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Correlation Of The Oxide-Reduction Potential And Study Of The Bacterial Population During The Copper Sulfide Bioleaching

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ABSTRACT- *The interrelation of bacterial population variables and oxide-reduction potential in the bioleaching of sulphided minerals was studied by bacterial strain of AciditiobacilusFerrooxidans, isolated from acid mine effluent, seeking the copper solubilization and the release of gold present in a mineral with sulfides greater than 80%.The experimental variables were: Pulp density at 1, 2 and 6% (W / V), ferrous sulphate concentration as part of the 9k medium of 0, 3, 6, 9 and 15 gr / Lt.; keeping constant the temperature, agitation of the medium and pH.The tests were performed in three consecutive phases of 24 days, starting with inoculum containing 7.05x107Cell / ml and then the one obtained in each previous phase, observing the variation in the periods of adaptation and growth.In the first phase, the maximum bacterial density reached was 4.75x107Cell / ml with 6 g / l of ferrous sulphate. In the second phase a maximum density of 6.30x107Cell / ml was obtained without the addition of ferrous sulfate.In the third phase, the bacterial density reached was 4.51x107Cell / ml., With exponential growth beginnings at approximately 13, 8 and 3 days, respectively. The bacterial strains were successfully adapted in different media containing varying amounts of iron and sulfur minerals, giving better results in the absence of iron sulphate in the added substrate.*

KEYWORDS: *Potential ORP, bacterial population, bioleaching, copper sulphides, adaptation of acidithiobacillus.*

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I INTRODUCTION

The redox potential is a measure of the activity of the electrons, as the pH is the measure of the activity of the protons, therefore the oxide-reduction potential (ORP) identification, is a critical factor in the development of the inoculum and in the evolution of the oxidation of the inorganic compounds, it was determined with a platinum electrode with a reference to a hydrogen electrode connected to a potentiometer.It is quantified in voltage units and it represents the amount of energy released by all the components on a time unit when a certain number of electrons travel from one phase to another; specifically, between the bioleaching substrate and the platinum electrode.

The biological oxidation of sulphide to sulfur, sulfate and other sulfur compounds and the reduction of oxygen in water represents the main redox changes that occur in this process. The ORP measurement in this way will be determined by the set of reactions.Similarly, the thermodynamic relation of the ORP represented by the Eh according to the composition of the solution is generally known as the Nernst equation, however, in practice, ORP measurement is mainly determined by the compound with the highest current exchange density, that is, the ability of the compound to exchange electrons with the surface of the platinum electrode, in this sense, several authors reveal that there are compounds that have a high capacity to exchange their valence electrons with the platinum surface, such is the case of hydrogen sulfide, for which there is a linear relationship between the ORP measurement and the logarithm of the concentration of hydrogen sulfide in natural environments. [8]

The utility of the ORP data is questionable, because the measurement probe is directly in contact with the extracellular environment sine which is totally different from the intracellular environment. One disadvantage of the ORP is its strong dependence on pH, decrements have been reported in the ORP of 33mV with the increase in one unit in the pH.[2]It has been known for a long time that microorganisms have different

degrees of sensitivity to the potential of oxide reduction, a fact that has been observed especially in culture media. It is thought that the redox potential is an important selective factor in all environments, including food, which probably influences the types of the current microorganisms and their metabolism. [9]In bioleaching tests for a prolonged period of 60 days it is possible to maintain the oxidation-reduction potential around 550-590 mV [14]as well, the evolution of the bacterial population showed increases in a certain period of time, that is between days 6 and 21 of the process, the average bacterial population was 1.70x108 cel.mL-1 and 8.00x107 cel.mL-1 in the bioleaching of ore whose granulometries corresponded to the 200 and 325 Tyler meshes, respectively. [13]

II ANTECEDENTS OF BIOPROCESSES

In recent years, the development of microbiological methods for the extraction of metals from minerals, has undoubtedly generated much interest and approach to several processes of bioleaching and biooxidation that operate in different parts of the world. There are fundamental reasons to carry out many investigations and give recognition to the discoveries obtained; In addition, it will surely become the cause of future development in the field of metal recovery. [5] The sources of inorganic electron donors are diverse and abundant in nature; they can be of geological, biological and anthropogenic origin. Volcanic activity is an important source of reduced inorganic sulfur compounds the same as the sulfatoreduction. The activities derived from agriculture and mining, as well as the burning of fossil fuels and other industrial activities, release reduced inorganic compounds of sulfur into the environment, which can be used as donors or electron receptors for the sulfoxidantchemolithotrophic bacteria.[7]The application of the bioleaching process to copper sulphide minerals has been industrialized during the last two decades, the combined flow of biooxidation - bioleaching - electrodeposition is successfully used in the extraction of uranium, gold, zinc and other metals. In addition, in the last ten years, interest has been shown in the application of biooxidation for the recovery of copper from refractory minerals. [16]

III METHODOLOGY

The design, implementation and development of the research was carried out in the Biometallurgy laboratory of the Professional Academic School of Metallurgical Engineering and the collaboration of students and faculty from the faculties of: Biological Sciences and Chemistry and Chemical Engineering, UNMSM, Peru.Potential measurements (Ev) and determinations of the bacterial population were made at different substrate concentrations, keeping the temperature constant at 22 ° C pH at 1.8 and stirring at 150 RPM. The test environment was formed of sulphide mineral, 100 ml of 9k solution and 10 ml of inoculum.The bacterial population count was performed in the Laboratory of Environmental Microbiology and Biotechnology of the Faculty of Biological Sciences.The chemical analyzes were took in the Biometallurgy laboratory of the E.A.P of Metallurgy Engineering, the Atomic Absorption and ICP (Induced Plasma Spectrometry) analyzes were carried out through private sector services.

1.1 Materials

An important aspect of the treated mineral in its nature, with diverse contents of sulfides, copper sulphides being of interest. The sulfurized ore was crushed to mesh -200 to 94%, allowing oxidation and the provision of nutrients for the growth of microorganisms.

1.2 Inoculum of AcidithiobacilusFerrooxidans

The start inoculum whose population was 7.05x107Cell / ml. was obtained after a process of isolation and adaptation from an acid mine drainage, from old mining works in the Huancavelica region, Peru. The culture environment used allowed to isolate and concentrate the bacteria and their identification using the technique of polymerase chain reaction (PCR) at a 98% probability. [3]

1.3 Mineral substrate as a metabolic environment

The mineralogical composition of the sulphide mineral that formed part of the substrate in the bioleaching, containing copper, gold and silver contents, was identified. Considering that presence of gangue with sulfur compounds, it would increase the pH in the leaching liquid and the inhibition or complete suppression of bacterial activity. [11] The leaching rate also depends on the total surface area of the substrate, a decrease in particle size means a surface increase, so that the dissolution or oxidation yields can be obtained without any change in the total mass of the particles. A particle size of approximately 42 µm is considered optimal. [4] In addition, a 9k breeding ground modified on its ferrous salt content was used to improve the reactivity.

1.4 Operating method

The first tests made corresponded to the chemical analysis of identification by elements, the results were submitted to the theoretical analysis based on the bibliographic information, with the purpose of defining the operational parameters to be chosen in the trials.

1.5 Work plan.

When the exploratory research work was considered, it was determined to perform in 3 consecutive phases, according to the previous results of each preceding one, the detailed conditions are shown in figure 1.

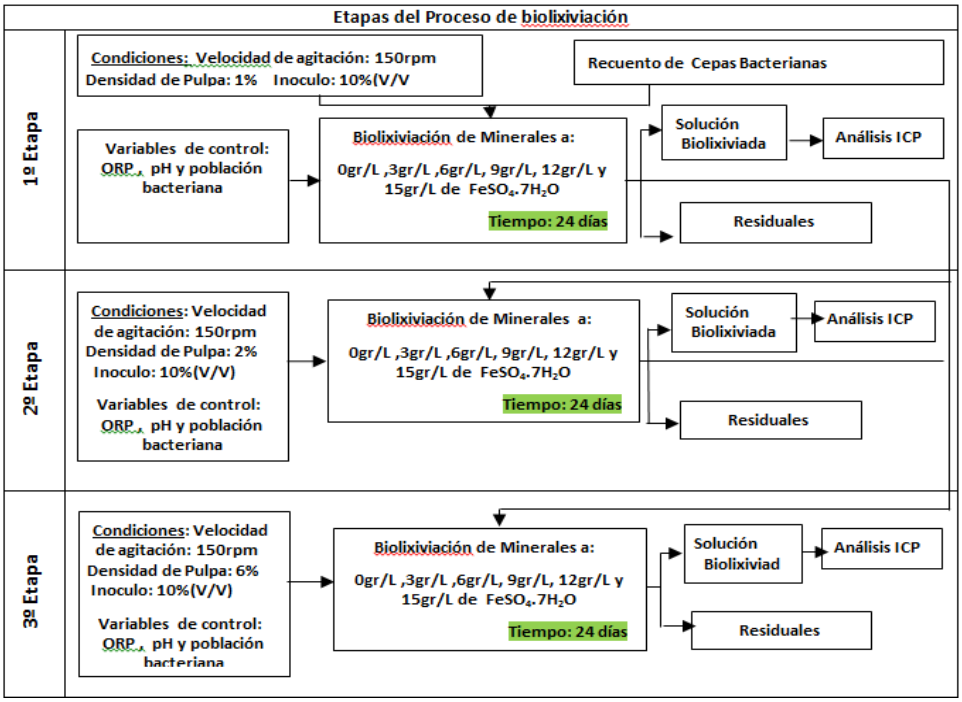

Fig. 1. Phases of the bioleaching process with 1, 2 and 6% pulp density.

2. BIOLIXIVIATION TESTS

The bioleaching tests were made in 250 ml flasks and, in 3 consecutive phases, with 1, 2 and 6% (W / V) of sulphide ore respectively, having 9K solutions at different concentrations of ferrous sulphate as substrate. Periodic measurements of potential oxidation reduction (ORP) and pH were made, and sampling of solution to determine copper and iron content.

2.1 FIRST PHASE OF BIOLEACHING

The Bioleaching substrate was the 9K environment, varying the concentrations of FeSO4.7H2O between 0.00 to 15.00 g / l. The tests were made using 500 ml flasks, where 3 gr. of mineral (1% W / V), 30 ml of bacterial inoculum of 7.05x107Cell / ml and 300 ml of medium 9k and amounts of FeSO4.7H2O equivalent to 3, 6, 9, 12 and 15 g / L. The pH was adjusted to 1.8 with sulfuric acid solution and then the process was started. The optimal dose of ferrous ions for the leaching of sulfides such as pyrite and chalcopyrite, differs depending on the nature of the mineral. [10,12]

2.2 EFFECT ON BACTERIAL GROWTH.

The bacterial growth during the bioleaching was identified according to the concentration of the ferric salt, showing an accelerated increase approximately, between the 12th and the 24th. day, producing a break in growth, with a tendency to remain constant and indicating the end of the growth phase. The maximum bacterial density reached at 24 days was 4.75x107Cell / ml with 6 g / l of FeSO4.7H2O reaching 67% of the inoculum. See Figure 2. The methodology commonly used in bioleaching processes includes the adaptation of the bacteria (A. ferrooxidans) to the presence of heavy metal ions, which consists of successive cultures in which the

microorganisms reproduce progressively and also the concentration of metal ions increases. [6,13]

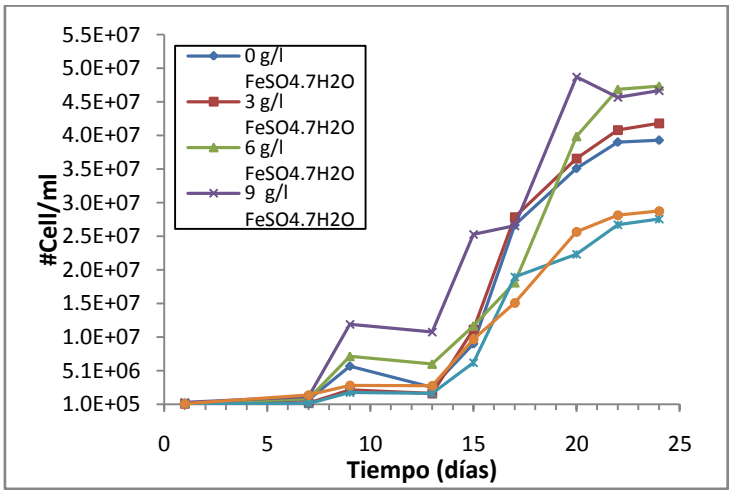

Fig. 2. Bacterial population variation during the first phase of bioleaching of a sulphide mineral.

2.3 PH VARIATION.

It started with a pH of 1.8 for all tests at different concentrations of FeSO4.7H2O, during the phase until 19 days, the minimum average pH was 1.6, while the maximum reached 2.1, maintaining an average pH of 1.9, later the pH tends to descend, probably by the generation of H + and the formation of sulfuric acid. See figure No. 3.

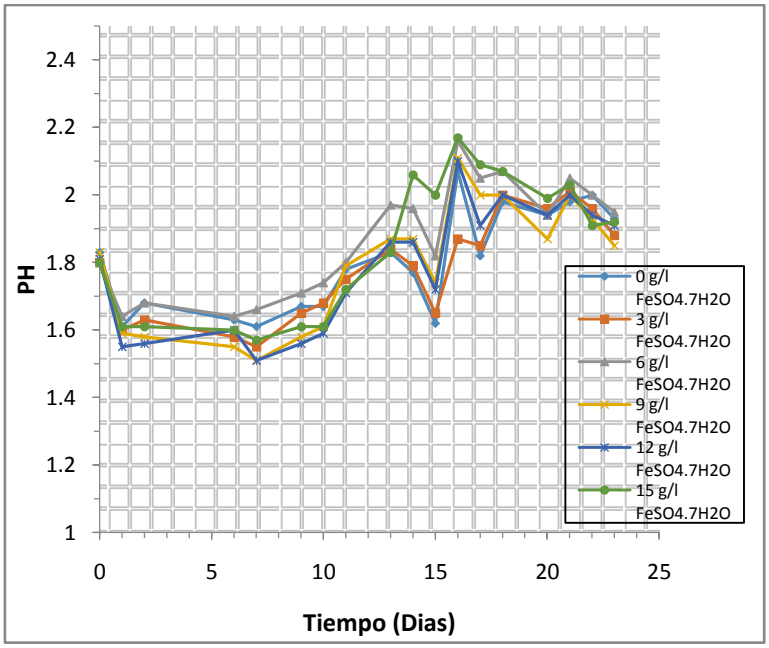

Fig. 3. pH variation during the first phase of bioleaching.

2.4 OXIDE-REDUCTION POTENTIAL MEASUREMENT.

Figure No. 4 shows values of ORP (mV) for each test made, at the first 6 days the sample of 0 g / l FeSO4.7H2O initiates an increase of 360 mV reaching a maximum value of 585 mV on the tenth day. After 10 days initiated the bioleaching, the sample of 15g / l FeSO4.7H2O initiates an increase until reaching a maximum of 560mV. Subsequently, all samples were maintained at an average of 575mV. The recovery of copper obtained in this first stage was 72.64%, with 6g / l FeSO4.7H2O and the minimum recovery of 30.96% with 15 g / l FeSO4.7H2O. After about 18 days, after the bioleaching started, it was observed that the copper recovery

percentage decreases considerably.

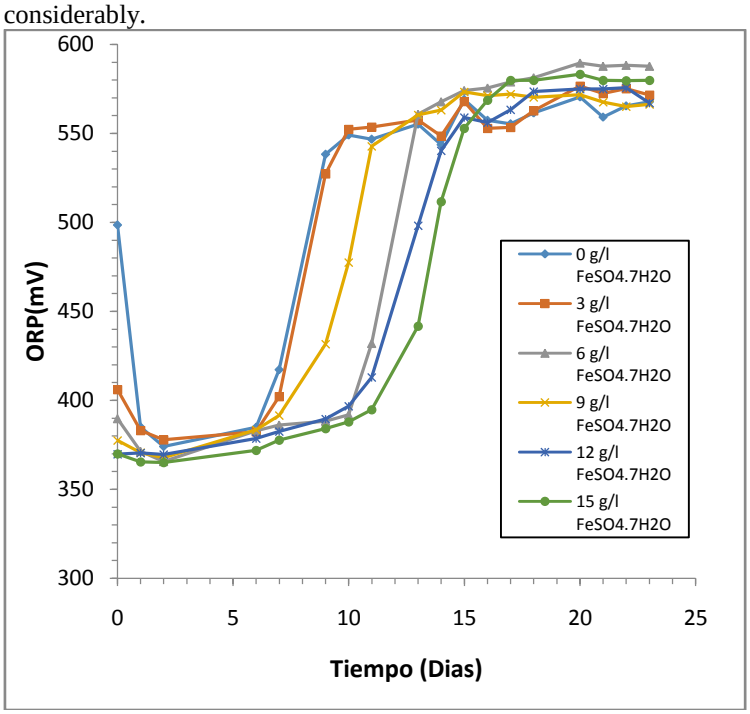

Fig. 4. Oxide-reduction potential (ORP) measurement, during the first stage of the bioleaching process of a sulphide mineral.

2.5 SECOND PHASE OF BIOLEACHING.

The samples were made using 500 ml, when 18 grams of mineral (6% w / v), 30 ml of bacterial inoculum (10% v / v) and 300 ml of medium 9k and amounts of FeSO4.7H2O equivalent to 0, 2, 4 and 6 g / L were added. The pH was adjusted to 1.8 with sulfuric acid solution and the process continued at a constant stirring of 150 RPM. The inoculum was obtained from the solution of the previous phase.

2.6 EFFECT ON BACTERIAL GROWTH.

Figure No. 5 shows the increase of the microbial density, taking as inoculum the solution of the previous stage that the concentration was 4.75x107 Cell / ml, it showed that the adaptation and exponential phases were the same tendency for all the concentrations of FeSO4.7H2O, Starting the exponential phase approximately to the 8th day. And achieving the maximum bacterial density of 6.30x107 Cel / ml, without addition of FeSO4.7H2O and, exceeding the inoculum concentration in 42%, compared to the first phase.

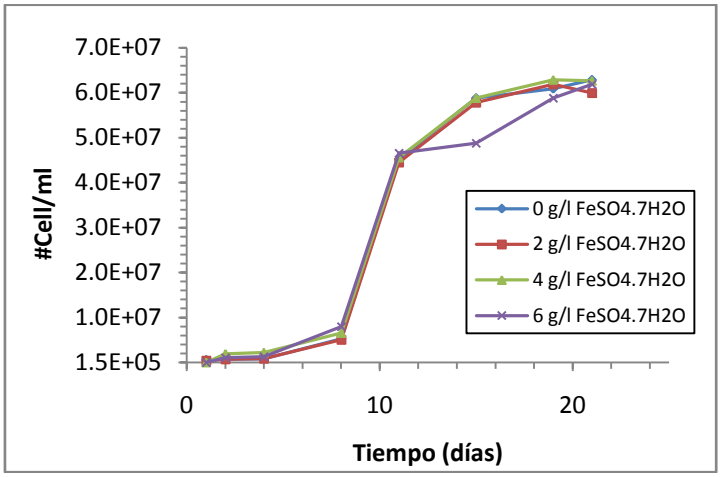

Fig. 5. Bacterial population variation during the second phase of bioleaching of a sulphide mineral.

2.7 VARIATION OF PH.

The effect of the PH of the mineral shows an increase during the first 7 days as the density of pulp has increased to 6%, because of these variation 5 drops of concentrated sulfuric acid have been added to each Erlenmeyer to correct the pH, showing as result a decrease in the subsequent days.

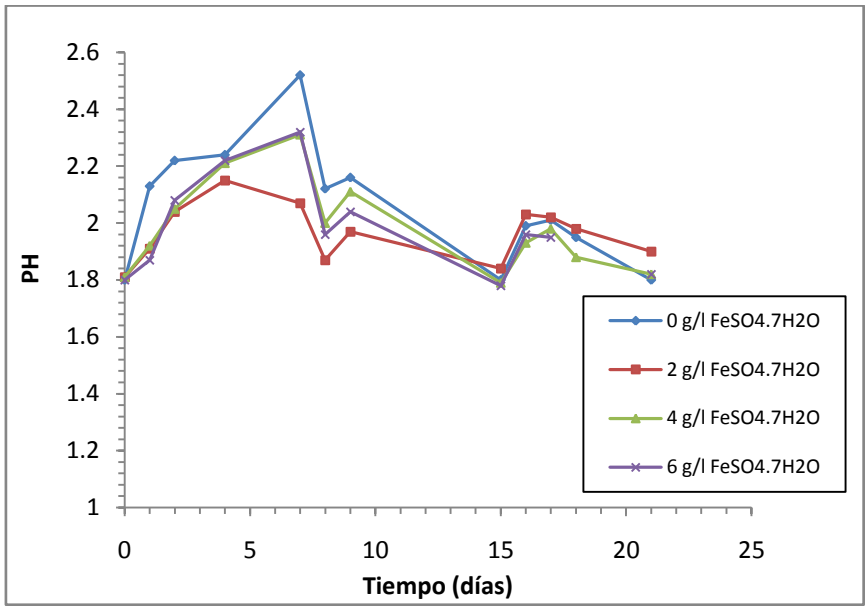

Fig. 6. pH variation during the second stage of bioleaching.

2.8 OXIDE-REDUCTION POTENTIAL MEASUREMENT.

The values in figure 7 show the increase of the redox potential for the different concentrations of FeSO4.7H2O. The maximum value in this phase is from 613.2mV to 2g / l of FeSO4.7H2O. It showed that the values exceed 600mV at day 9, concluding that in this phase there is a greater oxidation potential towards the mineral.

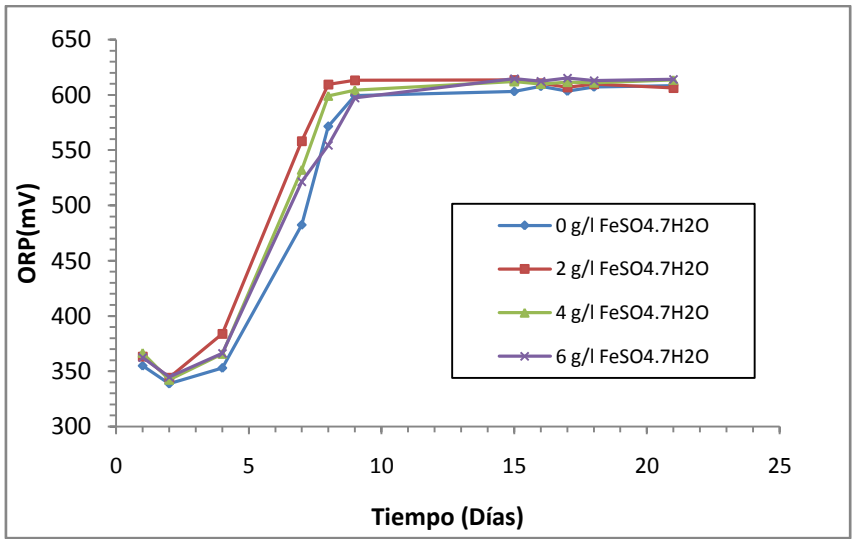

Fig. 7. Oxide-reduction potential (ORP) measurement, during the second phase of the sulphide mineral bioleaching process.

2.9 THIRD STAGE OF BIOLEACHING.

The liquor used or the Bioleaching substrate was the 9K environment, varying the concentrations of FeSO4.7H2O. The tests were made using 500 ml flasks, 6 grams of sulfurized mineral (2% W / V), 30 ml of

bacterial inoculum (10% V / V) and 300 ml of 9k and equivalent amounts of FeSO4.7H2O were added. at 0, 3, 9 and 15 g / L. The pH was adjusted to 1.8 with sulfuric acid solution and the process was continued at a constant stirring of 150 RPM. The inoculum is obtained from the second phase, taking into account its biological adaptation to the mineral. The control parameters are the same with respect to the first phase.

2.10 EFFECT ON BACTERIAL GROWTH.

Taking as inoculum the effluent of the second phase, whose bacterial density was 6.30x107 Cell / ml, achieving an exponential growth approx. after 3 days of the beginning of the experimentation; compared to the first phase it has been reduced by 9 days and compared to the second phase by 5 days. The exponential growth ends at approximately 10 days. In this phase it showed that at 0 g / l FeSO4.7H2O a maximum concentration of 4.51x107Cell / ml is achieved, with some similarity to the other concentrations. Concluding, the microbial adaptation with the provision of nutrients from the mineral substrate, confirming the chemolithotrophic characteristic of the bacterium AciditiobacillusFerrooxidans.

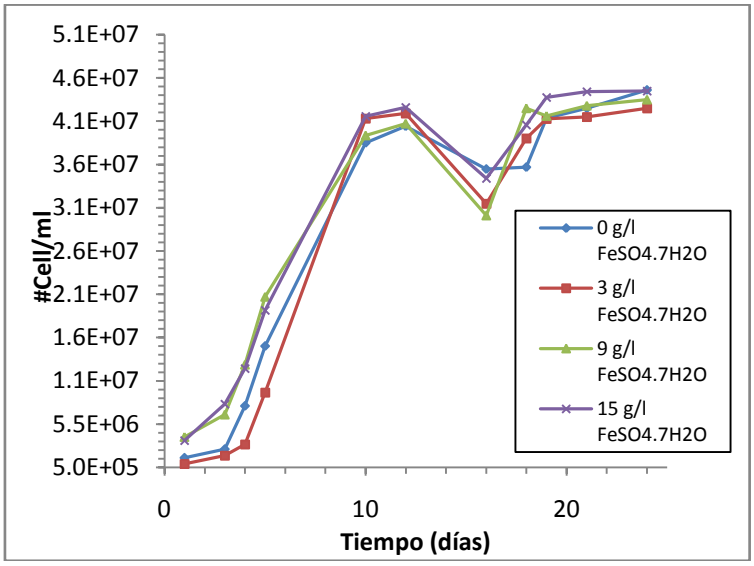

Fig. 8. Bacterial population Increase during the third stage of bioleaching of a sulphide mineral.

2.11 VARIATION OF PH.

An increase in pH was observed in the first 3 days, reaching a maximum of 2.08 to 15g / l $FeSO_4.7H_2O$, and it was decided to correct with H_2SO_4, then an increase in acidity was noticed, reaching a pH of 1.4, this increase was due to the greater amount of sulphide ore, compared to the second phase. During the following 17 days the pH has remained on average in 1.8, following a downward trend in recent days product of the mechanism of production of H^+.

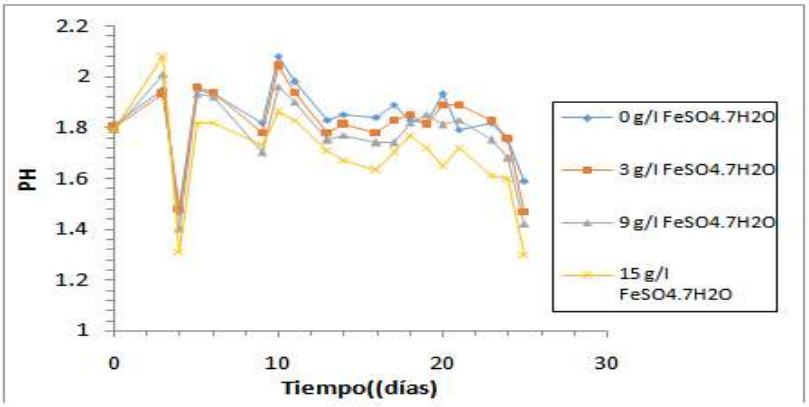

Fig. 9. pH variation during the third stage of bioleaching.

2.12 OXIDE-REDUCTION POTENTIAL MEASUREMENT.

Figure 10 shows that only in the first 3 days is it possible to obtain values close to the maximum, keeping constant throughout the phase, compared to the first phase this event occurred between days 7 to 15 approximately; in comparison to the second phase, it occurred between days 4 to 8, approximately. The average values of 585 mV for all tests, 15 mV lower than in the second phase and 10 mV higher compared to the first phase.

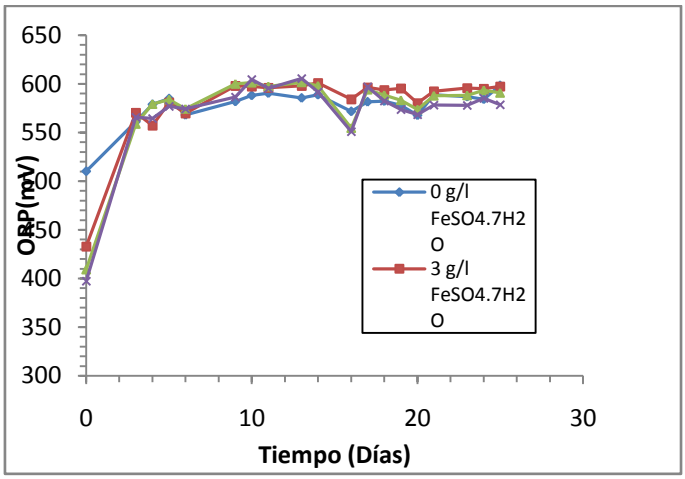

Fig. 10. Oxide-reduction potential (ORP) measurement, during the third stage of the bioleaching process of a sulphide mineral.

IV ANALYSIS AND DISCUSSION OF RESULTS

In the first phase of bioleaching, population growth is achieved approximately in the period of 12 to 24 days, producing a break in growth, with the tendency of remaining constant and indicating the completion of the phase. The maximum bacterial density reached was 4.75x107Cell / ml at 24 days on substrate with 6 g / l of $FeSO_4.7H_2O$ reaching 67% of the inoculum. While the reduction oxide potential shows a varied behavior in the growth period, at the first 6 days the sample with 0 g / l $FeSO_4.7H_2O$ initiates an increase of 360 mV reaching a maximum value of 585 mV on the tenth day approx., the sample of 15g / l $FeSO_4.7H_2O$ initiates an increase until reaching a maximum of 560mV, then all reach an average of 575mV.

In the second phase the inoculum had a concentration of 4.75x107Cell / ml, it was observed that the adaptation and exponential phases show the same tendency for all the concentrations of $FeSO_4.7H_2O$ Initiating the exponential phase to the eighth day, obtaining a maximum bacterial density from 6.30x107Cell / ml to 0g / l $FeSO_4.7H_2O$, exceeding the concentration of the inoculum in 42% with a maximum value of redox potential of 613.2 mV in the test with 2 g / l of $FeSO_4.7H_2O$ It showed that the values exceed 600mV. In the third phase, the start of exponential growth was noticed 3 days after the bioleaching began, compared to the first phase, it was able to reduce for 9 days compared to second phase for 5 days. The exponential growth ended approximately 10 days. In this phase, it showed that at 0 g / l $FeSO_4.7H_2O$ a maximum concentration of 4.51x107Cell / ml is achieved, with certain similarity than other concentrations of the iron salt. It was shown a highlight evolution of ORP values during the first 3 days, and then with a tendency of remaining constant throughout the test period with an average value of 585 mV, 15 mV lower than in the second phase and 10mV higher compared to the first phase and this event occurred between days 7 to 15 approximately, compared to the second phase, occurred between days 4 to 8.

Oxide reduction potential values in the first 3 days of the third phase are close to the maximum during the whole phase, compared to the first phase this event occurred between days 7 to 15 approximately and with the second phase, it occurred between days 4 to 8, approximately. The average values of 585 mV for all tests, 25 mV lower than second phase and 10 mV higher compared to the first one.

The redox potential as a factor that determines the growth and metabolism of the culture, indicates its capacity to accept or donate electrons, that is, the oxidizing or reducing characteristics of the components of the environment or substrate determined, by the concentration of oxygen. These oxidant characteristics are those required by the bacteria acidithiobacillus, favoring their growth and the development of an oxidative (or

respiratory) metabolism.The redox potential indicates the oxygen relation of living microorganisms and can be used to specify the environment in which a microorganism is capable of generating energy and synthesizing new cells without resorting to molecular oxygen: aerobic microorganisms require positive redox values and negative anaerobes.

The wide oxidation states range (from -2 to +6) favors the appearance of a large variety of redox enzymes that allow them to oxidize different inorganic sulfur compounds. However, nowadays, it is not clear which of these enzymes and metabolic pathways that microorganisms are used to oxidize different sulfur compounds at different pHs or oxygen concentrations, either in natural environments or in bioreactors. The identification of these enzymes and routes would allow to optimize the conditions of the sulfooxidation reactions and to improve the bacterial catalytic activity to look for their application to industrial bioprocesses. The potential (Ev) measurement is the dissolution of the electron donor and, on the other hand, the electron receptor at varied concentrations of substrate, pH 1.8 and 22 ºC. Showing increasingly positive values due to the growing tendency to accept electrons with the consequent formation of sulfates. The study addressed allowed us to acquire knowledge and obtain results with a view to its application on a larger scale and its exploration in various industrial effluents containing cyanide remaining.

V CONCLUSIONS

The oxide reduction potential offers many advantages in real-time monitoring and recording of media potentials in bioprocesses. The simple ions and compound ions, together with the bacterial consortium transfer the coming electrons from the oxidation of inorganic matter to the acceptors of available electrons of a more oxidizing nature, allowing to obtain the highest energy gain range by the oxidation of the organic and inorganic substrate present, of which the necessary carbon and energy are provided for its evolution, typical of chemolithotropic organisms. The bacterial strains are adapted successfully in different media containing varying amounts of iron as sulfur and oxides, from quarries of high mineralization (presence of copper, lead, zinc, sulfur, silica, gold, silver and others). However, the qualitative and quantitative determination is still a matter of investigation according to the constitution of the substrate provided. The increase in the dissolution of As, Fe, S and other elements, in the second and third phase of bioleaching, show favorable biological oxidation and the consequent degradation of the mineral species. Favoring the release of valuable species such as gold and silver that are native. The generation of H^+ as H_2SO_4 managed to buffer the acidic medium at an average pH of 1.8 in all the tests, as well as a decrease at the end of said tests.

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