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Anne-Gwenaëlle Guezennec, Marie Delclaud, Frederic Savreux, Jérome Jacob, Patrick d'Hugues

THE USE OF BIOLEACHING METHODS FOR THE RECOVERY OF METALS CONTAINED IN SULPHIDIC MINING WASTES

*A.G. Guézennec[1], M. Delclaud[2], F. Savreux[3], J. Jacob[1], P. d'Hugues[1]

[1]BRGM
3 av. C. Guillemin, BP.36009
45060, Orléans, France
*(*Corresponding author: a.guezennec@brgm.fr)*

[2]Air Liquide, CRCD
1 chemin de la porte des Loges, BP 126
78354 Jouy en Josas, France

[3]Milton Roy Mixing
10 rue du Bois Gasseau
77210 Samoreau, France

ABSTRACT

Mining wastes can contain base and precious metals, but also metalloids and rare earth elements that are nowadays considered as highly critical for the industrial development of the European Union. The development of alternative routes to conventional processing is still required in order to decrease the cost associated with the treatment of these resources, which are more complex in composition and with lower grades. An ecologically acceptable and yet economic alternative for processing of low-grade sulphidic primary ores as well as mining wastes is the extraction of metals using bioleaching processes. The purpose of this study was to test the potential of bioleaching procedures for the extraction of residual metals contained in sulphide-rich tailing wastes coming from a European copper mine. These wastes are mainly composed of pyrite (60%) and contain cobalt (0.06 %) and gold (0.95 g/t). Bioleaching experiments were performed in 2 L stirred reactors in batch mode and in pilot tanks (110L) in continuous mode, using the "BRGM-KCC" bacterial consortia. High metal extractions were obtained (cobalt dissolution > 90%), which confirm that bioleaching is an effective process for this tailings material. Experimental results were used to design a global treatment process scheme and to perform a preliminary economic evaluation, showing good profitability of a hypothetical industrial project.

KEYWORDS

Bioleaching, mining waste, floating agitator, low grade ore

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 EU industry (EC, 2011). For several years securing eco-efficient access to metals from primary mineral resources, combined with a minimum environmental footprint has thus 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. In this context, old waste deposits related to past mining activities are being investigated as potential significant reserves of valuable metals. The mining wastes can contain base and precious metals, but also metalloids and rare earth elements that are nowadays considered as highly critical for the industrial development of the European Union. Nevertheless, the development of alternative routes to traditional processing is still required in order to decrease the cost associated with the treatment of these unconventional resources, which are more complex in composition and with lower grades.

An ecologically acceptable and yet economic alternative for processing of sulphidic mining wastes is the extraction of metals using microorganisms. This procedure is called biomining and is based on biohydrometallurgy. It uses the metabolic activity of lithotrophic microorganisms which draw their energy from the oxidation of iron and/or reduced inorganic sulphur compounds, producing sulphuric acid and ferric iron. The result is a highly corrosive "bioleaching" solution that dissolves the sulphide minerals by oxidation, releasing the metals to solution. Progress in the engineering design of leaching plants and the management of bioleaching operations resulted in a worldwide spreading of this technology. Biohydrometallurgical techniques are increasingly implemented in the mining industry for processing of low-grade sulphidic ores. Nowadays the production of copper from low-grade ores is the most important industrial application and a significant part of the world copper production already originates from heap or dump/stockpile bioleaching (Dreisinger, 2006; Watling, 2006). Besides copper production, biohydrometallurgy is also used to produce gold, cobalt, nickel, zinc and uranium (Arrascue and van Niekerk, 2006; Van Aswegen *et al.*, 2007; Morin and d'Hugues, 2007).

Two types of bioleaching processes exist: bioleaching in stirred tank reactors (STR), which is dedicated to high-grade ores due to the relatively high costs of investments, and heap leaching, which is dedicated to low-grade ores. None of these technologies can be applied for the re-processing of tailings which requires the development of novel approaches to meet economic viability.

The purpose of this study was to develop an innovative bioreactor as an in-between pathway for bioleaching. This new concept consists in using floating agitators to inject gases, to mix and to suspend solids in the solution. The use of such floating agitators for bioleaching should enable the operation of bioleaching operations:

- at higher solid loading (> 15%) than in conventional stirred tank bioreactors,
- in lagoons or ponds instead of using costly tanks.

The waste materials chosen for this study come from sulphide-rich tailings of a European copper mine. They are mainly composed of pyrite (60%) and contain cobalt (0.06 %) and gold (0.95 g/t). Preliminary classical tests were performed to assess the amenability of such wastes to bioleaching. In a second step, experimental bioleaching tests were handled using a mini pilot agitator (scale ¼) designed from the innovative and unique floating agitation system (Turboxal 3) co-developed by Milton Roy Mixing (agitation system provider) and Air Liquide (Gas Provider) for waste water treatment applications. Experimental results were used to design a global treatment process scheme and to perform a preliminary CAPEX evaluation.

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 ($CuFeS_2$). 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 (60%), and they contain cobalt (0.06 %), Cu (0.19%) and gold (1 g/t). 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 (Battaglia, Morin, & Ollivier, 1994; 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 100 L prior to the beginning of the batch feed. The culture was grown in a nutrient medium called "0Km". This is a modified "9K" medium (9K without iron, "m" indicating modification of the basal salts) and it was optimised for bacterial growth on cobaltiferous pyrites. Its standard composition is the following: $(NH_4)_2SO_4$, 3.70 g L^{-1}; H_3PO_4, 0.80 g L^{-1}; $MgSO_4 \cdot 7H_2O$, 0.52 g L^{-1}; KOH, 0.48 g L^{-1}.

Laboratory apparatus

In a first step, the amenability of the sulphidic waste to bioleaching was tested in batch mode using 2 L laboratory scale glass reactors thermostated at 40 °C. Tests were carried out at 10% (w/w) pulp density and the inoculation was performed by adding 200 mL of the KCC culture in each reactor. The reactors were fully baffled; the agitation was performed using a dual impeller system consisting of a standard 6-blade flat-blade Rushton turbine in combination with a 6-blade 45° axial flow impeller. The impeller speed was set at 400 rpm. Air (120 L h^{-1}) enriched with CO2 (1%) was injected beneath the impeller at the bottom of the reactor via a stainless-steel pipe.

In a second step, a bioleaching batch test was carried out in a 2 m^3 stainless tank, 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 agitation speed was set to 1282 rpm. The test was carried out at 20% (w/w) pulp density and the inoculation was performed by adding a volume of the KCC culture corresponding to 10% of the total volume of slurry. The gas (air enriched with CO2 (1%)) was supplied directly by the floating agitator at a rate of 6 m^3/h.

Reactor monitoring

Both types of reactors were monitored daily for temperature, pH level, redox potential, dissolved O_2 (Mettler Toledo probe InPro 6850i). Copper, cobalt and total iron concentrations were measured by atomic absorption spectroscopy (Varian SpectrAA-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, copper, iron, elemental sulphur, sulphide and sulphate. These data were used further for the calculation of mass balance and metal extraction.

RESULTS AND DISCUSSION

Bioleaching amenability experiments in 2L reactors

The purpose of the batch tests performed in 2 L-reactors was to determine if the mining sulphidic waste used in this study was amenable to bioleaching using the KCC-BRGM acidophilic and moderate thermophilic consortium (40 °C).

Figure **1**a shows the solution potential (SHE) and pH profiles during the bioleaching experiments. The pH sharply decreased from 2.2 and then stabilized around 0.9 after 6 days. In the meantime, the potential increased from 700 mV and then stabilized around 900 mV. This decrease was followed by an increase in the concentration of Co and Fe in solution (Figure 1b). Final extractions of 97.8% Co and 83.2% Fe were achieved. According to the residue analysis, 97% of the sulphides were oxidized which indicates that most of the pyrite and chalcopyrite contained in the waste were leached. The difference between Fe extraction and sulphide rate of leaching is probably due to Fe precipitation as jarosite. Based on these promising results at 10% solids, bioprocessing using the floating agitation device was tested.

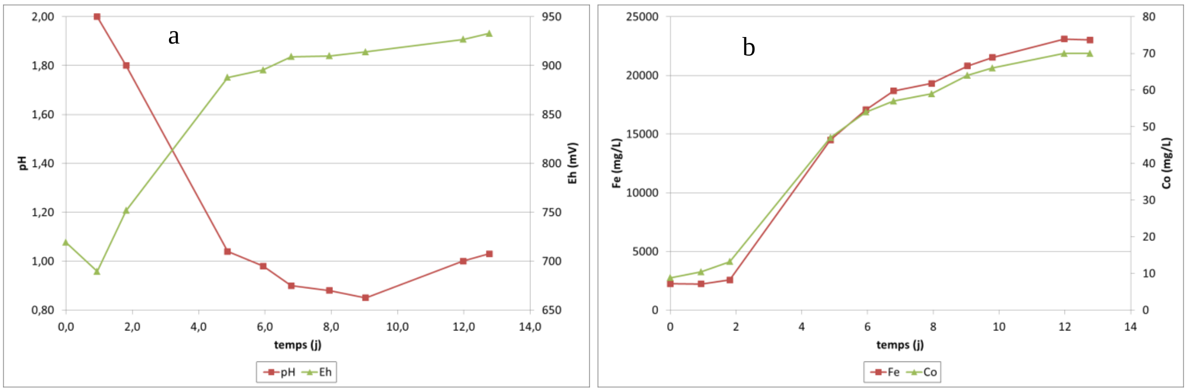

Figure 1 – (a) Evolution of the pH and Eh levels and (b) evolution of dissolved Fe and Co content with time during 2L batch tests

Bioleaching tests using the floating agitation device

The purpose of the second type of bioleaching batch tests using the mini floating agitator was (i) to test the ability of this device to suspend the pyrite particles and to form a homogeneous slurry, (ii) to study bacteria behaviour under high speed agitation and (iii) to evaluate metal extraction potential. The evolution of pH (Figure 2a) displays the same trend as that observed in traditional bioleaching batch test (see Figure 1a): pH decreased from 2.3 and stabilized around 0.9 after 4 days. The decrease of pH is linked to pyrite oxidation which leads to the formation of sulphuric acid. Bacterial activity being optimal for a pH above 0.8, pH is controlled by adding calcium carbonate to neutralize the excess acidity. In Figure 2b, it can be seen that the decrease of pH is followed by an increase of the potential of the solution as well as an increase of bacteria concentration (from 2.6 10^9 to 3.4 10^{10} bacteria/mL). 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.

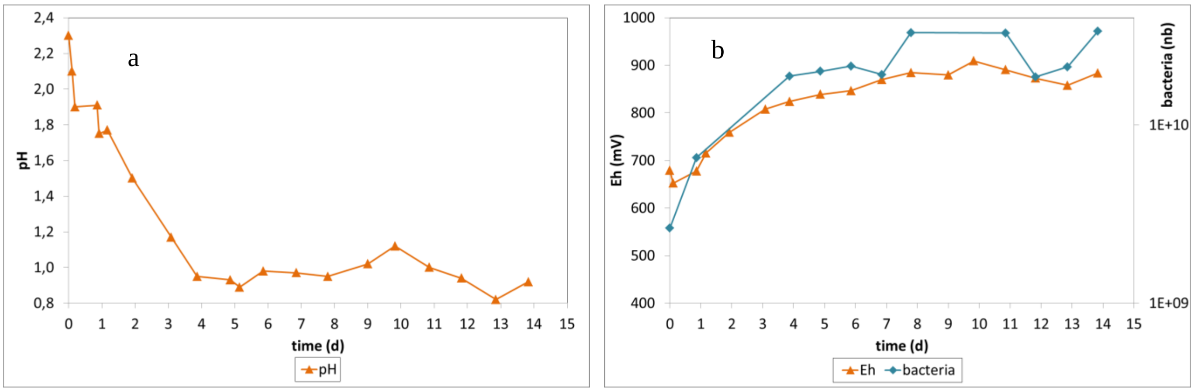

Figure 2 – (a) pH and (b) Eh and bacteria number (nb/mL) evolution with time during bioleaching tests with the floating agitator

The solution potential increase is mirrored by an increase in Fe, Cu and Co in solution (Figure 3a). Final metal extractions (obtained from the analysis of the residue and from the metal content of the solution at the end of the batch test) of 63% Fe, 76% Cu and 96% Co were achieved (Figure 3b). 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. Copper extraction is probably limited due to the incomplete dissolution of chalcopyrite. This well-known phenomenon has been addressed in numerous papers and is explained by the passivation of chalcopyrite at low operating temperatures (Stott, Watling, Franzmann, & Sutton, 2000; Parker, Klauber, Kougianus, Watling, & van Bronswijk, 2003; Sandstrom, Shchukarev, & Paul, 2005; Klauber, 2008). This batch test confirms that high Co extraction could be obtained at a solid concentration of 20% in an intensively agitated reactor without any apparent inhibitory effects or damage to the bacteria cells. The kinetics of the reaction remain however quite slow at that stage (1 day of lag phase + 7 days to reach a stable Co content). This point is the subject of ongoing research and development at the BRGM which involves a study for the improvement of gas transfer (O_2 and CO_2) as well as bioleaching tests in continuous mode to optimise and reduce the residence time.

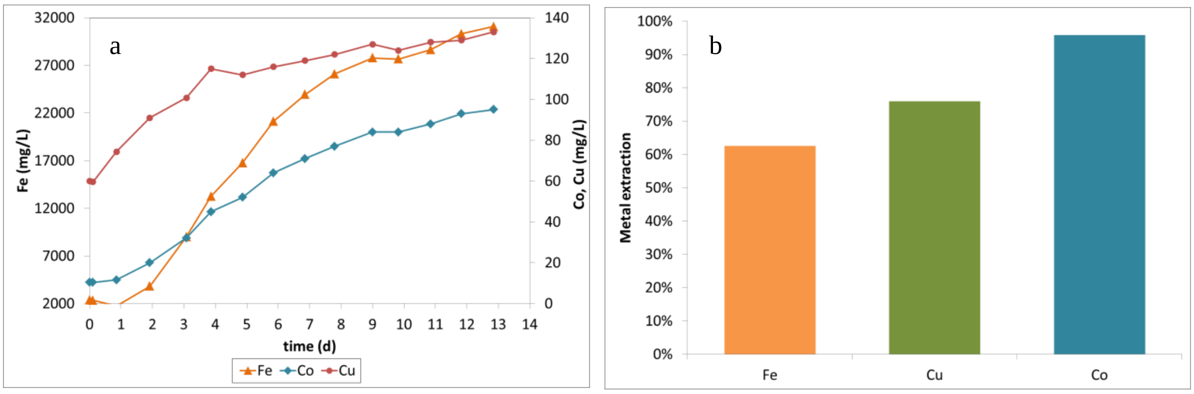

Figure 3 – (a) evolution of dissolved Fe, Cu and Co content with time during bioleaching tests with the floating agitator; (b) metal extraction rate reached at the end of this test

PRELIMINARY ECONOMIC EVALUATION: CAPEX CALCULATION

Experimental results were used to design a global treatment process scheme as shown in Figure 4. Major equipment items were sized based on mass balance and design specifications.

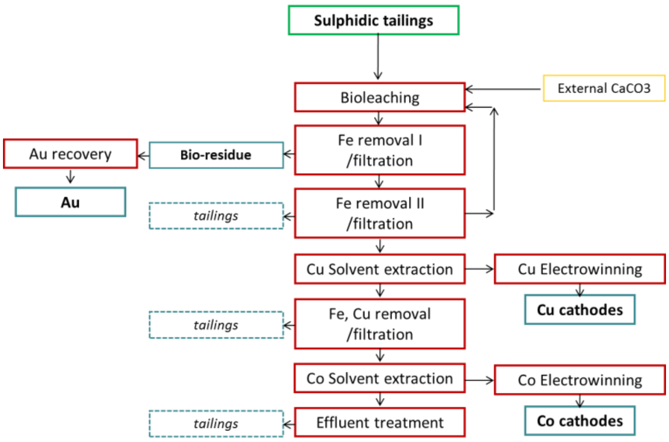

Figure 4 – Global treatment scheme for Co and Cu recovery in sulphide-rich tailings using bioleaching technology

From this process flowsheet, a preliminary evaluation of the investment costs was performed comparing classical bioleaching in stirred tank reactors (STR) to the use of floating agitators operating in lagoons. For the first case, sizing of the equipment was done on the basis of a feed solid content of 20% which is rather high for such an operation (usually 15%). For the latter case, two values of solid load were considered: 20% which corresponds to the one used in the test presented above and 30% which is currently being tested at the BRGM.

Compared to STR, the use of floating agitators at 20% solids leads to a decrease of 39% of the CAPEX. When the solid load is brought to 30%, the CAPEX decreases by 53% compared to STR. This can be explained by the costs of stainless steel reactors used in STR compared to the costs of lagoons used for bioleaching with floating agitator which are much cheaper. This is confirmed by the capital costs breakdown for the three options (see Figure 5): the investment costs required for the bioleaching step of the process are consistently higher for the STR. With floating agitation device, the investment costs for the bioleaching step decrease when the solid load increases.

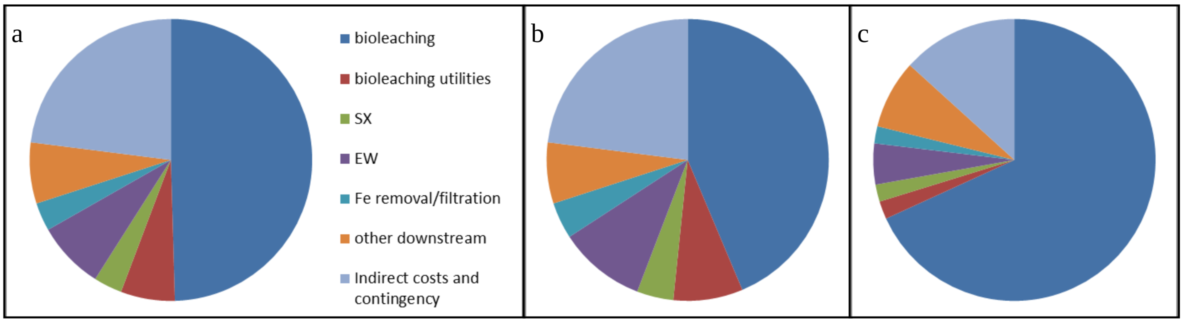

Figure 5 – CAPEX distribution for several technological options for sulphidic waste bio-reprocessing: (a) floating agitators at 20% solid load, (b) floating agitators at 30% solid load, (3) STR at 20% solid load

CONCLUSIONS

The results of the batch tests reported in this paper provide encouragement 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 reactors. Good microbial activity has been observed despite the high speed agitation and the high solids loading (20%, compared to 15% traditionally employed for bioleaching in STR). The basic calculation of the CAPEX performed from the experimental results confirms that a significant decrease of the investment costs might be obtained by implementing the floating agitation technology for bio-reprocessing of mining wastes. This study has also enabled the identification of questions that will need to be addressed further. The main one being strategies to improve the leaching kinetics, which is currently under examination at the BRGM where theoretical studies are performed to improve gas transfer (O_2 and CO_2). Bioleaching tests in continuous mode are also being pursued to optimize and reduce the residence time in the reactor.

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