



Selective removal of impurities from rare earth sulphuric liquor using different reagents



Ruberlan Gomes da Silva^{a,c,*}, Carlos Antonio de Moraes^b, Leandro Viana Teixeira^a, Éder Domingos de Oliveira^c

^a VALE Mineral Development Centre, Rodovia BR 381, Km 450, Distrito Industrial Simão da Cunha, CEP 33040-900 Santa Luzia, MG, Brazil

^b Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN), Av. Presidente Antônio Carlos, 6627, Pampulha, CEP 30123-970 Belo Horizonte, MG, Brazil

^c Department of Chemical Engineering, Universidade Federal de Minas Gerais (UFMG), Av Presidente Antônio Carlos, 6677, Pampulha, CEP 31270-901 Belo Horizonte, MG, Brazil

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ABSTRACT

In order to obtain a marketable rare earth product, purity requirements need to be met. More specifically, purification needs to be undertaken before precipitation. This addresses the technical feasibility of the use of different reagents such as limestone, lime, sodium hydroxide and magnesium oxide, to purify a rare earth sulphuric liquor containing impurities such as Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} , Th^{4+} , UO_2^{2+} , SO_4^{2-} and PO_4^{3-} . Moreover, it is important to avoid significant losses of rare earth elements during purification. To achieve this, experimental batch tests were carried out and the results obtained suggest that the best procedure for chemical precipitation requires neutralization in two consecutive steps: (i) limestone should be added until the pH level is about 3.5 and (ii) calcium hydroxide or lime is dosed until pH level rises to approximately 5.0. Under this optimum condition, some relevant impurities were fully removed, namely Fe, P, Al and Th. Also, about 98% of the initial uranium was removed, reaching the lowest uranium to rare earth oxides (REOs) mass ratio in the purified rare earth liquor considering all the experiments performed. Likewise, this was the condition in which the lowest sulphate content and U/REOs mass ratio in the purified rare earth liquor was obtained. Furthermore, the rare earth oxides recovery reached about 85%, preserving the same light (La + Ce + Pr + Nd)/total rare earth mass ratio observed in the purified liquors when compared to what was noticed in the initial rare earth sulphuric liquor. Moreover, the purified liquor is suitable to produce marketable rare earth salts to be processed in solvent extraction or ion exchange units.

1. Introduction

The term “rare earth” denotes a group of 17 elements which are chemically similar, comprising scandium, yttrium and lanthanides. Lanthanides is a group of elements in the periodic table having atomic numbers ranging from 57 to 71. Furthermore, the rare earth elements (REEs) invariably occur together in an ore deposit and behave as a single chemical entity (Gupta and Krishnamurthy, 1992). In addition, REEs are found in several minerals, such as bastnasite, mainly as RE-EsFCO₃, monazite, predominantly as REEsPO₄ or xenotime, largely as YPO₄ (Gschneidner, 1980; Sundaram, 1987). REEs are essential in an array of modern apparatus including wind turbines, smartphones, batteries and LEDs and the demand for these elements has been

increasing over the last decades by about 1% per year (Lima and Filho, 2015; Gras et al., 2017). In terms of processing, three precipitating agents – oxalic acid, ammonium/sodium hydroxide or ammonium/sodium bicarbonate – are usually applied in the production of rare earth oxides (REOs) (Lucas et al., 2015). More specifically, oxalic acid is used to precipitate high purity products, whereas the hydroxides and the carbonates are used to precipitate products with less rigorous purity requirements, and the choice of the agent to use depends on the physical characteristics required in the application of the final product (Lucas et al., 2015).

Nevertheless, the characteristics of the purity and quality will impact the final price of the rare earth products (Abreu and Moraes, 2010; Moraes and Ciminelli, 2004). The commercial value of the rare earth

* Corresponding author at: VALE Mineral Development Centre, Rodovia BR 381, Km 450, Distrito Industrial Simão da Cunha, CEP 33040-900 Santa Luzia, MG, Brazil.

E-mail addresses: ruberlan.silva@vale.com (R.G. da Silva), cmorais@cdtn.br (C.A. de Moraes), leandro.viana.teixeira@vale.com (L.V. Teixeira), eder@deq.ufmg.br (É.D. de Oliveira).

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products depends upon the purity and quality of the compound, which is based on the effective separation of the individual metals (Panda et al., 2016). However, the solvent extraction step is required in order to separate individually each REEs dissolved in either nitric or hydrochloric acid, but the presence of dissolved impurities can result in the emulsification of the extractants, which will have a negative impact on the purity of the final products (Ru'an et al., 1995).

According to Verbaan et al. (2015) most of applied flowsheets in the purification of rare earth liquors include a simple neutralization step using alkaline reagents such as lime, limestone, magnesium oxide, magnesium or sodium carbonate. Care must be taken when using calcium-based reagents in sulphuric media because REEs co-precipitation with gypsum can lead to significant REEs losses and, elements such as Th, Fe, P and Al are usually targeted to be removed in this stage. Ru'an et al. (1995) investigated a liquor containing only Al^{3+} ions and concluded that the pH used in the precipitation of rare earth and aluminium hydroxides are different, so the experiment was carried out by adjusting the pH of the leaching liquor to 5, resulting in spontaneous formation of insoluble $\text{Al}(\text{OH})_3$. According to Dutrizac (1983), Fernando et al. (2018) and Akcil and Koldas (2006), the impurities Fe^{3+} and Al^{3+} ions precipitate at pH 3.0 and 5.0, respectively, and any unoxidized iron will dissolve during leaching and remain in the solution as Fe^{2+} up to pH 6–8 (Onal et al., 2015). Verbaan et al. (2015) stated that a significant separation of REEs from impurities occurs due to the selectivity during precipitation as oxalate, which does not occur in the case of thorium.

In this context, the aim of this work is to devise a method to remove undesirable impurities prior to the rare earth precipitation step. In order to achieve this, different reagents were tested, including limestone, lime, sodium hydroxide and magnesium oxide. This purification aims at reducing the concentration of impurities such as Fe^{3+} , Al^{3+} , PO_4^{3-} and UO_2^{2+} in order to allow the production of marketable rare earth products, such as rare earth oxides or carbonates. Moreover, this purification is performed avoiding as much as possible any REEs losses, since this has a negative impact on the efficiency of the process.

2. Material and methods

2.1. Rare earth ore

The typical chemical and mineralogical compositions of the beneficiated rare earth ore are shown in the Tables 1, 2 and Fig. 1, respectively.

The main rare earth bearing mineral was monazite, which is represented by $(\text{REEs,Th})\text{PO}_4$. Both crandallite and apatite were also potential rare earth bearing minerals. A low REOs, MgO, Mn, ThO_2 and U_3O_8 content was found in the composition of the ore. Thorium and uranium can be expressed as $\text{Th}_3(\text{PO}_4)_4$ and $(\text{UO}_2)_3(\text{PO}_4)_2$ and are associated with monazite or apatite, respectively. In addition, a high iron content was found, mainly as hematite (Fe_2O_3). Likewise, this ore has high P_2O_5 and CaO contents mainly due to the presence of apatite, $\text{Ca}_3(\text{PO}_4)_2$, in the composition of the ore. Aluminium can be expressed as AlPO_4 , and is found in crandallite. Additionally, SiO_2 as quartz and TiO_2 as anatase were present in the ore structure used in the experiment, therefore these minerals do not react with sulphuric acid thus separation is not allowed.

According to Kumari et al. (2015), the REOs content in the monazite is about 65% w/w with 4–12% w/w of ThO_2 . These ores were expected to have a low Ca, Mg, Fe, Al, Si, Mn and U contents, given their high

REOs contents. The ore used in this investigation does not allow the application of conventional techniques to concentrate REEs, such as magnetic and density separation as well as flotation. Due to a rise in the REEs contents in the fine particles, the reclamation of the fraction below $74\ \mu\text{m}$ would be economically viable, if the REEs recovery reach amounts over 60% and REOs grade is above 5.0% (Testa et al., 2016).

2.2. Reagents and analytical methods

A 97.5% w/w sulphuric acid supplied by Química Moderna, a 97.0% w/w sodium hydroxide supplied by Anidrol Produtos Laboratórios, as well as a 95.0% w/w magnesium oxide and 98.6% w/w calcium hydroxide supplied by Sigma Aldrich, were used in the experiments. A commercial limestone (91.0% purity and 100% of particles below $74\ \mu\text{m}$) was used and its chemical composition is shown in Table 3.

The contents of the elements in the samples were determined according the analytical methods described in Table 4. The Fe^{2+} concentrations were analyzed through titration with $\text{K}_2\text{Cr}_2\text{O}_7$. In addition, the solids samples were dried in an oven at $100\ ^\circ\text{C}$ for at least 1 h and pulverized to a condition where 95% of the particles were below $74\ \mu\text{m}$.

The pH and redox potential measurements were performed with a Mettler Toledo type M400, having a reference electrode InPro3250SG/325/Pt10. Samples for X-ray diffraction were ground below $74\ \mu\text{m}$ and analysed on PANalytical Model XPERT PRO MPD (PW 3419) with PW3050/60 (θ/θ) goniometer, X-ray ceramic tubes, Cu anode ($K\alpha_1 = 1,540,598\ \text{\AA}$) model PW3373/00 – (2000 W-60 kV). Diffraction patterns were acquired from 5° to 75° in 0.02 steps. The identification of all minerals was done with a Xpert HighScore version 2.1b software from PANalytical. The mineralogical characterization has been conducted using Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN), equipped with energy-dispersive spectrometers (EDS).

2.3. Rare earth sulphuric liquor

The rare earth sulphuric liquor was obtained through the procedure shown in Fig. 2, and included the following steps:

- Ore beneficiation to classify the fine particles in the ore (100% smaller than $74\ \mu\text{m}$);
- Drying at $100\ ^\circ\text{C}$;
- Sulphation by reacting the beneficiated ore with a 97.5% w/w sulphuric acid (430 kg/t beneficiated ore);
- Pyrolysis or thermal treatment of the mass obtained after sulphation in a muffle at $700\ ^\circ\text{C}$ for 2 h
- Cooling at $20\ ^\circ\text{C}$. This is step is required, as $\text{REEs}_2(\text{SO}_4)_3$ reduces its solubility as the temperature rises.
- Water leaching at 10% w/w of solids at $20\ ^\circ\text{C}$.
- Filtration.

The REOs extraction from the ore was approximately 65.6%, but the amount of iron leached was only 6.3%. A complete chemical analysis of the rare earth sulphuric liquor produced is presented in Tables 5 and 6. Moreover, the density, pH and redox potential of the rare earth sulphuric liquor measured at $20\ ^\circ\text{C}$ were $1.021\ \text{g}\cdot\text{cm}^{-3}$, 1.7 and 489 mV, respectively. In fact, the presence of the cation Fe^{2+} was not detected in the liquor. The mass ratio between the light rare earth elements (LREEs) to the REEs in the liquor was approximately 96%. More specifically,

Table 1
Typical chemical composition of beneficiated rare earth ore (% w/w).

REOs	REEs	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	SiO_2	Mn	ThO_2	U_3O_8	TiO_2
7.11	5.93	11.1	1.14	33.8	3.96	12.7	10.7	1.25	0.035	0.0089	7.32

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