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HIGH PURITY NEODYMIUM ACETATE FROM MIXED RARE EARTH CARBONATES

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ABSTRACT

A simple and economical chemical process for obtaining high purity neodymium acetate is discussed. The raw material in the form rare earth (RE) carbonate is produced industrially from the chemical treatment of Brazilian monazite. Ion exchange chromatography technique with a strong cationic resin, proper to water treatment, and without the use of retention ions was used for the fractionating of the rare earth elments (REE). In this way, it was possible to obtain 99.9% pure Nd_2O_3 in yields greater than or equal 80%, with the elution of the REE using ammonium salt of ethylenediaminetetraacetic acid (EDTA) solution in pH controlled. The complex of EDTA-neodymium was transformed into neodymium oxide, wich was subsequently dissolved in acetic acid to obtain the neodymium acetates. Molecular absorption spectrophotometry was used to monitor the neodymium content during the process and sector field inductively coupled plasma mass spectrometry was used to certify the purity of the neodymium acetates. The typical neodymium acetates obtained contain the followings contaminants in $\mu g\ g^{-1}$: Sc(5.1); Y (0.9); La (1.0); Ce (6.1); Pr (34,4); Sm (12.8); Eu (1.1); Gd (15.4); Tb (29.3); Dy (5.2), Ho(7.4); Er (14.6); Tm (0.3); Yb (2.5); Lu (1.0). The high purity neodymium acetates obtained from this procedure have been applied, replacing the imported product, in research and development area on rare earth catalysts.

1. INTRODUCTION

Monazite is a heavy mineral composed of REE phosphates and thorium. Monazite occurs as an accessory constituent to granites, gneisses, pegmatites and the sands produced from the decomposition of these rocks [1]. It is found in the river beds of the Brazilian states of Bahia, Minas Gerais, Goias and Mato Grosso, and on the beaches of the coast of Bahia, Espirito Santo and Rio de Janeiro, wich contain from 25 to 30% of monazite. Other minerals present include quartz, zircon, ilmenite, magnetite and rutile [2].

The procedure for the separation of neodymium to obtain pure acetates was carried out using raw material RE carbonates that were industrially produced by the late NUCLEMON – Nuclebras de Monazita e associados Ltda using Brazilian monazite. Ion exchange chromatography without the use of retention ions and as eluent ammonium salts of EDTA in pH controlled was used to obtain high purity neodymium oxide.

Molecular absorption spectrophotometry and sector field inductively coupled plasma mass spectrometry (SF ICP-MS) techiniques were used as an analytical control to ensure the quality of neodymium oxide and neodymium acetates, respectively.

For several years, researches at Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP) have been working on the individual separation of REE, aiming to assist, with the obtained products, and internal demand in other researchs areas[3-12].

2. EXPERIMENTAL

2.1 Starting Raw Materials

A representative aliquot of the rare earth carbonates was used. Its chemical composition is show in Table 1. Nítric acid, acetic acid, ammonium salt of ethylenediaminetetraacetic acid (EDTA) and others reagents were of analytical grade. The solutions of RE nitrates were prepared by the dissolution to RE carbonates in nitric acid. The solutions of RE nitrates at 10-15 g L^{-1} in RE_2O_3 were filtered to get rid of small amount of insoluble products.

Table 1 – Composition of the RE Carbonates

Element	La	Ce	Pr	Nd	Sm	Gd	Y
Oxide (%)	42-47	3-7	5-6	30-34	4-5	2-4	1-3

2.2 Loading the Resin and Elution the Rare Earth to obtain $Nd_2O_3 \geq 90\%$

The strong cationic exchangers S-100, produced by Bayer Co. in 50 – 100 mesh, in the NH^{4+} form, were used in this investigation. The solutions of RE nitrates at 10-15g RE_2O_3 L^{-1} were continuously passed through column systems filled with strong cationic resin, which is used as a typical resin for water treatment and it is easy to find in the Brazilian market. Subsequently, the resin was rinsed with deionized water. The REE in the resin were eluted with ammoniacal EDTA at pH 4.0. The effluent was collected in fractions from which oxalates were precipitated and converted to oxides. The ion exchange system was built with columns connected in series, including 3 columns of 3 meter each and of 12 cm diameter. In this way, it was possible to obtain neodymium oxide with a purity of 90% and an 80% yield.

2.3 Neodymium Purification

The neodymium oxide obtained using the procedure in section 2.2 was refined by using the same strong cationic resin in an ion exchange system formed by 5 columns of 1 meter each and of 5 cm diameter connected in series.

The neodymium nitrate solution was prepared by dissolving of 90% pure neodymium oxide in hot nitric acid. The necessary dilution was made to obtain neodymium nitrates of 10-15g Nd_2O_3 L^{-1}. The neodymium nitrate solution was loaded into a strong cationic ion-exchange resin and then eluted using the ammonium salt of EDTA at pH 4.0. A final neodymium oxide with a purity greater than 99.9% was obtained.

2.4. Obtaining Neodymium Acetate of High Purity

For the preparation of neodymium acetates of high purity, the neodymium oxide with greater than 99.9% purity obtained using the procedure in section 2.3 was used. The experimental procedure was such that the neodymium oxide was added over the acetic acid. The mixture was stirred continuously until complete dissolution was achieved. After concentraton of the solution by evaporation the crystals of neodymium acetates were obtained.

The pilot plant of separation and purification of high purity neodymium oxide here produced is shown Fig. 1.

2.5. Characterization and Analytical Control of the Process

Molecular absorption spectrophotometry and sector field inductively coupled plasma mass spectrometry (SF ICP-MS), Element, from Finningan MAT (Bremen, Germany), was used to insure the quality of the neodymium oxide and the neodymium acetates, respectively. Table 3 shows values of REE determined as impurities in the neodymium acetates. This technique provides accurate results and reproducible contaminant values in the range of μ g^{-1}.

3. RESULTS

Table 2 shows the elution conditions and mass balance in the enrichment of neodymium from RE carbonates, using the pilot plant shown in Fig. 1. The first step of the process neodymium oxide of greater than 90 % purity was obtained with a yield of 80%. In the second step, using the 90% pure neodymium oxide, a feeding solution was prepared and percolated through a cationic exchanger system. Neodymium oxide of 99.9% purity was obtained. It is clear the enrichment of neodymium from 90,0 to 99,9%. Neodymium acetates were prepared using the 99,9% pure neodymium oxide, whose control of impurities of other REE is shown in Table 3.

Table 2 – Conditions of elution and mass balance in the enrichment of neodymium EDTA solution at pH 4.0 as eluent

Fraction.	Time (h)	Oxides (g)	Vol. (L)	Color	Nd_2O_3 (%)
1	120	116.1	300	Brown	
2	305	256.6	384	Beige	
3	456	901.6	584	Beige	
4	332	431.4	356	Beige	
5	576	490.5	596	Blue	90
6	666	236.6	469	Blue	90
7	600	401.2	550	Blue	90
8	96	78.5	130	Blue	90
9	72	56	70	Black	
10	72	23.5	28	Black	
11	26	18	23	Black	
12	98	73.3	80	Black	
13	48	51.5	80	Black	
14	172	110	75	Black	
15	72	38.6	60	Black	
16	24	27	40	Black	
17	72	115.5	65	Black	
18	48	43	40	Brown	
19	48	54	60	Brown	
20	24	69	50	Yellow	
21	72	--	50	Beige	

Table 3 - Values of rare earth impurities in the sample of neodymium acetate. Mass spectrometry inductively coupled with argon plasma (SF ICP-MS)

Element	$Nd(CH_3COO)_3$ (µg g^{-1} +/- σ)
Y	0.90 ± 0.20
Sc	5.10 ± 0.20
La	1.00 ±0.80
Ce	6.10 ± 0.70
Pr	34.40 ± 0.80
Nd	------------------
Sm	12.80 ± 0.80
Eu	1.10 ±0.90
Gd	15.40 ± 0.40
Tb	29.30 ± 0.50
Dy	5.20 ± 0.50
Ho	7.40 ± 0.10
Er	14.6 ± 0.70
Tm	0.30 ±0.10
Yb	2.50 ± 0.60
Lu	1.00 ±0.50

Figure 1. Rare Earths Pilot Plant

4-CONCLUSIONS

Neodymium acetates of high purity and quality have been obtained and can replace the imported product used in the development of nanocatalysts. Other studies to be published, describe the synthesis and chemical characterization of the neodymium acetates by Termogravimetry, X-ray Diffraction and Infrared Spectroscopy techniques.

Using a cationic ion exchange technique, without retaining ions and ammonium salt of EDTA at pH 4.0 as the eluent it was possible to obtain highly pure neodymium oxide and to obtain high purity neodymium acetates for use in the research on and development of catalysts.

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