

Solubility behavior of rare earths with ammonium carbonate and ammonium carbonate plus ammonium hydroxide: Precipitation of their peroxycarbonates

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Abstract

The purpose of this work is to report the significant behavior of the rare earths when treated with ammonium carbonate and with a binary mixture of ammonium carbonate plus ammonium hydroxide. The carbonates of some rare earths are completely soluble in ammonium carbonate or in ammonium carbonate plus ammonium hydroxide, while others are only partially soluble and finally some are completely insoluble. Addition of hydrogen peroxide to the soluble complexed rare earth carbonates results in the precipitation of a series of a new compounds described as rare earth peroxycarbonates. The rare earths have some different precipitation behavior in the carbonate–peroxide system. Some are completely and immediately precipitated, others are completely precipitated after an aging period, and finally other are not precipitated at all. These different behaviors open a new possibility for the separation chemistry of the rare earths. Sm, Gd, Dy, Y, Yb and Tm are fast and completely soluble in ammonium carbonate. Ho, Eu and Tb are completely soluble in ammonium carbonate but slowly dissolved. La, Ce, Pr and Nd are only partially soluble in ammonium carbonate. While Ce, Pr, Nd, Sm, Eu and Dy are completely and easily soluble in the ammonium carbonate plus ammonium hydroxide mixture, La is only partially soluble and Tb is completely insoluble in the same mixture. Concerning the peroxycarbonates, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Ho are quantitatively precipitated. The precipitation of the Er peroxycarbonate is quantitative, but after an aging period of 24 h. Y is not precipitated at all. The process is very easy, simple and economically attractive. Although proved in bench scale, its scale-up is easily feasible.

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1. Introduction

The separation and purification of rare earths (RE) it is still today a matter of utmost concern. Technology and procedures for the separation of macroscopic amounts of RE are always welcome. Brazil has a long tradition in rare earth technology, from the monazite ores mining until the industrial separation and production of rare earth concentrates. Using some rare earth concentrates produced industrially in the country a group of researchers at the Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN), São Paulo, have been working for several years with the individual separation of rare earth elements

(REE). Some high grade pure oxides, like lanthanum, cerium, neodymium, samarium and yttrium have been produced and used as standards.

One of the investigative lines at IPEN/CNEN is the dissolution of the REE concentrates with ammonium carbonate and the resultants complexes treated with hydrogen peroxide for the precipitation of the corresponding peroxycarbonates. Researchers exploited the different behavior of the REE solubilization and complex formation toward ammonium carbonate and the differential precipitation of the corresponding peroxides. The carbonate chemistry is of relevant importance to the rare earths from both analytical and industrial aspects. The rare earths can be precipitated and solubilized by alkaline carbonate as well [1,2]. Sinha [3] studied the solubility of Eu(III) with potassium carbonate and Firsching and Mohammadzadel [4] determined the solubility product of REE carbonates. Krumholz

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et al. [5] produced various rare earth concentrates using carbonate as precipitant, some of them for industrial application as a “rare earth carbonate”, “didymium-45 carbonate”, “didymium-50 carbonate”, “neodymium-85 carbonate” and “yttrium-85 carbonate”. More recently Abdel-Rehim [6] used ammonium carbonate–ammonium bicarbonate for the autoclave leaching and separation of thorium, uranium and rare earths. de Vasconcellos et al. [7,8] exploited the selective dissolution of yttrium in ammonium carbonate starting from an industrial low cerium carbonate concentrate. Queiroz et al. [9,10] reported that the addition of hydrogen peroxide to the carbonate rare earths complexes forms a precipitate, identified as rare earth peroxycarbonates. The present work discusses the dissolution behavior of the REE using a binary mixture of ammonium carbonate with ammonium hydroxide forcing the maximum dissolution of these rare earths. The treatment of the soluble REE carbonate complexes with hydrogen peroxide is reported as well. Every experiment was performed at room temperature and normal pressure, which offers considerable economic appeal.

2. Experimental

2.1. Starting raw materials

Chemically pure ammonium carbonate was used for the preparation of 50, 100, 200, 300 and 400 g L⁻¹ solutions. Ammonium hydroxide and the other reagents were of analytical grade. All solutions were prepared using deionized water. Several stock solutions of rare earth chlorides were prepared using the highly pure (>99.9%) oxides dissolved with hydrochloric acid. The La, Ce, Nd and Sm solutions were prepared using the corresponding oxides obtained at the IPEN/CNEN laboratories. The other oxides were from Johnson Matthey Chemical Co. The oxides were dissolved with hot hydrochloric acid. After concentration of the solutions by evaporation the residue was dissolved in deionized water. These stock solutions were diluted when necessary.

2.2. Solubility of rare earth carbonate in ammonium carbonate–ammonium hydroxide

An aliquot of lanthanum chloride solution was treated with a 200 g L⁻¹ ammonium carbonate. The precipitate formed was treated with an excess of carbonate solution and then with ammonium hydroxide. The lanthanum precipitate was not totally dissolved. It was separated by filtration. The filtrate, after acidification, was tested with oxalic acid indicating still the presence of lanthanum. This same procedure was applied to the other rare earth elements. The results are in Table 1.

2.3. Effect of the concentration of ammonium carbonate in the rare earth carbonates dissolution

The experimental procedure in this series was the addition of 10 g L⁻¹ RE solution over 25 mL of ammonium carbonate solution of 50, 100, 200, 300 and 400 g L⁻¹, respectively, at 20–25 °C. The mixture was stirred continuously until a permanent precipitate occurred. In this moment, the addition of the REE solution was stopped. Table 2 indicates the results.

2.4. Solubility of rare earth carbonates with ammonium carbonate plus ammonium hydroxide

In this series of experiments the scope was to learn the behavior of RE carbonate dissolution into more alkaline medium. As in the previous series, the work was done at room temperature. In this case only an ammonium carbonate solution of 400 g L⁻¹ was used. For each experiment over 10 g of ammonium

Table 1

REE solubility with ammonium carbonate, ammonium carbonate plus ammonium hydroxide and their peroxycarbonate precipitation

REE	Solubility in		Peroxycarbonate precipitation
	(NH ₄) ₂ CO ₃ (200 g L ⁻¹)	(NH ₄) ₂ CO ₃ /NH ₄ OH	
La	Partial	Partial	Total
Ce	Partial	Total	Total
Pr	Partial	Total	Total
Nd	Partial	Total	Total
Sm	Total	Total	Total
Eu	Total, but slowly	Total	Total
Gd	Total	Total	Total
Tb	Total, but slowly	Not	Partial
Er	Total	Total	Total after 24 h
Dy	Total	Total	Total
Y	Total	Total	Not
Ho	Total, but slowly	Total	Total
Tm	Total	Total	Partial

Table 2

Solubility of La, Ce, Pr, Nd, Sm, Gd, Tb, Y, Dy and Ho carbonate as function of ammonium carbonate concentration (20–25 °C)

REE 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

carbonate into a 25 mL volumetric flask was poured the ammonium hydroxide. The solution was transferred to a beaker and then the REE chloride solution was added with constant stirring. As before, the addition of the REE chloride solutions was interrupted after the commencement of the precipitate. The experiment allowed determination of the optimum volume of ammonium hydroxide for the maximum solubility of the rare earths. The results are shown in Table 3.

Table 3

Solubility of rare earth carbonates in ammonium carbonate 400 g L⁻¹ and in the 400 g L⁻¹ ammonium carbonate–ammonium hydroxide

REE carbonates solubility (g RE ₂ O ₃ L ⁻¹)	System	
	(NH ₄) ₂ CO ₃	NH ₄ OH/(NH ₄) ₂ CO ₃
La	1.50	2.06
Ce	2.31	3.13
Pr	2.86	3.90
Nd	3.33	4.51
Sm	4.25	5.33
Gd	4.84	5.71
Y	5.96	6.25
Dy	5.98	6.28
Ho	6.14	6.57

2.5. Addition effect of hydrogen peroxide over the rare earth ammonium carbonate complexes

Over the clear ammonium carbonate rare earth complexes, an excess of hydrogen peroxide (130 volumes) was added, at room temperature and with constant stirring. The practical results are very interesting. The elements La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Ho had their peroxycarbonates immediately and quantitatively precipitated. The precipitation of Tb and Tm as peroxides on the other hand is very slow. Dissolution commences 1 h after the addition of hydrogen peroxide and the precipitation is incomplete. The ammonium carbonate of yttrium did not yield the corresponding peroxycarbonate at all.

3. Results and discussion

In this paper we studied the treatment of rare earth carbonates with ammonium carbonate. The REE solubility with ammonium carbonate varies progressively from element to element, the heavy rare earth elements (HRE) being more soluble than the light rare earth elements (LRE). Table 1 indicates that the solubility of La, Ce, Pr, Nd with ammonium carbonate is partial and from Sm to Tm the solubility is complete, although slow for Eu, Tb and Ho. In all cases, the solubility is higher as the ammonium carbonate concentration increases. The addition of ammonium hydroxide to the ammonium carbonate enhances the solubility of the rare earths. As can be seen in Table 3 the solubility of the rare earths are higher with the admixture $\text{NH}_4\text{OH}/(\text{NH}_4)_2\text{CO}_3$ than with ammonium carbonate alone. The addition of hydrogen peroxide to the soluble rare earth ammonium carbonate complexes yields the corresponding peroxycarbonates, although notable differences were observed. For the rare earths La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Ho the precipitation of the peroxides is complete. The precipitation of the Er peroxide is also complete but

only after 24 h aging. The rare earths Tb and Tm are precipitated only partially. Yttrium is a notable exception being completely resistant to precipitation.

4. Conclusion

The different solubility behavior of the rare earths with ammonium carbonate as function of its concentration and their different behavior toward the addition of hydrogen peroxide suggest that the synthesis of peroxycarbonates is an attractive alternative for the separation and purification of the rare earth elements.

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