Hydrometallurgical/UV Process to Produce Ferrous Sulfate from the Pyrite Present in Coal Tailings

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Abstract Coal mining generates large volumes of tailings that may be responsible for serious environmental damage. The oxidation of pyrite (FeS_2), in the presence of air and water, promoted the formation of acid mine drainage (AMD), an aqueous and highly acid solution, rich in sulfate and iron (in the form Fe^{3+} and Fe^{2+}), along with other associated metals. The aim of this study was to develop a hydrometallurgical/UV route for the production of ferrous sulfate. This experimental study was carried out with a pyrite concentrate obtained from the gravimetric processing of a coal tailing. At the laboratory, the leaching of the material was performed in packed bed columns in an oxidizing environment, appropriate to provide pyrite oxidation in an aqueous medium. The recirculation of the liquor allowed a Fe^{3+} iron rich extract to be obtained. The conversion of Fe^{3+} to Fe^{2+} was performed using ultraviolet irradiation (UV). The heat provided by the UV lamps also promoted water evaporation and ferrous sulfate crystallization. The ferrous sulfate crystals were purified and analyzed by X-ray diffraction (XRD). The results demonstrated that it was possible to produce ferrous sulfate heptahydrate crystals (melanterite), with the pyrite present in coal tailings serving as the raw material.

Key Words pyrite, acid mine drainage (AMD), ferrous sulfate

Introduction

Coal mining generates large volumes of tailings that may be responsible for serious environmental damages. The oxidation of pyrite (FeS_2), in the presence of air and water, promotes the formation of acid mine drainage (AMD), an aqueous and highly acid solution rich in sulfate and iron (in the form Fe^{3+} and Fe^{2+}), along with other associated metals (Kontopoulos, 1998).

One potential method to extend the use of natural resources is to recover potentially valuable products from the AMD. These effluents have been previously processed for the production of ferric oxide nanoparticles (Wei and Viadero, 2007), inorganic pigments (Marcello et al., 2008); and coagulants (Rao et al., 1992; Menezes et al 2010).

The aim of this study was to develop a hydrometallurgical/UV route for the production of ferrous sulfate heptahydrate ($FeSO_4.7H_2O$ melanterite) from the pyrite present in the coal tailings. The study involved the steps of pyrite dissolution, the application of a photochemical technique to convert Fe^{3+} to Fe^{2+}, and, finally, the production of melanterite crystals.

Reactions

Pyrite Oxidation and Iron Dissolution

Oxidation of pyrite takes place through a complex series of reactions involving direct, indirect and microbial-assisted mechanisms. Some oxidation reactions result in acid generation, while others result in the dissolution and mobilization of iron and other heavy metals present in the environment (Kontopoulos, 1998). The direct mechanism, which occurs in the initial stages of pyrite oxidation, can be described using the following equation:

$$2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4H^+ + 4SO_4^{2-} \quad (1)$$

This reaction produces proton acidity; and, if the oxidation potential is maintained, oxidation of Fe^{2+} to Fe^{3+} by oxygen will take place; consuming part of the proton acidity:

$$4Fe^{2+} + O_2(aq) + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

Equation (2) proceeds abiotically at high pH and slows down as the pH decreases. However, at low pH, the rate can be accelerated by several orders of magnitude through the action of the

Acidithiobacillus bacteria. Yet, the Fe^{3+} generated will oxidize FeS_2 by the indirect reaction:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3}$$

The resulting Fe^{2+} will be oxidized to Fe^{3+} by reaction (2) and will again become available to oxide more pyrite (autocatalysis).

Iron Reduction with UV

Photoreduction, by means of ultraviolet radiation (UV), converts Fe^{3+} to Fe^{2+}. This reaction can be written as follows:

$$Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + \cdot OH + H^+ \tag{4}$$

The production of ferrous sulfate was studied considering the hypothesis that a Fe^{3+} rich solution, when flowing through a coal tailing rich in pyrite, under UV radiation, would be converted to Fe^{2+} by equations (3) and (4). Fe^{3+} photoreduction also created a short-lived $OH\cdot$ radical, which presented a bactericidal action in the environment, inhibiting equation (2) and the autocatalytic cycle.

Methods

The pyrite concentrate, produced by gravimetric processing of coal tailings, was obtained from Cambuí Mine, Paraná, Brazil. The characterization of the material indicated that it contained about 65% pyrite. The sample was crushed, screened, and washed, and the fraction comprising of -6 mm/ + 2 mm was employed in the experiments.

The production of the iron rich solution was carried out in three cylindrical columns (30 cm height ×7 cm diameter) containing 1 kg of the pyrite concentrate where 1 L of water was added in each column and pumped through the particles in close circuit, for a period of 11 weeks (Figure 1). At the end of each week, the evaporated fraction of water was brought up to 1 L and the solution was analyzed in terms of pH, Eh, and concentrations of Fe^{3+} and Fe^{2+}, as per the “Standard Methods for the Examination of Water and Wastewater” (APHA, 2005).

After this period of time, the UV reactors were coupled to two of the columns, to convert the Fe^{3+} to Fe^{2+}. Column 1 was the control. The reactors were constructed in plastic, and coated internally with aluminum paper. One reactor was equipped with 3 UV lamps (Column 2) and the other with 10 UV lamps (Column 3). The specification of the lamps was: wavelength 253.7 nm, power 15W, voltage 51V, and length 45 cm. The radiation intensity was measured as 77.7 mW/cm^2 in the reactor with three lamps and as 259.0 mW/cm^2 in the reactor with 10 lamps.

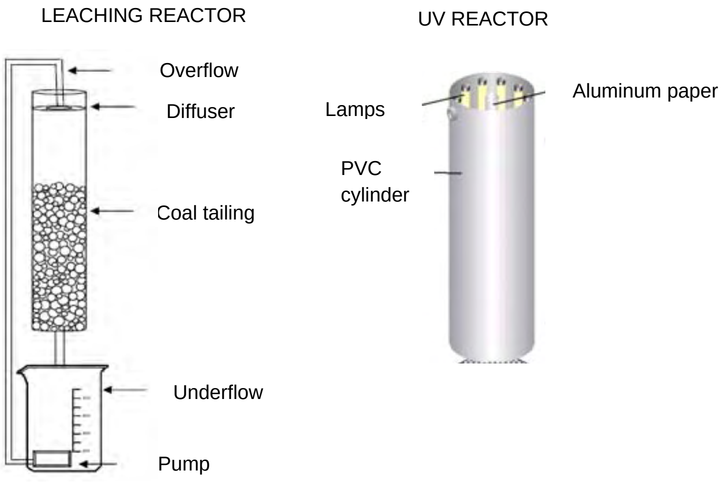

Figure 1 *Leaching column for dissolution of the pyrite and UV reactor for conversion of Fe^{3+} to Fe^{2+}*

Table 1 *Values of pH, Eh, and Iron (total, $Fe^{2+}$and Fe^{3+}) at end of the leaching step and at the end of the UV radiation step*

	Parameter	Column 1 Control	Column 2 UV radiation	Column 3 UV radiation
Leaching of pyrite for Fe dissolution (at the end of 11 weeks)	Fe total (g/L)	48.8	54.0	47.5
	Fe^{2+} (g/L)	23.7	23.0	23.2
	Fe^{3+} (g/L)	25.1	31.0	24.3
	pH	0.2	0.1	0.1
	Eh (mV)	586	590	589
Iron photoreduction (at the end of 96 hours)	Fe total (g/L)	45.8	52.5	50.2
	Fe^{2+} (g/L)	26.8	35.2	40.0
	Fe^{3+} (g/L)	19.0	17.3	10.2
	pH	0.4	0.6	0.6
	Eh (mV)	587	621	590

In each column, the amount of Fe^{3+} and Fe^{2+} was monitored as a function of time. When necessary, water was added to keep the volume constant at 1 L. The process was kept for 96 hours (four days). After that, no more water was added in the system, allowing evaporation of the running water and the crystallization of ferrous sulfate by the heat provided by the UV radiation. The ferrous sulfate crystals were purified with ethylic alcohol and their purity was analyzed by x-ray diffraction.

Results

Table 1 shows the results of the iron concentration obtained (total, Fe^{3+} and Fe^{2+}) after 11 weeks of leaching. The same procedure was applied to the three columns, which gave similar results of iron extraction. The iron concentration ranged from 47.5 to 54.0, with about 49% Fe^{2+} and 51% Fe^{3+}.

Following this, the study was continued for the conversion of Fe^{3+} to Fe^{2+} in columns 2 and 3, by submitting the system to UV radiation. It could be observed that, there was no significant increase in iron concentration in any of the columns. However, the proportion of Fe^{2+}:Fe^{3+}, after 96 hours, changed a great deal, as follows: 58%:42% for column 1, 67%:33% for column 2, and 80%:20% for column 3. The results clearly demonstrated the effectiveness of UV radiation for the conversion of Fe^{3+} to Fe^{2+}, by means of reaction (4) and the bactericidal effect.

In column 1, the low temperature of the system (close to 25°C) did not allow water evaporation or the start of the crystallization process. However, at the bottom of the beakers of columns 2 and 3, the crystallization of ferrous sulfate was abundant. The amount of ferrous sulfate heptahydrate crystals (melanterite) obtained was, 134.0 g/kg of pyrite concentrate in the column 2 and 127.1 g/kg of pyrite concentrate the column 3. In terms of recovery, the data obtained are resumed in Table 2.

The recovery of iron in the form of melanterite in relation to the initial iron concentration in the form of pyrite in the columns (approximately 0.30 kg per kg of coal tailings) ranged from 8.5 to 9.0%. However, the pyrite could be submitted to six or seven additional leaching steps as conducted in this study, to allow for an increase in the global recovery of the process.

The x-ray analysis of the purified hydrated iron sulfate obtained in both columns, showed that it was composed almost exclusively of melanterite crystals ($FeSO_4.7H_2O$, ferrous sulfate hep-

Table 2 *Recovery of melanterite in the process*

Column	Recovery (%)		
	Fe melant. / Fe^{2+} Ext.	Fe melant./ Fe Total Ext.	Fe melant. / Fe Pyrite
Column 1 Control	0.0	0.0	0.0
Column 2 UV-3 Lamps	75.0	50.0	9.0
Column 3 UV-10 Lamps	63.7	53.7	8.5

Figure2 *Melanterite obtained from the hydrometallurgical/UV processing of the coal tailing*

tahydrate), which had been largely applied for anemia control, both in humans and animals, as well as, a reagent for water and wastewater treatment (e.g., Fenton´s Reaction; Metcalf & Eddy, 2003).

Conclusion

The results demonstrated that it was possible to produce ferrous sulfate heptahydrate crystals having pyrite present in coal tailings as the raw material. The hydrometallurgical and UV radiation techniques applied in this study allowed production of a commercial grade product from coal mining waste material, thus minimizing the environmental impact.

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