Journal of Energy and Power Engineering 9 (2015) 616-621
doi: 10.17265/1934-8975/2015.07.003

Preparation of High Purity Neodymium Oxide from Brazilian Monazite by Ion Exchange

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Received: March 02, 2015 / Accepted: May 06, 2015 / Published: July 31, 2015.

Abstract: A simple and economical chemical process for obtaining high purity neodymium oxide is discussed. The raw material in the form of RE (rare earth) carbonates is produced industrially in Brazil from monazite. Using this concentrate as the feed material, ion exchange with a strong cationic resin, commonly used for water treatment, and without the use of retention ions was used for the fractionating of the REE (rare earth elements). The eluent was ammonium salt of EDTA (ethylenediaminetetraacetic acid) at pH 4.0. The complex of EDTA-neodymium was transformed into neodymium oxides via oxalate precipitation. We produced 99.9% pure Nd_2O_3 in yields greater than or equal to 80%. 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 oxides. The typical neodymium oxides obtained contained the followings contaminants in micrograms per gram: Sc (4.09); Y (0.39); La (0.78); Ce (5.62); Pr (4.56); Sm (11.10); Eu (1.10); Gd (14.30); Tb (29.3); Dy (4.15); Ho (8.39); Er (13.80); Tm (0.23); Yb (2.29); Lu (0.39). High purity neodymium oxides obtained from this procedure replaced the imported product used in research and development work on rare earth at IPEN/CNEN-SP (Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Eneergia Nuclear-São Paulo).

Key words: Neodymium oxide, elemental rare earths separation, rare earths.

1. Introduction

Neodymium is gaining more and more importance nowadays as an efficient component of permanent magnets which are used in generator motors, automobiles, hard disc drives and many other electronics devices. Another important application for neodymium is the production of lasers for use in dentistry and medicine. Also, neodymium is applied in advanced ceramics and special alloys. Currently, there are studies of new neodymium molecules for use in anticancer drugs [1, 2].

Brazil has a long tradition in industrial rare earth technology, from monazite ores mining to separation and production of rare earth concentrates. Using some rare earth concentrates produced industrially in Brazil, a group of researchers at the IPEN/CNEN-SP (Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Energia Nuclear-São Paulo), São Paulo, have been working for several years with the individual separation of REE (rare earth elements) [3-9]. Some high grade pure oxides, such as lanthanum, cerium, neodymium, praseodymium, samarium, gadolinium and yttrium have been produced and used as spec pure standards [10, 11].

In this work, the separation, enrichment and purification of neodymium was performed using a commercial rare earth carbonate concentrate low in cerium named LCC (low cerium carbonate) as the feed. This concentrate was produced industrially from the alkaline chemical treatment from Brazilian monazite sand. The separation of REE was achieved

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by a cationic ion exchange resin and ammonium salt of EDTA (ethilenediaminetetraacetic acid) as the eluent. Neodymium oxide at 99.9% purity was obtained. Molecular absorption spectrophotometry and SF ICP-MS (sector field inductively coupled plasma mass spectrometry) techniques were used as analytic controls to ensure the quality of neodymium oxide [12, 13]. This procedure simplifies the EDTA elution that requires the use the retaining ions such as Cu and Zn (exist as Cu-EDTA and Zn-EDTA complexes), reported widely in Refs. [14-16]. No retaining ions were used in this study.

2. Experiment

2.1 Starting Raw Materials

A representative sample of the LCC was used. Its chemical composition is shown in Table 1. Nitric acid, acetic acid, ammonium salt of EDTA and others reagents were of analytical grade. The solutions of RE (rare earth) nitrates were prepared by the dissolution of LCC in nitric acid. The solutions of RE nitrates at 10-15 g RE_2O_3/L were filtered to separate small amounts of residues left.

Table 1 Composition of LCC concentrate.

Constituent	%	Constituent	%
La_2O_3	42-47	Y_2O_3	1-3
CeO_2	3-7	CaO	4-5
Pr_6O_{11}	5-6	SiO_2	0.3
Nd_2O_3	30-34	U_3O_8	n.d.
Sm_2O_3	4-5	ThO_2	n.d.
Gd_2O_3	2-4		

Analysis by X-ray fluorescence, n.d. denotes not detected.

2.2 Loading the Resin and Elution of the REE to Obtain $Nd_2O_3 \geq 90\%$ Purity: Ion Exchange—Stage 1

The strong cationic exchanger S-100, produced by Bayer Co. in 50-100 meshes was used in this investigation. This resin is commonly used for water purification and freely available in Brazil. The solutions of REE nitrates at 10-15 g RE_2O_3/L were passed continuously through a column system filled with the resin and subsequently rinsed with deionized water. The REE loaded in the resin were eluted with ammoniacal EDTA (0.005-0.010 M) at pH 3.5-4.0. The eluate was collected in fractions, precipitated as oxalates and then converted to oxides, by calcining at 900 °C (1-4 h). The ion exchange system was built with three columns, 300 cm in height and 12 cm in diameter connected in series. The system was able to handle 10 kg of rare earth oxides, in total. This set up produced an eluate from which it was possible to obtain neodymium oxide greater than 90%-95% purity with a 80% yield.

2.3 Neodymium Purification—Ion Exchange Stage 2

The neodymium oxide obtained using the procedure described above was refined further by using the same strong cationic resin in an ion exchange system comprised of five columns, 100 cm in height and 5 cm in diameter, connected in series.

The feed neodymium nitrate solution for this stage was prepared by dissolving of 90%-95% pure neodymium oxide produced in the previous stage in hot nitric acid. The required dilution was made to obtain neodymium nitrates of 10-15 g Nd_2O_3/L. The resin was loaded with approximately 200 g RE_2O_3 (the maximum loading capacity of the system was 500 g RE_2O_3). As in the previous stage, the loaded resin was eluted with ammoniacal EDTA 0.01 mol/L at pH 3.5-4.0. A final neodymium oxide with purity greater than 99.9% was obtained. A block diagram of this process is presented in Fig. 1.

2.4 Oxalate Precipitation

The eluted fractions were acidulated with HNO_3 1/1 to pH 1. Then was added oxalic acid solution 20 g/L until complete precipitation of the rare earth oxalates and allowed to rest for 4 h. The precipitate was separated by vacuum filtration. Then, oxalates were calcined in a muffle furnace to 900 °C for up to 4 h in porcelain crucibles.

2.5 Characterization and Analytical Control of the Process

Molecular absorption spectrophotometry and SF

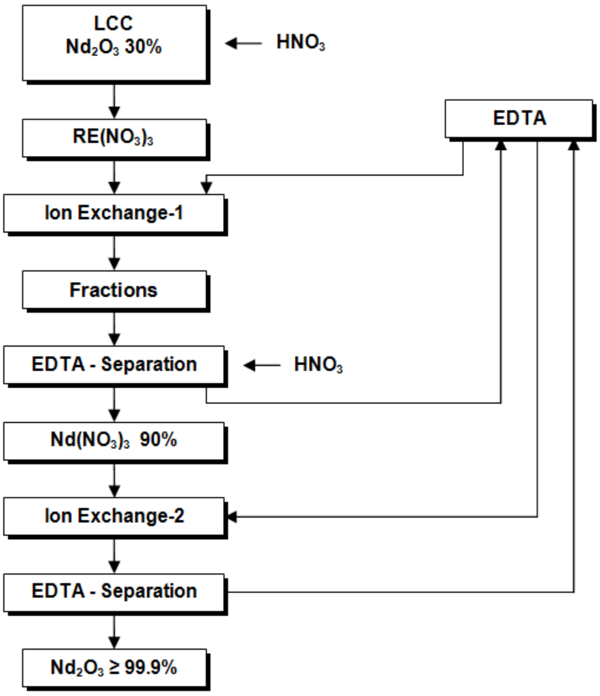

Fig. 1 Procedure for the preparation of pure neodymium oxides for use in research and development at IPEN/CNEN-SP (São Paulo).

ICP-MS, equipment supplied by Finnigan MAT (thermo mass spectometry), Bremen, Germany, were used to ensure the quality of the neodymium oxides. SF ICP-MS provided reliable and reproducible contaminant values in the range of µg^{-1}.

3. Results and Discussion

The color of the neodymium oxide usually indicates its purity. Highly pure neodymium oxide has a clear blue color. When contaminated with traces of praseodymium, for instance, the neodymium oxide acquires a brown color. This visual inspection was a helpful indication of the purity of neodymium during the elution of REs from the resin.

Tables 2 and 3 display the elution data for Stages 1 and 2, respectively. In the first stage of the process, neodymium oxide greater than 90%-95% purity was obtained with a yield of 80%. The feed for the second stage, was the 90%-95% pure neodymium oxide produced in the first stage. This stage produced neodymium oxide greater than 99.9% purity.

The detailed analyses of neodymium oxide produced from current study are shown in Tables 4 and 5.

Table 2 Data for elution and mass in the enrichment of neodymium, Stage 1.

Fraction	Time (h)	Vol. (L)	R_2O_3 (g)	Color	Nd_2O_3 (%)
1	120	300	116.1	Brown	
2	305	384	256.6	Beige	
3	456	584	901.6	Beige	
4	332	356	431.4	Beige	
5	576	596	490.5	Blue	90
6	666	469	236.6	Blue	90
7	600	550	401.2	Blue	90
8	96	130	78.5	Blue	90
9	72	70	56	Black	
10	72	28	23.5	Black	
11	26	23	18	Black	
12	98	80	73.3	Black	
13	48	80	51.5	Black	
14	172	75	110	Black	
15	72	60	38.6	Black	
16	24	40	27	Black	
17	72	65	115.5	Black	
18	48	40	43	Brown	
19	48	60	54	Brown	
20	24	50	69	Yellow	
21	72	50	-	Beige	

Table 3 Elution data for Stage 2: RE_2O_3 (g) = 215 g ($Nd_2O_3 \geq 90\%$), flow rate: 5 ± 2 mL/min.

Fraction	RE_2O_3 (g)	Sm_2O_3 (%)	Pr_6O_{11} (%)	Nd_2O_3 (%)
1 & 2	-	-	-	-
3	0.28	-	-	-
4	0.42	64	-	26
5	0.27	30	-	58
6	0.22	19	-	77
7	0.52	19	-	77
8	0.60	12	-	85
9	0.97	5	-	93
10	0.52	1	-	95
11	0.97	-	-	99
12	4.30	-	-	> 99
13	8.10	-	-	> 99
14	14.4	-	-	> 99
15	11.9	-	-	> 99
16	9.70	-	-	> 99
17	19.00	-	-	> 99
18	18.60	-	-	> 99
19	9.30	-	-	> 99
20	43.10	-	-	> 99
21	14.40	-	-	> 99
21-B	10.00	-	-	> 99
22	15.68	-	-	> 99
23	3.40	-	-	> 99
24	3.30	-	-	> 99
25	5.29	-	26.4	66

Table 4 Comparison of REE impurities in neodymium oxide produced at IPEN/CNEN-SP vs. imported.

Element	$Nd_2O_3 \geq 99.9\%$ IPEN/CNEN-SP (μg/g)	RSD (%) (*n* = 5)	$Nd_2O_3 \geq 99.9\%$ imported (μg/g)	RSD (%) (*n* = 5)
Sc	4.09	3.32	1.01	2.51
Y	0.39	4.15	0.28	3.14
La	0.78	3.97	0.81	2.94
Ce	5.62	2.08	4.23	1.08
Pr	4.56	0.35	5.81	0.13
Sm	11.80	3.22	2.23	2.22
Eu	1.10	2.67	0.81	3.79
Gd	14.30	1.46	2.31	2.18
Tb	20.30	3.97	15.40	1.95
Dy	4.15	2.17	6.25	2.78
Ho	8.39	0.74	7.46	1.37
Er	13.80	2.58	6.78	1.73
Tm	0.23	0.28	0.15	1.91
Yb	2.29	1.18	4.99	2.73
Lu	0.39	1.54	0.29	2.67

RSD: relative standard deviation (*n* = 5).

Table 5 Comparison of REE metallic impurities in neodymium oxide produced at IPEN/CNEN-SP vs. imported.

Element	$Nd_2O_3 \geq 99.9\%$ IPEN/CNEN-SP (μg/g)	RSD (%) (*n* = 5)	$Nd_2O_3 \geq 99.9\%$ imported (μg/g)	RSD (%) (*n* = 5)
B	0.46	3.85	0.31	2.51
Ti	0.50	2.64	0.11	3.14
V	0.66	1.71	0.21	3.95
Cr	0.30	3.81	0.20	2.75
Mn	0.84	4.81	0.38	2.55
Fe	32.8	4.92	16.5	3.37
Co	0.95	3.37	0.40	5.05
Ni	7.27	2.44	5.31	2.12
Cu	2.51	3,93	1.49	4.67
Zn	3.87	2.75	1.72	3.91
Sr	0.84	3.54	0.12	3.41
Nb	0.99	3.67	0.15	3.75
Mo	1.67	2.81	0.61	2.12
Pd	2.61	4.28	0.56	3.27
Sn	1.87	3.65	0.78	3.50
Cd	2.95	4.37	0.90	4.12
Sb	1.80	3.55	0.69	3.53
Pb	3.02	2.28	2.51	3.85
Bi	1.01	4.19	0.72	3.85
Th	1.51	3.81	0.82	4.50
U	2.05	3.38	0.94	3.24

4. Conclusions

Using a cationic ion exchange resin S-100 with 0.01 mol/L ammonium salt of EDTA at pH 4.0 as the eluent, it was possible to obtain a highly pure neodymium oxide that can be used in the research and development at IPEN/CNEN-SP. The purification procedure tested in this work can be scaled up to a semi industrial level.

We have also $CeO_2 \geq 99.9\%$, $La_2O_3 \geq 99.9\%$, $Pr_6O_{11} \geq 99.9\%$ and $Sm_2O_3 \geq 99.9\%$ to obtained by this method, that is used for preparing rare earths oxides nanoparticles and applied in automotive catalyst to increasing its life time.

Further studies undertaken on the synthesis and chemical characterization of the neodymium acetates by Thermogravimetry, X-Ray Diffraction and Infrared Spectroscopy techniques are yet to be published.

Acknowledgments

We thank to IPEN/CNEN-SP and Fundação de Amparo e Pesquisa do estado de São Paulo—FAPESP for financial support.

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