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PROGRESS IN METHODS FOR THE SEPARATION OF RARE-EARTH ELEMENTS

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INTRODUCTION

The position with regard to rare-earth elements (REE) has changed a good deal since our last review[1]. Experimental production of individual REE, based on Soviet raw materials, has been organised at a series of places in the USSR, and REE preparations with a very high degree of purity have become commercially available[2,3]. Work connected with the chemistry and technology of these elements has increased greatly.

In view of advances in this field which have been achieved recently in the USSR and abroad, another review of the methods for separating REE seemed timely. Not only have new, successful methods been developed — ion exchange, extraction, and electrochemical methods — but the classical methods of fractional crystallisation and fractional precipitation are also being perfected. The use of complexing agents[4] in the fractionation greatly improves these methods and makes it possible to use them industrially. A series of quite new methods of separation have been suggested: a so-called "dry" method based on differences in rates of chloride dehydration, an oxinesulphonic acid method, and others.

FRACTIONAL CRYSTALLISATION AND FRACTIONAL PRECIPITATION

In its classical form division of the total REE into subgroups by means of double sulphates is very laborious and time consuming. Complexing reagents, in particular ammonium acetate[5], have now been introduced to speed up this process. The maximum separation effect is achieved when a deficient amount of this reagent is used: the components forming more soluble double sulphates remain in solution. When separating a mixture of the yttrium-group elements to prepare 80–90% Gd and Dy concentrates, 25–30 precipitations are required instead of the 400–500 in the classical scheme. Still better results are obtained on introducing a deficient amount of a more powerful complexing agent, e.g. nitrilotriacetic acid (Complexone I), the use of which allows heavy REE, Tm, Yb, and Lu, to be isolated from a 9–10% solution in a comparatively short time.

Vagina[6], and also Gordon and Shaver[7], carried out the separation of some pairs of REE as oxalates in the presence of ethylenediaminetetraacetic acid (EDTA). When a hot solution containing oxalic acid and REE ions complexed with EDTA was slowly cooled, "homogeneous" precipitation of REE oxalates took place. The complex decomposes, to give M^{3+} ions which combine with $C_2O_4^{2-}$ ions and form difficultly soluble oxalates. The method is very selective compared with the usual oxalate method used in the absence of EDTA[8].

The same principle forms the basis of the gradual precipitation of REE by $C_2O_4^{2-}$ ions formed by hydrolysis of methyl oxalate[9]. The author considers that it does not possess any special advantage over other similar methods, but is to be recommended for purification of yttrium preparations.

Vickery[10] put forward a method of "homogeneous" precipitation of double sulphates. On adding an alkali-metal sulphite to a solution of mixed REE chlorides, soluble double sulphites are formed. By the action of oxidising agents such as O_2 or H_2O_2 in the presence of catalysts, e.g. Cu^{2+}, Mn^{2+}, Fe^{2+} (at pH 1.6–1.8), the double sulphites are gradually transformed into double sulphates. With controlled precipitation, a higher degree of separation of the total REE into subgroups is attained than is the case in the usual method employing double sulphates.

Virts[11] studied the influence of methods of crystallisation on the effectiveness of fractionation of mixtures of cerium earths in fractional crystallisation of double magnesium nitrates. The best results were obtained by seeding the hot solution of the double nitrates and allowing it to cool slowly with vigorous stirring.

Marsh[12] compared a method of crystallising basic nitrates of the type $M(NO_3)_3 \cdot M[M(OH)_5NO_3] \cdot 6.5H_2O$, where M = Ho, Er, or Y, with the ferricyanide method, and concluded that although the latter gives a higher separation coefficient, the nitrate method is to be preferred because of the difficulties connected with decomposing the ferricyanide and subsequently removing the iron.

A method of separating yttrium from REE using fractional crystallisation of carbonates has been described[13,14]. A solution of mixed REE nitrates was cooled to 0° and saturated with carbon dioxide. Crystalline NH_4HCO_3 was added to the mixture in amount sufficient for precipitation of 50% of the REE. The solution was stirred for three days, CO_2 was then passed for one day, and the precipitate was filtered off and dissolved in HCl. It was found that under these conditions the solubilities of the carbonates increase in the order: Pr, Nd, Sm, La, Gd, ... Lu, Y. A tenfold fractionation of a mixture containing 72 mole % Y_2O gave 98% Y_2O in 80% yield.

Marsh[15] prepared crystalline salts of REE with EDTA*, and determined their solubilities in water. The salts, made by heating the reagents,

$$M_2O_3 + 2NaOH + 2H_4E = 2Na[ME] + 5H_2O,$$

were recrystallised from weakly alkaline solution. The author considered that salts of this type are more suitable for fractional crystallisation than bromates or dimethylphosphates. Using EDTA, Marsh separated Lu and Y from a mixture.

Brunisholz et al.[16-20] recommended not only crystallisation of EDTA complexes of the type Na[ME] and NH_4[ME] with elements of the cerium group, but also fractional precipitation of the acids H[ME]. These authors isolated a

* In formulae EDTA is represented by H_4E.

series of crystalline EDTA salts of REE and determined their solubilities in water. In a study of the solubility isotherms at 0° for the system $NH_4[LaE]-NH_4[SmE]-H_2O$, it was shown that an α-phase separates, and that this consists of mixed crystals $NH_4[(Sm, La)E]$ rich in samarium, as well as a β-phase having the composition $NH_4[(La, Sm)E]$ and rich in lanthanum. When the α-phase has separated and been removed from the system, the β-phase begins to separate. It also was removed, and then a fresh portion of the mixture was added, and the crystallisation repeated. This is the basis of a cyclic process for separating REE, and the present authors have used it for fractionating mixtures containing La, Pr, Nd, and Sm.

Weaver[21] found that REE and mandelic acid give salts with formulae $M[C_8H_7O_3)_3 . nH_2O$ (n = 2.3), which differ considerably in solubility (the salts of the light metals are very soluble and those of the heavy ones sparingly so). Their solubility is greatly dependent on solution pH and temperature. The author turned this to account in fractionating an REE mixture. Mixed REE oxides (1 milligram to 100 grams) were converted to chlorides, and mandelic acid (crystalline or dissolved) or ammonium mandelate was added to their solution. The precipitates were separated and washed, then dissolved in hot dilute HCl and reprecipitated with ammonia, the resulting precipitates being combined with the appropriate filtrates and again fractionated at a definite pH. The method is recommended by the author for removing and separating heavy REE.

Freeman[22] published a preliminary communication about the application of organic solvents to the separation of mixtures of anhydrous chlorides. After a mixture of equivalent amounts of $NdCl_3$ and $DyCl_3$ had been shaken for 5 min with anhydrous acetone, 82% Nd and 18% Dy were found in the insoluble portion, and 24% Nd and 76% Dy were in solution. The method evidently deserves further development.

Indian workers[23] have suggested a method depending on the difference in the pH of precipitation of REE chromates for separating La from mixtures of elements of the cerium group not containing Ce.

Hall[24] used double chromates of the type $K_2CrO_4 . M_2(CrO_4)_3$ to separate Y from other REE. To a solution of nitrates equivalent to 100 grams of the oxides (M_2O_3 41%, Y_2O_3 58–59%), 216 grams of $K_2Cr_2O_7$ were added, the solution was made up to 1 litre and heated almost to boiling, 10% KOH solution was added dropwise with stirring, and the mixture heated for about an hour. Precipitation occurred in the order Nd, Gd(Tb), Dy, Ho, Er, and Y. The composition of the final fraction, i.e. that remaining in the mother liquor was (in %) Dy_2O_3 0.4, Ho_2O_3 0.2, Er_2O_3 0.4, and Y_2O_3 99.0.

Fractional precipitation of REE as hydroxides still remains important: it is used in work with kilogram quantities of REE. Mironov and Odnosevtsev[25,26] used it for extracting REE from industrial wastes and for obtaining concentrates of individual REE.

Trombe[27] used the ammonia method which he had worked out as long ago as 1943 to fractionate 82 kilograms of REE of the cerium group. The starting material consisted of a number of carbonates of La, Nd, Pr, Ce, Sm, and yttrium-group elements. It was dissolved in concentrated nitric acid, and the solution brought to pH 4 with ammonia (to separate Fe and Al present); then the pH was raised to 5.5 and $(NH_4)_2S_2O_8$ added to separate Ce. La was precipitated from the filtrate by passing in a mixture of gaseous ammonia and air. Precipitation was carried out in 300 litre ceramic vessels, and 4 fractions were taken: at pH 7.7, 8.1, 8.6, and finally from concentrated ammonia solution. The process was controlled by spectrophotometric and magnetic methods: 82 kilograms of mixed oxides yielded 10 kilograms of cerium oxide, 5 kilograms of oxides enriched in samarium and yttrium, 48 kilograms of mixed praseodymium and neodymium oxides, 5 kilograms of 95–97% La_2O_3, 7 kilograms of 97–98% La_2O_3, and 7 kilograms of La_2O_3 of purity greater than 99.5%.

Hilal[28] separated Ho by the ammonia method from a mixture of elements. Air containing ammonia was passed through a 4% solution of mixed nitrates, and the hydroxides were withdrawn as separate fractions. After 40 precipitations a good enrichment of holmium was attained, and there was an incidental concentration of ytterbium and yttrium. Hagiwara[29,30] carried out a series of investigations on the separation of REE mixtures as hydroxides, studying in particular the role of acidity of the medium on the process.

Misumi[31] fractionated La–Ce mixtures using urea hydrolysis at 90°–95° to effect fractional precipitation of basic salicylates and formates. He obtained cerium preparations of ~95% purity.

Kotlyarov and Kozhemyako[32] used Prandtl's method of fractional precipitation with ammonia in the presence of ammonium salts to separate La from Nd and Pr. These workers recommend a combination of fractional crystallisation with base precipitation in the presence of ammonium acetate as complexing agent for removal of small amounts of Pr in the La.

The iodate method[33,34] is often used to separate Ce from neighbouring elements. The mixture of oxides is dissolved in H_2SO_4 (1 : 1), diluted with water, and HNO_3 (specific gravity 1.42) is added, followed by H_2O_2 to convert all the cerium into the trivalent state. The whole is then left for a few minutes, cooled to 40°–60°, and NH_4IO_3 added. The reactants are well mixed and $(NH_4)_2S_2O_8$ is added to the resultant clear solution to oxidise all the cerium. Next the solution is stirred, heated to 70°–80°, and left on a hot plate for 2–3 h, after which it is stirred and cooled. A well-formed crystalline precipitate of $Ce(IO_3)_4$ forms slowly. It is separated, washed, and calcined to the oxide. The method is successful not only for the separation of cerium from REE, but also for its quantitative determination. Elements giving difficultly soluble iodates interfere: Sr, Ba, Bi, Sn, and others.

Ryabchikov and Vagina[35,36] suggest a separation of cerium from cerium-group elements, the ability of quadrivalent cerium to form complexes with acetate and oxalate ions, which are stable in solution. After using this method twice a 99% pure preparation is obtained in 96.8% yield.

EXTRACTION WITH ORGANIC SOLVENTS

The extraction method possesses a number of important advantages over crystallisation and fractional-precipitation methods: there is no need for repeated filtration or repeated dissolution of the precipitate. The time required for each separate operation is much less than for the latter two methods. Thanks to the possibility of carrying out the process continuously, it is coming into use for preparative purposes[37–41].

Thus Bock and Meyer[42] constructed a continuous countercurrent column and used it to extract quadrivalent cerium with ether. The optimum feed rate for the cerium

solution was 0.4–0.5 litres/h, while the optimum feed rate for the ether and for the wash nitric acid was 4–5 litres/h. The product contained ~99.5% Ce and the yield was 85%.

Weaver et al.[43] successfully used a countercurrent extraction method to separate large amounts of REE. In particular, this method was used to isolate more than 1 kg of 95–98% Gd_2O_3. The organic solvent used was tributylphosphate containing Varsol. The authors consider the liquid–liquid system extraction method to be the most promising for separating REE.

Fischer[44,45] used an arrangement of automatic extractors which allowed of approximately complete separation of components. Ether and pentan-2-one were the organic solvents, and $LiNO_3$ the salting-out agent. In one experiment 34 g of 90% gadolinium oxide (10% Sm and traces of Tb and Dy) gave, after putting 350 litres through a 25 stage apparatus, a 50% yield of 99% Gd_2O_3. All the samarium was removed after only 10 stages. Many more operations would be required in the crystallisation method to secure comparable results. In another extraction experiment, with an yttrium concentrate (660 g), 400 g of 99.5% Y_2O_3 were obtained after running 233 litres of pentanone through 76 stages.

The literature mentions every possible organic solvent for separating REE mixtures. To separate cerium as hexanitratoceric(IV) acid, $H_2[Ce(NO_3)_6]$, from an REE mixture, Klinaev and Senyavin[46] recommended ether, and other authors[47–50] ethyl and butyl acetates. Tributylphosphate, $(C_4H_9O)_3PO$, is widely used as a solvent[51–57]. Fomin[58] showed that from acid solution cerium goes into the organic phase as a compound of composition $Ce(NO_3)_3 \cdot 3(C_4H_9O)_3PO$. Tributylphosphate is also used to separate mixtures of light REE and to isolate yttrium.

The literature mentions[59] the use of di- and monoalkylphosphoric acids, and of a series of new trialkylphosphates, dialkylphosphates, and phosphine derivatives as solvents for REE. Peppard et al.[60,61] suggested bis(2-ethylhexyl)-orthophosphoric acid for use as the organic phase in separating tracer amounts of REE. This method is used for the separation of gadolinium. Various ketones: acetylacetone, thenoyltrifluoroacetone (TTA), pentan-2-one[62], 4-methylpentan-2-one (hexone), etc., are also widely used. As Keenan and Suttle[63] showed, when an aqueous solution of $PrCl_3$ is shaken with a benzene solution of TTA, the Pr^{3+} ions are distributed between the water and the organic phase, and form an inner complex with the TTA.

Dyrssen[64–66] made a series of studies of the extraction properties of various REE complexes, and he observed, in particular, that the oxine and cupferron complexes are extracted by chloroform and hexone. This can be used for the separation of REE mixtures. It has been mentioned that 1-nitroso-2-naphthol and disalicylalethylenediimine do not form complexes with REE, which are not therefore extracted by organic solvents in the presence of these reagents. Tropolone gives complex tropolonates with Y^{3+}, but they are difficultly soluble in chloroform.

Evidently research on the extraction method must proceed in two directions: synthesis of new complexes extractable by organic solvents, and selection of new organic solvents which can form complexes with REE, along with steady development of the extraction procedure itself.

ION EXCHANGE

The method of separation on ion-exchange columns was first suggested in 1947, and immediately became widely used. At first citric acid and its salts were exclusively used as eluents, and they are still being used for separating REE[67–70].

In 1954 Spedding and Powell[71,72] published a theory of the separation of REE citrates which was basically in agreement with a theory previously put forward by Ryabchikov[73]. Trombe and Loriers[74] made a real advance in the method of separating REE on columns. To extract REE from large volumes of eluates containing citric acid, the latter were acidified to pH < 2.7 and run through small auxiliary columns. The REE are absorbed and subsequently eluted with a small quantity of citric acid; the free citric acid can be used again. This method allows REE to be concentrated into a small volume without evaporating solutions.

To accelerate REE separation on columns the same authors[75] suggest using a series of small columns instead of one large one. The solution can be run through all the columns in succession. Before the most rapidly eluted REE component comes through, the mixture components are localised on individual columns. If the apparatus consists of a large number of columns, some of them can contain only one REE, and elution can be carried out on each column separately. The method was tested in an apparatus treating up to 1 kg of REE per cycle. At present all large-scale plants for separation usually consist of a series of columns.

In addition to citric acid, many other organic acids are at present used as eluents: lactic acid[76,77], glycolic acid[78], α-hydroxyisobutyric acid[79–81]. Mayers and Freiling[82] made a comparative study of the effectiveness of the separation of REE on Dowex 50 resin using citric, lactic, malic, and glycolic acids, as well as EDTA. The experiments were carried out at various temperatures, acidities, and complexing-agent concentrations. Of all the acids investigated the most selective was EDTA. Loriers and Carminati[83] eluted with a solution of nitrilotriacetic acid (Complexone I). Using a 130 × 3 cm Dowex 50 column and Complexone I at pH 4–6, 300–400 g of almost pure Nd, Pr, and La were obtained in one cycle. These authors also demonstrated that Complexone I is more selective than citric acid and its salts, and further that Complexone I allows more concentrated eluates to be obtained.

Holleck and Hartinger[84–86] confirmed the conclusions reached by the previous workers. On separating the same mixture under the same conditions (on Nalcite HCR), using citric acid, they isolated 44% pure Nd, whereas with Complexone I it was 83% pure.

Andreeva and Rozhdestvenskaya[87] determined the order of elution of Y when REE adsorbed on KU-2 cation-exchanger are eluted with Complexone I. The method consisted in introducing the REE mixture containing Y on to ten columns (10 × 1.8 cm) filled with the resin, and then running through an eluting solution of Complexone I until the REE appeared in the eluate from the last column. After washing the system through until there was no reaction for REE, the columns were disconnected and the REE eluted from each. It was established that, independently of the concentration and pH of the Complexone I solution, Y is washed out between Gd and the cerium REE. Using a 0.5% solution of Complexone I, pure yttrium was obtained from one concentrate containing 93% Y (remainder Dy, Tb, and Gd), and in another instance it was isolated from a concentrate containing 16.5% Y (remainder Dy, Er, and Ho).

EDTA has been more widely used as an eluent than has Complexone I. In 1953 Spedding[88] established that the preparation of individual REE can be much accelerated if the starting mixture is first fractionated with an acid ammonium salt of EDTA. The EDTA salt (pH 10) was added, in amount sufficient to form complexes with the heavy REE, to a neutral solution of 312 g of mixed oxides, and diluted with water to 90 litres. When equilibrium had been attained, the pH was adjusted to 4.5 with hydrochloric acid. After 24 h, the solution was rapidly run through a short Dowex 50 column, which was then washed with distilled water to remove all REE–EDTA complexes. The REE remaining on the resin were eluted in fractions using a solution of the calculated amount of EDTA. Pretreatment of a crude REE mixture raises the heavy REE concentration fivefold, and accelerates separation.

Achard[89] used ion-exchange columns in series to resolve mixtures of cerium earths (La, Pr, and Nd) with the aid of EDTA. Five 150 × 11 cm columns were packed with sulphonic acid cation exchanger, and a 1% EDTA solution (pH 4) used as the eluent. After passing 600 litres solution, the first column no longer contained REE, Pr was found in the second, Nd in the third and fourth, and Sm plus a small quantity of yttrium-group elements at the top of the fifth column. In a few days 600 g of crude Nd_2O_3 gave more than 200 g of Nd_2O_3 > 99.8% pure, 125 g > 99% pure, and 100 g > 98% pure.

With two columns in series packed with cation exchanger and using EDTA as the eluent, Topp[90] successfully separated a mixture of Pr, Nd, and Sm. Loriers et al.[91-93] used EDTA solution to separate Y from REE mixtures. For the separation of 200 g of mixed yttrium earths on a 150 × × 11 cm column, 125 litres of 1% sodium salt of EDTA (pH 3.5) were used for complete elution of the REE, the elements being eluted in order of decreasing atomic weight: Y was eluted between Dy and Tb. Using a more concentrated eluent solution at a higher pH, Y was eluted sooner, among elements with a higher atomic number, and this can be turned to account for isolating Y from mixtures rich in it. When EDTA is used, a three- or fourfold repetition of the operation is sufficient for the separation of a pure yttrium-group element.

To isolate Tm from an REE mixture of the yttrium group, Loriers used a mixture of EDTA and citric acid as the element. From a natural mixture containing 0.02–0.03% Tm, a product ten times richer in thulium was obtained by fractional precipitation. Separation was effected in two stages with columns in series. In the first stage EDTA at pH 4.5 was the eluent, and an Er–Yb concentrate was obtained containing 2–3% Tm. In the second stage elution was by means of a 5% citric acid solution (pH 2.7) and an 80–90% thulium concentrate was secured. The final purification was effected by elution with hot (90°) sodium citrate solution (pH 3.2), and the final product contained 99.5% Tm.

Spedding's[94,95] introduction of the Cu form of cation-exchanger resins was an important advance in the technology of REE separation. This improvement considerably increases the effectiveness of separation on ion-exchange resins. In practice separation is effected thus: one column with the resin is impregnated with the REE mixture, and the second column, more precisely its upper part*, is charged with copper. The columns are washed with distilled water to remove free ions, and then placed in series, the end of the first column being joined to the top of the second one. The columns are then eluted with EDTA solution of definite pH. The eluate (up to the time of appearance of REE ions), containing mainly $[CuE]^{2-}$, is acidified with H_2SO_4 and electrolysed to remove copper[95]. A solution containing REE then flows out; fractions of it are collected, their compositions being followed by any suitable method. The REE from the solutions are isolated as oxalates and then calcined to oxides. In this way such "difficult" mixtures as Pr and Nd can be quite successfully separated, as well as mixtures of yttrium-group elements, and the majority of REE are obtained 99.9% pure.

Many workers now use a combination of two columns[96-99], and, in particular, Noddack and Oertel[100-102] obtained pure REE on an industrial scale by this means. In four months they obtained from 96 kg of mixed starting oxides: 450 g of Lu and 2700 g of Yb, each 99.9% pure; 180 g of Tm and 1900 g of Er, each 99.6% pure; 10 500 g of Y and 3840 g of Sm 99.5% pure; and a series of other REE.

Separation was effected on a column 4 m long. The first column was made of plastic and its internal diameter was 15 cm, while the second column was of glass and had a diameter of 10 cm. Both were packed with Lewatit S-100, converted to the Na form. The first column was washed with the REE mixture to be separated and the second was converted to the Cu form. The columns were joined in series, and a 2% solution of the sodium salt of EDTA (Complexone III) was run into the first. Gradually the REE were transferred to the second column, the copper being displaced from it. After removal of all the copper, separation of fractions of REE was begun. The first stage of separation gave concentrates rich in yttrium earths, as well as pure Nd (100%) and 92% Pr (mixed with Nd and Ce). The second stage of the separation, effected with six pairs of columns each 2 m long, gave 99.0–99.9% pure preparations. The third stage was carried out when particularly pure salts were required.

Wolf and Massone[103-105] recommend the use of 2-hydroxyethyliminodiacetic acid for rapid separation of La in kilogram quantities. For example, separation of La from a mixture consisting of 86.2% La_2O_3, 6.9% CeO_2, 2.0% Pr_2O_3, 4.2% Nd_2O_3, 0.7% Sm_2O_3, and traces of yttrium earths was carried out thus: the starting mixture was converted to chlorides and run through a column (57 × 2 cm) in the upper part of which the REE were adsorbed, the resin in the lower part being in the H or Cu form (particle size 0.2–0.4 mm). The second column was charged with the H form of the same cation exchanger. Elution with a 4% solution of the hydroxyethyliminodiacetic acid was begun at 70°. With an elution rate of 0.7 cm/min, all the REE save La were concentrated in a volume of 3.7 litres of eluate. The La remaining on the column was extracted with a 4% Complexone III solution containing 2% NH_4Cl, along with NH_4OH added to bring it to pH 9. At this stage of the separation the column heating was switched off. With an elution rate of 1.5–2.0 cm/min, all the La went into 1.8 litres of eluate. By this method it was possible to separate 15.1 g of La_2O_3 in 95% yield and 99.5% purity, in 35 h. The method is recommended for separating La on a semi-industrial scale.

As well as 2-hydroxyethyliminodiacetic acid, *o*-hydroxycyclohexyliminodiacetic acid has been tried as an eluent[106]. Compared with other Complexones, these acids and their REE compounds are more soluble in water and do not give precipitates on the columns. They can give both cationic

* The reader is advised to consult ref. 95 (Ed. of Translation).

and anionic complexes with REE, the cationic ones being the more stable.

James and Bryan[107] found that thenoyltrifluoroacetone (TAA), usually used for separation of REE mixtures by the extraction method, can be employed as an eluent in separating REE mixtures on ion-exchange resins. Since TTA has a low solubility in water, a solution of it in water–dioxane is used. TTA rapidly elutes REE from the column and is recommended for separating short-lived isotopes. The method has been used for an Eu–Y mixture.

Okabe's method of separating cerium[108] is somewhat unique. The author made use of the ability of Ce(IV) to form basic salts which do not dissociate and which are not adsorbed by cation exchangers. When a solution of $Ce(NO_3)_4$ with other REE was run through an Amberlite IR-120 (NH_4 form) column, a solution of Ce(IV) free from other REE was immediately obtained. The effectiveness of the separation was greater, the higher the solution pH, while the magnitude of the flow rate affected separation but little.

A method of separating REE has been worked out[109,110] which is based on differences in rates of oxidation of complex sulphites of various REE, followed by adsorption of liberated REE cations on an ion-exchange resin.

When sulphur dioxide is passed through an aqueous suspension of REE oxides, hydroxides, or carbonates, they dissolve to give complex ions $[M(SO_3)_3]^{3-}$, stable at pH 5.5-6.1. These complex ions are oxidised by oxygen, in the air, when the metal complex goes over to the simple cation M^{3+}, which is adsorbed by a cation-exchanger. Fractionation is effected by a series of successive partial oxidations and absorptions by the resin. REE adsorbed by the resin are eluted with EDTA solution, the heavy REE being first displaced. According to the author, this method gives much purer products than the usual ion-exchange method, large quantities of REE can be processed, and it is not limited by the exchange capacity of the resin.

To separate tracer amounts of REE obtained as fission fragments in an atomic reactor, the same eluent is employed as on a macroscale; e.g. lactic acid and its salts are much used[111-120]. Here Freiling recommends the following procedure: the irradiation products are dissolved in 6 *N* HNO_3, and 20 mg of Ce, Pr, Nd, and Sm are added to the solution to act as carriers. The REE mixture is isolated as hydroxides, washed, and dissolved in a minimum amount of concentrated $HClO_4$. The resultant solution is passed through a Dowex 50 (NH_4 form) column, which is then washed with boiling distilled water. The adsorbed REE are eluted with lactic acid solutions of increasing concentration, 0.85 *N*, 0.90 *N*, 0.95 *N*, and 1 *N*, the elution temperature being 87°, and the pH 3. Freiling separated Y, Tb, Gd, Eu, Sm, Pm, Nd, and Pr quantitatively by taking fractions of the eluate. Stewart[121] suggests ammonium glycolate solution as an eluent. Elution is then effected on a column a few centimetres long and with 1 mm internal diameter, packed with Dowex 50. The eluent is a 0.25 M ammonium glycolate solution at pH 3.48. A sharp separation of Tm and Tb is obtained in 15 min on a column 3 cm long; with a 10 cm column a mixture of Lu, Tm, and Er is separated in 20 min. If the Al or Ca form of the resin is used, there is almost no separation.

Lavrukhina[122] recommended trihydroxyglutaric acid for elution of microquantities of REE. Duyckaers and Fuger[123] recommended EDTA solution. TTA is used for separating radioactive isotopes, particularly short-lived ones[107].

PAPER CHROMATOGRAPHY AND ELECTROPHORESIS

The principle of the first of these methods is based on the difference in the rates of migration of REE ions on filter paper. A drop of an aqueous solution of the REE mixture under investigation is placed at some distance from the end of a sheet of the paper which is some tens of centimetres long and a few centimetres wide. One end of the sheet is put into a vessel containing solvent and the vessel raised above the level of the bench, while the other end is put into another vessel. The solvent moves slowly in a descending stream over the paper, and the REE ions begin to migrate, different ions migrating at different rates. If the ions are quite colourless, the sheet of paper is dried, treated with a developer, and examined in daylight or by ultra-violet light, when separate coloured spots show up.

Lederer[124-131] has done the basic work in this field. He succeeded in finding conditions for identification of some REE and in separating mixtures of them. For comparison of the behaviour of a series of REE ions, a sample (sometimes 5–6 separate drops) of solution was put on a strip of Whatman No. 1 filter paper (15 × 60 cm) using a capillary tube; it formed a line 1 cm long 20 cm from the end of the strip. One end of the strip was fixed in a glass trough containing alcohol mixed with 10% of 2 *N* HCl, and the other end was put in a lower vessel. After some days the resultant chromatogram was air-dried, and then immersed in an ammonia-alcohol solution of 8-hydroxyquinoline, after which it was viewed by ultra-violet light: La, Y, Er, and Lu gave a yellow or green fluorescence, and all the other REE showed as brown or dark spots. In daylight all the spots appeared light yellow, and darkened to a brown colour after some days. Only one, Ce, five minutes after treatment with the reagent gave a brown spot.

Lederer's experiments showed that when acetone–2 *N* HCl was used as the solvent, separation took ~ 20 h. For the separation of a mixture of elements of the gadolinium group, ethanol mixed with 2 *N* HCl and NH_4SCN was used as the solvent, and an ammoniacal alcoholic solution of 8-hydroxyquinoline as developer. A mixture of Nd, Sm, and Eu, and also one of Eu and Yb, were completely separated in 48 h. The spots of Eu, Gd, and Tb partly overlapped.

A filter paper impregnated with a colloidal mass of the cation-exchange resin Dowex 50 (NH_4 form) was also used for chromatographing a mixture of La, Ce, and Y, 3% ammonium citrate solution being used as the solvent, and, as before, the spots were made visible by means of an ammonia-alcohol solution of 8-hydroxyquinoline. Spots corresponding to the La, Y, and Ce showed up.

To speed up the separation of a mixture of macroquantities of REE, Lederer developed the method of continuous paper electrophoresis. The ends of a sheet of paper carrying a drop of the mixture under investigation are placed in a solution of an electrolyte, and a direct current passed. With 300 V and a current of approximately 10 μA separation can be effected in 45 min. As the atomic number increases so does the distance traversed by an individual ion on the paper.

Lederer considers that in some cases electrophoresis is better than ion exchange or fractional crystallisation. However, in view of the small amount used, the method cannot be used for preparative work, but it is useful for effecting quicker analysis.

Moeller et al.[132] chromatographed a mixture of Y and Gd

acetylacetonates on columns packed with hydrated and anhydrous D-lactose*. The eluent was a mixture of benzene and petrol ether. Mixtures of complexes were partly resolved into optically active fractions.

METHOD BASED ON DIFFERENCES IN RATES OF ION MIGRATION

A solvent in a glass tube moves against a stream of ions at a rate greater than that of the less mobile ions, which are thus held back; the more mobile ones, however, are faster than the solvent stream and can move against it[133]. When an electric field is applied, the least mobile ions collect in the anode space and the most mobile ones in the cathode space. Convection currents, which may arise during the electrolysis, are prevented by inserting a large number of dialysis paper diaphragms into the separation tube.

Quantitative separation of La from Nd and Sm, and of Pr from Sm, was attained with a tube 40 cm long (with 105 diaphragms), at 600 V and 130 ± 10 mA, a countercurrent rate of 55 ml/h, and solution concentration 0.15–0.18 N (with respect to M^{3+}). Separation of a mixture of Pr and Nd at 60° was effected in a tube 100 cm long (having 245 diaphragms), using a 2300 V field, a 105 mA current, solution concentration (with respect to M^{3+}) 0.09 N, and a countercurrent rate of 85 ml/h. The separation took some weeks: finally the anode-space liquid contained 82% Pr and 18% Nd, and the cathode-space liquid 98% Pr (no Nd) and 2% La (?). Because the apparatus required is too complex, this method cannot in its present form be recommended for preparation of large amounts of REE.

METHODS BASED ON VALENCY CHANGES OF ELEMENTS

1. Reduction Methods

Effective methods of separating REE which can go over to the divalent state were developed long ago. However, separation of a small amount of a single element from a much larger amount of another still present difficulties, and the problem is at present under investigation. Thus Onstott[134,135] worked out an electrolytic method which allowed samarium to be freed from europium in a single operation.

The cathode was lithium amalgam, and the anode a platinum plate. Electrolysis was carried out in a 600 ml beaker with side tubes for contacts. The starting solutions were made by heating a freshly prepared mixture of Sm_2O_3 and Eu_2O_3 (98.4% and 1.6%) in 20% acetic acid, followed by addition of the hot solution to a lithium citrate solution, the pH being adjusted by adding LiOH. At the beginning of electrolysis the cathode potential was approximately -1.6 V (normal hydrogen electrode); thereafter it rose somewhat and stayed at about -2 V. The cathode current density varied from 0.0027 to 0.0162 A/cm², and experiments lasted 6 to 20 h. The Eu content was followed with the aid of the isotopes ^{152}Eu and ^{154}Eu. When electrolysis was finished the mercury phase was removed and then treated, first with water, then with dilute HNO_3. Under optimum conditions, 99.9% Eu went into the amalgam. From the solutions oxalates were precipitated, and were then calcined to the oxides. The amount of Eu was determined by its activity.

Ryabchikov et al.[136] perfected a method involving electrolytic reduction of ytterbium in the presence of citrate ions. They found that the best conditions for carrying this out were: pH 6.0, 5°, $Yb_2O_3 : K_3Cit = 1:2$, current density 0.05 A/cm², Yb concentration in the starting solution 2.0%. The method elaborated is recommended for final precipitation of ytterbium preparations from traces of neighbouring elements.

Chang[137] showed that when solutions containing mixed nitrates of Sm, Eu, and Gd, 8-hydroxyquinoline-5-sulphonic acid ("oxinesulphonic acid"), and acetic acid are electrolysed at 12 V and 0.02 A/cm² for 12 h, a greenish-yellow precipitate of composition $H_2[Eu(C_9H_5NOSO_3)_2] \cdot 4H_2O$ is formed; it is insoluble in the usual organic solvents. Spectrophotometry reveals 1–2% Sm in the precipitate, while the filtrate is free from Eu.

Achard[138*–140] suggested a new "dry" method of separating REE. When REE oxides of formula M_2O_3 are heated in vacuo with carbon, elements which can be reduced to the divalent state (Sm, Eu, and Yb) yield MO oxides which sublime owing to their higher vapour pressure.

To separate Yb, the oxide mixture is compressed with 20–30% of graphite and heated in a graphite crucible in an induction furnace. At 1400° and $< 10^{-3}$ mm Hg, YbO plus a small amount of carbon collect on a tantalum water-cooled condenser in 3 h. Three repetitions of the process separate quantitatively a mixture of Yb (52%) and La (48%). At a higher temperature (~1550°) the separation is not so good.

When YbO is heated at 1250° and $< 10^{-4}$ mm Hg in a tantalum crucible without the addition of any reducing agent, pure ytterbium metal collects on a tungsten condenser as a glistening deposit.

To separate Sm and Eu from other REE of the yttrium group, the oxides mixed with carbon are heated in a column with three graphite plates whose temperature varies from 1100° to 1600°. The deposit on the first plate consists almost entirely of SmO contaminated with traces of Eu, Yb, and Dy oxides. On the second plate there is SmO with a significant amount of Yb and traces of EuO, while on the third plate there is YbO mixed with EuO. The SmO concentrate is purified by repeated sublimation. To prepare Sm metal, the product isolated is heated at 1300°–1400° and 10^{-4} mm Hg. Pure EuO is obtained from a mixture containing Sm and Gd oxides by heating the mixture plus carbon at 1300° for 4 h; 80% of the Eu sublimes uncontaminated with other oxides.

2. Oxidation Methods

Quadrivalent cerium and ammonium oxinesulphonate give a water soluble complex[141]. This property of cerium is used to separate it from lanthanum. Oxinesulphonic acid is neutralised with excess ammonia, diluted with

* The Russian original confirmed an error which has been corrected (Ed. of Translation).

* Reference 138 appears in the authors' list of references apparently in error (Ed. of Translation).

water, and added to a mixture of cerium and lanthanum nitrates. The resultant solution is treated at 55° with a mixture of oxygen and ammonia, when Ce^{3+} is very readily oxidised to Ce^{4+}. After some hours oxidation stops and Na_2CO_3 is added. A precipitate of lanthanum carbonate forms, but the cerium stays in solution.

Misumi[142-144] worked out a method of separating praseodymium, based on its ability to undergo oxidation to the quadrivalent state when electrolysed in a melt. Praseodymium oxide containing neodymium is converted into hydroxide by fusion with KOH containing a definite amount of water. Then the melt is electrolysed at 360° in a nickel crucible, the latter being the anode and a platinum wire the cathode. The electrolytic oxidation gives a black precipitate of praseodymium oxide $PrO_{1.83}-PrO_{1.94}$* along with a small amount of hydrated neodymium oxide, and the praseodymium oxides are more than 95% pure. Repetition of the process gives a still further enriched product.

METHOD BASED ON DIFFERENCES IN RATES OF CHLORIDE DEHYDRATION

Freeman and Smith[145] found that boiling with thionyl chloride was an effective method of preparing anhydrous REE chlorides:

$$MCl_3 . xH_2O + xSOCl_2 \rightarrow MCl_3 + xSO_2 + 2xHCl.$$

Freeman published a paper[146] about experiments on separating mixtures of REE chlorides based on differences in the rate of dehydration by thionyl chloride.

A mixture of equal amounts of Nd_2O_3 and Dy_2O_3 was dissolved in hydrochloric acid, and the solution of chlorides heated with thionyl chloride; part of the chlorides become dehydrated. The mixture was then heated strongly in an argon atmosphere, and the chlorides which had not been dehydrated were converted to water insoluble oxychlorides. The anhydrous chlorides could be leached out with water: the water-soluble fraction contained 70% Nd and 30% Dy, while the residue contained 38% Nd and 62% Dy. The inventor of this method does not believe that it will find much application.

MAGNETIC METHOD

Noddack and Wicht[147-149] showed that when an REE solution flows at right angles to lines of magnetic force, fractionation of ions takes place in a way depending on their magnetic moments, the most paramagnetic ions migrating to the region of greatest field strength.

A mixed REE solution is placed in a trough provided with a capillary tube for introducing and withdrawing solution. A small platinum wire is welded to the bottom of the trough, and by heating this wire electrically, convection circulation of the liquid is brought about. The trough is put between the poles of an electromagnet for about half an hour. The effectiveness of separation depends on the circulation of solution in the vessel, degree of inhomogeneity and strength of the magnetic field, the duration of the experiment, and the initial concentration of the REE solution.

A way of separating Y from heavy REE has been elaborated, and is more effective than fractional crystallisation and fractional precipitation. The fundamental disadvantage of the method is the impossibility of working with a large amount of material.

CONCLUSION

Trials under production conditions of many methods of separation described in the literature showed that only a few of them deserve attention. It is evident that the most rational schemes of separation are those combining the most effective aspects of different methods. Ryabchikov et al.[2,3] worked out a detailed scheme for the separation of all the individual REE from a naturally-occurring mixture.

It is absolutely necessary to effect an initial separation of a mixture into cerium and yttrium groups, even if only one of the groups predominates in the mineral. It is undoubtedly easier to separate the cerium group because the series of elements which it comprises (cerium, samarium, and europium) exhibits marked variability of valency. The separation of this group is also facilitated by the absence of promethium in natural raw material. These factors make it possible to use purely chemical methods for separating the individual members of this group.

In the subsequent separation of elements it is naturally expedient to remove first the most abundant ones, cerium and lanthanum, from the mixture. Conversion of cerium to the quadrivalent state without difficulty effects its separation from adjacent elements, the mass of the starting material being reduced by about two-thirds. Lanthanum is separated from the residual mixture by crystallisation or by base precipitation, using ammonia. After that Eu and Sm are isolated by electrochemical means, and then separated.

Separation of a mixture of praseodymium and neodymium presents the greatest difficulty. Here crystallisation is not very effective, and the conversion of praseodymium into a higher valency state offers greatest promise. If it is necessary to obtain the individual REE in a highly pure state, further purification by ion-exchange and extraction methods is used.

The ytterbium group is, for a number of reasons, much harder to resolve than the cerium one. Firstly, it contains a large number of elements; secondly, these resemble one another more closely than the cerium elements do; thirdly, natural raw material always contains an excess of yttrium, an element not formally related to this group of elements but always accompanying them in nature. The old methods of separation, crystallisation, and fractional precipitation, even in conjunction with the recent improvements in them, are of little use here.

Firstly, the entire main mass of yttrium has to be removed from the mixture. This can be rapidly accomplished by treating the starting material with the calculated amount of complexing agent (EDTA) and then precipitating the elements which have not formed complexes. In this way not only is the main mass of yttrium removed, but the remaining elements are divided into small subgroups, which much facilitates separation of the mixture into its individual components. The next step is conveniently effected by ion exchange. From the last portion of the heaviest elements, ytterbium is removed electrochemically. This method gives considerably improved yields of thulium, an element of practical importance.

Now that a large number of investigators have obtained adequate amounts of very pure individual REE preparations,

* This corresponds to a mixture of $Pr_2O_3 + PrO_2$ with the latter predominating.

it can be hoped that the study of the physical and chemical properties of this large and interesting group of elements will develop much faster than has hitherto been the case.

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