

Sequential separation of the yttrium—heavy rare earths by fractional hydroxide precipitation

Mari E. de Vasconcellos*, Carlos A. da S. Queiroz, Alcídio Abrão

Instituto de Pesquisas Energéticas e Nucleares (IPEN), Cx. Postal 11049, CEP 05422-970 Pinheiros, São Paulo, Brazil

Abstract

In the course of the treatment of monazite in Brazil a fraction of crude yttrium carbonate is obtained. The main constituents of this fraction are: Y_2O_3 (76.7%), Dy_2O_3 (9.31%), Er_2O_3 (3.21%), Yb_2O_3 (2.34%), Lu_2O_3 (1.56%), Ho_2O_3 (1.40%), Tb_4O_7 (0.97%), Gd_2O_3 (0.69%), CeO_2 (0.43%), Tm_2O_3 (0.33%), Nd_2O_3 (0.22%), La_2O_3 (0.21%), Sm_2O_3 (0.14%), Pr_6O_{11} (0.13%), and minor impurities like nickel, calcium, and iron. An alternative process based on the homogeneous precipitation technique has been studied for sequential separation of yttrium from heavy rare earths. The first step of the process is the dissolution of the crude yttrium carbonate using hot hydrochloric acid. The resultant filtered solution of pH 2–3 has 30–35 g l⁻¹ total rare-earth elements (REE). From this solution the lanthanides were precipitated by the controlled hydrolysis of hot urea and the precipitate filtered off. The homogeneous precipitation is repeated once more. Yttrium is kept in the filtrate. The final yttrium fraction has 86.2% Y_2O_3 . If the original rare-earth solution is spiked with an amount of lanthanum a most efficient separation of yttrium was obtained. In this paper, the influence of lanthanum to improve the yttrium separation is discussed. This separation envisages an industrial application.

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1. Introduction

In recent years the separation chemistry of the rare-earth elements (REE) continue to receive a growing interest. The major reasons for this stand from the high application interest of the REE in many fields. Elements such as Y, Nd, Sm, La, and Gd and their compounds find various commercial applications. For instance, Y and Sm have an interesting application in the field of nuclear technology due to the low cross-section for neutron capture and high temperature stability of their oxides. La, Y, Sm, and Nd oxides find application in ceramic industry for coloring glass and as glaziers. Gadolinium is useful in nuclear technology in fuel element fabrication and as control rods, and as refractory material and in ceramic industries. Yttrium is used in many applications, as in the manufacture of superconductors, in the composition of phosphors, and in the thermoluminescent $CaSO_4(Y)$ dosimeters, in superalloys of nickel and cobalt as well, and in electronic materials and solid oxide fuel cells

[1,2]. Lanthanum continues to be used in the fabrication of mischmetal alloy, in the composition of special glasses [1] and, more recently, into catalyst zeolite for use in the cracking of petroleum. In view of the above mentioned applications, the separation and purification of Y, Nd, Sm, La, and Gd is desired.

From the industrially alkaline chemical processing of monazite sand in S. Paulo, Brazil, various REE concentrates were produced. The present investigation was carried out primarily to separate yttrium and lanthanum from two concentrates, namely yttrium carbonate and low cerium carbonate (LCC) concentrate.

Research being conducted by the IPEN, CQMA Division, to improve the REE technology of yttrium and lanthanum includes the separation by homogeneous urea precipitation and selective dissolution of the yttrium from the concentrates by the aid of ammonium carbonate [3–5]. Preparation of rare-earth carbonates by the homogeneous precipitation was reported first by Salutsky and Quill [6], who made use of trichloroacetic acid as precursor. Akinc et al. [7] studied the precipitation of lanthanide basic carbonates via hydrolysis of urea. Panchula and Akinc [8] prepared lanthanum carbonate particles using the homogeneous precipitation of

* Corresponding author.

E-mail address: mstela@baitaca.ipen.br (M.E. de Vasconcellos).

Table 1
Typical analysis of yttrium carbonate and LCC XR fluorescence analysis

Constituent (%)	Yttrium carbonate	Low cerium carbonate (LCC)
Y ₂ O ₃	76.7	2.4
Dy ₂ O ₃	9.3	0.6
Er ₂ O ₃	3.2	<0.1
Yb ₂ O ₃	2.3	–
Lu ₂ O ₃	1.6	–
Ho ₂ O ₃	1.4	–
Tb ₄ O ₇	1.0	–
Gd ₂ O ₃	0.7	2.7
CeO ₂	0.4	2.5
Tm ₂ O ₃	0.3	–
Nd ₂ O ₃	0.2	33.2
La ₂ O ₃	0.2	40.3
ThO ₂	0.2	–
Sm ₂ O ₃	0.1	4.1
Pr ₆ O ₁₁	0.1	7.5

–: Not detected.

pure lanthanum nitrate with urea. Umeda and Abrão [9] reported a procedure for the separation of individual REE using the homogeneous urea precipitation applied to the natural rare-earth chlorides obtained from the monazite sand.

In this work the authors exploit the homogeneous precipitation of lanthanides from an industrial low cerium carbonate concentrate and a rare-earth solution prepared from a crude yttrium carbonate and performed their separation envisaging the recovery of lanthanum and yttrium in the filtrate.

The used yttrium concentrates have the chemical composition depicted in Table 1.

2. Experimental

2.1. Starting raw materials

As can be seen from Table 1, the yttrium carbonate concentrate is high in yttrium and low in lanthanum content, while the LCC is low in yttrium and high in lanthanum content. The yttrium carbonate stockpile today is low but the IPEN has many tonnes of the LCC waiting for an adequate technology for its elemental fractionation.

2.2. Apparatus

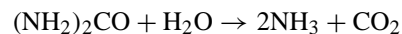
A RIGAKU model RIX 3000 (1996) spectrometer was used for the measurement of the X-ray fluorescence. pH measurements were carried out on a MICRONAL model B 474 digital pH meter equipped with combined glass electrode.

2.3. Homogeneous precipitation with urea

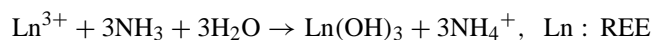
For the yttrium carbonate, previously rich in yttrium, the homogeneous fractionation using urea was performed first.

This concentrate was dissolved with hydrochloric acid and filtered to get rid of some small amount of insoluble products. The rare-earth chloride solution of 30–35 g l⁻¹ had the pH ascertained to 2–3. Using this rare-earth chlorides two solutions were prepared by dilution with distilled water, with concentrations of 11.77 and 20.56 g l⁻¹ total rare-earth oxides (R₂O₃), respectively.

In this work, the homogeneous fractional precipitation using the hydrolytic decomposition of urea was performed aiming the precipitation of the other rare-earth elements and keeping the yttrium in solution, since this earth requires higher precipitation pH. So the homogeneous precipitation is based on the differences in the rare-earth hydroxides (or hydroxycarbonates, like hydroxichlorides or hydroxycarbonates) pH values as function of temperature and atomic weight from La to Lu. In this work, several fractional precipitates were obtained as function of pH with the help of the controlled hydrolysis of urea. The decomposition of urea was kept at 90 °C, according to the reaction:



followed by the precipitation reaction:



For the precipitation of the bulk of the other REE, the chloride solution was warmed to 70 °C and then a calculated quantity of urea for their precipitation was added and the temperature raised to 90 °C. The reaction was so maintained during 4 h, and then filtered off. The main component of the filtrate was yttrium. This filtrate was submitted to a new urea precipitation with the scope of obtaining a sequential precipitation for the enrichment of yttrium.

2.4. Improvement of the enrichment of yttrium with the addition of lanthanum

Still working with the homogeneous precipitation of REE by the urea hydrolytic technology, the REE chloride solution was spiked with lanthanum chloride and then submitted to the precipitation as before. We expected that with this resort the final yttrium precipitate could be enriched.

An experiment was performed using the REE chloride solution of 20.56 g l⁻¹ and without addition of lanthanum chloride. A second one was performed using the 11.77 g l⁻¹ solution plus the addition of lanthanum chloride 13.23 g l⁻¹.

2.5. Leaching the concentrates with ammonium carbonate as an alternative process

Considering that both concentrates are solid REE carbonates we put forward a process that exploits the selective solubilization of yttrium with ammonium carbonate, while lanthanum and other rare earths are less dissolved or not dissolved at all by this treatment. The proposed process has several advantages, as for instance, it works at room temperature, has a selective dissolution of yttrium, the starting

material is solid, and keeps the undissolved REE as carbonate anyway, avoiding the use of acids. Add to this that the process is less time-consuming.

Solid LCC concentrate was treated with a solution of ammonium carbonate of 200 g l^{-1} at room temperature, being covered with the solution and agitated during 10 min and filtered. Yttrium was recovered in the filtrate after acidified with hydrochloric acid and precipitated with oxalic acid. The oxalate was fired to oxide, which was white.

3. Results and discussion

With some exploratory precipitation experiments using pure solutions of yttrium and lanthanum and a mixture of both elements, the threshold pH was determined at 21°C . For the mixture of La and Y the 1:1, 2:1, and 3:1 ratios were used. For the precipitation was used an aqueous ammonia solution. The result can be seen in Table 2. It is clear that lanthanum is precipitated at pH higher than the precipitation of yttrium, allowing in this way a convenient separation of both.

In Table 3 are shown the results of the fractionation of yttrium and other RE using the solution prepared by the dissolution of the yttrium carbonate without and with spiked lanthanum chloride, by the homogeneous precipitation with urea. In the first case, it is clear the enrichment of yttrium, from 76.7 to 86.2%, while processing the solution spiked with lanthanum fractionation was unsuccessful. As expected,

Table 2
pH values in which precipitation starts for La, Y, and their mixtures at 1:1, 2:1, and 3:1 ratios at 21°C

Rare earths	pH
La	8.18
Y	6.75
La/Y (1:1)	6.92
La/Y (2:1)	6.97
La/Y (3:1)	7.03

Table 3
Composition of the starting solution and filtrate after precipitation with urea

Constituent (%)	Starting solution A and B	Filtrate	
		A	B
Y_2O_3	76.7	86.2	36.5
La_2O_3	0.2	0.3	53.8
Dy_2O_3	9.3	6.2	2.2
Er_2O_3	3.2	2.1	0.7
Yb_2O_3	2.3	1.4	0.5
Lu_2O_3	1.6	0.7	0.3
Ho_2O_3	1.4	0.5	0.1
Tb_4O_7	1.0	0.7	0.3
Gd_2O_3	0.7	0.6	1.2
Tm_2O_3	0.3	0.1	–
CeO_2	0.4	0.4	0.2
Nd_2O_3	0.2	0.1	–

A: without spiked LaCl_3 ; B: with spiked LaCl_3 ; (–): not detected.

Table 4
Composition of the yttrium precipitate obtained by the leaching of LCC with ammonium carbonate

Constituent	Content (%)
Y_2O_3	52.9
Gd_2O_3	23.7
Nd_2O_3	13.7
Dy_2O_3	9.7
Sm_2O_3	7.5

in this experiment (spiked with lanthanum), the final oxide is rich in lanthanum. Summarizing, this process using solution spiked with lanthanum is not reliable for the proposal of fractionation for separation and enrichment of yttrium from its concentrates.

On the other hand, the proposed process of leaching the solid REE carbonates with ammonium carbonate solution gave rather reliable results, being a simple technique allowing the separation of yttrium from the other rare-earth elements and concentrating them, with special interest in lanthanum and heavy rare earths. The composition of the yttrium concentrate is indicated in Table 4. The XR fluorescence analyses are semi-quantitative with standard deviation of 10%.

Additional work is being done to extend the separation and purification of yttrium and to upgrade and improve the purification ammonium carbonate leaching technology.

As a conclusion, the ammonium carbonate solution as describe above is a simplified method developed for the separation and concentration of yttrium and lanthanum from their concentrate, specially from the solid rare-earth carbonates as the LCC and yttrium carbonate. Advantage is clear considering the elimination of the need for an acidity dissolution of the concentrate.

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