

Separation of rare earths by ion exchange

G S RAO and G M PHATAK

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

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Abstract. Separation of rare earths from monazite source by ion-exchange process is discussed. Optimum conditions for obtaining kilogram quantities of individual rare earths of high purity are reported.

Keywords. Separation ; rare earth ; ion-exchange ; eluent ; EDTA.

1. Introduction

The fact that the rare earths have yet to earn a place as materials of primary technology is generally attributed to the restricted availability of individual rare earths and their compounds in substantial purities and the cost factor involved therein to compete with other industrial materials which have already established their importance in technology. This drawback is mainly due to the fact that the group of rare earths (At. No. 57-71) and yttrium (At. No. 39) which is also included in the group of rare earths) have similar chemical properties and consequently the processes involved for the separation of rare earths are generally complex, slow and associated with unfavourable economic factors.

Of the free world resources of rare earth elements estimated at about ten million tons (as oxides) India contributes nearly one-third ranking next to the USA. The chief source for rare earths in India is the monazite although a few isolated pockets of samarskite are reported.

The ion-exchange process is highly successful for their separation with high yields of pure materials and hence is now universally adopted for this purpose. Though the separation of rare earths by ion-exchange is well-known (Powell *et al* 1959), detailed data for scaling up the process were not available.

Realising the importance of making available of individual rare earths in the country for research and development towards their application in technology, the Chemistry Division of the Bhabha Atomic Research Centre has carried out extensive development work on the separation of rare earths by ion-exchange process leading to pilot plant scale operations (Bhat *et al* 1966).

2. Process description

Didymium carbonate produced by Indian Rare Earths from monazite was used as the starting material (composition: La_2O_3 49.2%, CeO_2 1.1%, Nd_2O_3 34.5%, Pr_6O_{11} 7%, Sm_2O_3 6%, Gd, Tb, and heavy rare earths 2%).

Utilising the large difference in the basicities of lanthanum and other rare earths, the didymium carbonate was further fractionated into lanthanum-rich and neodymium-rich concentrates. This was achieved by passing air-borne ammonia through rare earth chloride solution (10 gpl as R_2O_3) at 60° C and at a pH of 7.8–7.9. Praseodymium, neodymium, samarium and gadolinium contents of these fractions were determined by spectrophotometric analysis (Banks and Klingman 1956). Lanthanum content was obtained by difference.

The ion-exchange method of separation of rare-earths consists of in brief, absorbing the mixed rare earths on the top of a cation exchange resin column with a copper cycle and then eluting the rare earths selectively from the resin column with a suitable aminopolycarboxylate solution. In this process the chelating properties of some of the aminopolycarboxylates mainly ethylenediaminetetraacetate are made use of for selective separation of rare earths. One of the most important physical properties of the rare earth ions that has come to the rescue of the chemist is the gradual decrease of crystal/ionic radius from lanthanum to lutetium (1.061 to 0.848 Å). This property has a great inverse influence on the stabilities of the rare earth chelates mentioned above, with the result that there is an increase in the stability of the complexes from lanthanum to lutetium. ($\log_{10} K$ values of EDTA complexes vary from lanthanum to lutetium 15.50 to 19.83 (Schwarzenbach *et al* 1954). The selective absorbability of the rare earth ions, when eluted in the

Table 1. Experimental conditions for optimum separation of rare earths by ion exchange.

Loading	5 kg mixed rare earths as R_2O_3 /unit.
Total number of units	6
Cation exchange resin	Dowex-50 W × 8 Zeocarb 225
Eluting agent	EDTA (0.015 M) pH 8.2–8.4
Retaining bed	Copper form of resin
Linear flow rate	
(a) loading	1 to 1.2 cm/min
(b) elution	0.5–1.5 cm/min
Columns	PVC, Glass Dia. 6.5–15 cm.
Distance of elution in band lengths	0.66–1

form any of the chelates mentioned above, depends on the stability of the chelate ; the higher the stability the lesser is the absorption. The sequence of the elution thus follows from lutetium to lanthanum. A better separation and resolutions of individual rare earths is effected when the rare earth chelates are allowed to interact on the resin bed with transition metal ion such as Cu^{2+} , whose stability constant with EDTA is comparatively high ($\log_{10} K = 18.8$).

In the present work various parameters such as pH of the eluent, flow rates for effective loading and elution and distance of elution for obtaining optimum yields of individual rare earths, were studied in detail and are summarised in table 1.

The individual rare earths from the effluent were precipitated as oxalates and converted to oxides by ignition. The purity was ascertained by spectrophotometric and spectrographic analysis and the results are shown in tables 2 and 3.

Table 2. Some typical plant data on the per cent yield of spec. pure and A. R. grade materials obtained on elution through different number of band lengths.

Total loading : 5 kg of oxide. Starting material : Didymium carbonate

Product and quality		Distance of elution in band lengths					
		0.66		1		1.5	
		wt. of oxide in gms	% of total originally present	wt. of oxide in gms	% of total originally present	wt. of oxide in gms	% of total originally present
Starting material : Lanthanum-rich fraction							
Lanthanum oxide	spec. pure	600	24	1200	48	1350	54
	AR	1400	56	1100	44	1000	40
Praseodymium oxide	spec. pure	80	13	140	23	200	33
	AR	320	52	320	54	270	45
Neodymium oxide	spec. pure	750	44	900	53	1200	70
	AR	800	47	730	43	450	26
Samarium oxide	spec. pure	36	12	50	16
	AR	70	23	54	18	75	25
Starting material : Lanthanum-rich fraction							
Lanthanum oxide	spec. pure	1000	25	2400	60	2550	64
	AR	2800	70	1400	35	1300	32
Praseodymium oxide	spec. pure	40	11.4	75	21	125	35
	AR	170	49.6	190	54	150	43
Neodymium oxide	spec. pure	135	40	210	52	275	65
	AR	200	40	200	40	145	30
Starting Material : Neodymium-rich fraction							
Lanthanum oxide	spec. pure	300	30	370	37	400	40
	AR	550	55	520	52	500	50
Praseodymium oxide	spec. pure	100	14	300	43	380	54
	AR	400	55	300	43	220	32
Neodymium oxide	spec. pure	800	32	1700	68	1800	72
	AR	1000	50	700	28	600	24
Samarium oxide	spec. pure	70	12	150	25	250	42
	AR	170	28	150	25	150	25

Table 3. Some typical analysis of rare earth oxides produced by ion-exchange separations.

	Spec. pure		Analytical Grade	
Lanthanum oxide	CeO ₂	<0.01%	CeO ₂	0.08%
	Pr ₆ O ₁₁	<0.001%	Pr ₆ O ₁₁	0.08%
	Nd ₂ O ₃	<0.005%	Nd ₂ O ₃	0.04%
	Fe	0.0008%	Fe	0.001%
Praseodymium oxide	La ₂ O ₃	<0.01%	La ₂ O ₃	0.06%
	CeO ₂	<0.01%	CeO ₂	0.1%
	Nd ₂ O ₃	<0.1%	Nd ₂ O ₃	0.05%
	Sm ₂ O ₃	<0.01%	Fe	0.001%
Neodymium oxide	Pr ₆ O ₁₁	<0.02%	Pr ₆ O ₁₁	0.08%
	Sm ₂ O ₃	<0.05%	Sm ₂ O ₃	0.08%
	Fe	<0.0008%	Fe	0.001%
Samarium oxide	Gd ₂ O ₃	<0.05%	Nd ₂ O ₃	0.08%
	Nd ₂ O ₃	<0.025%	Eu ₂ O ₃	0.06%
	Eu ₂ O ₃	<0.025%	Gd ₂ O ₃	0.08%
	Fe	0.0008%	Fe	0.001%
Gadolinium oxide	Eu ₂ O ₃	<0.001%	Sm ₂ O ₃	0.08%
	Sm ₂ O ₃	<0.03%	Tb ₄ O ₇	0.05%
	Tb ₄ O ₇	<0.05%	Eu ₂ O ₃	0.1%
	Fe	0.0007%	Fe	0.001%
Yttrium oxide	Gd ₂ O ₃	<0.03%	Dy ₂ O ₃	0.1%
	Dy ₂ O ₃	<0.02%	Tb ₄ O ₇	0.08%
	Tb ₄ O ₇	<0.025%	Fe	0.001%
	Ho ₂ O ₃	<0.01%		
	F ₂	0.0006%		

Some typical impurity levels of other elements; Mg = 0.0006%; Cu = 0.0001%; Ni = 0.0008%; Ag = 0.0001%.

3. Conclusion

Ion-exchange plays an important role in the separation of rare earths. Under optimum conditions of operation it is possible to produce large quantities of high purity rare earths by this technique.

References

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