

Enrichment of yttrium from rare earth concentrate by ammonium carbonate leaching and peroxide precipitation

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Abstract

The rare earth elements (REE) solubility with ammonium carbonate vary progressively from element to element, the heavy rare earth elements (HRE) being more soluble than the light rare earth elements (LRE). Their solubility is function of the carbonate concentration and the kind of carbonate as sodium, potassium and ammonium. In this work, it is explored this ability of the carbonate for the dissolution of the REE and an easy separation of yttrium was achieved using the precipitation of the peroxide from complex yttrium carbonate. For this work is used a REE concentrate containing (%) Y_2O_3 2.4, Dy_2O_3 0.6, Gd_2O_3 2.7, CeO_2 2.5, Nd_2O_3 33.2, La_2O_3 40.3, Sm_2O_3 4.1 and Pr_6O_{11} 7.5. The mentioned concentrate was produced industrially from the chemical treatment of monazite sand by NUCLEMON in São Paulo. The yttrium concentrate was treated with 200 g L^{-1} ammonium carbonate during 10 and 30 min at room temperature. The experiments indicated that a single leaching operation was sufficient to get a rich yttrium solution with about 60.3% Y_2O_3 . In a second step, this yttrium solution was treated with an excess of hydrogen peroxide (130 volumes), cerium, praseodymium and neodymium peroxides being completely precipitated and separated from yttrium. Yttrium was recovered from the carbonate solution as the oxalate and finally as oxide. The final product is an 81% Y_2O_3 . This separation envisages an industrial application. The work discussed the solubility of the REE using ammonium carbonate and the subsequent precipitation of the correspondent peroxides.

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1. Introduction

Yttrium compounds find interesting application in many fields. High pure yttrium oxide (Y_2O_3) is used in the composition of phosphors emitting wavelengths of red, blue and green [1]. Yttrium is used in the manufacture of superconductors, in superalloys of nickel and cobalt as well, and solid oxide fuel cells. Yttrium oxide has high melting point, its greater use is for advanced ceramics, as for instance yttrium stabilized zirconia. It is used in electronic ceramic as oxygen sensor [2]. The compounds of yttrium are used as catalysts. Considering its thermoluminescent properties yttrium is now used for the man-

ufacture of incandescent mantle for gas illumination, where it substitutes the thorium. The garnets Y–Fe and Al–Gd–Y exhibit interesting magnetic properties. Y–Al garnets are considered gemstone like diamonds [2].

The growing industrial applications of the rare earth elements (REE) led to a growing interest in the research of new technologies for extraction and use of alternative sources of rare earths. In nature, the REE are associated in quite complex mixtures and due to the similarity of their chemical properties it is difficult and laborious to separate the individual elements. Usually, the synthesis of pure rare earth compounds first requires their separation in groups. Then the element of choice is isolated from the group. With the scope to obtain a rich fraction of yttrium the present work started performing an ammonium carbonate leaching of an yttrium concentrate. This raw material is a rare earth concentrate low in cerium named low cerium carbonate (LCC) produced in

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the country from the industrial treatment of monazite. This work explores the selective solubilization of yttrium with ammonium carbonate while lanthanum and the other REE are little dissolved or not dissolved at all. The solubility of the REE carbonates in water is low. From aqueous solutions the lanthanum carbonate, for instance, is crystallized as $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$. Generally, it is reported in the literature that the carbonates of cerium group (La, Ce, Pr, Nd and Sm) are insoluble in water and in ammonium carbonate, while the yttrium group rare earths are soluble in this salt. The carbonate chemistry is very important for the precipitation of the rare earths and for their solubilization as well. Although lanthanum, cerium, praseodymium and terbium are little soluble in ammonium carbonate, the other REE are completely soluble. The normal carbonates and the double REE carbonates as well, are reasonably soluble in alkaline carbonate, especially potassium carbonate, due to the complexation [3,4]. The REE carbonates system is of utmost importance from both the analytical and industrial aspects. Taketatsu [5] reported over the dissolution of REE with ammonium carbonate, potassium carbonate and hydrogen potassium carbonate. Sinha [6] studied the solubility of Eu(III) with potassium carbonate and Firsching and Mohammadzadel [7] determined the solubility product of REE carbonates. To mention here the local industrial importance of the REE-carbonate system, Krumholz et al. [8] produced various concentrates of rare earth carbonates at the Orquima Indústrias Químicas Reunidas S.A., São Paulo, as “rare earth carbonate”, “low cerium carbonate”, “didymium-45 carbonate”, “didymium-50 carbonate”, “neodymium-85 carbonate” and “yttrium-85 carbonate”. Vasconcellos et al. [9] exploited the selective dissolution of yttrium in ammonium carbonate starting from the “low cerium carbonate” with 1–3% Y_2O_3 and obtained a final fraction with 52.9% of Y_2O_3 . Queiroz et al. [10,11] reported that the addition of hydrogen peroxide to the carbonate rare earths complexes forms a precipitate, identified as rare earth peroxycarbonates.

2. Materials and methods

2.1. Starting raw materials

A representative aliquot of the “low cerium carbonate” was used. Its chemical composition is shown in Table 1. Ammonium carbonate, ammonium hydroxide and others reagents were of analytical grade. The rare earth stock solutions were prepared by the dissolution of the correspondent oxides with hydrochloric acid. After concentration of the solutions by evaporation the residue was taken with deionized water. Using this solution, the necessary dilutions were made.

2.2. Apparatus

The X-ray fluorescence analyses were obtained using a RIGAKU model RIX 3000 (1996) spectrometer.

2.3. Solubility of yttrium carbonate in ammonium carbonate

To an aliquot of yttrium chloride a 200 g L^{-1} ammonium carbonate was added, the precipitation of the correspondent carbonate occurred immediately. Then, to the precipitate an excess of ammonium carbonate solution was added, the solubilization being complete. This same procedure was applied to the other REE. The results are in Table 2.

Table 1

Typical analysis of LCC and chemical composition of yttrium oxide from experiments A, B and C

Constituent (%)	Low cerium carbonate	Experiment		
		A	B	C
Y_2O_3	2.4	52.9	60.3	81.0
La_2O_3	40.3	n.d.	14.9	3.0
Dy_2O_3	0.6	9.7	4.3	4.3
Er_2O_3	<0.1	n.d.	n.d.	2.0
Yb_2O_3	n.d.	n.d.	n.d.	n.d.
Lu_2O_3	n.d.	n.d.	n.d.	n.d.
Ho_2O_3	n.d.	n.d.	0.79	0.98
Tb_4O_7	n.d.	n.d.	0.74	0.76
Gd_2O_3	2.7	23.7	8.3	6.90
Tm_2O_3	n.d.	n.d.	n.d.	n.d.
CeO_2	2.5	n.d.	0.40	n.d.
Nd_2O_3	33.2	13.7	6.0	n.d.
Sm_2O_3	4.1	7.5	1.40	0.63
Pr_6O_{11}	7.5	n.d.	1.1	n.d.
Eu_2O_3	n.d.	n.d.	n.d.	0.14
ThO_2	n.d.	n.d.	n.d.	n.d.

XR fluorescence analysis. n.d., not detected; A and B, leaching with ammonium carbonate and directly precipitated with oxalic acid. Leaching time 10 and 30 min, respectively; C, leaching with ammonium carbonate, soluble RE precipitated with H_2O_2 and the filtrate precipitated with oxalic acid.

2.4. Effect of the concentration of ammonium carbonate in the rare earth carbonate dissolution

In this work, we studied the solubility of the rare earths as function of the excess of ammonium carbonate at 20–25 °C. The experimental procedure was such that the 10 g L^{-1} RE solution was added over the carbonate solution using 25 mL of carbonate solution of 50, 100, 200, 300 and 400 g L^{-1} , respectively. The mixture was stirred continuously until a permanent precipitate occurred. In this moment, the addition of the RE solution is stopped. Table 3 has the results of the above-mentioned experiments.

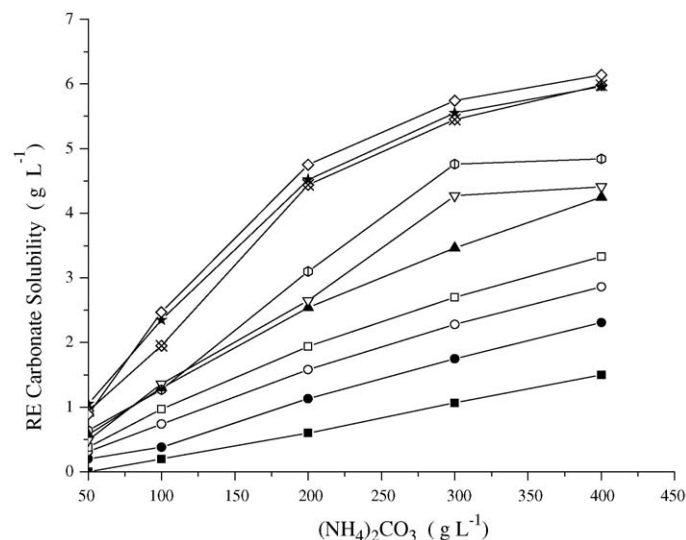
2.5. Treatment of yttrium carbonate with hydrogen peroxide

To the soluble yttrium carbonate complex a little excess of solution of hydrogen peroxide (130 volumes) was added. No precipitation occurred. This same test was applied to the other pure REE. In Table 2 are the results of the mentioned tests.

Table 2

REE solubility with ammonium carbonate and their peroxycarbonate precipitation

REE	Solubility in $(\text{NH}_4)_2\text{CO}_3$ 200 g L^{-1}	Peroxycarbonate precipitation
La	Partial	Total
Ce	Partial	Total
Pr	Partial	Total
Nd	Partial	Total
Sm	Total	Total
Eu	Total, but lengthily	Total
Gd	Total	Total
Tb	Total, but lengthily	Partial
Er	Total	Total after 24 h
Dy	Total	Total
Y	Total	Not
Ho	Total, but lengthily	Total
Tm	Total	Partial



Legend	—■— La	—●— Ce	—○— Pr	—□— Nd	—▲— Sm
	—▽— Tb	—◊— Gd	—⊗— Dy	—★— Y	—◇— Ho

Fig. 1. RE carbonates solubility as function at ammonium carbonate concentration (legend: (■) LA; (●) CE; (○) Pr; (□) Nd; (▲) Sm; (▽) Tb; (◊) Gd; (⊗) Dy; (★) Y; (◇) Ho).

2.6. Leaching the LCC with ammonium carbonate

Solid LCC concentrate was treated with a 200 g L⁻¹ solution of ammonium carbonate at room temperature. The rare earth concentrate was covered with the ammonium carbonate solution and agitated from 10 to 30 min and then filtered. Yttrium was recovered from the filtrate after acidified with hydrochloric acid and then precipitated with oxalic acid. The dried oxalate was fired to oxide. Its chemical composition determined by X-ray fluorescence analysis is listed in Table 1.

2.7. Precipitation of LRE with hydrogen peroxide

The leached yttrium carbonate filtrate prepared as above-mentioned procedure was treated now with little excess of hydrogen peroxide (30 volumes). The suspension was kept under mechanical agitation during 90 min and then centrifuged. The light yellow precipitate was dried and then fired to the oxide. Yttrium was recovered from the filtrate after being acidified with hydrochloric acid and then precipitated with oxalic acid. The dried oxalate was fired to oxide. Table 1 has its chemical composition. In this table are the results

Table 3
Rare earth carbonates solubility as function of ammonium carbonate concentration (20–25 °C)

RE carbonates solubility (g RE ₂ O ₃ L ⁻¹)	(NH ₄) ₂ CO ₃ (g L ⁻¹)				
	50	100	200	300	400
La	–	0.20	0.60	1.07	1.50
Ce	0.20	0.38	1.13	1.75	2.31
Pr	0.31	0.74	1.58	2.28	2.86
Nd	0.38	0.97	1.94	2.70	3.33
Sm	0.57	1.30	2.54	3.46	4.25
Gd	0.64	1.27	3.10	4.76	4.84
Tb	0.49	1.36	2.65	4.27	4.41
Y	1.05	2.35	4.52	5.55	5.96
Dy	0.94	1.95	4.44	5.45	5.98
Ho	0.89	2.47	4.75	5.74	6.14

of two representative experiments according to the protocol of this paper, i.e., experiment A leaching with ammonium carbonate, acidified and precipitated as oxalate; C leaching with ammonium carbonate and LRE directly precipitated with hydrogen peroxide. Yttrium was recovered from this peroxide filtrate.

3. Results and discussion

3.1. The XR fluorescence analyses are semi-quantitative with standard deviation of 10%

The precipitation of Tb, Er and Tm is quite slow. The precipitation started after the first hour. After 24 h, the maximum of precipitation was reached, but even so it was incomplete. After separating the precipitate, the filtrate was treated with oxalic acid to complete the recovery of the rare earths. This fact allows to state that the rare earths have differential behavior since Ce, Pr and Nd are precipitated immediately. So, it is clear that this behavior provides a way of separation by the synthesis of the peroxycarbonates.

Observing Fig. 1 it is possible to see the increasing of the solubilization of the rare earths as function of the atomic number.

4. Conclusions

The procedure described in this work is very simple, adequate and economical. The solid “low cerium carbonate” is leached at room temperature (about 20–25 °C), for a short time (10–30 min). The filtered solution can be treated directly with oxalic acid to obtain the yttrium oxide or treated directly with hydrogen peroxide to get the LRE peroxycarbonate that can be fired directly to the oxide. Starting with the LCC of 2.4%

Y₂O₃, one simple leaching with ammonium carbonate allowed to obtain a final yttrium oxide of ca. 80%. The ammonium carbonate leach procedure has a reasonable selectivity when it is complemented and ameliorated by a peroxy carbonate precipitation technique.

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