BIO_FP07 - BIOLEACHING OF A PYRITE GRAVITY CONCENTRATE SO AS TO SYNTHESIS IRON OXIDE PIGMENTS.

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ABSTRACT

During the coal prospecting operation nearly 60% of the mined coal is considered as tailings. The reason for such high amount of that residue is an attempt to produce low sulphur content coal for energy generation purpose. Therefore, this technical contribution aimed at gravity concentrating, in the first place, the iron sulphide minerals, pyrite in particular, for bio-assisted digesting them to produce ferric sulphate bearing leachates, considering two different particle size ranges (12% as +3mm -6mm, and 88% as +6mm -9mm). Those leachates were used as raw material for producing iron oxide pigments, goethite, for instance, intensively used in different industrial sectors such as ceramic, paint etc. The bioleaching test were accomplished using different consortium of microorganisms in a four metre pilot scale column in a sort of ramping up mode so as to reach, separately, the potentiality of those particular groups of microorganisms. According to the results out of the in progress bioleaching test of the aforementioned concentrate, the iron extraction is about 45%, which is the result of 220 days of test, and prone to be enhanced as the operation parameters are being optimised.

Keywords: Bioleaching, iron oxide pigment and mineral coal.

1. INTRODUCTION

The coal is a chemically and physically heterogeneous mineral. Essentially, it consists of carbon with small quantities of sulphur, nitrogen and hydrogen [1]. Coal from the Brazilian mines possesses high sulphur content. Consequently, in the coal combustion process, for electricity generation, sulphur oxides (SOx) are released. These chemical compounds are recognized as highly polluting and inducing the formation of acid rain ([2],[3]). For this reason, in the coal industries large quantities of wastes are generated out of the coal
processing operation. Such wastes contain high iron contents, mostly from pyrite (FeS$_2$). With the objective of minimizing the environmental impact in the regions where the exploitation of such coal takes place, some coal mines have produced pyrite concentrates, from coal wastes, aiming at using them in the production of different chemicals, which contain some added value.

One of those chemicals is the iron oxide pigment. Before this scenario, it is necessary to develop process ways of promoting the dissolution of pyrite aiming at obtaining liquor containing high concentrations of iron ionic species that will be further used to produce the above mentioned pigment. A technological alternative that has been shown to be quite attractive is the bio-hydrometallurgical route, more specifically, the biolaching, which enables us to reach high extraction yields of the metal of interest with low investment and operating costs.

Bioleaching is a sulphide minerals dissolution process that takes place as a result of action of a group of microorganisms [4]. The microorganisms capable of promoting the leaching of sulphide minerals are acidophilus, quimiotrophics (obtains energy from the oxidation of inorganic compounds), autotrophic organisms, as they are implementing the biosynthesis of all cellular constituents using the carbon dioxide (CO$_2$) as the only source of carbon and are classified according to the temperature at which it develops, such as: mesophiles ( ~ 40°C), moderate thermophiles ( ~40 - ~ 55°C) and extreme thermophiles ( ~55 - ~ 80°C) [ 5].

The biolaching process consists of a series of chemical and biochemical reactions that solubilise metals from oxidative mechanisms that may occur, simultaneously, in a leaching reaction system [6, 7]. In the direct contact mechanism (Equation 1) the interaction of the cell with a surface area of sulphide mineral takes place, followed by an enzymatic attack to the components of the mineral likely to be oxidized, such as Fe$^{2+}$. In this mechanism, the microorganism withdraws electrons straight from the mineral, which will be used for producing energy.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

The so-called indirect mechanism, the ferric ion (Fe$^{3+}$) in solution promotes the chemical oxidation of the mineral (Equation 2). This occurs as the
ferric sulphate, generated from the Equation 3, is an efficient oxidant agent, which is able of promoting the sulphides dissolution, in general, including the pyrite (FeS\textsubscript{2}) [8].

\begin{align*}
  \text{FeS}_2 + 7\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} & \rightarrow 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \\
  2\text{FeSO}_4 + 0.5\text{O}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\end{align*}

During the indirect mechanism, the ferric ion (Fe\textsuperscript{3+}) is reduced to ferrous ion (Fe\textsuperscript{2+}). The role of iron-oxidising microorganisms, in this case, is to oxidize the Fe\textsuperscript{2+} to Fe\textsuperscript{3+}, regenerating, thus, such oxidizing agent. In addition, while generating elemental sulphur (Equation 4), it is important the activity of sulphur oxidising microorganisms to occur (Equation 5), so as to prevent the deposition of elemental sulphur (S\textsuperscript{0}) on the mineral, forming a barrier to the diffusion of the oxidising agent up to the surface of the mineral, which may hinder, or even prevent, the oxidation of the mineral constituents.

\begin{align*}
  \text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow 3\text{FeSO}_4 + 2\text{S}^0 \\
  2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} & \xrightarrow{\text{microorganisms}} 2\text{H}_2\text{SO}_4
\end{align*}

The adhesion of microorganisms to the mineral surface can also be mediated by extracellular polymeric substances (EPS - Extracellular Polymeric Substances), which are produced by some used microorganisms [9]. The excretion of exopolymeric material is important for microbial adherence, and the subsequent mineral dissolution, as the iron, which is bound to the polymeric material, gives a positive charge to the cell. Thus, it is established an electrostatic attraction between the microbial cell and the negatively charged surface of some minerals [10].

The Goethite (\(\alpha\)-FeOOH) is one of the most important iron oxides. It is present in a wide variety of soils [11] and in the aquatic environment, and it is a common constituent in bottom and in suspension sediments and it is associated, in a complex way, with other clay minerals, organic matter and even the microorganisms [12]. Other elements present in the surface, but in concentrations sufficient to form minerals themselves, can be associated to goethite by superficial adsorption and/or incorporation into its structure [13]. The sorption of heavy metals is strongly influenced by its hydrolytic properties.
Metals such as manganese, lead, nickel, cadmium, cobalt, and copper, with high affinity for hydroxyl ions in solution, also have a high affinity for hydroxyl of goethite.

In the market for inorganic pigments, the iron oxides play an important role, mainly due to the high opacity, stability and high coverage power. Among the most important ones is the goethite ($\alpha$-FeOOH), of yellow colour, the hematite (Fe$_2$O$_3$) of red colour and the magnetite (Fe$_3$O$_4$), a black colour iron oxide. The goethite is used as colouring agent for paintings and water-based paints formulation, in addition to the production of ceramic articles and use in the building construction.

2. EXPERIMENTAL

2.1 Mineral Sample

The mineral sample used in this study is a pyrite gravity concentrate, a product of coal waste processing, which was referred for crushing and subsequently for a dry classification in Kason’s sieve on 3 particle size ranges: < 3mm, +3 and -6mm and +6 and -25mm. The iron content of that sample was 34.2 %.

2.2 Microorganisms and Culture Medium

The mesophile micro-organisms used in this study are species of the genera Leptospirillum and Acidithiobacillus, cultivated at 30 °c. The consortium of moderate thermophile microorganisms used consists of species of the genera Acidithiobacillus, Sulfobacillus and Acidimicrobium being cultivated at 50°C. The consortium of extreme thermophile microorganisms used is composed of species of the genera Acidanus brierlyi, Acidianus infermus, Metallosphaera sedula, Sulfolobulus metallicus, Sulfolobulus acidocalrius, Sulfolobulus shibatae, being cultivated at 68°C.

The cultures were accomplished in MKM culture medium (Modified Kelly Medium), which has the following composition: (NH$_4$)$_2$SO$_4$:0,8 g/l; MgSO$_4$.7H$_2$O: 0.8 g/l, K$_2$HPO$_4$:0,08 g/l e 0,2 g/l of yeast extract (the latter is offered only for the thermophile consortium). As An energy source 25 g/l of FeSO$_4$.7H$_2$O and
2.5 g/l of $S^0$ were used. The pH was adjusted to 1.8 by adding 5M $H_2SO_4$ solution.

From of the microorganism consortia successive sub-cultures were prepared established with increasing contents of mineral sample under study. As the pyrite content was increased, the microbial population was established and achieved cellular concentrations equivalent to $1.21 \times 10^8$, $6.19 \times 10^6$ and $5.42 \times 10^6$ cells/mL for consortia of mesophile, moderate thermophile, and extreme thermophile micro-organisms, respectively. As they are growing in medium containing pyrite concentrate, the microorganisms become used to oxidize the substrate even in the presence of soluble sources of energy that are more easily oxidized, such as $FeSO_4$.

### 2.3 Bioleaching Test work

The bioleaching test was carried out in a 4-meters high column made out of glass fibber, with 0.45 meters in diameter. This column was loaded with 900 kg of mineral sample, so that 12% of the total weight was in the particle size range of +3mm -6mm and 88% in the range of +6mm -9mm and microbial consortia (mesophile microorganisms, moderate thermophiles and extreme thermophiles) in a concentration of $10^5$ cells/g. A column liqueur drained into a 200 litters tank where the pH was controlled by adding 5M sulphuric acid solution using a metering pump. A liqueur out of the 200 litters tank was then pumped, by a metering pump, to the top of the column for irrigating the ore bed, as a spray, by using a sparger located in the lid of the column. This solution, apart from containing iron and sulphur oxidising microorganisms, also contains source of nitrogen (N), phosphor (P) and potassium (K).

The injection system, at the bottom of the column, ensures the supply of air as sources of oxygen and carbon, whose flow is monitored/controlled by flow meters. However, the flow of air is first bubbled into a water-bearing humidifier bottle to avoid water evaporation and dryness of the mineral bed.

### 2.4 Experiment of pigment synthesis

Particles of iron oxide pigments were synthesized using a lecheate from the bioleaching of pyrite gravity concentrate. That lecheate, after being diluted, contained 12.0 g.L$^{-1}$ of total iron, where 84.5 % of iron species were as $Fe^{2+}$.
ions. The reaction system used in synthesis of iron oxide pigment is composed, as can be seen in Figure 1, by a jacketed reactor of 4 litters useful capacity, manufactured in refractory glass (borosilicate glass), equipped with temperature control, variable mechanical stirring provided by a special impeller and solution aeration device. The reactor was completed with 2.6 litters of liquor, which fills 2/3 of its capacity, and, then, hydrogen peroxide (H₂O₂) was slowly added, as oxidising agent, equation 7, up to reaching an Fe³⁺ /Fe²⁺ ratio of 0.9, blowing 5 L/min of air and agitation of 1400 rpm. Then, the reaction system pH was raised using 1 mol/L NaOH solution up to 3.5. After such pH control and generation of the hydrolyzed material, the stirring and air blowing were continued at room temperature, 30 °C, for 36 hours. The solid obtained was filtered, washed with deionised water and dried in an oven.

\[
2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{7}
\]

![Figure 1. Outline of the 3 litters reactor for goethite precipitation.](image)

### 2.5 Goethite Characterization

The X-Ray powder diffractogram (XRD) of the pigment sample was generated in an equipment Bruker-D4 Endeavor, under the following operation
conditions: radiation Co Kα (35 kV/40 mA); speed of the goniometer of 0.02° by step with counting time of 1 second per step and collected from 4 to 80°. The qualitative interpretations of the spectra were determined by comparison with standards contained in the database PDF02 (ICDD, 2006) in software Bruker Diffrac Plus.

2.6 Chemical Analysis

The pH and redox potential (Eh) measurements were accomplished directly in the reaction system by using a micro-processed Analion pHmetro AN2000 using a glass combined electrode and platinum electrode (against Ag/AgCl reference electrode), respectively. The iron ionic species (Fe³⁺ and Fe²⁺) concentrations were determined by colorimetric method (Herrera, et al., 1988). This method is based on the complexation reaction of ferrous ion (Fe²⁺) by orthophenanthroline (FenH⁺) generating an orange colour complex (Fe(Fen)³²⁺). The absorbance reading was carried out at a wavelength of 510 nm (where a maximum absorption of the complex formed is reached) in a spectrophotometer Lamatte Smart Spectro.

3. RESULTS AND DISCUSSION

The iron extraction is directly related to the performance of acting microbial consortia in their respective ranges of temperature, i.e., temperatures of the mineral bed inside the column. Figure 2 shows the heating ramp imposed on the system, by means of an external heating, in addition to the iron extraction curve that indicates an extraction of 45% after 220 days of test.

It can be seen that the heating ramp, imposed to the bioleaching column, throughout the test, it covers a range of optimum temperature of the three microbial consortia used, mesophiles (30 °C), moderate thermophile (50 °C) and extreme thermophile (70 °C); however, there were no major changes in the iron extraction kinetics in different temperature ranges.
The iron ionic species concentrations are directly related to the redox potential (Eh). Thus, the Eh values, measured during the bioleaching process, can be used to determine whether the experimental conditions are favourable to the maintenance of ferric ions in the reaction system, as can be seen in the thermodynamic equilibrium diagram of the Fe-H₂O system. It is observed in Figure 3, that the ferric ion stability region is very restricted, and dependent on high Eh values in combination with low pH values. For this reason, the Fe³⁺ precipitation, in the bioleaching systems as insoluble species (MFe₃(SO₄)₂(OH)₆⁺, Fe(OH)₃, FeOOH etc.), is an inconvenience that must be avoided, as, apart from hindering the metal extraction process, by restricting the access of microorganisms to the sulphide mineral surface, may, additionally, imprison nutrients, ferric ions and other metals on their structures [14].
Figure 3. Thermodynamic equilibrium diagram of the Fe-H₂O system at 25°C. Source: Software HSC [15].

Figure 4 shows the values observed during the monitoring of the redox potential and iron concentration in the PLS (pregnant leach solution). It is observed the increase in the redox potential to values close to 650 mV vs. SHE, with peaks around 700mV vs. SHE, from the second week of operation. This may be related to the increase of the microorganisms population density in the interior of the column and in the lecheate tank, which can be followed by an increase in the iron extraction. The variation of iron concentration in the lecheate is due to the frequent bleedings accomplished throughout the process. This procedure is important to avoid increasing the salinity and, as a consequence, the decrease in the availability of dissolved oxygen, causing a reduction in the oxidative process efficiency, as can be observed in the region next to the 80th day of leaching, where there is a reduction in the redox potential due to the high iron concentration in the leaching solution (~40.0 g.L⁻¹). The concentrations of iron ionic species, i.e., the ratio between those species are directly related to the redox potential as can be observed in the Nernst equation (equation 8).
Figure 4. Monitoring of redox potential and iron species concentrations.

\[
E = E^\circ_{Ox,red} + \frac{0.0591}{n} \log \left( \frac{[Ox]}{[Red]} \right) \tag{8}
\]

Where:

Eh: Potential (V vs. SHE) measured, experimentally, with platinum electrode against Agº/AgCl reference electrode;

Eº: Standard Potential (V) of the couple Fe³⁺/Fe²⁺;

R: The constant of gases, 8.31441 Joule.K⁻¹.mol⁻¹;

T: Temperature in Kelvin;

F: Faraday constant (96493.5 Coulombs.mol⁻¹); and

n: Number of electrons involved in the reaction (in this case, 1 electron)

It is observed in Figure 5, the mineral bed irrigation rate, which is carried out by using an acid solution (H₂SO₄), containing fundamental chemicals, biomass (bacteria and archaeas) and nutrients. In the bioleaching column operation it was used a maximum irrigation rate of 23.30 L.m⁻².h⁻¹. In relation to the pH variation during the experiment, as expected, occurred generation of
sulphuric acid, from the pyrite oxidation reaction, which drops the pH down to values close to 1.0 from the 30th day. For this reason, dilutions of the reaction system lecheate were necessary to avoid high salinity to be reached, as well as to prevent high hydrogen ion concentration that could decrease the activity of microorganisms acting in the oxidative process.

From the bioleaching process lecheate, the iron oxide pigment precipitation, the goethite (α-FeOOH), in particular, was conducted in the experimental conditions described above. From the initial of Fe$^{3+}$ and Fe$^{2+}$ species concentrations values, respectively, 1.86 g.L$^{-1}$ and 10.14 g.L$^{-1}$, there is an increase, after the first hour of test, of the Fe$^{3+}$/Fe$^{2+}$ concentration ratio to 0.95, due to the addition of hydrogen peroxide (H$_2$O$_2$), oxidizing agent that does not depend on the salinity of the reaction system, which was not the case of oxygen, that was supplied by blowing air in the bulk of the solution.

For this reason, the Eh values can be used to determine whether the experimental conditions are favourable to maintain the ferric ions in the reaction system, as can be observed in the thermodynamic equilibrium diagram for the Fe-H$_2$O system. It can be observed in Figure 3, that the ferric ion stability region

![Figure 5. Variation of pH and irrigation rate.](image)
is very restricted, dependent on high Eh values in combination with low pH values [14].

It is observed in Figure 6, the diffractogram of the precipitated material at the end of the test for producing the iron oxide pigment using the leachate from the bioleaching of pyrite gravity concentrate. The peaks are characteristic of low crystallinity goethite. The hydrolysis of Fe$^{3+}$ ionic species in solution at room temperature results in an amorphous iron hydroxide (III) precipitate. This amorphous compound, as all other amorphous precipitates, are thermodynamically unstable and may be gradually transformed in structures more crystalline with a longer aging time or even using higher temperatures.

![Figure 6. X-ray diffraction of synthetic pigment aged for 36h at 30ºC.](image)

4. **CONCLUSION**

It was obtained from the bio-oxidative process, by using consortia of mesophile, moderate and extreme thermopiles microorganisms, iron extraction of 45.05 % at the end of 220th day of test.

The bioleaching of pyrite gravity concentrate is configured as a technological alternative to low investment and operating costs due to the origin of the pyrite concentrate, which is produced from wastes generated during the processing of mineral coal. Such high iron contents bearing wastes, basically from pyrite (FeS$_2$), and may cause potential environmental impact in regions where such waste are disposed generating the so-called acid rock drainage.
The use of consortium containing extremes thermophile microorganisms did not show a significant improvement in the iron extraction rate if compared to the activity periods of consortia containing mesophile and moderates thermophile microorganisms. Although the moderate thermophile microorganisms present resistance to mechanical stress due to the characteristics of their cell walls, their use is interesting due to possibility of generating heat from the oxidation of sulphides present at larger scales, or even in heap bioleaching, once the column bioleaching may be considered as an aliquot of the entire heap.

The pigment obtained in the aforementioned experimental conditions, did not show high crystallinity, which is a prerequisite to configure as a high quality one; however, it can be used for incorporation as a load in ceramic artifacts or even in civil construction.

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REFERENCES


