PRESSURE LEACHING OF A HIGH ARSENIC COPPER CONCENTRATE UNDER CESL PROCESS CONDITIONS

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ABSTRACT

Two copper concentrate with medium and high enargite content were leached in a 3 L autoclave reactor under conditions based on the CESL process. Copper, arsenic, sulfur and iron were checked in all the experiments and antimony, zinc and molybdenum were evaluated in selected tests. The 98% of the obtained copper extraction is agree with others authors, but the behavior of arsenic, iron an sulfur have some differences. The solid residue was characterized by chemical analysis, DRX and QEMSCAN®. Finally a comparative analysis with neutral roasting as an option for the treatment of this concentrate is done.

KEYWORDS

Pressure leaching, copper concentrates, arsenic,

INTRODUCTION

Arsenic is an impurity frequently found in copper concentrates in Chile and it is most commonly present as enargite, Cu3AsS4, which makes it a challenge in order to separate it from the copper product.

Copper concentrates are treated almost exclusively via smelting and refining, technology that allows to process material with up to 1% arsenic, being able to control emissions and to deliver a good quality product. However, environmental regulations are becoming more stringent and at the same time higher arsenic levels are being found in copper concentrates, which render current smelting and refining plants incapable of processing these materials. Thus, alternative technologies to smelting or technologies that allow decreasing the content of arsenic are being considered in order to make these materials suitable for processing in a conventional smelting and refining plant. One of these technologies is the arsenic volatilization via controlled roasting of concentrates.

Amongst alternatives technologies to smelting and refining, the CESL process has been successfully evaluated to recover copper from concentrates (Mc Donald and Muir, 2007; Defreyne et al, 2004; Defreyne et al, 2009) and from high arsenic concentrates (Bruce et al, 2011; Barrios et al, 2011).

This technology, which has been widely promoted, operates at 150°C with an O_2 pressure of 7 atm. and a chloride concentration of 12 g/L. Under these conditions, copper sulphides are transformed into basic copper sulphate which can be easily leached, leaving most of the sulphur as native sulphur. The dissolution reaction for chalcopyrite is as follows:

$$12\text{CuFeS}_{2} + 15\text{O}_{2} + 4\text{H}_{2}\text{O} + 4\text{H}_{2}\text{SO}_{4} \rightarrow 4[\text{CuSO}_{4} \cdot 2\text{Cu(OH)}_{2}] + 6\text{Fe}_{2}\text{O}_{3} + 24\text{S}^{\circ}$$
(1)

The arsenic is dissolved and precipitates with iron as insoluble ferric arsenate. The overall reaction for enargite is as follows (Bruce et al, 2011):

$$2Cu_{3}AsS_{4} + 5.5O_{2} + Fe_{2}(SO_{4})_{3} + 3H_{2}SO_{4} + H_{2}O = 6CuSO_{4} + 2FeAsO_{4}.2H_{2}O + 8S^{\circ}$$
(2)

EXPERIMENTAL

Materials

Two copper concentrates with medium and high arsenic content were used in the experiments. The chemical analysis of these concentrates are shown in Table 1 and the mineralogical components obtained by Qemscan analysis, are presented in Table 2.

Table 1: Chemical composition of copper concentrates									
Sample	Chemical composition (%)								
	Cu	Fe	Мо	Zn	As	Sb	S		
Concentrate 1	27.7	18.6	0.15	1.3	0.65	0.04	22.4		
Concentrate 2	27.1	15.0	0.05	1.59	5.94	0.56	28.6		

	Conc. 1	Conc. 2
Chalcopyrite	26,95	9.95
Bornite	10,26	2.6
Cu-sulphides	14,28	23.77
Pyrite	16,07	16.92
Fe-oxide	1,42	0.44
Fe-(Si) spinel	2,15	0.11
(Cu)-Fe 'Oxide' phase	0,91	0.02
Cu-Fe-Si 'Oxide' phases	0,55	
Cu-oxide	1,94	2.09
Fe-As-S-O phases		0.25
Cu-As-S		21.18
Cu-S (As)		2.44
Total As phases	2,28	23.87
Molybdenite	0,47	0.084
Galena	0,38	0.23
Sphalerite	1,08	1.29
Cu-Fe-Zn phases	3,11	
Quartz	5,9	2.4
Gangue	12,2	14.2

Table 2: Mineralogical composition of copper concentrates obtained by QEMSCAN® analysis

Apparatus and procedure

Pressure leaching experiments were conducted in a batch stainless steel autoclave reactor with a glass vessel inside to avoid corrosion. The reactor comprises a variable speed mechanical agitation system with a reinforced glass teflon propeller, electric heating, a sampling device to extract samples and a cooling system. Figure 1 shows photography of the autoclave reactor.

The experimental procedure consisted in preheating the leaching solution with the solid sample to produce a 5 to 10% solids pulp under nitrogen atmosphere. Once at the set temperature the oxygen was injected to maintain the oxygen partial pressure for the reaction time. Samples taken at regular intervals were filtered and the solids were submitted for analysis for the elements Cu, As, Fe and Mo, Sb and Zn were included for selected samples. The final leach residue was also analyzed by X–ray diffraction and Qemscan.



Figure 1: Autoclave reactor

RESULTS

Copper extraction

Figure 2 shows the effect of the particle size on the copper extraction for concentrate 1. It can be see that the concentrate ground to P80 60 microns needs over 150 minutes to reach a 90% copper extraction, while the finer concentrates ground to P80 of 36 and 13 microns require 45 and 30 minutes respectively.

The high arsenic concentrate (concentrate 2) had a P80 of 48 microns and was leached without a regrind. The influence of the temperature and sulphuric acid concentration were tested and the results are shown in Figure 3. Results shows a more favourable kinetics of copper extraction for concentrate 2 compared with concentrate 1, considering that similar results were obtained with coarser particle size, which appears to indicate that enargite is more leachable than chalcopyrite under these conditions. Increasing sulphuric acid concentration from 25 to 50 g/L also increase the copper extraction, but no effect in copper extraction was observed when the temperature increased from 150 to 180°C.



Figure 2: Copper extraction from concentrate 1 at 5% solids, Po2 7 atm, Cl⁻ 12 g/L, quebracho 1.5 g/L



Figure 3: Copper extraction from concentrate 2 at 5% solids, P₀₂ 7 atm, Cl⁻12 g/L, quebracho 1.5 g/L

Extraction of arsenic and others elements

As it is shown in Table 3 for the copper concentrate 1, arsenic is mostly leached and retained in the solution. This effect is clearer for the finer particle size. For copper concentrate 2 (high arsenic) most

of the arsenic finished in the solid residue and this distribution increase with a lower sulphuric acid concentration in the leaching solution. Antimony and molybdenum are partially leached and the extraction of zinc is almost complete for both of types of concentrates.

Table 3: Extraction of elements										
Copper P80 conc. microns	P80	Tomn °C	H ₂ SO ₄ ,	Extraction (%)						
	Temp. C	g/L	Cu	As	Fe	Sb	Mo	Zn		
1	60	150	25	93.4	68.1	68.4	46.9	32.2	93.0	
1	36	150	25	97.0	81.4	67.0	49.3	60.9	99.1	
1	13	150	25	98.6	91.9	80.1	39.5	80.4	99.9	
2	48	150	25	93.8	23.1	66.5	53.2	29.7	94.9	
2	48	150	50	98.3	46.0	76.9	57.8	35.1	99.5	
2	48	180	25	95.3	28.5	52.7	52.3	31.8	98.2	
2	48	180	50	96.0	35.6	87.8	42.8	45.4	94.9	

Conditions: 5% solids, P₀₂ 7 atm, Cl⁻ 12 g/L, quebracho 1.5 g

Solid residue characterization

The characterization of the residue was essential to confirm the reactions proposed. Chemical analysis of a solid residue obtained from copper concentrate 1 and 2 are presented in Table 4. Table 5 shows the Qemscan analysis of the leaching residue of concentrate 1.

Copper	P80 micron	Temp.	H ₂ SO ₄ ,	H ₂ SO ₄ , Elements (%)							
conc.	S	°C	g/L	Cu	As	Fe	Sb	Mo	Zn	S	
1	36	150	25	1.3	0.29	15.6	0.06	0.15	0.03	26.7	
2	48	150	25	4.7	12.9	14.2	0.74	0.08	0.23	32.7	
2	48	150	50	1.9	13.3	14.4	0.98	0.11	0.03	19.0	

Table 4: Chemical characterization of the solid residues

Table 5: Mineralogical analysis of the concentrate 1 leaching residue

Chalcopyrite	0.55
Bornite	0.07
Pyrite	3.38
Cu-sulphides	2.44
Fe-oxide/hydroxide	0.64
As phases	40.17
Molybdenite	2.01
Pb-sulphides	0.17
Zn-sulphides	0.00
Quartz	7.97
Gangue	42.12

The 60 to 80% of the sulphur in the solid residue shown in Table 4 is elemental sulphur and it represents between 35 to 40% of the initial sulphur present in the concentrate.

Table 5 shows that the arsenic phases are the main components of the residue, but the Qemscan analysis could not indentify the mineralogical species. Since no concentrated iron species were found, mostly of the iron should be associated to the arsenic phases. This result is agreement with the proposed reaction for enargite.

A X-ray diffraction analysis identified elemental sulphur, hematite, jarosite and enargite, but no arsenic species was identified.

Roasting - pressure leaching comparison

A comparison of pressure leaching and roasting to process high arsenic copper concentrates has the following characteristics:

Copper recovery: roasting for arsenic volatilization is a selective process and a calcine of copper and iron sulphides is obtained. Smelting and refining has been considered to recover the copper from the calcine, but, all the concentrate labile sulphur reacts in the roaster and a low sulphur calcine is obtained, which is could be a problem for the heat balance in the smelting stage. For pressure leaching, copper is recovered by SX-EW.

Precious metals recovery: pyrometallurgical rout allows an efficient recovery from the anode slimes which is a highly concentrated precious metals material. Hydrometallurgical treatment requires another leach process such is cyanidation of the leach residue.

Costs: Roasting – smelting – refining has higher capital costs but lower operating costs than pressure leaching – SX - EW. However depending on local conditions, the recommendation to process high arsenic copper concentrates could be different.

CONCLUSIONS

The CESL process extract copper efficiently from chalcopyrite and enargite concentrates.

Copper extraction from enargite concentrate shows faster kinetics than chalcopyrite concentrate.

Between 65 to 75% of the arsenic finished in the solid residue as Fe-As compounds which were not identified.

Only 35 to 40% of the sulphur finished as native sulphur and 60 to 65% is oxidized to sulphate, but the effect of some variables that can modify this result, it was not considered in this study.

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