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HIGH PURITY SAMARIUM OXIDE FROM MIXED RARE EARTH CARBONATES

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ABSTRACT

A simple and economical chemical process for the production of highly pure samarium oxides is discussed. The raw material, which was used in the form of rare earth carbonates was produced industrially from the chemical treatment of Brazilian monazite. Ion exchange chromatography was performed using a strong cationic resin that is typically employed in water treatment processes to fractionate rare earth elements (REE) without the use of retention ions. Under these conditions, 99.9% pure Sm_2O_3 was eluted using the ammonium salt of ethylenediaminetetraacetic acid (EDTA) at a controlled pH. The EDTA-samarium complex was separated from EDTA and then precipitated as oxalate and fired to samarium oxide. Molecular absorption spectrophotometry was used to monitor the samarium content during the proposed process, and sector field inductively coupled plasma mass spectrometry was used to certify the purity of the samarium oxide. Typical samarium oxide obtained from the proposed procedure contained the following contaminants in micrograms per gram: Sc (20.90); Y (11.80); La (8.4); Ce (4.3); Pr (2.5); Nd (5.1); Eu (94); Gd (114); Tb (3.6); Dy (2.5), Ho (2.3); Er (3.0); Tm (2.3); Yb (38,2); Lu (25.6). The high-purity samarium oxides produced in the present study can be used as an alternative to imported products in research and development applications.

1. INTRODUCTION

Samarium is currently used in many applications, such as catalysts, lasers and metal alloys. For instance, samarium-cobalt alloys are used to prepare magnets that are resistant to demagnetization. Samarium is also employed to absorb neutrons in nuclear reactors and is used in sensitizers matches, optical glasses and carbon arc lamps. In medicine, samarium is used in the form of radioactive Sm_{153} to produce radiopharmaceuticals, which are used to reduce bone pain in patients with cancer. Moreover, new compounds containing samarium have been investigated as drugs. In Brazil, the extraction of rare earth metals occurs during the industrial exploitation of monazite. Herein, we use mixed rare earth carbonates depleted in cerium and lanthanum from the monazite processing industry to obtain high-purity Sm_2O_3, via ion exchange chromatography.

Monazite is a heavy mineral composed of REE phosphates and thorium. Monazite occurs as an accessory constituent to granites, gneisses and pegmatites, as well as sands from the

decomposition of the aforementioned rocks [1]. In Brazil, monazite is found in riverbeds located in Bahia, Minas Gerais, Goias and Mato Grosso, and the beaches off the coast of Bahia, Espirito Santo and Rio de Janeiro, which contain 25% to 30% on monazite. Other minerals present in monazite include quartz, zircon, ilmenite, magnetite and rutile [2-4]. The present procedure for the separation of samarium was carried out using raw material from the separation of uranium, thorium and rare earths in monazite. Fractional precipitation and ion exchange chromatography were employed to obtain high-purity samarium oxide. Molecular absorption spectrophotometry and sector field inductively coupled plasma mass spectrometry (SF ICP-MS) were used to ensure the quality of the samarium oxide.
At IPEN-CNEN/SP, the separation of rare-earth metals is performed to meet internal demands in other research areas[5-14].

2. EXPERIMENTAL

2.1. Starting Raw Materials

A representative aliquot of commercial rare earth (RE) carbonates (17% Sm_2O_3) was used. Hydrochloric acid, acetic acid, the ammonium salt of ethylenediaminetetraacetic acid (EDTA) and all other reagents were of analytical grade. Solutions of RE chlorides were prepared by dissolving the RE carbonates in hydrochloric acid. Solutions of RE chlorides with a RE_2O_3 concentration of 10 g L^{-1} were filtered to remove insoluble products.

2.2 - Loading the resin and eluting the rare earth metals to obtain 20%-93% pure Sm_2O_3

Rare earth chlorides solutions with a concentration of 10 g L^{-1} were pumped into a system of columns filled with a strong cationic resin, which is typically used as a resin for water treatment and that is easy to obtain in the Brazilian market. Subsequently, the resin was rinsed with deionized water. REEs in the resin were eluted with EDTA solution at pH 3.5-4.0. The effuent was collected in fractions, from which the oxalates were precipitated and converted into oxides. Ion exchange-system 1 contained several columns connected in series, including 3 columns with a lenght of 1.4 meters and a diameter of 12 cm and 4 columns with a length of 1.0 meter each and a diameter of 5 cm. In this way, samarium oxide with a purity of 20% to 93% was obtained.

2.3-Loading the resin and eluting the REEs to obtain ≥ 99.9% Sm_2O_3

Several fractions (20%-93%) were combined to obtain 100g of oxide yelding a 65% Sm_2O_3 concentrate, and the combined fractions were dissolved in hot 1:1 HCl. The resulting solution was diluted to 10 g L^{-1} of 65% Sm_2O_3. Subsequently, this solution was percolated in another ion exchange system containing 5 columns with a length of 1 meter and a diameter of 5 cm, which were connected in series and filled with a strong cationic resin. The same resin used in section 2.2. was employed in the second ion exchange system, and an EDTA solution at pH 3.5-4.0 was used to elute the REEs. As a result, Sm_2O_3 with a purity of 99.9% was obtained. A block diagram of this process is presented in Figure 1.

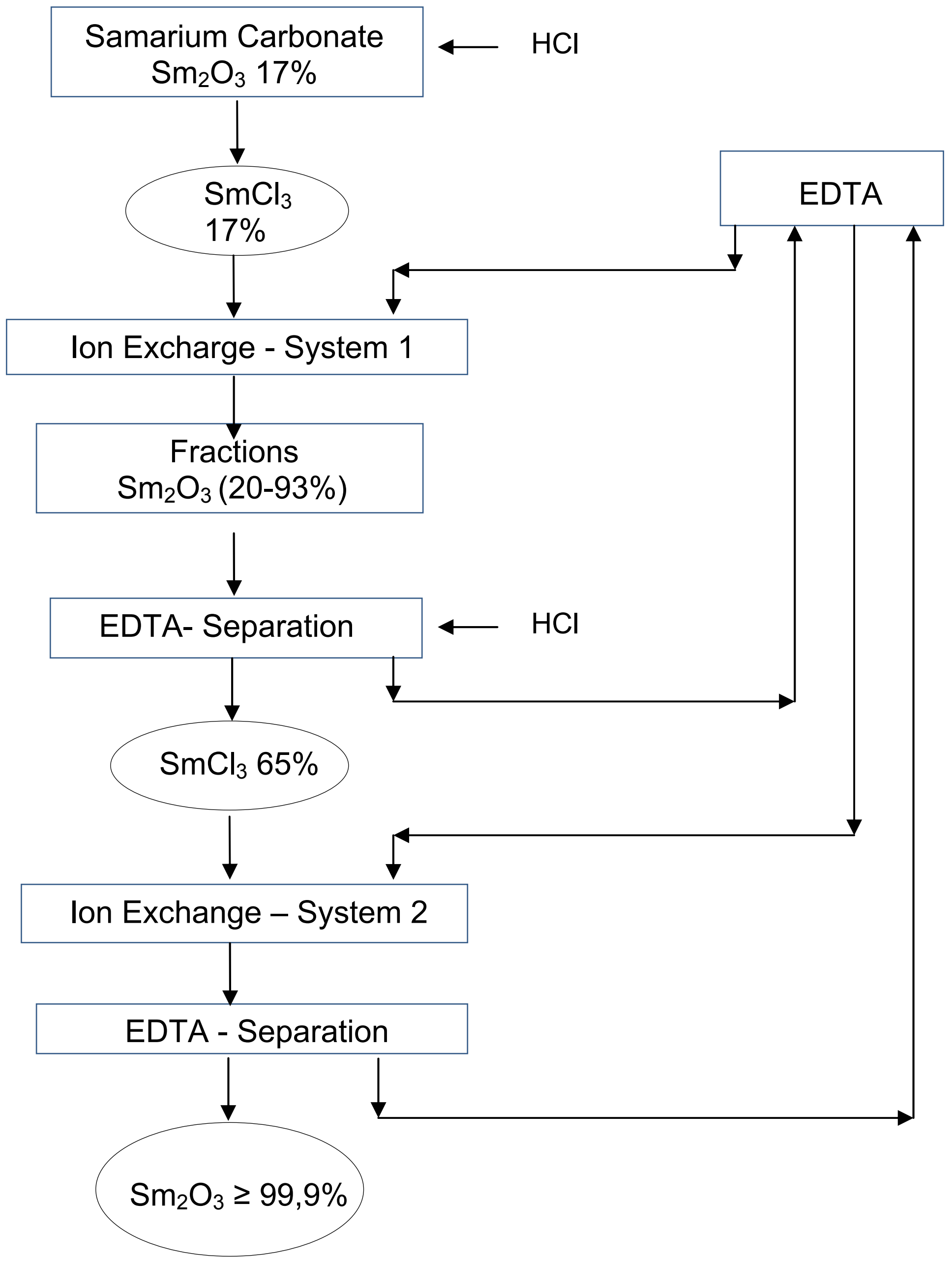

Figure1: Procedure for the preparation of pure samarium oxides for use in P&D at IPEN- CNEN/SP

2.3. Characterization and analytical control of the proposed process

Molecular absorption spectrophotometry and sector field inductively coupled plasma mass spectrometry (SF ICP-MS, Element, Finningan MAT Bremen, Germany) were used to ensure the quality of the samarium oxide. This technique provided accurate results and reproducible contaminant values in the µg $^{-1}$ range.

3. RESULTS

Table I shows the elution conditions and mass balance in enriched samarium from RE carbonates (17% Sm_2O_3) using ion exchange-system 1. Various fractions with a samarium oxide content between 20% and 93% Sm_2O_3 were obtained. Several fractions were combined to obtain a 65% Sm_2O_3 concentrate, which was used in ion exchange-system 2 to increase the purity to $\geq$ 99.9% Sm_2O_3. In Table II it's presented a typical samarium oxide obtained by this process with analytical control by ICP-MS.

Table I: Ion exchange - system 1. Elution and mass balance of enriched samarium from mixed rare earth carbonates (17%Sm_2O_3). Eluent: EDTA solution-acetic acid-NH_4OH at pH 3.5-4.0. Elution rate: 8 ± 2 mL/minute.

Fraction	pH	Time (h)	Oxide (g)	Oxide Color	Sm_2O_3 (%)
1	3.5	583	623	-	-
2	4.0	30	30	White	-
3	4.0	24	14	White	20
4	4.0	48	30	yellow	26
5	4.0	96	88	yellow	35
6	4.0	24	30	yellow	45
7	4.0	24	27	yellow	60
8	4.0	48	46	yellow	76
9	4.0	24	31	yellow	93.5
10	4.0	48	50	yellow	93
11	4.0	24	30	yellow	93.4
12	4.0	48	42	yellow	93
13	4.0	96	121	brown	72

Table II: Rare earth impurities present in samarium oxide. Sector field inductively coupled plasma mass spetrometry (SF ICP-MS)

Element	Sm_2O_3 ($\mu g.g^{-1}$ +/- σ)
Y	11.80 +/- 2.59
Sc	20.90 +/- 3.64
La	8.43 +/- 3.75
Ce	4.39 +/- 4.76
Pr	2.52 +/- 5.02
Nd	5.19+/- 4.48
Sm	……………
Eu	94.1 +/- 3.69
Gd	114.0 +/- 3.55
Tb	3.60 +/- 2.44
Dy	2.55 +/- 3.13
Ho	2.31 +/- 2.71
Er	3.09 +/- 2.31
Tm	2.30 +/- 2.36
Yb	38.2 +/- 2.90
Lu	25.6 +/- 3.93

4. CONCLUSIONS

Using cationic ion exchange chromatography, highly pure samarium oxide was obtained as an eluent, without the retention of ions and EDTA solution at pH 3.5-4.0. High-purity samarium oxide can be used as an alternative to imported products employed in research and development applications. Further studies on the synthesis and chemical characterization of the samarium acetates by thermogravimetry, X- ray diffraction and infrared spectroscopy will be published in due course.

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