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THE USE OF OXYGEN INSTEAD OF AIR IN BIOLEACHING OPERATIONS AT MEDIUM TEMPERATURE

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ABSTRACT

The lack of adequate gas mass transfer is a potential rate limiting step in many bacterial leaching processes. Oxygen can become a limiting factor because of its low solubility compared to the high demand induced by sulfide oxidation. One way of increasing the solubility of oxygen in water or in media solution is by increasing the driving force, i.e. raising the oxygen partial pressure in the gas stream supplied to the leach pulp. The use of oxygen is a well-known practice in high-temperature bioleaching reactors (above 70°C) whereas air is usually preferred in medium and low-temperature operations, mainly for practical and economic reasons in classical CSTR bioleaching condition. Another reason associated with not using enriched oxygen gas is to avoid too high dissolved oxygen concentrations which could impact negatively the bacterial activity. The purpose of this study was to investigate the use of oxygen-enriched gas in bioleaching reactors at 40°C in order to improve the gas transfer in the system when operating at high solid load (20% and more). Bioleaching experiments were performed on a sulfide-rich tailing waste (pyrite 60%) using the "BRGM-KCC" bacterial consortia. The reactor used for the tests was designed on the basis of a new bioleaching reactor concept developed by Air Liquide, Milton Roy Mixing and the BRGM which uses a floating agitator to inject gases, and to mix and suspend solids in the bioleaching solution. Two types of tests were carried out: with air injection and with oxygen enriched gas mix injection. The aim of this work was to confirm the capacity of bacteria to grow and to dissolve pyrite in this type of bioreactors in oxygen-rich atmosphere, and to compare sulfides dissolution rates during the two types of bioleaching tests. The profitability of this new concept of bioreactor will rely on the optimisation of oxygen transfer. The results obtained show that the use of oxygen enriched gas mix does not negatively impact bioleaching performances compared to air injection. High metal extraction yields were achieved (above 80%). No deleterious effect due to oxygen use was observed on the bacteria despite the high level of dissolved oxygen reached in oxygen tests (up to 14 mg.L⁻¹). This result is very encouraging in the development of the new type of bioreactor where limited gas flows can be combined with high oxygen transfer rates and efficiency.

KEYWORDS

Bioleaching, gas transfer, oxygen, agitation, tailing waste, pyrite

INTRODUCTION

The countries of the European Union are heavily dependent on metal imports that play a central role in guaranteeing industrial and economic sustainability. A recent report of the European Commission also demonstrated that metal recycling from end of life products, even though absolutely necessary, would not be sufficient to cover the needs of the industry (EC, 2011). Therefore securing eco-efficient access to metals from primary mineral resources, combined with a minimum environmental footprint has become a critical economic, social and scientific challenge. In Europe, most of the primary resources that possess a high or moderate amount of metals, have a reasonable accessibility and are easy to process are exhausted. Therefore there is a need to identify new potential resources which could be used for the recovery of rare and/or valuable materials in order to face the needs in raw materials. In today's context of resource scarcity, two types of "deposits" deserve attention:

- "old waste deposits" related to past mining and metallurgical activities: they contain residual quantities of base and precious metals (Cu, Ni, Zn, Co, Au, Ag) as well as significant reserves of valuable metals (associated metals) which were not exploited in the past.
- complex low grade ores which were not considered as valuable and profitable deposits up to now: in Europe, primary resources still available for exploitation are more complex showing a complex mineralization (e.g. polymetallic and polymineral, carbon rich), or a low metal content; these complex deposits also have higher levels of toxic impurities such as arsenic, antimony and mercury, penalizing current pyrometallurgical technologies.

The exploitation of such resources would require improving the efficiency and the sustainability of current methods and developing innovative technologies to optimize the global recovery of metals, whether they are base metals (Cu, Ni, Zn, ...) or associated ones (Ag, Co, Ni, Ga, Au, PGE, etc) i.e. As existing processes and technologies are not profitable on unconventional resources, alternative routes still need to be developed to address the complexity of composition while remaining cost effective.

In this context, bio-hydrometallurgy appears more and more as an ecologically acceptable and yet economic alternative for processing of low-grade ores as well as old mining wastes that can contain significant reserves of valuable metals. Biohydrometallurgy is well established for the treatment of certain sulphide minerals, where iron and sulphur-oxidising bacteria are used for the leaching of low grade copper ores and the pretreatment of pyritic gold ores and concentrates. Even though heap, dump and in-situ bacterial leaching of sulphide minerals are well established and the bacterial treatment of refractory gold concentrate using Stirred Tank Reactors (STR) is an industrial reality, the European mineral industry is still sceptical and reluctant to adopt biohydrometallurgical techniques. Heap leaching is often considered as unadapted due to space constraints, slow leaching kinetics and low recovery rate. The interest of using STR for the treatment of other minerals than refractory gold ores, such as the base metal sulphides, has already been demonstrated but some improvements are still needed to meet economic viability (D'Hugues *et al.*, 2008; Spolaore *et al.*, 2009). The main costs of bioleaching operations in STR are the costs of the leaching tanks and the costs of gaseous mass transfer to the leach pulp (these costs include the capital costs associated to agitators and gas injection devices, and the operating costs associated to energy consumption required for slurry agitation and air compression, since air is usually used to provide oxygen in bioleaching operations).

Air Liquide, Milton Roy Mixing and the BRGM (French geological survey) developed an innovative bioleaching process using floating agitators to mix and to suspend solids in the solution as well as to inject gases in the pulp. This new concept enables to decrease the costs of bioleaching processes by operating:

- in lagoons or ponds instead of using costly tanks,
- at higher solid loading (>20%) than in conventional stirred tank bioreactors.

In these conditions of high solid load, the microbial and chemical demand for oxygen is significantly increased and air could be replaced by oxygen enriched gas to provide an adequate oxygen supply in order to satisfy the oxygen demand. However the use of such conditions can lead to much higher

dissolved oxygen (DO) concentrations than those encountered with air sparging. Very few papers have been devoted to the study of the optimal range of DO concentrations for bioleaching processes. However most of them reported an inhibitory effect of DO concentrations above 5 mg L⁻¹ (de Kock *et al.*, 2003; Wang *et al.*, 2015).

The purpose of this study was to investigate the use of a floating agitator injecting oxygen-enriched air in bioleaching reactors at medium temperature (40°C) with moderately thermophilic bacteria. Bioleaching experiments were performed in batch mode on sulfide-rich tailings wastes using the “BRGM-KCC” bacterial consortia. Two types of tests were carried out: with air injection and with oxygen-enriched air injection. The aim of this work was to confirm the capacity of bacteria to grow and to dissolve pyrite in oxygen-rich atmosphere and to compare sulfides dissolution rates during both types of bioleaching tests. The detailed objectives of the tests were as follow: (i) to test the ability of this device to suspend the pyrite particles and to form a homogeneous slurry, (ii) to study bacterial activity under high speed agitation, (iii) to study the influence of the oxygen enrichment in the injected gas on the bacterial activity and (iv) to quantify metal extraction potential under these unconventional conditions.

MATERIALS AND METHODS

Characterization of the sulphidic materials

The experiments were performed using flotation tailings coming from a European copper mine whose mineral of economic interest in the ore body is chalcopyrite (CuFeS₂). At site, the ore is ground and valuable chalcopyrite is then separated from pyrite by flotation. Copper contained in the chalcopyrite is recovered by smelting whereas pyrite is discharged in tailings, from which the material used in this study was sampled. The tailings are mainly composed of pyrite (50%), and they contain cobalt (550 ppm), Cu (980 ppm) and gold (1 ppm). This waste has been chosen as test materials for its high content of pyrite, which makes it particularly suitable for bioleaching.

Bacterial culture and nutrients

The experiments were run using the BRGM-KCC microbial consortium, which has already been fully described (d'Hugues *et al.*, 2003). The predominant organisms in the culture are affiliated to the genera *Leptospirillum*, *Acidithiobacillus* and *Sulfobacillus*. The culture used as an inoculum originated from BRGM stock culture, stored at -80 °C. The culture was subcultured several times in batch mode from 2 mL up to 120 L prior to the beginning of the batch feed. The culture was grown in a nutrient medium called “0Km”. This medium is a modified “9K” medium (9K without iron, “m” indicating modification of the basal salts) which was optimised for bacterial growth on cobaltiferous pyrites. Its standard composition is the following: (NH₄)₂SO₄, 3.70 g L⁻¹; H₃PO₄, 0.80 g L⁻¹; MgSO₄•7H₂O, 0.52 g L⁻¹; KOH, 0.48 g L⁻¹.

Laboratory apparatus

The bioleaching tests were carried out in batch mode in a 2 m³ stainless tank (working volume: 1.2 m³), thermostated by means of a water jacket maintained at the desired temperature (40°C) with a cryothermostat. The agitation was performed using a small floating agitation device built on the model of TurboxAL agitators designed by MRM and Air Liquide for water treatment applications. The dimensions of the industrial agitator were divided by four for the purpose of the study (diameter: 750mm, height: 850 mm). The agitator performs pulp mixing together with gas injection. Figure 1 shows a schematic view of the whole experimental setup (tank and agitator).

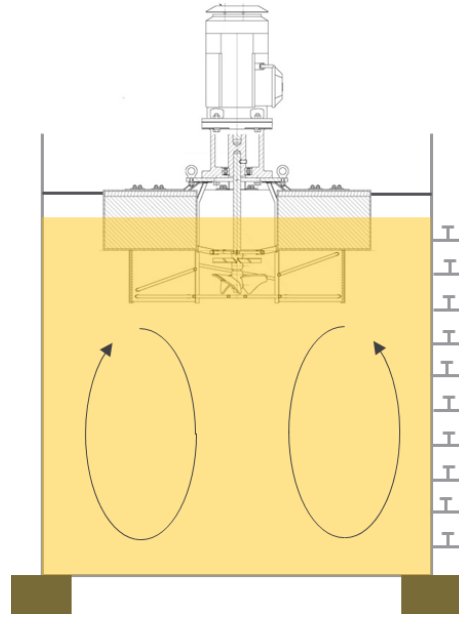


Figure 1 – Schematic view of the experimental setup used for the bioleaching tests (tank & mini floating agitator)

Operating conditions

The reactor was inoculated by adding a volume of the KCC culture corresponding to 10% of the total volume of slurry. The agitation speed was set to 1282 rpm. The operating conditions corresponding to each batch test are summarized in the table below. Four tests were performed at 20% (w/w) solid load. The last test was carried out at 30% solid load. The oxygen partial pressure in the injected gas was increased from one test to another. The gas contains also 1% CO₂ in order to supply the carbon required for the bacterial growth. Generally bioleaching tests in batch STRs can be divided into 3 phases: a lag phase corresponding to the bacterial growth and the biomass production where the demand in oxygen is low, an active phase where the bacterial activity is high and the demand in oxygen increases and a latent phase where the bacterial activity decreases due to a lack of substrate. To maintain a rather constant DO concentration throughout each test the gas flow rate was increased progressively during the lag phase up to the maximum gas flow rate indicated in Table 1. The gas flow rate was then maintained constant during the active phase and then decreased again when the bacterial activity decreased at the end of the test. The mean DO concentrations reached in the bioreactor are reported in Table 1.

Table 1 – Main operating conditions of the tests

	Test 0	Test 1	Test 2	Test 3	Test 4
<i>Solid load</i>	20%	20%	20%	20%	30%
<i>O₂ partial pressure</i>	air	30%	50%	70%	70%
<i>Maximum gas flow rate (m³/h)</i>	6	2	1,2	0,9	0,9
<i>Mean dissolved oxygen concentration (ppm)</i>	2	4	8	14	14

Reactor monitoring

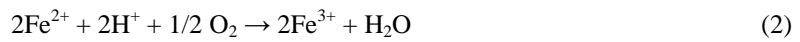
The bioreactor was monitored daily for temperature, pH level, redox potential, dissolved O₂. Cobalt and total iron concentrations were measured by atomic absorption spectroscopy (Varian SpectraAA-300) in the supernatant fraction from 0.45 µm filtered culture samples. Bacterial cells were counted

regularly in slurry samples. The leach residue was collected at the end of each batch test and analyzed for cobalt, iron, elemental sulphur, sulphide and sulphate. These data were used further for the calculation of mass balance and metal extraction.

RESULTS AND DISCUSSION

pH and redox potential

The evolution of pH (Figure 2) displays the same trend as the one observed in traditional bioleaching batch test: pH decreased from 2 and stabilized between 0.8 and 1 after a couple of days. The decrease of pH in the bioreactor is linked to pyrite oxidation which leads to the formation of sulphuric acid according to the following chemical reactions:



The reactions (2) and (3) are biologically catalysed by acidophilic Fe- and S-oxidizing bacteria, whereas the reaction (1) occurs through chemical oxidation. Bacterial activity being optimal for a pH above 0.8, pH is controlled by adding calcium carbonate to neutralize the excess acidity. It must be noticed that in the batch test 3 pH decrease was slowed down after 2 days because of an agitator failure. The bacterial activity was thus delayed due to the lack of agitation. In test 4 the lag period is a little higher than in the other tests (2 days vs. 1 day respectively) but the profile of the pH decrease is the same.

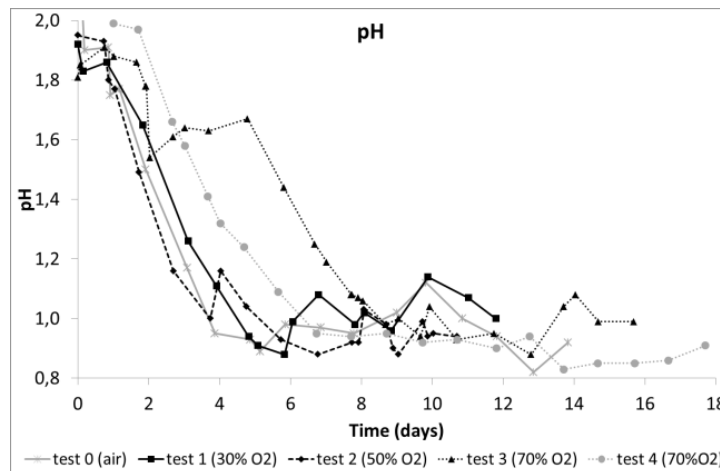


Figure 2 – pH profiles of the leach solutions, effect of O₂ partial pressure

The decrease of pH is followed by an increase of bacteria concentration (from $8.0 \cdot 10^8$ to $4.0 \cdot 10^{10}$ bacteria/mL, data not shown). In parallel the redox potential (Eh) of the leach solution was rapidly increased from 680 to 900 mV (SHE, data not shown). In bioleaching solutions the redox potential is driven by the couple FeII/FeIII. Ferrous iron is released by the oxidation of pyrite (Equation 1) whereas FeIII is used as an oxidising agent in this reaction. FeIII is constantly “recycled” in the leaching solution through the catalytic activity of the bacteria (equation 2). The value of Eh reached in the solution (up to 900 mV) shows that most of the iron in the solution is under the form of FeIII, which indicates a good biological oxidising activity. This result is confirmed by the analysis of FeII in the leaching solution by colorimetric titration (detection limit ~ 10 mg/L): at the beginning of the bioleaching tests [FeII] is comprised between 1500 and 2000 mg L⁻¹ whereas at the end of the lag period (1 to 4 days, depending on the course of the tests) FeII is no more detected.

The composition of the gas injected in the reactor and the DO concentration did not show any obvious impact on the redox and pH profiles of the leaching solutions which remain similar for the different conditions tested. The only difference appears in test 5 where the pH decrease is delayed compared to the other tests. This may be explained by the higher solid load (30% vs 20% for the other tests). A longer lag phase is then probably required to enable the adaptation of the bacteria to these unusual operating conditions.

Metal solubilization

The solution potential increase is mirrored by an increase in Fe and Co in solution (see figure 3). Co being hosted in the crystal lattice of pyrite, the release of this element in the solution is a good indicator of the pyrite oxidation kinetics. The activity phase lasts between 5 and 6 days in the tests carried out at 20% solid load. In test 5 where the solid load was increased from 20% to 30% the activity phase is longer (around 11 days) but the amount of substrate for bacterial activity (namely FeII coming from pyrite) is also much higher.

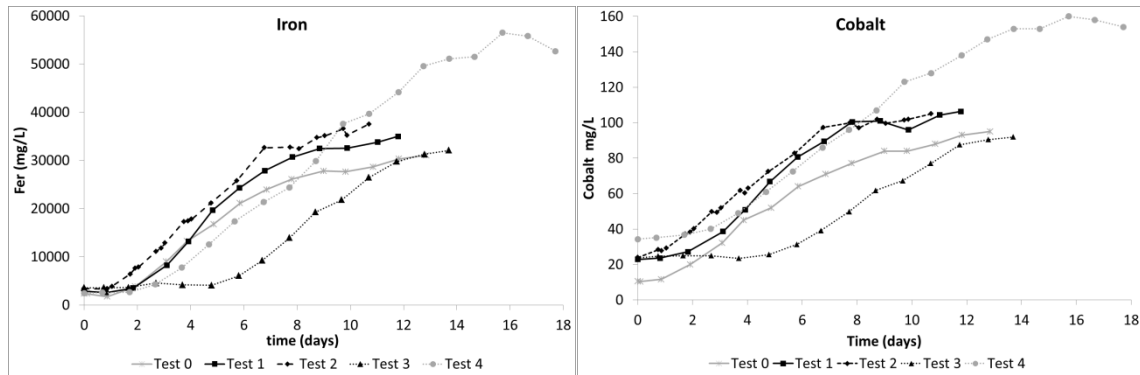


Figure 3 – Fe and Co release in the bioleaching batch tests

The leaching rate (corresponding to the rate of Co release in the solution during the active phase) is reported in Table 2. Due to the lack of precision of this calculation it can be considered that the leaching kinetics is rather the same in the five trials.

Table 2 – Leaching rate corresponding to the rate of Co released in the solution during the steady-state active phase

	Test 0	Test 1	Test 2	Test 3	Test 4
<i>Leaching rate (mgCo/L/d)</i>	9 (± 1)	13 (± 1)	12 (± 1)	11 (± 1)	12 (± 1)

Final metal extractions and sulphides dissolution yields (obtained from the analysis of the residue and from the metal content of the solution at the end of the batch test) are shown in figure 4. All the bioleaching trials exhibit high sulphide dissolution yields (between 80 and 97%), which confirms the good oxidising activity already noticed in the previous section. It must be noted that iron release is consistently underestimated because of the addition of calcium carbonate for pH control, which leads to the precipitation of dissolved iron as jarosite. Like for pH and redox profiles the composition of the gas injected in the reactor or the DO concentration in the leaching solution do not influence the leaching efficiency (kinetics and sulphides dissolution yields).

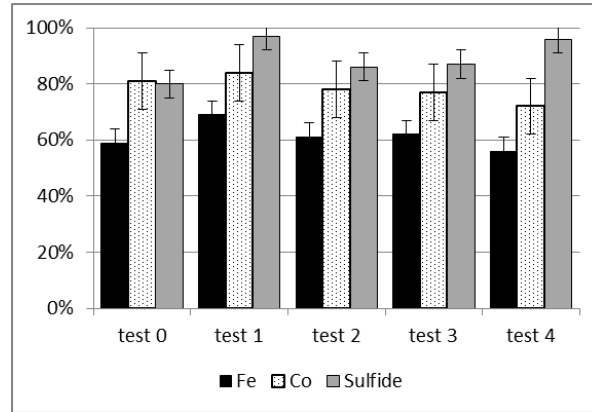


Figure 4 – Fe, Co and sulfides leaching yields

Particle suspension

In bioleaching reactors complete particle suspension is generally looked for to achieve good bioreactor homogeneity and to maximize the liquid-solid interfacial area for optimal bacterial activity and sulphides conversion. To assess the mixing quality and the homogeneity of the pulp in the bioreactor used for this study sampling were performed at three different depths in the reactor. The pulp samples were filtered to separate the liquid and the solid phase and the subsamples were characterised for pulp and liquid density, solid load and dissolved metal contents. As can be seen in Table 3 which gathers the sampling data corresponding to test 1 the characteristics of the pulp are the same at any depths in the reactor, which shows that the mixing of the pulp achieved by the floating agitator is adequate and enables to obtain a good homogeneity of the suspension.

Table 3 –Characteristics of the pulp sampled at three different depths in the bioreactor at the end of bioleaching test 1

	D1	D2	D3
<i>Pulp density</i>	1,20	1,20	1,20
<i>Leach solution density</i>	1,06	1,06	1,06
<i>Leach solution/pulp (w/w)</i>	75,8%	74,9%	75,5%
<i>Solid load (w/w)</i>	14,4%	14,2%	14,6%
Fe^{liq} (ppm)	31410	31510	32630
Cu^{liq} (ppm)	223	228	229
Co^{liq} (ppm)	95	96	93

CONCLUSION

The results of the bioleaching tests reported in this paper showed promising results and demonstrated that a new type of bioreactor could be developed to perform bioleaching operations using floating agitation devices. They show that high metal extraction can be achieved using moderate thermophile bacteria in intensely agitated reactor sparged with oxygen-enriched air. Good microbial activity has been observed despite the high speed agitation and the high solids loading (from 20% to 30%). In contrary to what is reported in the literature the increase of DO concentration (from 2 to 14 ppm) linked to the oxygen enrichment of the gas injected in the leaching solution had no noticeable impact on the microbial activity neither on the leaching efficiency in terms of leaching rates and sulfide dissolution yields. The use of oxygen-enriched air appears as a good solution to improve gas-liquid mass transfer and to provide an adequate oxygen supply in order to satisfy the high oxygen demand induced by the high solid load.

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