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Non-traditional operating conditions for a copper concentrate continuous bioleaching

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ABSTRACT

The Polish copper concentrate subject of this study is produced by flotation from a black shale organic rich ore. Due to ore specific properties, flotation indexes have always been poor in the Polish concentrator. Moreover, in the last 5-6 years, ore characteristics dramatically changed and the concentrate grades (mostly Cu and As) degraded. As a consequence, research on alternative technologies to pyrometallurgy is necessary.

Bioleaching efficiency was already demonstrated during the Bioshale FP6 European project. However, some improvements were still needed to be achieved in order to meet process economic viability. In the frame of Promine FP7 European project, our study aimed at improving the profitability of the continuous bioleaching of the copper concentrate in stirred tank reactors. Non traditional operating conditions were tested: high solids concentration (> 20% solids), reduced agitation and aeration rates. The follow-up of the experiment consisted in both physical parameters measurements (pH, Eh, oxygen uptake rates...) but also in the monitoring of the bacterial population using molecular biology techniques.

Keywords: Sulphide ore, bioleaching, ore mineralogy

INTRODUCTION

There are nowadays two principal production paths to treat copper ores. Smelting, converting and electrorefining has dominated the copper industry since the 1800s and represents 80% of the copper production. The other 20% are produced via hydrometallurgy (Schüller *et al* (2008); Dreisinger (2006); Watling (2006)). Research is going on to develop alternative routes to conventional processing as there is a need to exploit more diverse resources, more complex in composition and with lower grades. The dissolution of chalcopyrite must also be addressed as it is a real challenge.

Biohydrometallurgy is a proven technology already industrially applied all over the world for the exploitation of refractory gold ores and in one case for cobaltiferous pyrite (Arrascue and van Niekerk (2006); Morin and d'Hugues (2007)). However, it remains a niche application which can compete with other pyrometallurgical or hydrometallurgical technologies only for specific resources. The economy can be one advantage of biohydrometallurgical process and is also one of the most important drivers for the industry. Another advantage is the low environmental impact, sulphur dioxide and arsenic emission to air occurring during smelting being completely avoided (Brierley and Brierley (2001); Rawlings *et al* (2003)).

Promine project, "Nano-particle products from new mineral resources in Europe" is a FP7 European project that aims at enhancing the efficiency of the overall European production chain putting higher quality and added value products on the market (<http://promine.gtk.fi/>). A part of Promine research

focuses on the demonstration of the reliability of new (bio)technologies for an ecoefficient production of strategic metals.

One of the Promine case studies is a Polish concentrate originating from a black shale ore. This resource is a carbonate-rich, multi-element (Cu, Ag) and polymineral concentrate containing chalcopyrite. Due to ore specific properties, flotation indexes have always been poor in the Polish concentrator. Moreover, in the last 5-6 years, ore characteristics dramatically changed and the concentrate grades (mostly Cu and As) degraded. This is to the detriment of the economy of the pyrometallurgical process currently applied and has pushed the research work on a possible alternative technology. Bioleaching demonstrated to be a viable option during the Bioshale project but to meet economic interest, improvements are still to be made (Spolaore *et al* (2009)).

The aim of our study was to improve the profitability of the continuous bioleaching of the copper concentrate in stirred tank reactors. Non traditional operating conditions were tested: high solids concentration (> 20% solids), reduced agitation and aeration rates. The follow-up of the experiment consisted in both physical parameters measurements (pH, Eh, oxygen uptake rates...) but also in the monitoring of the bacterial population using molecular biology techniques.

MATERIALS & METHODS

Bacterial inoculum

The Bioshale-BRGM bacterial consortium has already been fully described (Spolaore *et al* (2009)). The predominant organisms in the culture were affiliated to the genera *Leptospirillum*, *Acidithiobacillus* and *Sulfobacillus*.

The inoculum used to start the continuous bioleaching operation was prepared in two stages. The Bioshale-BRGM consortium was first subcultured several times at 42°C in batch mode on 10% copper concentrate (wt v⁻¹). Then, a 15% solids batch culture was conducted in the first reactor of the unit (R1, 50 L). When the bacteria entered the exponential growth phase, continuous feed started.

Copper concentrate

The copper concentrate was produced from a black shale ore in a Polish concentrator. The main characteristics of the sample were as follows: Cu 14.6%, Ag 900 mg/kg, Fe 7.5%, sulphur as sulphide 15.9%, inorganic C 1.9% and organic C 8.2%, particle size (cumulative passing 80%) 60 µm. Copper sulphides in the concentrate mainly consisted of bornite (Cu₅FeS₄), chalcocite (Cu₂S), chalcopyrite (CuFeS₂) and covellite (CuS).

Nutritive medium

The nutrient medium was derived from the 0Km medium (Battaglia *et al* (1994)). Following the Bioshale project, it was demonstrated that a dilution of the 0km medium by a factor 3 did not affect bioleaching performances. For economic reasons, the 0km/3 medium was used in this study. Its standard

composition was the following: $(\text{NH}_4)_2\text{SO}_4$, 1.23 g.L⁻¹; H_3PO_4 , 0.27 g L⁻¹; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.17 g L⁻¹; KOH, 0.16 g L⁻¹.

Laboratory-scale continuous operation

The continuous bioleaching operation was carried out in a laboratory-scale unit equipped with three stirred reactors, one of 50 L (R1) followed by two of 20 L operating capacity (R2, R3). The tanks were all made from 316-L stainless-steel and had a height/diameter ratio equal to 1. The reactors were arranged in cascade so that the pulp passes from one tank to the next one by overflowing. CO₂-enriched air (1%) was injected beneath the turbine at the bottom of the tank. The top of the reactors were connected to a condenser system to prevent excessive evaporation. The same mixing system (BROGIM® - BRGM/MRM) was mounted in all tanks on a rotating shaft.

The feed was made up of a high density pulp of concentrate flow (50% wt wt⁻¹ in water), a concentrated nutritive medium flow and a H₂SO₄ (20% v v⁻¹) flow. The three feed flows were pumped separately into the first tank to obtain the desired solids ratio for the feed pulp (20% or 25%) and a pH below 1.8.

Temperature was maintained constant at 42°C by circulating cold water through an internal stainless-steel coil for cooling and by an external electric ribbon for heating. When necessary, the pH was regulated in the second tank of the unit (R2) between 1.5 and 1.7 by adding H₂SO₄ (20% v v⁻¹) in the pulp. pH regulation was not necessary in the last tank. The main operating conditions in the pilot are presented in Table 1.

Table 1 Main operating conditions of the continuous bioleaching unit. Comparison with best operating conditions applied during the Bioshale project.

Configuration	Solid concentration (%)	Tank	Residence time (days)	Agitation rate (rpm)	Aeration rate (L h ⁻¹)
1	20	R1	2.5	450	800
		R2	1.3	420	400
		R3	1.3	420	400
2	20	R1	2.4	340	100
		R2	1.1	420	400
		R3	1.1	420	400
3	25	R1	2.4	340	100
		R2	1.1	300	50
		R3	1.1	300	50
Bioshale	15	R1	2.1	390	500
		R2	2.2	250	100
		R3	2.3	250	100

Analytical techniques

Redox potential (vs. Ag/AgCl), pH and dissolved oxygen concentration (Mettler Toledo probe InPro 6850i) were measured directly in the pulp. Copper and total iron concentrations were measured by atomic absorption spectroscopy (Varian SpectrAA-300) in the supernatant fraction from 0.45 µm filtered culture samples.

The oxygen concentration in the inlet and outlet gas of each reactor was measured using a paramagnetic analyser (ADC – MGA 3000). The gas balance was used to calculate the oxygen uptake rate (OUR).

When the laboratory pilot-scale unit was operating at steady state, samples were collected from the overflowing pulp at the exit of the reactors and from the initial pulp feed. Samples of pulp were first filtered with a Büchner funnel. The filtered solid material was then rinsed with a sulphuric acid solution at pH

close to the one of the reactors and then dried. Copper, iron and other chemical elements contained in the solid and liquid phases were analysed by atomic absorption.

BILCO® software was used to analyse experimental data and to calculate a consistent material balance of the process. The consistent data were then processed to estimate copper dissolution efficiency.

Bacterial community structure

Bacterial community structure was monitored at the end of the batch experiment in the 50-L reactor, just prior starting the continuous operation, and then once a week during the continuous operation itself.

Genomic DNA extraction

0.5 mL of homogenous bioleaching pulp was centrifuged (10 min, 10 000 g) and the resulting pellet was washed twice by re-suspension in 100 mM citrate (pH 4). DNA was extracted from the washed pellets with the FastDNA Spin Kit for Soil (Bio101) using a modified procedure that included a treatment with 5.5 M guanidine thiocyanate recommended by the manufacturer for high organic matter content samples. A slight modification of the protocol was introduced: the mechanical lysing step was repeated twice for better cell disruption.

CE-SSCP monitoring

The V3 region (*E. coli* position 331 to 533) of 16S rRNA genes of members of the *Bacteria* domain was amplified (25 cycles, hybridization at 61°C) from DNA extracts with the universal reverse primer w34 (5'-

TTACCGCGGCTGCTGGCAC-3') and the eubacterial forward primer w49 (5'-ACGGTCCAGACTCCTACGGG-3') 5' end-labelled with the fluorescent dye FAM. CE-SSCP analyses were performed on formamide and heat denaturated, 5- to 200-fold diluted PCR products. Assignment of strain names was performed by comparison of peak migration position on the profile obtained for reactor samples with that of pure reference strains.

RESULTS & DISCUSSION

How to improve process economy ?

Before undertaking any new testwork, elements on process economy were reviewed in order to point out the most pertinent ways to improve it. Information coming from several pre-feasibility studies of bioleaching installations was analysed and combined to literature data. It appeared that the most important investments costs generally come from bioleaching and electrowinning unit operations. When focusing on bioleaching itself, capital costs largely depends on global tank volume and agitators. The higher operating costs are power (mainly related to oxygen supply) and chemical compounds (Rossi (2001); Morin and d'Hugues (2007); van Aswegen *et al* (2007)). The latter are of particular importance in this study because of the sulphuric acid injection needed to neutralise carbonates of the concentrate.

Starting from the experimental work and the pre-feasibility study undertaken during the Bioshale project (Spolaore *et al* (2009)), it was decided to try and improve process economy by working on:

- increasing revenues by improving process efficiency. Copper recovery was limited to 92% in continuous mode. By controlling redox potential, it should be possible to better dissolve chalcopyrite and improve global copper recovery;
- reducing operating costs. Working with reduced agitation and aeration rates will reduce power consumption;
- reducing capital costs (i.e. reducing global bioleaching tank volume). This will be tested by decreasing global residence time in the unit from 6.6 days down to 4.7 days. The feed solids content will also be increased from 15% to 25%. In the literature, there is a controversy on the feasibility of working at such high solids content. Some authors think that bioleaching operations are limited to 20% pulp densities because beyond this limit, physical mixing and microbial problems occur (Rawlings (2005)). On the contrary, van Aswegen *et al* (2007) explain that the maximum solid concentration is linked to maximum oxygen mass transfer capacity. As a consequence, depending on the resource sulphide content, it is conceivable to work with pulp density above 20%. Another challenge related with bioleaching at very high solids content concern bacterial metal tolerance. It is generally considered that mesophiles are less tolerant to copper than thermophiles: 25 g L⁻¹ vs. 35 g L⁻¹ (Batty and Rorke (2006); Clark *et al* (2006)). During Bioshale continuous operation, copper concentration reached almost 25 g L⁻¹ for 15% pulp density proving the high tolerance of Bioshale-BRGM consortium to this metal. However, at 25% solids,

copper concentration could be high above the tolerance limit considered and bacterial activity could be affected.

Feed at 20% solids concentration (configuration 1)

After 15 days of continuous operation, all physico-chemical parameters (pH, Eh, Cu and Fe concentrations) were stable in the first reactor of the unit (R1): the reactions reached a steady-state. R2 was also close to a steady-state but in R3, redox potential and iron concentration were decreasing constantly and the pH was gradually increasing. It reached values around 2.2. It was assumed that bacterial activity in this reactor was affected by the high pH, limiting iron oxidation rate and causing Eh and iron concentration decrease. At this pH, iron precipitation also occurred. As the pH was already high in R2 (between 1.8 and 1.9), it was decided to start pH regulation in this reactor. It would help to decrease the pH in R3 and stabilise bacterial culture and bioleaching performances. Sulphuric acid (20% v v⁻¹) addition started in R2 to obtain a pH between 1.5 and 1.7. This was successful and after 24 days, the whole unit reached a steady-state.

With this first set of operating conditions, in R1, copper dissolution rate was 355 mg L⁻¹ h⁻¹ and copper recovery was 48%. After 5.2 days of residence time, global copper dissolution was 60% (Figure 1). Almost no copper dissolution occurred in the last reactor.

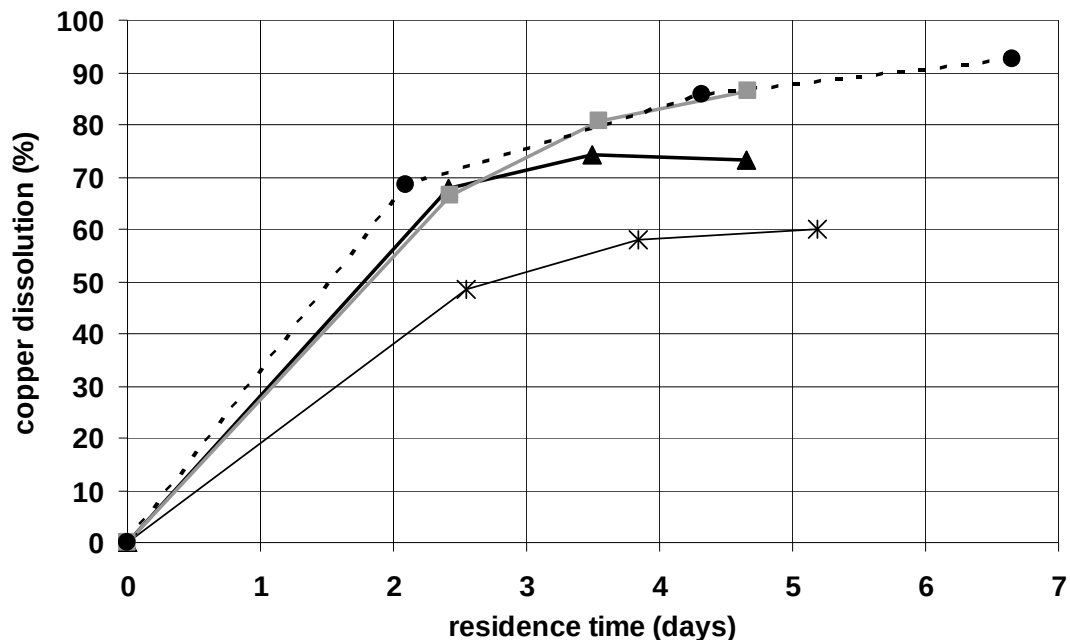


Figure 1 Influence of operating conditions on copper dissolution vs. residence time during continuous bioleaching X configuration 1 ▲ configuration 2 ■ configuration 3 • Bioshale

Feed at 20% solids concentration and reduced agitation/aeration rates in R1 (configuration 2)

During the Bioshale project, the limitation of copper recovery was demonstrated to be linked to incomplete dissolution of chalcopyrite. So as to improve chalcopyrite dissolution, many authors recommend working at reduced redox potential (< 420 mV) to limit passivation of the mineral surface. The reduction of redox potential is obtained by controlling oxygen transfer rate (Córdoba *et al* (2008); Pinches *et al* (2000), Third *et al* (2002); Tshilombo *et al* (2002)). This was at that time applied in R2 and R3 but was not successful. It was supposed that passivation already occurred in R1 and that the decrease of redox potential in R2 and R3 could not be efficient. In this study, the limitation of redox potential was applied in the first reactor. As bacterial growth

mostly takes place in this reactor, a particular attention was taken to provide sufficient oxygen in order to maintain the necessary growth rate avoiding a washout of the unit.

Agitation and aeration rates were gradually decreased to their lower acceptable limit to obtain a good homogeneity of the pulp (340 rpm, 100 L h⁻¹, Table 1). A slight decrease of dissolved oxygen concentration was observed and OUR was divided by 2. This was not sufficient to allow a redox potential decrease (Table 2).

Redox potential increased in R2 and R3 but OUR in these reactors did not changed significantly.

Table 2 pH, redox potential, dissolved oxygen concentration and OUR values reached at steady-state in the three reactors of the continuous bioleaching unit. Comparison between the three different sets of operating parameters.

Configuration		1	2	3
pH	R1	1.6	1.8	1.3
	R2	1.5	1.5	1.6
	R3	1.7	1.6	1.9
Eh	R1	600	592	601
	R2	611	642	472
	R3	616	639	480
dissolved O ₂ (mg L ⁻¹)	R1	5.6	3.2	1.9
	R2	5.6	5.1	0.6
	R3	5.4	5.3	0.5
OUR (mg L ⁻¹ h ⁻¹)	R1	193	86	115
	R2	202	163	101
	R3	147	126	79

Copper dissolution was positively impacted by these changes of operating parameters: copper dissolution rate in R1 reached 445 mg L⁻¹ h⁻¹, copper

concentration was 24 g L^{-1} and recovery was 68%. Global copper dissolution did not improve in the same proportions. After 4.7 days residence time, final copper concentration was 28.4 g L^{-1} corresponding to 73% recovery. No significant copper dissolution was again observed in R3.

Feed at 25% solids concentration and reduced agitation/aeration rates in R1, R2 and R3 (configuration 3)

R1 performances at 20% solids being satisfactory, the feed solid content was increased to 25%. In the same time, as the agitation and aeration rates limitation was efficient in improving copper dissolution in R1, a similar modification was applied to R2 and R3.

After 10 days of continuous running with these new operating parameters, a steady-state was reached. A decrease of pH in R1 was observed. Dissolved oxygen concentration also decreased and OUR increased in proportion to the solids content (Table 2). Copper recovery in R1 was identical to the one at 20% solids (67%, Figure 1). Copper dissolution rate was in consequence improved from $445 \text{ to } 538 \text{ mg L}^{-1} \text{ h}^{-1}$.

In R2 and R3, the decrease in agitation and aeration rates caused a limitation in oxygen transfer: dissolved oxygen concentration dropped under 1 and OUR significantly decreased. Redox potential also decreased but its value remained above 420 mV (Table 2). In R3, an increase in pH was observed. Copper recovery in these two reactors was positively impacted by the reduction of agitation and aeration rates. It was 81% in R2 and 86% in R3 (Figure 1). The copper concentration reached very high values all along the continuous unit: 31.7 g L^{-1} in R1; 37.2 g L^{-1} in R2 and 40.6 g L^{-1} in R3.

Structure of the bioleaching consortium

The structure of the bioleaching consortium at the end of the 50-L batch culture just prior the start-up of the continuous operation was the following: *Sulfobacillus* (*Sb.*) *benefaciens* 6%, *Sb. thermosulfidooxidans* 10%, *Leptospirillum* (*L.*) *ferriphilum* 64% and *Acidithiobacillus* (*At.*) *caldus* 20%. All species of the Bioshale-BRGM consortium were still present.

When the unit was run in continuous mode, the diversity of the population in R1 decreased gradually. After 21 days, *Sb. thermosulfidooxidans* was not detected anymore and after 46 days, *At. caldus* was also under the CE-SSCP fingerprinting technique detection level (Figure 2). The final population was only composed of two organisms, *Sb. benefaciens* and *L. ferriphilum*, which is even less diverse than what is usually observed in continuous operations (Okibe *et al* (2003); Norris (2007)). Nevertheless, all the functions needed in a bioleaching consortium were still present: iron and sulphur oxidation and autotrophic and heterotrophic growth. The fact that *Sb. benefaciens* developed over *Sb. thermosulfidooxidans* could be due to the faster growth rate of *Sb. benefaciens* in autotrophic condition. *Sb. thermosulfidooxidans* is more likely to washout in a stirred tank continuous operation (Johnson *et al* (2008)).

The population evolution was similar in the two other reactors (R2 and R3, data not shown).

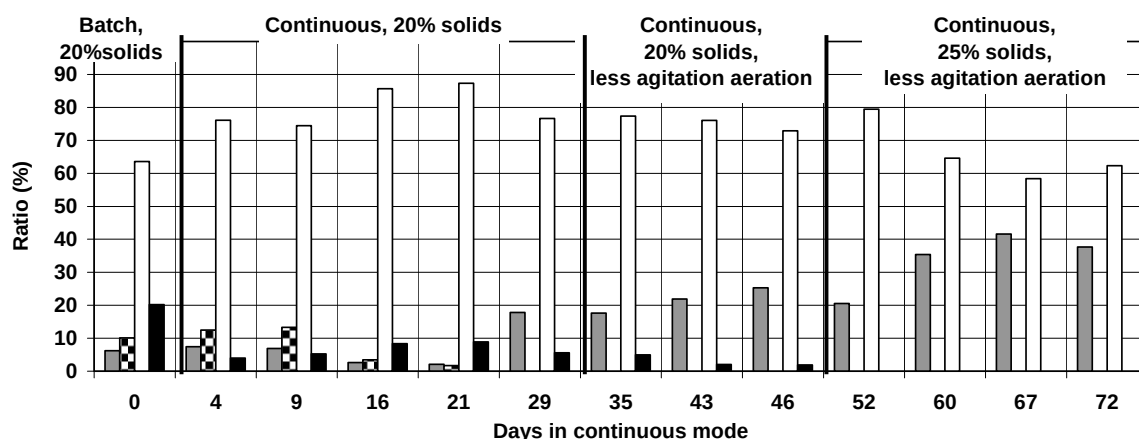


Figure 2 Evolution of the bacterial community structure determined from CE-SSCP fingerprints in the first reactor of the continuous unit. Grey bars *Sb. benefaciens*; black and white bars *Sb. thermosulfidooxidans*; white bars *L. ferriphilum*; black bars *At. caldus*.

CONCLUSIONS

During this study, non-traditional operating conditions were tested on the bioleaching of a carbonate-rich, multi-elements (Cu, Ag) and multi-minerals concentrate. The process performances obtained were compared to the ones reported in the Bioshale project on the same resource. In the latter, 92% copper recovery in 6.6 days residence time was the best performance reached at 15% solids. In this study, the best result was 86% copper recovery at 25% solids after 4.7 days residence time. On figure 1, it appears that both processes reached the same recovery after 4.7 days of residence time. So, it should be assumed that at 25% solids, if residence time was extended, recovery would at least reach 92%.

The feasibility of the copper concentrate bioleaching at high pulp density (25%) was demonstrated. No mixing or microbial issues were encountered. Bioshale-BRGM consortium has shown a rare copper tolerance. In terms of

economy, the results were also very encouraging. To reach 86% recovery, “Promine process” would need 2.3 less tank volume than “Bioshale process”. That would significantly reduce investment costs. This opens new perspectives in the design of an alternative process to smelting. Results concerning downstream metal recovery (copper and silver) should have to be taken into account to complete the overview of the bioleaching capabilities.

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