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BIO-HYDROMETALLURGY: AN ALTERNATIVE TO PYROMETALLURGY FOR COPPER RECOVERY IN A POLYMINERAL CONCENTRATE

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ABSTRACT

The copper concentrate used in this study is produced by flotation of a black shale organic rich ore. This resource is a carbonate-rich, polymineral concentrate. In the last 5-6 years, ore characteristics changed and the concentrate grades degraded. This study evaluated bioleaching of the concentrate in stirred tank reactors as an alternative to the pyrometallurgical technology that is currently applied, and which may no longer be feasible in future given the concentrate chemistry.

The first part of the study focused on testing non-traditional operating conditions during continuous bioleaching experiments: high solids concentration (> 20% solids), reduced agitation and aeration rates. For the same residence time, bioleaching performance at high solids loading (25%) were the same as those reached during previous bioleaching experiments at 15% solids. No mixing or microbial issues were encountered. The bacterial consortium used in the experiments demonstrated a high copper tolerance.

The second part of the study was devoted to technology development for metal recovery from copper bearing solutions obtained during bioleaching experiments. Due to the high copper concentration of the leachate, solvent extraction prior to electrowinning was not necessary. After iron removal, high quality copper cathodes (morphology and composition) were obtained from the PLS by electrowinning.

KEYWORDS

Bioleaching, copper, low grade ore, electrowinning

INTRODUCTION

Biohydrometallurgy is a proven technology already industrially applied all over the world for the exploitation of refractory gold ores, low-grade copper ores and in one case for cobaltiferous pyrite (Arrascue & van Niekerk, 2006; Van Aswegen, Van Niekerk, & Olivier, 2007; Morin & d'Hugues, 2007; Dreisinger, 2006; Watling, 2006). However, it remains a niche application which can compete with other pyrometallurgical or hydrometallurgical technologies only for specific resources. Cost can be one advantage of biohydrometallurgical processing and is also one of the most important drivers for the industry. Another advantage is the low environmental impact, sulphur dioxide and arsenic emissions to air occurring during smelting being completely avoided (Brierley & Brierley (2001); Rawlings, Dew, & du Plessis (2003)).

The copper concentrate subject of this study is produced by flotation from a black shale organic rich ore. The main copper-bearing minerals are: chalcocite, bornite, chalcopyrite and covellite. In the last few years, an increase of organic carbon and As contents as well as a decrease of Cu content in ore were observed, resulting in a decrease of the concentrate quality. There was a need to look for new methods of concentrate treatment. Bioleaching efficiency for this type of ore was previously demonstrated in the frame of the Bioshale FP6 European project (D'Hugues *et al.*, 2008). However, some improvements were still needed to be achieved in order to meet process economic viability (Spolaore, Joulain, Gouin, Morin, & d'Hugues, 2009). In bio-hydrometallurgy, the most important investment costs generally come from the bioleaching and electrowinning unit operations. When focusing on bioleaching itself, capital costs largely depend on global tank volume and agitators. Our study aims at improving the profitability of the bioleaching of the copper concentrate in stirred tank reactors with the following objectives:

- increasing revenues by improving chalcopyrite dissolution and thus bioleaching operation efficiency;
- reducing capital costs by reducing global bioleaching tank volume, which means decreasing residence time in the bioleaching unit and increasing the feed solids content from 15% to 25%;
- reducing capital and operating costs by performing electrowinning without solvent extraction step.

The first part of the experimental study consisted in testing non-traditional operating conditions during continuous piloting bioleaching experiments: high solids concentration (> 20% solids), reduced agitation and aeration rates. In the second part of the study, electrowinning experiments were conducted on copper bearing solutions obtained during the bioleaching experiments cited above. Current efficiency and energy consumption were monitored. The influence of iron and chloride removal from the bioleaching solution on copper recovery was also tested.

MATERIALS AND METHODS

Characterization of the sulphidic materials

The copper concentrate used in the study is produced from a black shale ore. The main characteristics of the sample are 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 (80% cumulative passing) 60 μm . Copper sulphides in the concentrate mainly consist of bornite (Cu_5FeS_4), chalcocite (Cu_2S), chalcopyrite (CuFeS_2) and covellite (CuS).

Bacterial culture and nutrients

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

Nutritive medium

The nutrient medium is derived from the "0Km" medium (Battaglia, Morin, & Ollivier, 1994). Following the Bioshale project, it was demonstrated that a dilution of the 0Km medium by a factor 3 did not affect bioleaching performance. For economic reasons, the 0Km/3 medium is used in this study. Its standard composition is the following: $(\text{NH}_4)_2\text{SO}_4$, 1.23 $\text{g}\cdot\text{L}^{-1}$; H_3PO_4 , 0.27 $\text{g}\cdot\text{L}^{-1}$; $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 0.17 $\text{g}\cdot\text{L}^{-1}$; KOH, 0.16 $\text{g}\cdot\text{L}^{-1}$.

Pregnant leach solution

The initial solution used in the electrolytic copper recovery experiments was sampled during bioleaching of the copper concentrate. This copper rich solution is called PLS1 and its main characteristics are the following: Cu^{2+} , 44.91 g.L⁻¹; Fe^{3+} , 5.5 g.L⁻¹; Fe^{2+} , 0.27 g.L⁻¹; Cl^- , 0.46 g.L⁻¹; pH, 1.78.

Laboratory-scale continuous bioleaching operation

Apparatus

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 are all made from 316L stainless-steel and have a height/diameter ratio equal to 1. The reactors are arranged in cascade so that the pulp flows from one tank to the next one by overflowing. CO₂-enriched air (1%) is injected beneath the turbine at the bottom of the tank. The top of the reactors is connected to a condenser system to prevent excessive evaporation. The same mixing system (BROGIM® - BRGM/MRM) is mounted in all tanks on a rotating shaft.

Operating conditions

The feed was made up of a high density pulp (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. Three configurations were tested during these experiments:

- Configuration 1 (solid concentration of the feed pulp: 20%) corresponds to the first attempt to test the feasibility of a bioleaching operation at high solid content. This configuration was tested during 24 days.
- In Configuration 2 (solid concentration of the feed pulp: 20%, reduced agitation/aeration rates in R1), the objective was to reduce redox potential (< 420 mV Ag/AgCl) by controlling oxygen transfer rate in order to improve chalcopyrite dissolution. This configuration was tested after Configuration 1, for a period of 16 days.
- Configuration 3 (solid concentration of the feed pulp: 25%, reduced agitation/aeration rates in R1, R2 and R3) combines both objectives of Configurations 1 and 2, i.e. increasing solid content of the feeding pulp and decreasing redox potential. This configuration was tested after Configuration 2, for a period of 27 days.

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

The residence time was reduced from 5.1 days in Configuration 1 to 4.6 days in Configurations 2 and 3.

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 analyzer (ADC – MGA 3000). The gas balance was used to calculate the oxygen uptake rate (OUR).

Laboratory-scale electrowinning tests

Apparatus

Copper removal by electrowinning was tested in an experimental stand which consists of a main electrolyte tank, electrolytic cell and spent electrolyte tank with stirrer. Thus the electrolyte flows through a circuit. The characteristics of the cell are as follows:

- cell tank volume: 2 dm^3
- electrode set-up: 2 anodes – PbAg, 1 cathode – 316 L stainless steel
- cathode operating dimensions (cm): 8.2 x 10.2 x 0.2
- cathode operating surface: $P = 167.28 \text{ cm}^2$
- anodes operating dimensions (cm): 7.5 x 10.0 x 0.25
- anode spacing: 90 mm

Operating conditions

Before electrowinning trials, several pre-treatment processes were tested on the copper rich bioleaching solution:

- Hydrolytic Fe(III) removal using calcium carbonate: 8.5 dm^3 of bioleaching solution was heated up to the temperature of 90 – 95°C. 115 g of CaCO_3 was then proportioned with continuous mechanical stirring for 1 hour. The precipitated suspended matter was filtered on Buchner funnel and the cake was washed with water. The solution obtained is called PLS1-IR1.
- Fe(III) removal by jarosite precipitation: bioleaching solution was brought to pH of 1.7, and then maintained in the state of boiling under reflux condenser for 20 h. The process was conducted in 5 steps where 1.5 dm^3 of the bioleaching solution was treated. To accelerate precipitation of iron in a form of jarosite, crystal nuclei were added to the solution. After cooling the solution down, the precipitated residue was filtered (easy filtration) on Buchner funnel and the cake was washed with water. The solution obtained is called PLS1-IR2.
- Fe(III) removal by jarosite precipitation combined to Cl^- removal: Fe(III) was removed from the bioleaching solution as described above. The excess of chloride ions was removed from the solution by weighed amount of Ag_2SO_4 added in a form of aqueous solution. The precipitated silver chloride was filtered and the excess of silver ions was then cemented on metallic copper. The solution obtained is called PLS1-IR2-CR.

Continuous copper removal by electrowinning was then tested using the bioleaching solution without pre-treatment (PLS1) and the three solutions obtained after pre-treatment (PLS1-IR1, PLS1-IR2, PLS1-IR2-CR). The tests were conducted in the conditions of maintaining the Cu^{2+} content in the solution at a constant level of about 30 g/dm^3 . Electrolyte flow was equal to 33.3 cm^3/min which means that volume of the electrolytic cell was exchanged after one hour. Inhibitors (glue and thiourea) were continuously proportioned to the spill tank. The temperature of the electrolyte was maintained at 55°C. The cathode current density was 200 A/m^2 .

Analytical techniques

Current intensity, bath voltage, current efficiency and electrical energy consumption were continuously registered during the tests. Copper content of the electrolyte was measured by means of iodometric copper titration. The composition (Cu, Fe, Ag, Pb, Zn, As contents) of the copper cathodes was determined by means of inductively coupled plasma optical emission spectroscopy (ICP-OES).

RESULTS AND DISCUSSION

Bioleaching experiments

Results obtained with configuration 1 (solid concentration of the feed pulp: 20%)

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 stabilize 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. Table 2 presents the values of pH, redox potential, dissolved oxygen concentration, OUR and copper concentration in the liquid phase reached at steady-state in the reactors R1, R2, R3.

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 O₂ (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
Cu (mg.L⁻¹)	R1	21.0	24.4	31.7
	R2	25.6	25.7	37.2
	R3	26.8	27.6	40.6

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.

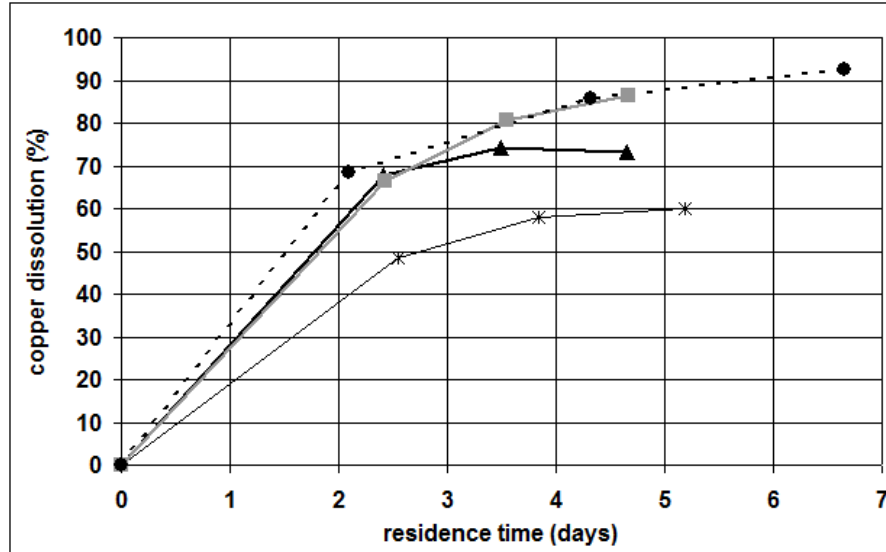


Figure 1 – Influence of operating conditions on copper dissolution vs. residence time during continuous bioleaching (X, configuration 1; ▲, configuration 2; ■, configuration 3; ●, Bioshale)

Results obtained with configuration 2 (solid concentration of the feed pulp: 20%, reduced agitation/aeration rates in R1)

During the Bioshale project, the limitation of copper recovery had been demonstrated to be linked to incomplete dissolution of chalcopyrite. 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 the oxygen transfer rate (Córdoba *et al.*, 2008; Pinches *et al.*, 2000, Third *et al.*, 2002; Tshilombo *et al.*, 2002). 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, $100 \text{ L}\cdot\text{h}^{-1}$, Table 1). A slight decrease of dissolved oxygen concentration was observed and OUR was cut in half. 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 change significantly.

Copper dissolution was positively impacted by these changes of operating parameters: in R1, copper dissolution rate reached $445 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$, copper concentration was $24 \text{ g}\cdot\text{L}^{-1}$ and copper recovery was 68%. When considering the whole operation (R1, R2, R3, R4), global copper dissolution did not improve in the same proportions. After 4.7 days residence time, final copper concentration in R4 was $28.4 \text{ g}\cdot\text{L}^{-1}$ corresponding to 73% recovery. No significant copper dissolution was again observed in R4.

Results obtained with configuration 3 (solid concentration of the feed pulp: 25%, reduced agitation/aeration rates in R1, R2, R3)

R1 performances at 20% solids being satisfactory, the feed solid content was increased to 25%. Similarly, as the agitation and aeration rate limitation improved copper dissolution in R1, the same 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 to $538 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$.

In R2 and R3, the decrease in agitation and aeration rates caused a limitation in oxygen transfer: dissolved oxygen concentration dropped under 1 mg/L 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.

The results obtained in this last part of the bioleaching continuous experiment can be compared to those obtained 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. In 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%.

Bioleaching consortium

The bioleaching consortium at the end of the 50L 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).

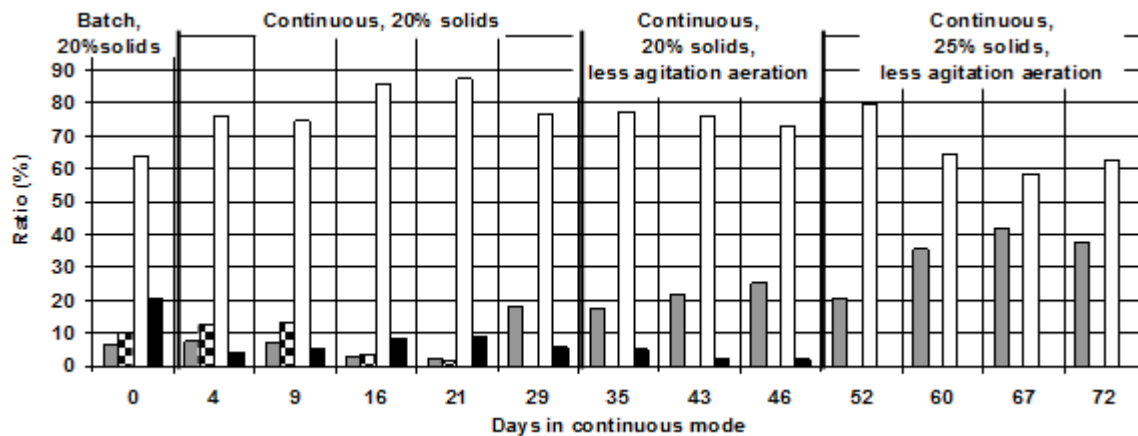


Figure 2 – Evolution of the bacterial community structure determined from CE-SSCP fingerprints in the first reactor of the continuous unit. Grey bars *Sb. benefaciens*; black and white bars *Sb. thermosulfidooxidans*; white bars *L. ferriphilum*; black bars *At. caldus*.

Electrowinning experiments

Efficiency of the Fe(III) removal processes

The results of Fe(III) removal experiments (Table 3) show that 96% of Fe(III) is removed from PLS1 solution by hydrolysis. There is, however, significant loss of copper in the residue which most probably results from

difficulties in filtration of the precipitated iron residue. Jarosite precipitation removes only 70% of the iron from the solution, but the precipitate is much easier to filter than the precipitate obtained with the hydrolysis method and the loss of copper in the residue is much lower.

Table 3 – Results of the Fe(III) removal tests

Fe(III) removal tests	Initial solution (g.dm ⁻³)		Mass of precipitated residue (g)	pH	Final solution (g.dm ⁻³)		Removal to residue (%)	
	Cu ²⁺	Fe			Cu ²⁺	Fe	Cu ²⁺	Fe
Hydrolytic Fe(III) removal using calcium carbonate	44,91	5,76	161,8	3,0	43,08	0,23	4,07	96,0
Fe(III) removal by jarosite precipitation	44,91	5,76	51.9	1,24	43,58	1,67	2,93	71,0

Results of the electrowinning experiments

The results of the continuous electrowinning experiments performed on PLS1 (see Table 4) show that copper removal is efficient and copper cathodes are produced in a compact metallic form. However, the current efficiency is quite low during the operation (in the range 61 – 77%), which entails high energy consumption. Fe(III) removal from the PLS1-IR1 solution radically increases current efficiency (above 91%) and decreases electrical energy consumption (to the level of 2000 kWh/Mg Cu). Copper deposits obtained from electrowinning of PLS1, PLS1-IR1 and PLS1-IR2 are characterized by smooth metallic surface and presence of loosely bounded bushy accretions mainly located on the cathode rims whereas the cathode obtained from PLS1-IR2-CR exhibits a significant decrease of dendritic accretions. These results confirm that chloride removal improves the quality of copper cathodes. The qualities of the copper deposits obtained were very good and average impurities level in the cathodes was as follows [ppm]: Ag, 24.24; Pb, 1.74; Fe, 2.15; Zn, 3.04; As, 0.37.

Table 4 – Results of the continuous electrowinning tests

Initial solution	Cu ²⁺ content in solution (g.dm ⁻³)		Mass of copper cathode (g)	Average current (A)	Cell voltage (V)		Current efficiency (%)	Energy consumption (kWh/t Cu)
	initial	final			average	stand. deviat.		
PLS1	44.9	29.9	133.8	3.341	2.21	0.06	70	2653
PLS1-IR1	43.1	30.5	106.3	3.345	2.26	0.09	96	1828
PLS1-IR2	43.6	28.8	97.6	3.347	2.22	0.08	91	2055
PLS1-IR2-CR	41.3		90.8	2.348	2.18	0.07	91	2012

CONCLUSIONS

Non-traditional operating conditions were tested on the bioleaching of a carbonate-rich, multi-element (Cu, Ag) and multi-mineral concentrate. Electrowinning of the bioleaching solution for downstream copper recovery was also examined.

The bioleaching 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. It appears that both processes reached the same recovery rate 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 also demonstrated. No mixing or microbial issues were encountered. The Bioshale-BRGM consortium has shown a rare copper tolerance: copper content increased up to

more than 40g/L without any negative effect on the bacterial community. Combining high solid content and reduced residence time, this bioleaching process would need 2.3 less tank volume than the “Bioshale bioleaching process” to reach a copper recovery of 86%, which would significantly reduce capital costs.

Electrowinning experiments performed using solution coming from bioleaching tests show that copper removal can be achieved directly by electrowinning without any solvent extraction step. Preliminary removal of Fe(III) from the bioleaching solution significantly increases current efficiency of electrowinning operations. Iron can be successfully removed by precipitation as jarosite, which demonstrated good filtration properties at low copper loss in the residue. An improvement of the structure of copper cathodes can be achieved by decreasing chloride ion content in the bioleaching solution from the level of about 0.5 g.dm⁻³ to 0.01 g.dm⁻³. Chloride content reduction should be done in a separate process of concentrate washing before bioleaching. These results offer new perspectives for the design of an alternative process to smelting.

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