

# Selective Extraction of Rare Earth Elements from Complex Monazite Ores



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**Abstract** Rare Earth Elements (REE) are fundamental for modern life products and green technologies. Supply constraints and the price peak of 2011 boosted intensive research for alternatives for processing and separation. Complex monazite-type, rare earth ores usually contain high acid consumption impurities, such as iron and aluminum, and radioactive thorium in their composition. These impurities are not removed by conventional concentration processes due to fine, micro-level association between the REE carrying minerals and the gangue minerals. This work presents a selective process route for REE extraction from iron-rich, monazite ores. The process involves sulfation by addition of concentrated sulfuric acid and pyrohydrolysis at temperatures of approximately 700–750 °C. Experimental results show REE extraction higher than 70% and low iron (below 5%) and thorium extraction (below 10%). A method based on thermogravimetric analyses was shown to be adequate to predict the behavior of a given ore sample in the sulfation-selective pyrolysis-leaching process.

**Keywords** Rare earth extraction · Sulfation · Selective pyrolysis  
Leaching · Thermodynamics · Monazite · Thermo-gravimetric analyses

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## Introduction

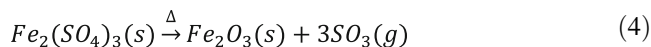
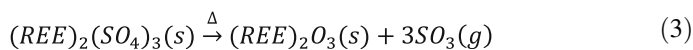
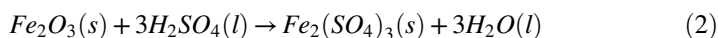
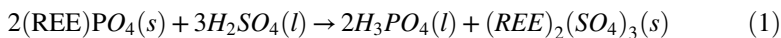
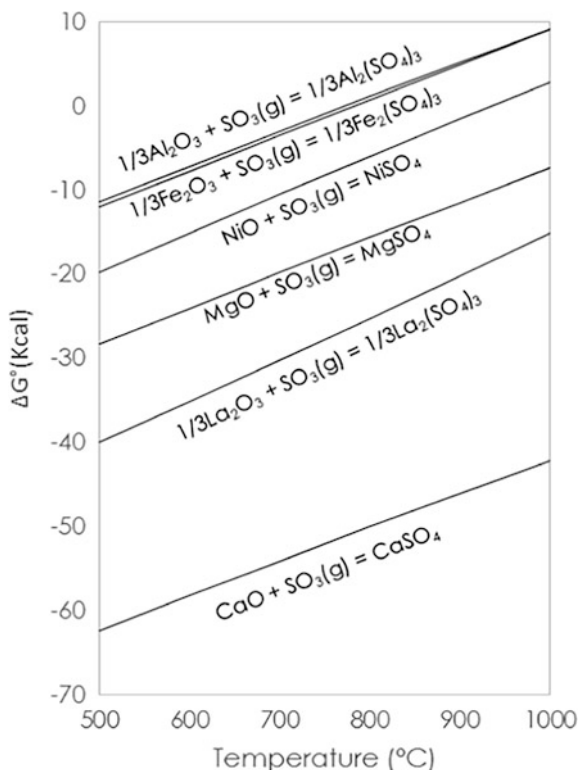
The extraction processing of rare earths usually includes a physical beneficiation stage and a hydrometallurgical stage. The former produces a physical concentrate that is further processed in a hydrometallurgical plant to produce a chemical concentrate. A typical hydrometallurgical route for REE extraction comprises three stages: extraction, purification and separation. In the first stage the REE are leached from the ore by an acid (or alkaline) solution. Some impurities are also dissolved and should be removed before the REE are precipitated (e.g., hydroxide, oxalate, carbonate, chloride) to produce a REE concentrate. This concentrate will finally feed a separation plant (usually a solvent extraction facility—SX) to produce the high-purity individual or mixed products [1]. A pyrometallurgical step may be introduced prior to the hydrometallurgy processing. The presence or not of this stage depends on the ore type and composition.

Ores containing monazite (a rare earth phosphate mineral) usually show a greater number of processing options due to its large variation in composition and weathering degree when compared to ores containing bastnaesite (a rare earth carbonate mineral). Based on the leaching conditions, the process options can be separated in two main groups: sulfuric acid and hydroxide.

The conventional sulfuric acid process is comprised by sulfuric acid addition to the ore (ratio varying largely), followed by heating in a furnace and dissolution in water [2]. The acid/ore weight ratio is very important, since it directly impacts the economic feasibility of the chosen process as well as the amount and type of impurity that will be loaded in the downstream pregnant leach solution—PLS. In most cases, this ratio varies between 1/1 and 1/2. Higher ratios result in higher impurity dissolution. The pyrometallurgical pre-treatment, when included prior to leaching, can be further classified as low-temperature (below 300 °C) and high-temperature (above 300 °C) process. The low-temperature process is older and generates a more complex PLS, difficult to be treated. The high-temperature process minimizes thorium extraction, due to the formation of insoluble  $\text{ThP}_2\text{O}_7$  [3]. Several variations of this process were developed recently, mostly in response to the 2011 price peak. Verbaan et al. [4] evaluated 26 projects and showed that all of them involve a hydrometallurgical extraction and seven projects also require an acid roasting stage. A pyrolysis stage, as investigated in the present work, may also be included prior to the leaching to enhance selectivity in the REE extraction and minimize acid (or base) consumption.

In 1973, Bainbridge [5] reported the possibility of achieving a selective nickel extraction by using  $\text{SO}_3$  gas as sulfation agent and exploiting the difference in the sulfate stability region for Ni and Fe. This selectivity may also be applied to REE sulfates, as illustrated in Fig. 1, taking lanthanum sulfate as a representative of the REE sulfates. The figure shows that REE is well below the iron sulfate decomposition line, thus generating a window that may allow selective extraction of rare earths. Based on this concept, the sulfation and pyrolysis stages in a sulfuric acid based extraction is represented by the following reactions:

**Fig. 1** Gibbs standard free energy for the sulfation reaction for several oxides (HSC V.8) [6]



The aforementioned approach, if successful, would generate a PLS with low iron content and the opportunity to recover sulfur from the decomposition of iron sulfate. This manuscript discusses the conditions that allow the selective extraction of REE from a monazite, iron-rich ore. It is also shown that thermogravimetric analyses allow the identification of samples that are more susceptible to a combination of sulfation/selective pyrolysis/leaching. This analytical approach proved to be a useful tool to be applied in variability testwork carried out during the development of mineral deposits.

## Experimental

### Materials

Reagent grade ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ , Fe 22.0%min), 97.5% w/w sulfuric acid (Anidrol) and natural fines ( $<74 \mu\text{m}$ ) of a monazite ore from a phosphate mine were used in the experiments. The composition of the ore sample is shown in Table 1 (rare earth oxide—REO base).

### Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

The TGA-DTA analyses were performed in a NETZSCH STA 449F3 equipment, under synthetic air atmosphere in an alumina crucible with heating rate of  $10 \text{ K min}^{-1}$  up to  $1000 \text{ }^\circ\text{C}$  ( $1400 \text{ }^\circ\text{C}$  for  $\text{La}_2(\text{SO}_4)_3$ ).

### Rare Earth Extraction

The extraction experiments comprised the following steps: (i) separation of natural fines ( $<74 \mu\text{m}$ ) by scrubbing a 50% w/w suspended solids ore pulp during 15 min and passing this material through a  $74 \mu\text{m}$  sieve [7]; (ii) sulfation by mixing the ore with sulfuric acid 97.5% w/w using an EIRICH intensive mixer; (iii) pyrolysis in a muffle-type furnace for 2 h; (iv) cooling the charge to  $20 \text{ }^\circ\text{C}$  and (v) leaching the solids in water at 10% w/w for 2 h at room temperature, under mechanical mixing (200–300 rpm). The REE extraction was performed following the procedure described by Teixeira and Silva [8] and Berni et al. [9]. Direct leaching experiments were performed following the steps described above, but without the pyrolysis step.

### Chemical Analysis

The concentration of Al, Fe, P, S, La, Pr, Nd and Sm in aqueous solution were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry-ICP-OES (Varian, VISTA PRO model). The concentration of the remaining rare earth

**Table 1** Chemical composition of the ore (%) for the sample used in Fig. 3

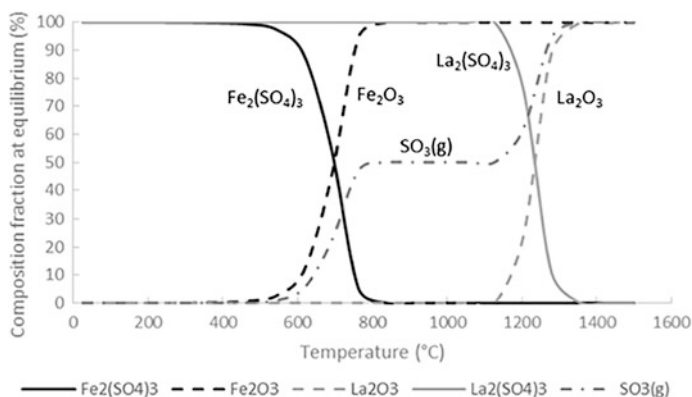
REO	CaO	MgO	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{SiO}_2$	Mn	$\text{ThO}_2$	$\text{U}_3\text{O}_8$	$\text{TiO}_2$
4.86	2.22	1.59	34.39	5.28	4.84	17.43	0.77	0.026	0.00059	0.0016

elements and other impurities were analyzed by Inductively Coupled Plasma Mass Spectrometry (PerkinElmer ICP-MS, model NexION 300D). Before the analysis, the samples were diluted in nitric acid (65% v/v) solution 2% v/v. The ferrous iron concentration in the PLS was measured by titration with  $K_2Cr_2O_7$ . Solid samples were dried at 100 °C for 3 h, cooled to 20 °C and pulverized to 95% below 74  $\mu m$ . Solid samples containing REE, Th and U were treated by fusion with  $Li_2B_4O_7$  or with  $H_2O_2$  and dilution in 10% (v/v) nitric acid (65% v/v). Iron was analysed by fusion with  $Na_2CO_3$  and  $Na_2B_4O_7$ , dilution in 67% (v/v) hydrochloric acid.

## Results and Discussion

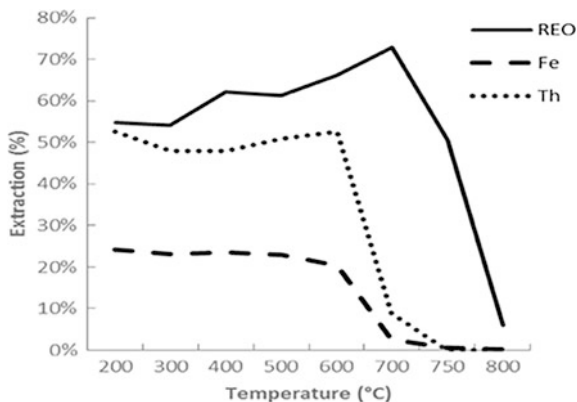
Thermodynamic simulations using the software HSC 8 (HSC Chemistry, 2015) is shown in Fig. 2, where lanthanum sulfate represents the REE family. The initial molar composition of the system was set at 12.5%  $La_2O_3$ , 12.5%  $Fe_2O_3$  and 75%  $H_2SO_4$ . The simulation confirms that the selective pyrolysis of iron over the rare earths can be achieved in a relatively wide temperature window of 700–1200 °C. An ore sample (Table 1) was submitted to steps (i) to (v) described in section “Rare Earth Extraction”. Figure 3 shows the extraction of REO, Fe and Th, given by the amount of the target element in the aqueous phase after leaching relatively to the initial amount in the solid sample. It can be noticed a maximum of REO extraction (73%) with low Fe (below 5%) and Th (below 10%) extraction at 700 °C, making this temperature the best one for selective pyrolysis. Acid consumption was less than 0.250 kg per kg of ore.

It is important to notice that the selectivity window attained from the experiments (between 700 °C and 750 °C) is much narrower than the window expected from the thermodynamic simulation (between 700 °C and 1200 °C). The temperature window may depend on several factors, such as the deformation level of the



**Fig. 2** Thermodynamic simulation of ferric and lanthanum sulfate decomposition

**Fig. 3** Temperature effect in the rare earth, iron and thorium extraction after sulfation (acid/ore mass ratio of 1/4), selective pyrolysis and water leaching



crystalline structure, the weathering degree of the ore and the presence of secondary elements, like phosphor. This element, not considered in the present thermodynamic simulation, may play an important role in the formation of insoluble REE compounds.

The overall test procedure of a RE sample includes sulfation, pyrolysis, leaching and chemical analysis of solid and liquid phases. This procedure is time-consuming and therefore a simpler approach to predict the sample behavior during selective pyrolysis would be advantageous, in particular for carrying out variability tests of a deposit under development. Variability studies on the thermal behavior of the ore samples were performed as an attempt to identify a relationship between the TGA pattern of sulfated samples and the REE extraction. This study was carried out together with the metallurgical variability study for the deposit. The samples used in this study have different weathering degrees and different chemical compositions, although all of them belongs to the same lithotype.

The first step was to determine the mass loss during decomposition at 700 °C and calculate how much could be attributed to the decomposition of ferric sulfate. The total amount of ferric sulfate formed during the sulfation step was calculated by leaching the sulfated samples (without pyrolysis) in water (direct leaching). It was assumed that all ferric sulfate present in the sample was dissolved. This allows the calculation of the theoretical mass loss to be expected from the sample if only the ferric sulfate is decomposed. Those numbers were compared with the results from TGA, considering five ranges, as follows:

- Z1 (up to 200 °C)—Free humidity and/or adsorbed water
- Z2 (200–320 °C)—Dehydration of weathered minerals (e.g., goethite).
- Z3 (320–600 °C)—Other type of mass loss (e.g., phosphoric acid and related compounds).
- Z4 (600–750 °C)—Zone of interest. Ferric sulfate decomposition.
- Z5 (750–900 °C)—Other decompositions (sulfates, carbonates and others)

Figure 4 shows the ratio between the total mass loss by SO<sub>3</sub> gas release in zone 4 (from TGA) and the expected mass loss attained from the iron concentration in the aqueous phase after direct leaching. The SO<sub>3</sub> mass loss attributable to the decomposition of ferric sulfate in Z4 is given by Eq. (5).

$$\text{Mass loss (ferric sulfate decomp., \%)} = \frac{\text{SO}_3 \text{ mass loss by direct leaching of the sample}}{\text{(Z4) mass loss attained from TGA}} \times 100 \tag{5}$$

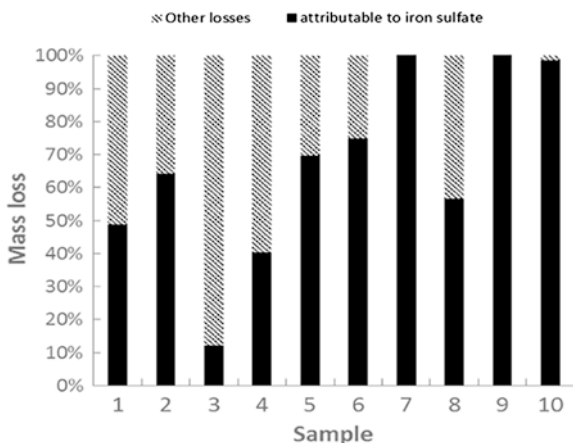
Figure 4 shows a significant variation in the mass loss attributable to the decomposition of ferric sulfate by different ore samples. The matching of these results with the rare earth extraction is shown in Fig. 5. It is possible to notice a correlation between the mass loss attributable to ferric sulfate decomposition and the rare earth extraction. Losses not attributable to ferric sulfate decomposition may indicate a premature (not predicted in Fig. 2) decomposition of RE sulfates. This decomposition may imply in the formation of REE insoluble compounds, thus decreasing the REE extraction and liberating SO<sub>3</sub>.

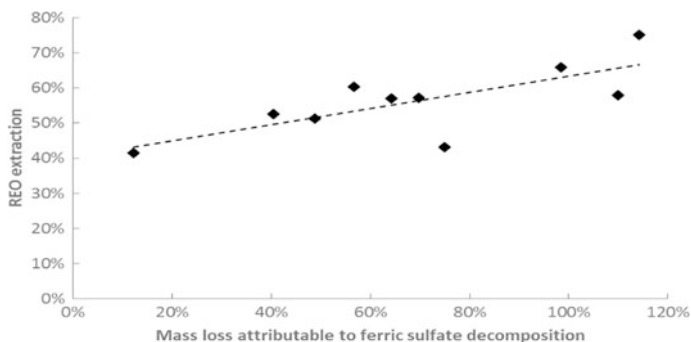
Based on the results from Figs. 4 and 5 it is possible to divide the ore samples in 3 main groups:

- GI—Samples that show mass loss attributable to ferric sulfate decomposition between 80–100%.
- GII—Samples that show mass loss attributable to ferric sulfate decomposition between 40–80%.
- GIII—Samples that show mass loss attributable to ferric sulfate decomposition below 40%.

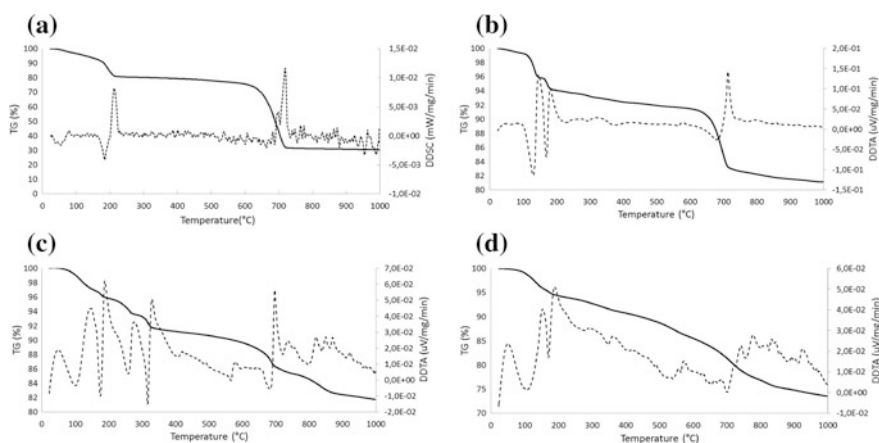
Figure 6 shows the TGA of samples belonging to the three groups defined above and reagent grade ferric sulfate. The final objective is to predict the rare earth extraction of a sulfated sample from the TGA features.

**Fig. 4** Mass loss attributable to the decomposition of ferric sulfate at temperatures between 600 and 700°C





**Fig. 5** Relationship between the mass loss attributable to ferric sulfate decomposition and the rare earth extraction after sulfation, pyrolysis and water leaching



**Fig. 6** TGA results for reagent grade ferric sulfate and sulfated rare earth ore samples divided in three distinct groups: **a** analytical grade ferric sulfate, **b** Group I sample, **c** Group II sample, **d** Group III sample. Solid lines represent TGA results and dashed lines represent DDTA/DDSC results

It can be noticed (Fig. 6) that the group I samples (b) show a mass loss zone well-defined, with a decomposition peak ranging between 700 °C and 750 °C, similarly to ferric sulfate (a). Samples from group II (c) show other thermal events around 750 °C but the characteristic peak for ferric sulfate decomposition is still clear. Samples from group III (d) do not display the characteristic peak for ferric sulfate decomposition. There are several thermal events taking place below and above 700 °C, which cannot be discerned and, among these events, rare earth sulfates may have been decomposed into insoluble compounds. This is reflected in the low rare earth extraction.



In addition to the hypotheses of a premature sulfate decomposition, TGA and extraction results also suggest poor performance during the sulfation, pyrolysis and leaching stages. The increased complexity in DDTA pattern indicates that the sample itself is relatively more complex. Side reactions, like generation of phosphoric acid, may allow the formation of unwanted compounds (e.g. monocalcium phosphate) that can increase the viscosity during the sulfation stage, leading to incomplete mixture. Phosphoric acid may also decompose and generate gaseous  $P_2O_5$ , promoting the formation of insoluble, rare earth phosphates. The partial pressure of  $SO_3/SO_2$  gas is also important since lower concentrations would facilitate sulfate decomposition. Higher degree of weathering may create a more refractory monazite to sulfation, decreasing its conversion in sulfate. All these factors are under investigation.

## Conclusion

The selective pyrolysis of iron-rich, monazite ores prior to leaching allows over 70% rare earth extraction with low iron (below 5%) and thorium (below 10%) dissolution. A simple approach to predict the sample behavior during selective pyrolysis was developed. The results demonstrate that samples with complex TGA/DTA patterns and mass loss superior to that ascribed to ferric sulfate decomposition at 600–750 °C are expected not to respond well to the sulfation-selective pyrolysis-leaching process.

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