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Production of rare-earth oxides of high purity

Zuying Zheng, Daren Ling*, Ying Sun

Department of Applied Chemistry, Jiangsu Institute of Petrochemical Technology, Changzhou, 213016, China

Abstract

A novel industrial technology for producing rare earth oxides of high purity (>99.99%) by temperature pressurized ion-exchange displacement chromatography is reported. It was concluded from the technological parameters that the concentration of complex agent in the eluent can be several times higher than that used in the classical ion-exchange method if a certain amount of buffer is present; the height equivalent to a theoretical plate (HETP) decreases linearly with increase in the operating temperature, increases slightly with increase in the flow-rate of the eluent and depends on the particle size of the ion exchanger. Rare earth oxides of high purity were manufactured on an industrial scale using a solution of special composition as eluent, and enriched rare earth mixtures or single rare earth oxides with low grade as raw and processed material on a temperature pressurized ion-exchange multi-column operating system containing polytetrafluoroethylene as the inner liner.

1. Introduction

Ion-exchange displacement chromatography with an amino-carboxylic complex agent as the eluent has been an important and effective method for industrially separating rare earth mixtures. However, because of its intrinsic shortcomings, such as long run period, low eluate concentration of rare earths and high production costs, its application in industry is limited. Recently, the temperature pressurized ion-exchange technique has been improved [1–3]. Owing to the patenting of the key techniques for processing, the separation of rare earths on an industrial scale has rarely been reported [4–6]. This paper briefly reports a novel industrial technology for producing rare earth oxides of high purity (>99.99%) by temperature pressurized ion-exchange displacement chromatography.

2. Experimental

The experiments were carried out using a temperature pressurized stainless-steel multi-column system [7], which consisted of five pressurized columns with jackets, three tanks for storing feed, eluent and ion exchanger sludge, three types of pumps (reciprocating pump, pressure air pump and vacuum pump), two types of valves (needle cut-off valve and safety valve) and five pipelines for vacuum, exhaust, feed, eluent and ion-exchanger sludge. In addition, another simple temperature pressurized glass multi-column system was built for parts of the experiments [8].

In the separation of rare earths by the temperature pressurized ion-exchange method, the factors that affect the efficiency of the separation are mainly the composition of eluent, the volume ratio of adsorption column and displacement column, the type of ion exchanger and its par-

* Corresponding author.

Table 1
Calculation of acidity of eluent with simulated titration curve

Resin	Composition of eluent			pH of eluate	
	$C_C^0 (M)^a$	$C_B^0 (M)^a$	pH	Calculated	Measured
D01 × 8	0.015	0	8.8	3.0	3.0
D01 × 8	0.015	0.114	6.5	5.4	5.4
D01 × 8	0.015	0.022	6.2	3.9	4.0
D01 × 12	0.015	0.114	6.5	5.4	5.4
D001 × 8	0.015	0.114	6.5	5.4	5.4
D001 × 8	0.015	0.022	6.2	3.9	4.0

^a C_C^0 = concentration of complexing agent in the eluent; C_B^0 = concentration of buffer agent in the eluent.

ticle size, the flow-rate of the eluent, the operating temperature and the carrier ions. In this work, a strongly acidic cation exchanger with a cross-linked polystyrene structure (degree of crosslinking is 8%, crosslinking with divinylbenzene) was used. The particle diameter of the ion exchanger was between 30 and 90 μm . Copper ion and hydrogen ion were the carrier ions.

2.1. Eluent

When the light rare earths were separated with an eluent of 0.015 M complexing agent (pH 8.8) at 60°C, precipitation occurred in the lanthanum region [9]. The pH in this region was 3.0. If the pH of the eluent was not suitably controlled, failure of the separation occurred owing to blocking of the columns. However, the precipitation disappeared if a buffer salt formed by a weak acid and a weak base was added to the eluent. The amount added and its corresponding buffering capacity can be determined from simu-

lated titration curves. From this, the pH of the eluate can be controlled [9]. A comparison is shown in Table 1.

When the buffer agent was added, it changed the composition of the eluent and the concentration of rare earths, the complex formability and the pH of the eluate. Table 2 gives the results of the separation of Eu(II) using eluents with the different composition.

As shown in Table 2, because of the added buffer agent, it is possible to use a solution with a high concentration of a complexing agent as the eluent. Under these conditions, the concentration of the driving ion increases considerably, which makes the migration rate of the band and the rare earth concentration in the eluate increase proportionally, although the complex formability (C_f) decreases slightly [3]. Observing the values of the slopes (s) of the displacement curves at the rear boundaries, the boundaries did not collapse; to the contrary, they became sharp. This conclusion has been tested and verified in many experiments.

Table 2
Effect of composition of eluent on complex formability of Eu(II)

$C_C^0 (M)$	$C_B^0 (\%)$	pH	k	$C_f (\%)$	v	s
0.015	Moderate	8.0	30	86	970	3
0.050	Moderate	8.0	11	74	400	4
0.075	Moderate	8.0	6.2	73	230	7

pH = pH of the eluent; k = column distribution ratio; C_f = complex formability; v = volume of eluent consumed; s = slope of displacement curve at rear boundary.

2.2. Temperature

In order to study the effect of temperature on the separation, Sm–Nd and Gd–Tb were separated at flow-rates of 13 and 3.6 cm/min, respectively, on a Cu–H resin bed. The eluent was a solution of pH 7.5 containing 0.050 M complexing agent and a moderate amount of buffer agent (Table 3). HETP was used to express the separation efficiency, which was calculated according to the boundary equation based on the distillation equilibrium plate model [2].

As shown in Table 3, the calculated values of HETP are lower at an operating temperature of 75°C than at lower temperatures according to the boundaries of the displacement curves of the Nd–Sm pair. When the temperature was decreased to 25°C, the HETP increased, the boundary of the curve collapsed and the separation efficiency became worse. The effect of temperature on the separation of Gd–Tb exhibited the same tendency.

In the process of ion exchange without chemical reaction at a low reaction rate, the diffusion rate of ions depends on the liquid film diffusion and interparticle diffusion. When an ion exchanger of micrometre particle diameter is used as the packing of column, the controlling step of the ion-exchange rate is the rate of liquid film diffusion [2]. Therefore, an increase in the operating temperature undoubtedly increases the diffusion of ions, decreases HETP and gives a good separation efficiency. However, in practice, it would not be convenient to operate at high temperatures. The column temperature is suitably controlled below 80°C when Cu–H columns are used as the carrier ion beds.

2.3. Flow-rate and particle size

The results of the experiments at different linear flow-rates of the eluent and particle sizes of the ion exchanger are given in Tables 4 and 5, respectively. As shown, HETP increases only slightly with the increase in flow-rate from 16 to 25 cm/min. Comparing the efficiency of separation of Sm–Y on columns filled with ion exchangers of particle diameter 30–40 μm and 40–60 μm, the former is better.

It has been reported that the relationship between HETP and the flow-rate (V) and the particle size of ion exchanger (r) follows the expression $HETP = CV^a r^b$, where C is a constant, $0.3 < a < 0.6$ and $1.4 < b < 1.8$ [10]. In this work, the calculated values of a and b were about 0.5 and 1.7, respectively, in good agreement with the above values.

In addition, an increase in the flow-rate in-

Table 4
Relationship between HETP and linear flow-rate of eluent (V)

V (cm/min)	HETP (Eu–Sm) (cm)	HETP (Sm–Y) (cm)
16	0.53	0.17
20	0.80	0.19
25	0.84	0.20

Table 5
Relationship between HETP and particle size of ion exchanger (r)

r (μm)	V (cm/min)	HETP (Sm–Y) (cm)
30–40	20	0.18
40–60	20	0.43

Table 3
Effect of temperature on separation efficiency

Parameter	Nd–Sm				Gd–Tb		
	Cu–H				Cu–H		
Eluent	$C_i^0 = 0.050 M$, pH = 7.5, buffer = moderate						
Flow-rate (cm/min)	13				3.6		
Temperature (°C)	75	70	50	25	75	50	25
HETP (cm)	1.6	1.6	2.2	2.8	0.7	3.3	6

increases the HETP slightly and leads to a decrease in column efficiency to a certain extent; however, the production time is considerably shortened. A decrease in particle size can obviously enhance the efficiency of the column, but it will greatly increase the resistance of the column, which is not advantageous for practical operation if an ion exchanger with too small a particle size is used as the column packing.

3. Industrial production of rare earth oxides of high purity

A flow diagram of the scheme for the industrial production of rare earth oxides of high purity by temperature pressurized ion-exchange chromatography is shown in Fig. 1.

Fig. 2 shows the scheme of the temperature pressurized multi-column system. It consists of columns with different diameters (600×3000 mm, 300×1500 mm), pressurized reciprocating pumps, valves and pipelines with different functions. The columns, the pipelines and the parts of valves were lined with PTFE. The packing in the columns was an ion exchanger with micrometre particle diameter which was hydrodynamically sieved. Ion exchangers of different particle sizes were filled into the different columns according to the functions of the columns.

The enriched rare earth mixture or a single rare earth of low grade was dissolved in the acidic solution. The feed solution was pumped

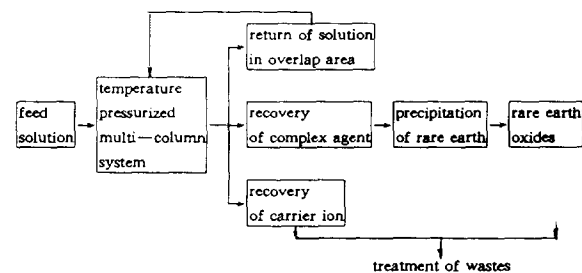


Fig. 1. Flow diagram of scheme for products of rare earth oxides.

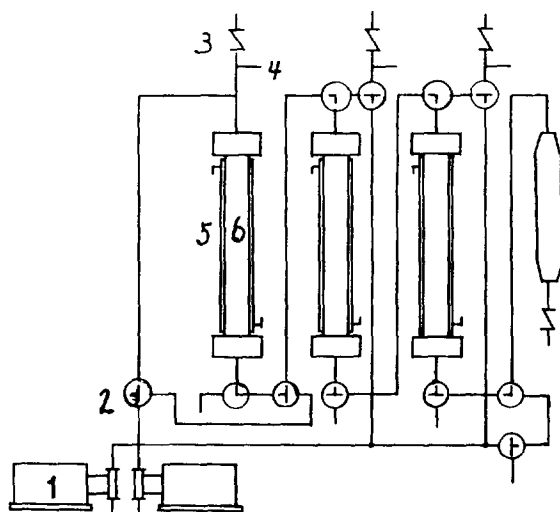


Fig. 2. Temperature pressurized ion-exchange multi-column system. 1 = Reciprocating pump; 2 and 3 = valves; 4 = pressure indicator; 5 = water jacket; 6 = column.

into the adsorption column after the acidity of the feed solution had been adjusted. After washing the column with deionized water, the rare earth adsorption band was eluted to the Cu–H carrier columns with an eluent of the special composition. According to the separation factor of the rare earths, the different displacement distances (the column ratio) were chosen.

The solution of the carrier agent from the columns was treated to recover the carrier agent and the complexing agent by electrolysis and precipitation, respectively. The solutions collected at the overlap areas were returned to the column system in the next run. The solutions of the rare earths were acidified in order to recover the complexing agent, then the rare earths were precipitated and scorified to the oxides as the products. Some measurement results for Er and Y products are given in Table 6. The measurements were made using a JY-38-Plus inductively coupled plasma instrument.

The production capacity for a run (2–3 days) was over 100 kg of rare earth oxides in an industrial plant (Wuxi TIO Ultrapure Materials Company, Wuxi, Jiangsu, China).

Table 6
Some measurement results for rare earth products

Element	Impurity (ppm) ^a							
	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y
Er	–	–	0	0	–	0	0	0
	–	–	0	0	–	0	0	0
	–	–	0	0	–	13	0	0
Y	0	0.4	0.07	–	0	0.05	0	–
	0	0.4	1.1	–	0	0.03	0	–
	0	0.5	0	–	0	0.03	0	–

^a Value 0 indicates an amount lower than the detection limit of the instrument.

4. Conclusion

The technology reported here overcomes the intrinsic shortcomings of the classical ion-exchange method (CIEM). The concentration of rare earths in the eluate is several times higher than that obtained with CIEM. The production time per run is much shorter than that using CIEM. In comparison with CIEM, the characteristics for the present process are a shorter production period, much less reagent consumption and waste, higher concentration of rare earths in the eluate and higher column efficiency.

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