



Beneficiation of pyrite from coal mining



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ABSTRACT

An abundant mineral in nature and despite its potential as raw material for different segments of industry, when it comes from coal mining, pyrite (FeS_2) is treated as waste, and its disposal culminates in environmental problems for the coalfields. Increasing the purity of pyritic tailings, increasing its iron disulfide content, strengthen the possibility of turning it into a value-added by-product. In this work, an analysis of impurities in the pyrite of southern Santa Catarina (Brazil), including organic matter, sulfates, iron oxides, calcite, clay and sandstone, suggests a processing route for pyrite based on separation by density in bromoform and subsequent leaching in water and acetone solution. Statistical methods were applied to set the leaching parameters, and the process efficiency was evaluated and confirmed by fluorescent X-ray (XRF) elemental analysis (CHNS/O), X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR). The proposed method extracted ferrous sulfate, calcite and quartz present in clayey and sandy fractions.

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1. Introduction

Pyrite, a mineral with a chemical formula of FeS_2 , is an iron disulfide, which is usually associated with other sulfides and oxides. It is abundant in the earth's surface, being found in the composition of sedimentary and metamorphic rocks, in coal beds and as a replacement mineral in fossils (Klein and Hurlbut, 1993).

There are occurrences of high crystallinity pyrite in the United States, Peru, China and Spain (Klein and Dutrow, 2012), with Navajún mine, located on Spanish soil, the only known place in the world where this mineral forms perfect cubic crystals (Boronat, 2008).

In Brazil, pyrite is present in greater amounts in the 60% of the solid waste generated for every ton of coal drawn (Nascimento et al., 2002). Brazilian coal reserves account for 1% of world reserves, with 7 billion tons concentrated in southern Brazil: Rio Grande do Sul (89.25%), Santa Catarina (10.41%) and Paraná (0.32%) (ANEEL, 2008).

Due to its high content of impurities, to meet the parameters required by the thermoelectric industry, Brazilian coal is subjected to concentration methods (Amaral Filho et al., 2013), including density separation and washing. The disposal of solid waste generated during this process is responsible for the main environmental impact associated with mining and coal processing (Evangelou, 1995).

Waste, rich in sulfide minerals, favors the occurrence of acid drainage, which contaminates water with bio-accumulative metals, making the water unsuitable for domestic and agricultural use. Both air and water promote the oxidation of wastes containing iron sulfides, leading to the drainage acidification process (Evangelou, 1995).

To balance coal extraction with environmentally sustainable development, attention must be paid not only to the coal but also to pyrite, abolishing its classification as waste, and treating the mineral as a raw material for various chemical processes (Peterson, 2008).

Pyrite may be used as a precursor of products, such as sulfur, sulfuric acid, hematite, sulfur dioxide, fertilizers and ferrous sulfate (Peterson, 2008). Pyrite is also one of the metal sulfides whose electrochemical properties are evaluated for use as cathodes in lithium batteries (Kim et al., 2007).

There is research data from the 1980s and 1990s viewing pyrite

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as semiconductor materials for use in photovoltaic panels. However, the poor performance of the devices led to the abandonment of the studies, which were taken up recently given the low cost of producing FeS₂ (Hadlington, 2012).

In this context, this paper suggests methods of concentration of pyritic waste to raise its iron disulfide content and to contribute to the sustainability of the coal extraction process.

2. Experimental procedure

2.1. Materials

The pyrite from the coal waste was collected in the city of Treviso/SC, Brazil. After comminution processes, the average particle size determined by a Cilas 1064 laser granulometer, was reduced to 11.75 μm.

2.2. Methods

To evaluate the purity of “in natura” pyrite, the pyrite was characterized by:

X-ray fluorescence spectrometry (XRF): wavelength dispersion X-ray spectrometer - WDXRF Axios Max Panalytical;

Elemental analysis in a PerkinElmer 2400 Series II CHNS/O elemental analyzer, for the determination of carbon, hydrogen, nitrogen and sulfur;

Infrared spectroscopy (FTIR): Samples prepared by pressing with a dilution ratio (approximate) of 95% potassium bromide (KBr) and 5% of material to be analyzed. The equipment used was a spectrophotometer IRPrestige-21, from Shimadzu. The analysis was performed by transmittance with a speed of 0.2 cm/s and a resolution of 4 cm⁻¹, ranging from 400 to 4000 cm⁻¹;

X-ray diffraction (XRD): testing X-ray diffractometer (Shimadzu, Model XRD-6000), theta-theta goniometer, K-α radiation with copper tube with a wavelength of (λ) of 1.5406 Å. The analysis was performed at 2°/min. The measuring range was 10–80°, with a 30 kV voltage and 30 mA current.

Processing routes were suggested based on the results of the characterizations.

2.2.1. Leaching in water

To reduce the soluble content, such as ferrous sulfates, pyrite was immersed in distilled water - 0.02 kg/L - and the system was subjected to magnetic stirring (Fisatom, model 752A). Further, pyrite was separated by vacuum filtration (Primatec vacuum pump, model 131). The drying of the material was performed in a vacuum oven (Marconi model MA 030/12) at 40 °C.

The evaluation of some parameters, such as the water temperature, time of agitation and reproduction of the process (number of times that pyrite is leached), were defined according to 2^k statistical experimental factorial planning, with three factors, as shown in Table 1.

2.2.2. Leaching in organic solvent solution

To reduce the organic content, a similar procedure to that described for leaching in water was performed but substituting the water with an organic solvent solution. Statistical 2^k experimental factorial planning was used with two factors, as shown in Table 2.

The experiments shown in Table 2 took place at room temperature with three different solvents: i. acetone (Lafan, 99.5% P.A.) diluted in the proportion 1:1; ii. ethyl alcohol (Lafan, 95% P.A.) diluted in the proportion 1:1; iii. saturated solution of dichloromethane (0.23 M) (Vetec, 99.5% P.A.). For leaching, pyrite was immersed in the appropriate solution at a concentration of 0.02 kg/L.

Table 1

Statistical 2^k experimental factorial planning for the analysis of leaching in water.

Experiment	Levels			Factors		
				Temperature (°C)	Time (min)	Reproduction
1	-1	-1	-1	50	20	1
2	+1	-1	-1	90	20	1
3	-1	+1	-1	50	60	1
4	+1	+1	-1	90	60	1
5	-1	-1	+1	50	20	3
6	+1	-1	+1	90	20	3
7	-1	+1	+1	50	60	3
8	+1	+1	+1	90	60	3
9	0	0	0	70	40	2
10	0	0	0	70	40	2
11	0	0	0	70	40	2

Table 2

Statistical 2^k experimental factorial planning for the analysis of leaching in organic solvent solution.

Experiment	Levels		Factors	
			Time (min)	Reproduction
1	-1	-1	20	1
2	+1	-1	60	1
3	-1	+1	20	3
4	+1	+1	60	3
5	0	0	40	2
6	0	0	40	2
7	0	0	40	2

The response of the experimental design was the sulfur content of the samples, measured on an elemental analyzer (LECO SC632).

The experiments of Tables 1 and 2 used “in natura” pyrite. After statistical analysis of the data and setting of the leaching parameters, pyrite was subjected to density separation by immersion in very pure bromoform (AP 97% Vetec mark) at a concentration of 0.25 kg/L and, sequentially, to water leaching and organic solvent leaching. After separation by density, the settled pyrite was washed with ethanol.

The recovered pyrite was characterized using the same techniques employed for the “in natura” material.

3. Results and discussion

Through stoichiometric calculations (Eq. (1)), it was found that pure pyrite has approximately 53.4% sulfur (Concer, 2013).

$$\%S_2 = \frac{m_{S_2}}{m_{FeS_2}} \times 100 \quad (1)$$

Where,

%S₂: sulfur content of pure pyrite;

m_{S₂}: sulfur mass in a mole of iron disulfide (~64.1 g);

m_{FeS₂}: molar mass of pyrite (~120.0 g).

The sulfur content in pyritic waste is 36.33%. Applying Eq. (2), the approximate percentage of pyrite present in the composition is 68.0%.

$$\%FeS_2 = \frac{\%S_2}{\%S_{2Teor}} \times 100 \quad (2)$$

Where,

%FeS₂: pyrite content of the sample and

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