

Biohydrometallurgical Production of Heptahydrate Iron Sulphate Crystals from the Pyrite Present in Coal Tailings

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Abstract

The Brazilian coal mines generate 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 the acid mine drainage (AMD), an aqueous and highly acid solution rich in sulphate and iron (in the forms Fe^{3+} and Fe^{2+}), along with other associated metals. In this study, the objective was to develop a biohydrometallurgical/UV radiation route to produce ferrous sulphate from the pyrite present in coal tailings. The experimental work was carried out with a pyrite concentrate obtained from gravimetric processing of a coal tailing. I was performed, at laboratory scale, the oxidation of pyrite in aqueous medium in packed bed leaching columns at oxidizing environment and the presence of acidophilic bacteria (*Acidithiobacillus ferrooxidans*). The recirculation of the liquor allowed obtaining an iron rich extract. The conversion of Fe^{3+} to Fe^{2+} was performed using ultraviolet irradiation (UV). Finally, the solution was evaporated allowing the formation of iron sulphate crystals. The results demonstrated that it is possible to produce high purity heptahydrate iron sulphate crystals having coal tailings as a raw material.

Keywords: pyrite, acid mine drainage (AMD), ferrous sulphate.

1. Introduction

Brazilian run-of-mine (ROM) coal contains high levels of impurities (rock minerals and pyrite). Thus, it requires concentration methods to reach the conventional Brazilians power station's standards. Approximately, 50-60% of the ROM material is discharged as waste in tailings deposits. It is estimated that more than 300 millions tonnes of coal tailings exists in the south of Brazil, generating AMD with the well known environmental impacts (Amaral Filho et al, 2010).

The oxidation of the 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 sulphate and iron (in the form Fe^{3+} and Fe^{2+}), along with other associated metals (Kontopoulos, 1998; Skousen et al, 1998). In Brazil, part of the generated AMD has been treated in effluent treatment plants using sodium hydroxide or lime for neutralisation. The metal precipitates are removed in settling ponds, conventional settling tanks, lamellar tanks, and dissolved air flotation units (Silveira et al., 2009). Although active treatment can provide effective remediation, it has the disadvantages of high operational costs and problems related to the disposal of the bulky sludge that is produced.

Another possible way to minimize the effects of coal mining tailings is to concentrate the pyrite and convert this mineral to valuable products. The pyrite can be processed by

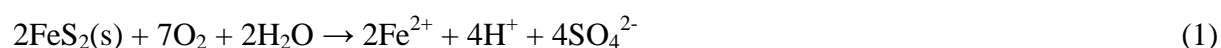
hydrometallurgical and/or pyrometallurgical techniques to sulphuric acid, iron salts (like ferric sulphate and ferrous sulphate) and iron oxides (goethite, hematite and magnetite) (Peterson, 2008; Menezes, 2009; Madeira, 2010). Concerning the production of ferrous sulphate from coal tailings in Brazil, a pyrometallurgical route was developed by Peterson (2008). The author applied a thermal process at 300°C, obtaining a maximum conversion of pyrite to ferrous sulphate of 5,7%.

The aim of this study was to develop a biohydrometallurgical/UV route for the production of ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - melanterite) from the pyrite present in the coal tailings. The study involved the used of biohydrometallurgical techniques to oxidize and dissolve the pyrite, the application of a photochemical technique to convert Fe^{3+} to Fe^{2+} , and, finally, an evaporation/crystallization step to produce melanterite crystals.

2. Reactions

(a) Pyrite Oxidation and Iron Dissolution

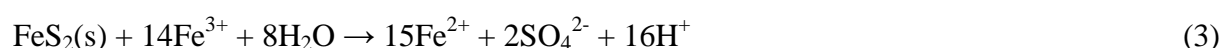
Oxidation of pyrite takes place through a complex series of reactions involving direct, indirect and microbial-assisted mechanisms. Some oxidation reactions result in acid generation, while others result in the dissolution and mobilization of iron and other heavy metals present in the environment (Kontopoulos,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



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:



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:



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

(b) Iron Reduction with UV

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



The production of ferrous sulphate 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 $\text{OH}\cdot$ radical, which presented a bactericidal action in the environment, inhibiting equation (2) and the autocatalytic cycle.

3. Materials and 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 x 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). Bacteria inoculums was added in the system to accelerate the leaching process. It was consisted of a 10 mL of an acid mine drainage (AMD) obtained from the coal site containing 6.8×10^5 cells/mL of *A. ferrooxidans*. 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+} following the procedures described in the “Standard Methods for the Examination of Water and Wastewater” (Eaton et al, 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 aluminium 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/cm² in the reactor with three lamps and as 259.0 mW/cm² in the reactor with 10 lamps.

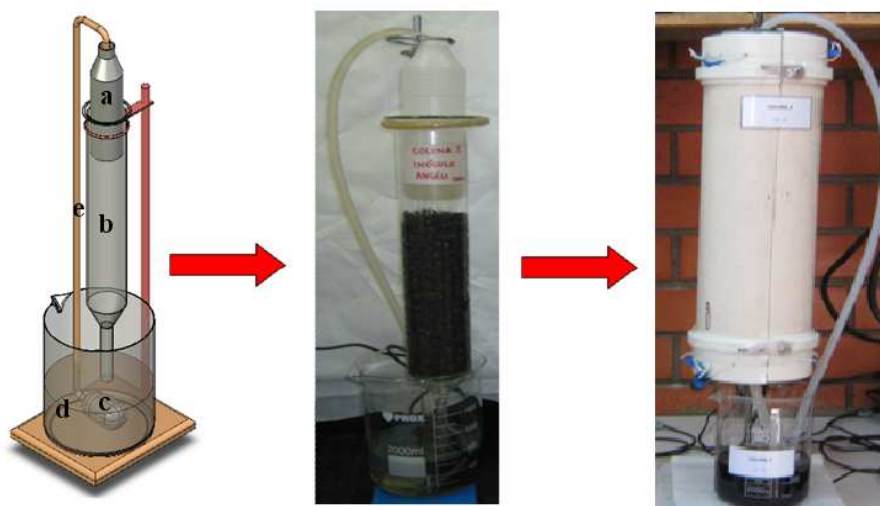


Figure 1. Leaching column for dissolution of the pyrite and UV reactor for conversion of Fe^{3+} to Fe^{2+} .

In each column, the amount of Fe^{3+} and Fe^{2+} was monitored as a function of time as well the most probable number of suspended cells of *Acidithiobacillus ferrooxidans*. The number of

suspended bacteria was estimated by multiple tube technique using the medium “9K”, which is specific for this microorganism (APHA, 2005). 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 sulphate by the heat provided by the UV radiation. The ferrous sulphate crystals were purified with ethylic alcohol and analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

4. Results and Discussion

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+} . At the end of the leaching process, the amount of *Acidithiobacillus ferrooxidans* suspended in the liquor was in the order of 1×10^8 cells/100mL.

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 $\text{Fe}^{2+}:\text{Fe}^{3+}$, after 96 hours, were the follows: 49%:51% 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.

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	0.5	0.6	0.6
	Eh (mV)	586	590	589
	<i>A. ferrooxidans</i> (MPN/100mL)	1×10^8	1×10^8	1×10^8
Iron photoreduction (at the end of 96 hours)	Fe total (g/L)	45.8	52.5	50.2
	Fe^{2+} (g/L)	22.4	35.2	40.0
	Fe^{3+} (g/L)	23.4	17.3	10.2
	pH	0.4	0.6	0.6
	Eh (mV)	587	621	590
	<i>A. ferrooxidans</i> (MPN/100mL)	1×10^8	0.0	0.0

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 sulphate was abundant. The amount of ferrous sulphate 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.

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

The recovery of iron as melanterite (Figure 2) 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.



Figure 2. Melanterite obtained from the biohydrometallurgical/UV processing of the coal tailing.

The x-ray analysis (Figure 3) of the purified hydrated iron sulphate obtained in both columns, showed that it was composed almost exclusively of melanterite crystals ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, ferrous sulphate heptahydrate), which had been largely applied for anaemia control, both in humans and animals, as well as, a reagent for water and wastewater treatment (e.g., Fenton's Reaction) (Metcalf & Eddy, 2003). The results were also confirmed by scanning electron micrographs (SEM) and energy dispersive spectrometry (EDS) (Figura 4 and 5).

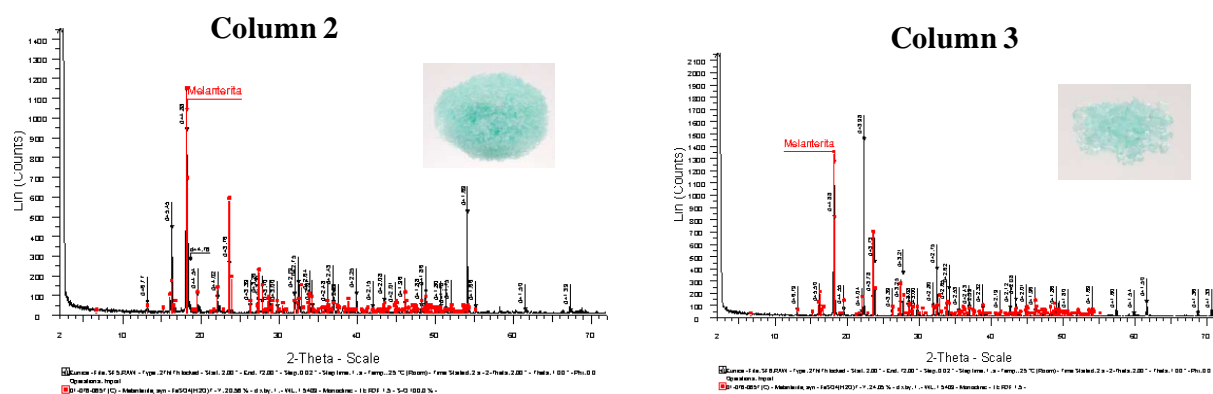


Figure 3. X-ray diffraction (XRD) of ferrous sulphate crystals

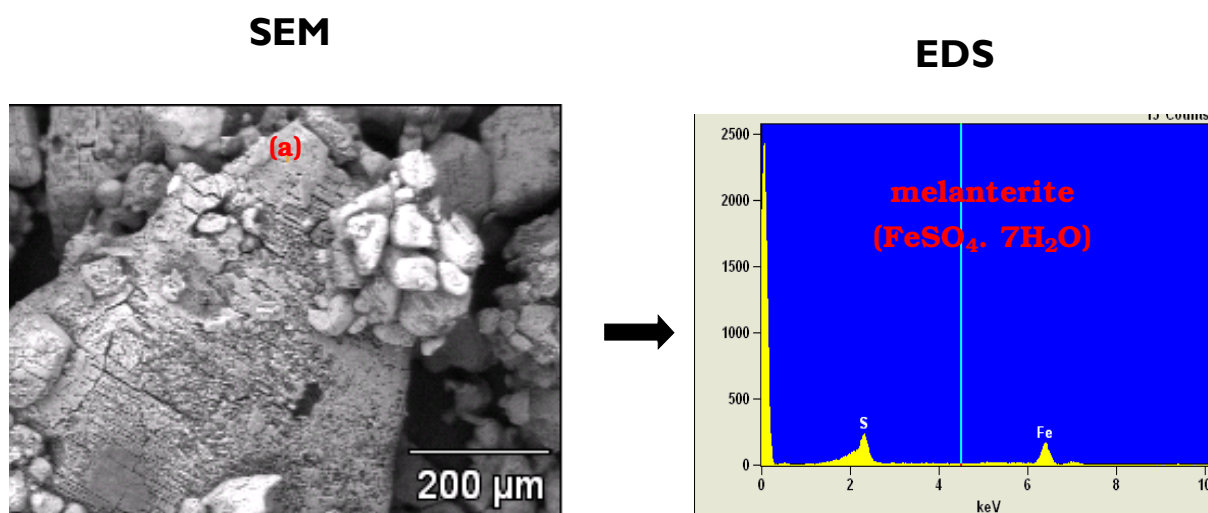


Figure 4. Scanning electron micrograph (SEM) and energy dispersive spectrometry (EDS) analysis of the ferrous sulfate crystals.

5. Conclusion

The results demonstrated that it was possible to produce ferrous sulphate 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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References

- Amaral Filho, J., Schneider, I.A.H., Tubino, R.M.C., Brum, I.A.S., Miltzarek, G., Sampaio, C.H., Schneider, C.H., 2010. Characterization of a coal tailing deposit for zero waste mine in the Brazilian coal field of Santa Catarina. In: Wolkersdorfer, C. & Freund, A. (Eds). International Mine Water Association 2010 Symposium, Sydney, Canada. Mine Water & Innovative Thinking. University of Cape Breton, Canadá, pp. 639-642.
- Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E. (Eds.), 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, DC.
- Kontopoulos, A., 1998. Acid mine drainage control. In: Castro, S.H., Vergara, F., Sánchez, M.A. (Eds.), Effluent Treatment in the Mining Industry. University of Concepción, Chile, pp. 7-118.
- Madeira, V.S. 2010. Aproveitamento de Resíduos da Mineração de Carvão para Fabricação de Produtos com Elevado Valor Agregado. Doctoral Thesis. Universidade Federal de Santa Catarina, Brazil.
- Menezes, J.C.S.S. 2009. Produção de Coagulantes Férricos na Mineração de Carvão. Universidade Federal do Rio Grande do Sul, Brazil.
- Metcalf & Eddy, 2003. Wastewater Engineering: Treatment and Reuse. 4th Ed., McGraw-Hill Book Company, New York.
- Peterson, M. 2008. Produção de Sulfato Ferroso a Partir da Pirita: Desenvolvimento Sustentável. Doctoral Thesis. Universidade Federal de Santa Catarina, Brazil.
- Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., Hellier, W.A., 1998. Handbook of Technologies for Avoidance and Reclamation of Acid Mine Drainage. National Mine Land Reclamation Center. West Virginia University, Morgantown, WV.
- Silveira, A.N., Silva, R.D.R., Rubio, J., 2009. Treatment of acid mine drainage (AMD) in South Brazil. Comparative active processes and water reuse. International Journal of Mineral Processing 29, 92-202.