dowex 50x4 indicates 4 percent DVB and Dowex 50x12 indicates 12 percent DVB. Increased cross-linking results in decreased swelling in aqueous solution and in decreased speed of ion exchange; however, this effect tends to be offset by an increase in differences in resin affinities between pairs of ions with increase in cross-linking. Control of porosity of such resins permits selection of the best resin for a specific need. These resins are also chemically and physically stable and possess high exchange capacity.

The ion-exchange resin beds in applicant's invention are employed in the form of conventional ion-exchange columns. The columns consist of glass tubing fitted with rubber stoppers and a porous material, such as Cynel, Teflon cloth or fritted glass to support the resin bed. The exact length and diameter of the column as well as the porosity and mesh size of the resin will vary according to the particular elements being separated. The columns are filled to the desired height with the sulfonic acid type resin as received from the manufacturer. The resin fines are removed by backwashing at a rate sufficient to expand the beds 100 percent. Backwashing also serves to classify the resin and insure a uniform particle-size distribution across the bed to minimize channeling. Electrical heating tapes are used to maintain the column-skin temperature at the desired value.

FIG. 11 is a diagram of the apparatus employed in the invention. The eluting solution is pumped from reservoir 1 by means of pump 2 through columns 3, 4 and 5 and the effluent solution is collected from line 6 by means of needle valve 7. The collection line is cooled by means of cooling coils 8 and dilute ammonia solution is metered into the collection line via line 9 and needle valve 10.

Fresh resin beds are conditioned by elution with a 25 percent excess of a 5 percent solution of hydrochloric acid, followed by a similar solution of ammonium hydroxide; any traces of metal impurities in the resin are removed by elution with a solution of the ammonium salt of the eluent. The beds are washed with deionized water to remove the excess ammonium-salt solution and a similar wash after each run removes excess eluent from the interstices and pores of the resin.

The desired stoichiometric amount of the rare-earth chloride solution is passed through and adsorbed on the first resin bed of each series of beds to be concatenated in the series are placed in the hydrogen cycle by treatment with acid.

The eluent consists of EDTA in aqueous ammoniacal solution, the optimum pH and concentration of which will vary according to the nature of the rare earth charge stock, speed of elution, nature of the resin and physical arrangement of the resin beds. The concentration of the EDTA may vary over a range of about 1 gram per liter to about 6 grams per liter and the pH may range from about 6 to 9. In general the pH of the influent eluting solution should be such that the first lutetium samples collected will have a pH of approximately 1.8, then the pH of subsequent rare earth fractions increases as the succeeding species are collected to approximately 3.2 for lanthanum. Provided the temperature is kept above the solubility of the EDTA in all cases, the process could be operated, for example, with an EDTA influent concentration of 6 grams per liter and a pH of 8.0 or with the same pH and a concentration of 3 grams per liter. For practical considerations it is best to use the highest possible eluent pH since at lower pH values much of the EDTA passes through the system unused. However, if the eluent pH is too high (above about 9.0) rare earth elements will leak through the bed resulting in loss of separation efficiency. In systems such as that of the

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instant case, a portion of the resin downstream from the rare earth saturated resin is used in attaining the equilibrium pH. Therefore, if short beds are used, the equilibrium pH may be reached faster by carrying out initial stages of the elution cycle with the eluting solution at a pH of approximately 5.

Flow of eluent is from top to bottom, through the rare-earth-cycle resin bed and then through the hydrogen-cycle resin bed. By continued elution the effluent is collected as a series of equal-size fractions or samples and the pH of each sample is measured. At least the column containing the resin in the hydrogen cycle and preferably both columns are maintained at elevated temperature sufficient to insure solubility of the free acid form of the EDTA. The temperature required will depend on the concentration of the EDTA in the eluent solution and on the pH of the eluent solution and may range from about 200° F. to 250° F.

The following example will serve to more particularly describe the invention.

Example I

19 grams of a mixture of rare earth oxides was prepared by leaching of a bastanite concentrate assaying 55 percent rare-earth elements, removal of most of the cerium and one half of the lanthanum by conventional chemical means, precipitation as oxalates and conversion to oxides by ignition at 1750° F. The mixture of oxides which had the following analysis:

Element	Oxide basis, weight percent
Lanthanum	18.0-19.5
Cerium	0.4-3.0
Praseodymium	18.0-21.5
Neodymium	46.0-49.5
Samarium	4.0-5.0
Heavier rare-earth elements	4.0-6.0

was dissolved in hydrochloric acid, evaporated to near dryness and redissolved in deionized water. A few drops of hydrochloric acid were then added to complete the solution of the chlorides. The solution of rare earth chlorides was then loaded on the first of two columns to be connected in series by passing the solution of chlorides through the resin-containing column. The second column was placed in the hydrogen cycle by passing a solution of hydrochloric acid through the column.

The ion-exchange columns consisted of glass tubes, of 1.7 cm. inside diameter and 110 cm. in height, filled with resin to a height of 104 centimeters. The columns were arranged vertically in series with the rare earth loaded column at the top and the column in the hydrogen cycle in series below the rare earth column. The temperature of both columns was maintained at 200° F. by means of electric heating tape and the column surface temperature was measured with a pyrometer.

The rare earths were eluted from the columns with a .015 molar solution of EDTA in aqueous ammonia having a pH of 8. Vacuum degassed water was used for the solution in order to minimize bubble formation in the heated columns. Elution was accomplished by forcing the eluent through concatenated rare-earth and hydrogen cycle columns by means of a polyethylene acid egg pump. Dilute ammonia solution was metered into the collection line leading from the bottom of the last column to prevent EDTA from precipitating in the line as it cooled, the flow of ammonia being stopped just before rare-earth breakthrough. The collection line was jacketed with cooling water to prevent the hot EDTA solution from evaporating at the outlet valve.

Following separation, the rare earth elements were precipitated as oxalates, ignited to oxides at 1600° F. and analyzed by X-ray emission spectroscopy.

The results of the separations using Dowex 50x4 resin and a flow rate of 10 ml./min./sq. cm. are shown

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in FIG. 1. FIG. 2 shows the results obtained using Dowex 50x12 and the same flow rate while FIG. 3 shows the results using Dowex 50x12 and a flow rate of 17 ml./min./sq. cm. In the figures the percentage of each rare-earth element in a fraction of the collected eluate was plotted against the cumulative volume of the fractions, i.e., fraction analysis versus cumulative fraction volume. Fractions in the center of individual rare-earth bands were plotted as 100% when analysis showed only one element present; however, 0.1% of other elements may be present.

Example II

The experimental arrangement in this example was similar to that of Example I except that three columns were employed instead of two as in Example I. A charge stock consisting of 20 grams of a mixture of heavy rare earth oxides having the following analysis:

Element	Oxide basis, weight percent
Holmium	25
Erbium	24
Thulium	14
Ytterbium	33
Lutetium	4

was dissolved in hydrochloric acid and the mixture of rare-earth elements absorbed from the chloride solution on the first of three ion exchange columns containing 50 to 100 mesh Dowex 50x4 resin connected in series. The second and third columns were placed in the hydrogen cycle by passing hydrochloric acid through them. The eluent consisted of aqueous ammonia solutions of EDTA adjusted to the desired value of pH with ammonium hydroxide and in concentrations of 2, 3, 4, 5 and 6 grams of EDTA per liter.

The results of the elution using a 5 gram per liter EDTA solution having a pH of 8 as eluant are given in Table I and are shown graphically in FIG. 4.

FIGURES 5 and 6 show the effect of concentration of the EDTA solution on separation and on the pH of the erbium eluate respectively. Erbium was chosen to represent the separation efficiency because it was one of the dominant species present in the charge and data regarding hydrogen ion concentration in the eluate fractions were more consistent. Hydrogen ion concentration values for early lutetium and ytterbium fractions were considered unreliable due to the addition of ammonia to the collection line leading from the bottom of the last column, as described in Example I, resulting in considerable variation in pH values of lutetium and first ytterbium samples.

FIG. 5 shows that separation efficiency increases with the concentration of EDTA in the eluting solution. The increase in separation with concentration of the eluting solution is attributed to the decrease in effluent pH of the erbium fraction (FIG. 6). As the EDTA concentration in the eluting solution is increased, the pH in the rare-earth-saturated resin bed decreases, thus creating conditions more favorable for the separation mechanism.

FIG. 7 shows the variation in amount of erbium recovered (with a purity in excess of 99 percent) with a change in the pH of the influent eluting solution. These data show that separation declines moderately with an increase in pH of the eluting solution until it is raised above 8. Between pH 8 and 9, separation declines markedly. Presumably, this decline in separation is due to an increase in pH in the rare-earth band. The variation in pH of the rare-earth effluent with change in pH of EDTA eluting solution is shown in FIG. 8. The reason for decline in separation with increasing pH in the rare-earth band is not clear. Apparently, two major factors are involved; at influent pH values above 8, the excess ammonia converts the hydrogen cycle resin to the ammonia cycle and as a result, the chelated rare-earth mixture passes through the resin with little or no exchange

taking place; at influence pH values of 8 and below, the rare-earth elements are retained in a compact band upstream from the hydrogen cycle resin. The continued increase in separation with decreasing pH in the rare-earth band may be due to an increase in relative amounts of the HMY chelate species over the MY-species (where M is the trivalent metal ion and Y is the EDTA). A preponderance of the HMY species at low pH values may account for the increased separation either because of more rapid and/or complete exchange of rare-earth elements between the resin and the EDTA or because of a greater difference between the stability constants of the HMY chelates for different rare-earth species.

Example III

This example shows the results of macro-scale separations employing five 8-foot long columns, two of which were of 4 in. interior diameter, two 3 in. interior diameter and one 2 in. interior diameter, all the columns being filled with 50-100 mesh Dowex 50x4 resin. The charge was loaded on the first 4 in. diameter column and eluted through the other four columns in the hydrogen cycle, with an ammonia-EDTA solution having a pH of 8.0 and an EDTA concentration of 4 grams per liter. All columns were again maintained at a temperature of 200° F. by means of electrical heating tapes.

The charge stock for the first macro-scale run consisted of a mixture of oxides of rare-earth elements and yttrium prepared from a euxenite concentrate and having the following analysis:

Element	Oxide basis, weight percent
Lanthanum	0.1
Cerium	10.6
Praseodymium	.9
Neodymium	2.6
Samarium	3.8
Europium	.5
Gadolinium	7.9
Terbium	2.7
Yttrium	58.1
Dysprosium	5.8
Holmium	1.0
Erbium	2.7
Thulium	.3
Ytterbium	2.5
Lutetium	.3

The second macro-scale run employed a charge stock of the following composition:

Element	Oxide basis, weight percent
Terbium	33
Ytterbium	34
Dysprosium	33

FIGURES 9 and 10, in which the percent of each element present is plotted against the volume of effluent collected, represent a summary of the data for runs one and two, respectively.

FIGURES 9 and 10 show that good resolution is obtained between all the elements except dysprosium and yttrium. Under similar conditions at ambient temperature, yttrium is nearly centered between dysprosium and terbium in the elution sequence and its separation from each of these elements is almost equally difficult. The data shown in FIGURES 9 and 10 indicate that temperature has the effect of shifting yttrium toward dysprosium in the elution sequence so that its separation from dysprosium is more difficult, and its separation from terbium easier. Inasmuch as the shift of the yttrium is toward dysprosium and holmium where it lies in the selectively sequence of the resin for the rare-earth elements, one may suspect that the elevated temperature has increased, to a degree, the resin's influence as compared to that of EDTA.

All of the column effluent in the examples, collected before breakthrough of the rare earth elements, contained EDTA which was free of impurities and therefore ready to be recycled in the system without further treatment, other than adjustment of the pH with ammonia.

The advantage of applicants' process in avoiding the use of metal ions such as copper and thus obtaining reusable EDTA in effluent solutions before rare earth breakthrough is believed to be readily apparent. Further advantages of the use of elevated temperature are increased separation efficiency of the ion-exchange columns and ready recovery of EDTA from the solutions of rare-earth-EDTA complexes since the rare earths may be precipitated from the hot solution with oxalic acid, the EDTA remaining in solution. A further advantage of applicants' invention is that the large quantities of high purity water used in the system may be recycled. Further, regeneration or conversion of the resin between runs with sulfuric acid is simple and economical.

A still further advantage of applicants' method is the possibility of increased throughput by allowing the use of either shorter length of elution or faster flow rate.

The invention is obviously not limited to the specific mixtures of rare earths employed in the examples and may be used with a wide variety of types and amounts of rare earth mixtures. The process may also be varied widely with respect to the pH and concentration of the elutriant solution, the composition and mesh size of the resin, the physical arrangement of the resin beds, etc., without departing from the essential spirit and scope of the invention. Furthermore, the invention is applicable to other resins which are characterized by insolubility of the acid form at ambient temperature such as DCTA (1, 2 diaminocyclohexanetetraacetic acid).

What is claimed is:

1. A process for the separation of rare earth metals comprising providing at least two cation-exchange resin beds in series, contacting the first bed with an aqueous solution of salts of the rare earth metals to adsorb the rare earth ions on the resin, contacting the succeeding resin beds with an acid capable of placing the resin in the hydrogen cycle to place the resin in the hydrogen cycle, maintaining at least the hydrogen cycle resin at an elevated temperature of about 200° F. to about 250° F., sufficient to ensure solubility of the acid form of EDTA, passing an eluant comprising an aqueous ammoniacal solution of EDTA having a pH in the range of about 6 to about 9 through the rare earth cycle resin whereby the rare earth ions in the resin are complexed by the EDTA, subsequently passing the solution of complexed rare earth ions through the hydrogen cycle resin whereby ion-exchange takes place between the complexed rare earth ions in solution and the hydrogen ions on the hydrogen cycle resin, continuing elution with an aqueous ammoniacal EDTA solution having a pH in the range of about 6 to about 9 and collecting initially the acid form of EDTA in solution and subsequently successive portions of eluate each containing a separated rare earth in solution.

2. The process of claim 1, in which both the hydrogen cycle resin bed and the rare earth cycle resin bed are maintained at elevated temperature.

3. The process of claim 1, in which at least the hydrogen cycle resin bed is maintained at a temperature of 200° F.

4. The process of claim 1, in which concentration of the EDTA in the eluant solution is from 2 to 6 grams per liter.

5. The process of claim 1, in which the pH of the EDTA solution is 8.

6. The process of claim 1, in which the resin is a sulfonic acid type resin.

7. A process for the separation of rare earth metals comprising passing an eluting solution comprising an aqueous ammoniacal solution of EDTA having a pH in the range of about 6 to about 9 through a first cation-

exchange resin bed in a rare earth cycle and subsequently through a second cation exchange resin bed in hydrogen cycle, at least the second resin bed being maintained at an elevated temperature of about 200° F. to about 250° F., sufficient to ensure solubility of the acid form of EDTA which is formed during the elution, and collecting successive portions of the resultant eluate containing initially the acid form of EDTA in solution and subsequently the separated rare earth ions in solution.

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