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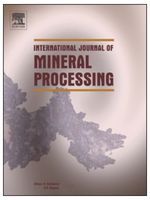

Rare earths concentration from phosphogypsum waste by two-step leaching method☆

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ABSTRACT

In the present work, Tunisian phosphogypsum was considered as a source of rare earths. After examining the particle size distribution of the raw sample and its rare earths repartition by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), a double sulfuric leaching of the sample led to rare earths dissolution, then, the evaporation of the acid liquor allowed to recover a rare earths-rich solid. During the process, all the obtained solids were identified by infrared spectroscopy and X-ray powder diffraction, and rare earths content was also measured after each step by ICP-MS. Analytical results showed that the first acid leaching allowed essentially to impurities dissolution (such as fluorides and phosphates) and so rare earths enrichment in the residue (about 52%), whereas the second leaching led to the dissolution of such elements in the sulfuric acid liquor (about 50%). The crystallized solid obtained after the evaporation stage corresponds to a mixture of anhydrite-monetit phases with a total rare earths enrichment of about 86%. The method showed also its efficiency for purifying the phosphogypsum which can be used safely in industrial applications. Photoluminescence measurements carried on the phosphogypsum sample and the crystallized solid allowed the observation of some rare earths emissions (cerium, europium and samarium) and confirmed as well their enrichment in the final solid at the end of the process.

1. Introduction

Industrial wastes stir the interest of multiple researches. A special category of industrial wastes is the hazardous waste and especially radioactive waste. The great quantities of hazardous waste arise from chemical industry (organic and inorganic); oil refining and thermal processes (Zirnea et al., 2013). Among the main type of hazardous waste present in large amount in Tunisia we cite phosphogypsum (PG).

Phosphogypsum is the main by-product of the production of phosphoric acid and it is formed by the acidic digestion of phosphate rock (Koopman and Witkamp, 2000). It contains various impurities such as residual acid (P_2O_5), fluorine compounds, trace elements including radioactive elements and rare earth elements (Karagoz and Oguz, 2005; Taybi et al., 2011). Because rare earths are regarded as one of the important development indicators of modern technologies, we are interested in our research works especially on these elements. The rare earths are concentrated in phosphogypsum during the production of phosphoric acid. About 70 to 85% of them originally present in the phosphate rock end up in the phosphogypsum. The rest remains dissolved in the leaching solution, which also contains the phosphoric acid (Binnemans et al., 2013). Given the enormous amounts of phosphate rock processed every year and the fact that rare earths are just a by-product of the phosphoric acid production, phosphogypsum presents a valuable source of rare earths (Binnemans et al., 2013). Phosphogypsum, containing low rare earths concentrations, could provide thus significant amounts of these elements when its large volumes are taken into account.

The aim of the present work consists on a detailed investigation of rare earths recovery from phosphogypsum waste by the leaching method. In fact, previous studies proved that leaching phosphogypsum with mineral acids creates favorable conditions for rare earths migration from the solid to solution (Binnemans et al., 2013; Grabas et al., 2014; Habashi, 1985; Jarosiniski et al., 1993; Kijkowska et al., 1989). It is true that nitric acid is the most effective medium for leaching than sulfuric acid leaching for the recovery of rare earths, but the latter (H_2SO_4 leaching) is preferred in the industry because of economical reasons (nitric acid would necessitate an additional acid circulation whereas sulfuric acid is already available in the phosphoric acid plant). Thus, the authors decided to investigate the effect of a double sulfuric lixiviation on rare earths dissolution from a recent Tunisian phosphogypsum sample and recover a rare earths-rich solid after evaporation of the acid liquor. This latter, after rare earths separation, will be sufficiently concentrated to be recycled to the phosphoric acid process. Therefore, there is no liquid effluent problem. To make a detailed study, several

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analytical techniques were used for solids identification and rare earths content's monitoring during the process (infrared spectroscopy, X-ray diffraction, ICP-MS and photoluminescence).

2. Materials and methods

The PG studied in this work is a recent sample having as origin Sfax (Tunisia) stockpiles.

After drying and grinding the phosphogypsum, the bulk sample was sieved with a series of sieves (from 1 mm to 53 μm) vibrated for 15 min. This operation allowed us to determine the particle size distribution of the studied sample.

ICP-MS analyses were performed at the Department of Biology, Ecology and Earth Sciences, University of Calabria, Italy. The samples were powdered in an agate mortar and then dissolved by microwave digestion using a Mars5 microwave apparatus (CEM technologies). About 100 mg (±0.01 mg) of each powder was placed in a microwave vessel with a mixture of Merck “suprapur” quality hydrofluoric acid (6 ml HF), nitric acid (5 ml HNO_3) and perchloric acid (3 ml $HClO_4$), covered and sealed with a cap and subjected to an oven method that consisted of a 15 min ramp to 200 °C and a pressure of 600 PSI, then held at temperature for 15 min and then a 15 min cool down. Unclear solutions containing some residues were obtained. The content of each vessel was allowed to heat up to 200 °C. Before the complete evaporation of acid we added 3 ml of pure $HClO_4$ and we maintain heating up to 200 °C. Before the complete evaporation, 5 ml of HNO_3 (5%) was then added. Clear and colorless solutions were finally obtained. These latter, were left to cool down gently and made up to a standard volume in a 100 ml volumetric flask with Millipore water in order to prepare the mother solutions. External calibration curves were prepared using Perkin Elmer “multi-element Calibration Standard 2 solution” to analyze rare earth elements. Standard reference materials Micaschist (SDC1) were prepared in the same way and were used as unknown samples during the analytical sequence. Concentrations of the elements were compared with certified values to evaluate accuracy and precision of analytical data (Mastandrea et al., 2010).

The X-ray powder diffraction (XRD) patterns of all samples were recorded on an X'PERT Pro PANAnalytical diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm).

Infrared spectra were performed on a FT-IR System Perkin Elmer spectrometer using KBr pellets in the region of 4000–400 cm^{-1}.

Photoluminescence measurements were recorded on samples pellets with Perkin Elmer spectrometer LS55. All the pellets were prepared in the same conditions (mass, pressure) in order to allow a reliable comparison of emission intensities.

3. Results and discussions

3.1. An overview of the phosphogypsum sample

The phosphogypsum used in this work has been recently produced. Its analysis by different techniques was detailed in a previous work (Hammas et al., 2013). The results showed that it consists mainly of the dihydrated calcium sulfate phase ($CaSO_4 \cdot 2H_2O$) with coexistence of other impurity phases which correspond mainly to ardealite $Ca_2(HPO_4)(SO_4)(H_2O)_4$ and malladrite Na_2SiF_6. Low contents of Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O were also obtained (Hammas et al., 2013). ICP-MS analysis, summarized in Table 1, showed total rare earths content of about 225 ppm in the studied Tunisian phosphogypsum.

3.2. Particle size distribution and fraction analysis by ICP-MS

The study of the particle size distribution of the phosphogypsum sample showed that about 83% of its particles have a diameter greater than 600 μm (Fig. 1).

Table 1
Thorium and rare earths content in the raw phosphogypsum sample (expressed in ppm).

Element	PG sample
Y	44.48
La	35.86
Ce	49.99
Pr	8.90
Nd	52.63
Sm	7.14
Eu	1.68
Gd	7.20
Tb	1.10
Dy	6.62
Ho	1.32
Er	3.89
Tm	0.47
Yb	3.31
Lu	0.34
Th	0.95
Σ REE	*224.93*

Each fraction was analyzed thereafter by ICP-MS spectrometry in order to determine the fraction in which rare earth elements are concentrated. The results, depicted on Fig. 2, showed a uniform distribution of rare earths regardless the size of PG particles. The most plausible explanation is that the sulfuric attack of the Tunisian phosphate ore led to the genesis of very fine phosphogypsum particles having similar compositions. Indeed, the fractions obtained after granulometric separation are the result of such $CaSO_4 \cdot 2H_2O$ fine grains agglomerations. Thus, we have drawn the conclusion to use the entire sample without the need to carry a granulometric separation during phosphogypsum processing.

3.3. Process of rare earths concentration from phosphogypsum

500 g of the phosphogypsum sample was firstly washed with distilled water and then underwent a double leaching with a sulfuric acid solution (10%) at 60 °C, for 1–2 h of continuous stirring, with a weight ratio (liquid/solid) about 1.3. Indeed, after a first lixiviation with the acid solution, the residue (R1), obtained after filtration, was remixed with the same leach liquor. Then, after a solid–liquid separation, evaporation of the final filtrate at 100 °C resulted in a solid crystallization (the process is detailed in Fig. 3). This latter was filtered off,

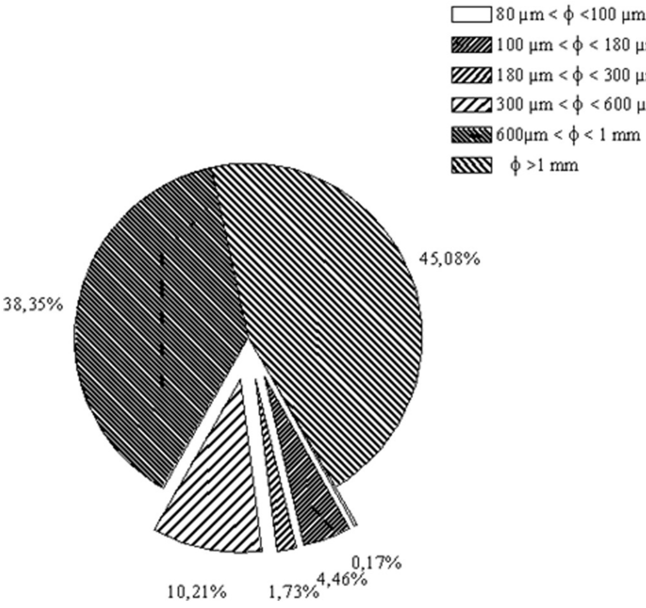

Fig. 1. Particle size distribution of a fresh Tunisian phosphogypsum sample.