Use of seawater and discard salts of caliche industry to improve the copper extraction from leaching process

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Abstract– ***The objective of this research is to study the acid-nitrate-chloride system in the chalcopyrite leaching process ($CuFeS_2$) in order to propose a hydrometallurgical process that allows the use of salts or discarding solutions from the caliche industry as well as saline discard solutions (such as the rejection solution of the reverse osmosis process) or raw seawater. The methodology used is to use low grade ore, concentrate and pure chalcopyrite samples which are conditioned and leached by stirring, varying concentrations of chloride, solvent, source of nitrate and pretreatment. The system has shown good copper extraction results at atmospheric pressure, over 60% and up to 90%. Salts and discard solutions have been used and it has been proven that they could be alternatives of raw materials in the process. A conditioning stage is essential to accelerate the dissolution kinetics of copper in the systems studied.***

Keywords—Seawater, chalcopyrite, chloride, nitrate, leaching.

I. INTRODUCTION

The northern of Chile is characterized by having reserves of metallic minerals such as copper and nonmetals such as caliche [1]. In addition, the weather is desert therefore water is a scarce resource. It is necessary to consider that copper oxides are increasingly scarce due to the exploitation of the deposits. This in the future will cause hydrometallurgical plants to stop being used. The sulfide minerals to be increasingly predominant in mining companies. An alternative solution would be hydrometallurgical treatment of sulfur species, such as chalcopyrite ($CuFeS_2$). It is known from the literature that chalcopyrite tends to be refractory to leaching in sulfate media [2]. This does not occur in chloride media [3] and especially in oxidizing media [4]. Several authors have studied the use of nitrogen species for leaching sulfur minerals such as nitric acid [5], nitrate [6, 7], nitrite [8], among others. Due to the caliche industry, present in the northern part of Chile, it is expected that salts or discarding solutions from this industry are expected to be used for leaching chalcopyrite. In addition, the chlorinated medium could be supplied by seawater or brines.

The objective of the research is to study the acid-nitrate-chloride system in the chalcopyrite leaching process ($CuFeS_2$) in order to propose a hydrometallurgical process in the future, which allows the use of salts or discarding solutions of the caliche industry as well as saline discard solutions (such as the rejection solution of the reverse osmosis process).

II. METHODOLOGY

A. *Ore*

Different chalcopyrite samples from Antofagasta and Atacama Regions of Chile were used (Table I). The samples were low grade ore (1.6% Cu), concentrate (12.9% Cu) and pure samples (29.1% Cu). The mineralogical species were obtained by optical microscopy, semi-quantitative X-ray diffraction and the chemical composition was determined by atomic absorption spectrometry (AAS). Different particle sizes were used according to the methodology determined.

TABLE I
MINERALOGICAL CHARACTERIZATION OF SAMPLES USED IN THE TESTS

Minerals	Formula	Low copper grade	Concentrate	Pure sample
		Amount (%)		
Chalcopyrite	$CuFeS_2$	4.8	37.2	85.2
Covellite	CuS	0.0	12.5	0.0
Digenite	Cu_9S_5	0.0	2.9	0.0
Pyrite	FeS_2	8.1	34.0	2.1
Magnetite	Fe_3O_4	36.7	0.0	0.0
Gangue		50.4	13.4	12.7
Total		100.00	100.00	100.00

B. *Reagents*

Analytical grade of reagents, H_2SO_4, $NaNO_3$ and $NaCl$ were used in the tests. Seawater was obtained from San Jorge Bay (Antofagasta). Seawater was filtered (1 µm, sand quartz and polyethylene membrane). Discard brine from reverse osmosis process was obtained from desalination plant of Antofagasta. Table II shows the concentration of ions in the seawater and brine obtained by different analytical techniques (AAS, volumetric and gravimetric analysis, inductively coupled plasma atomic emission spectroscopy ICP-AES)

TABLE II
CHEMICAL ANALYSES OF SEAWATER AND BRINE (MG/L)

Element	Seawater	Brine
Mg^{2+}	1256	2297
Na^+	11250	19768
K^+	401	746
Cl^-	20289	36074
SO_4^{2-}	2758	5063
NO_3^-	2.40	6.40

C. *Procedure*

Leaching tests by stirring used 1 L of jacketed glass reactors. A thermostatic bath controlled the temperature at 45 °C. Mechanical stirring was providing at 400 rpm. Copper extraction was monitored over time to obtain kinetic curves. For

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this, solution samples of the tests were periodically taken for analysis of copper concentration by AAS. In addition, solid waste was analyzed by chemical and mineralogical analysis (AAS and optical microscopy).

In addition, pretreatment tests were performed with concentrate samples. When the pretreatment was used, the concentrate was conditioned. A sample of concentrate was placed on a plastic sheet and solid reagents were added: 23 kg of sodium nitrate/ton of solid sample and 12 kg of chloride/ton of solid sample. This mixture was homogenized and 17 kg of sulfuric acid/ton of solid sample was added. Finally, seawater was added to complete 15% moisture of the mixture. The conditioned sample was allowed at rest (20 days) in a plastic sheet at 25 °C. When the resting time was reached, the solid sample was leached using 0.7 M of sodium nitrate, 0.7 M of sulfuric acid and seawater as solvent. The other test, called “repose in solution”, considers that the conditioned sample was left in a reactor with leaching solution (0.7 M of sodium nitrate, 0.7 M of sulfuric acid and seawater as solvent) for 20 days and then the stirring began.

The variables studied in this research were: concentrations of chloride, type of solvent, source of nitrate and pretreatment of the solid sample.

III. RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the copper extraction in function of type of solvent used (water, seawater and brine from the reverse osmosis process) when different solid samples were used. In all cases, the water shows a lower copper extraction in comparison to use seawater or brine. This is due to chloride presence that improve the copper extraction from chalcopyrite.

When the concentrate is leached, seawater showed a better copper extraction than when brine was used. This could be due concentrate sample contain covellite and digenite, copper sulfides more soluble in chloride media than chalcopyrite. Better copper extractions were obtained when brine was used for the other tests, pure sample and low grade ore. In both cases, it is observed that the brine has better copper extraction results, mainly due to the greater presence of chloride in the system (36 g/L).

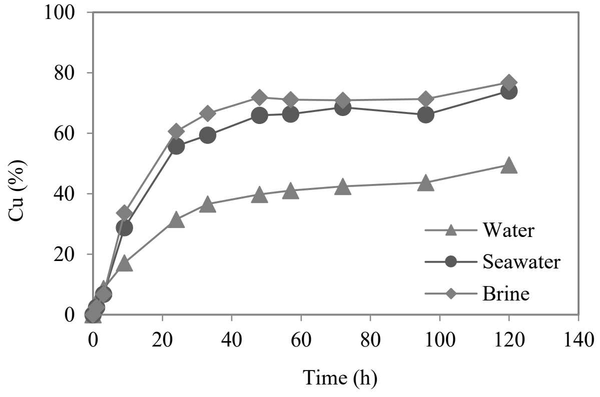

Fig. 1 Copper extraction (%) vs. time (h) in function of solvent used: water, seawater and brine. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.5$ M, 100 g of ore/1000 mL solution, 5 days of leaching, particle size under 150 µm, low grade ore 1.6% Cu)

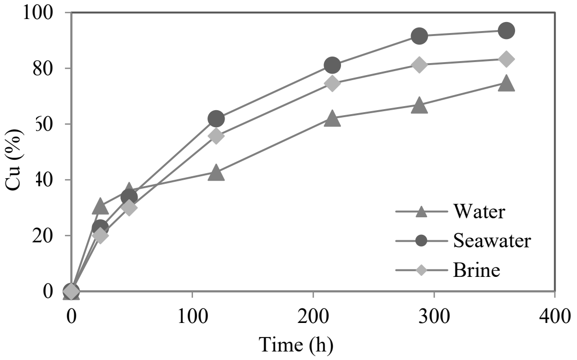

Fig. 2 Copper extraction (%) vs. time (h) in function of solvent used: water, seawater and brine. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.7$ M, 50 g concentrate/500 mL solution ,15 days of leaching, particle size under 150 µm, concentrate copper grade 12.9% Cu)

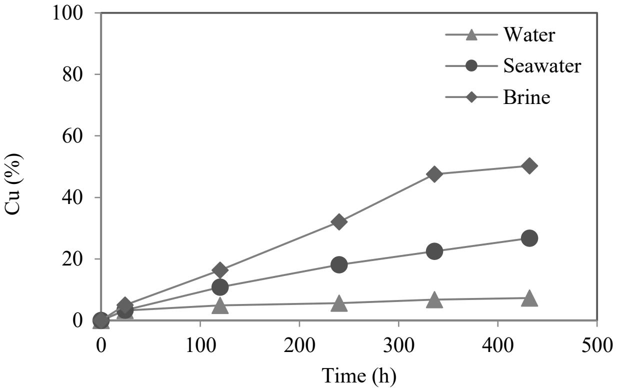

Fig. 3 Copper extraction (%) vs. time (h) in function of solvent used: water, seawater and brine. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.7$ M, 1 g of ore/500 mL solution ,18 days of leaching, particle size under 150 µm, sample chalcopyrite grade 29.1% Cu)

A maximum of 76.8%, 93.7 and 50.3% Cu were obtained by leaching of low grade ore, concentrate and pure sample, respectively.

Figures 4, 5 and 6 show the copper extraction in function of chloride concentration when different solid samples were used.

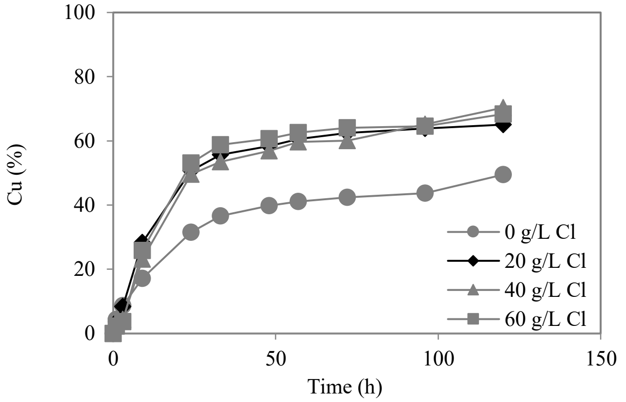

Fig. 4 Copper extraction (%) vs. time (h) in function of chloride concentration: 0, 20, 40 and 60 g/L. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.5$ M, water as solvent, 100 g of ore/1000 mL solution, 5 days of leaching, particle size under 150 μm, low grade ore 1.6% Cu)

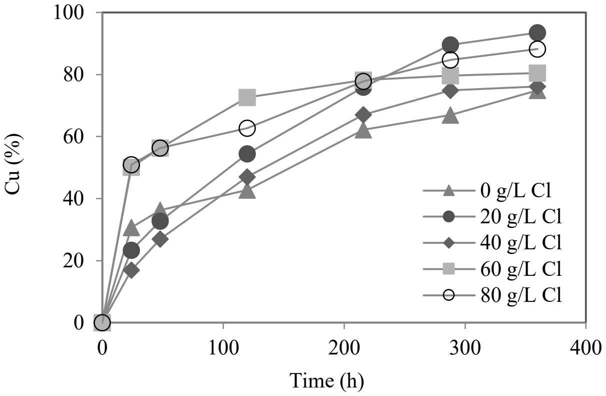

Fig. 5 Copper extraction (%) vs. time (h) in function of chloride concentration: 0, 20, 40, 60 and 80 g/L. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.7$ M, water as solvent, 50 g concentrate/500 mL solution ,15 days of leaching, particle size under 150 μm, concentrate copper grade 12.9% Cu)

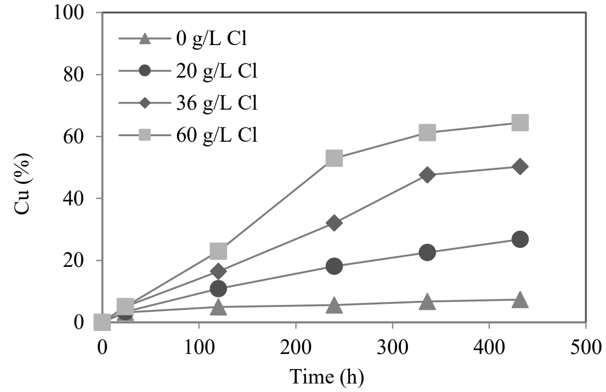

Fig. 6 Copper extraction (%) vs. time (h) in function of chloride concentration: 0, 20, 36 and 60 g/L. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.7$ M, water as solvent, 1 g of ore/500 mL solution ,18 days of leaching, particle size under 150 μm, sample chalcopyrite grade 29.1% Cu)

Figure 4 shows that an increase in the concentration of chloride from 0 to 20 g/L, produces a 30% increase in copper extraction in comparison with chloride is not present in the media. Moreover, a slightly increase was observed when chloride concentration increases in the media over 20 g/L. It is appreciated that the presence of this ion is important, but that an excess does not have a greater influence on the conditions studied when low grade ore is used.

Figure 5 shows a similar behavior of the Figure 4. When 80 g/L of chloride concentration was used, the copper extraction achieved was lesser than 20 g/L of chloride was present in the media.

Figure 6 shows something different. In this case, the increase of chloride concentration produced an increase on copper extraction. Due to this results, the gangues or other mineralogical species influenced in the results showed in Figure 4 and 5.

A maximum of 70.3% Cu (40 g Cl^-/L), 93.5 Cu(20 g Cl^-/L), and 64.4% Cu (60 g Cl^-/L), were obtained by leaching of low grade ore, concentrate and pure sample, respectively.

Figure 7 shows the copper extraction over time when comparing a test using analytical sodium nitrate and a discarding salt from the caliche process that contains 64% nitrate. It can be seen that both extraction curves are very similar to each other. This would verify that it is possible to use these salts in the process.

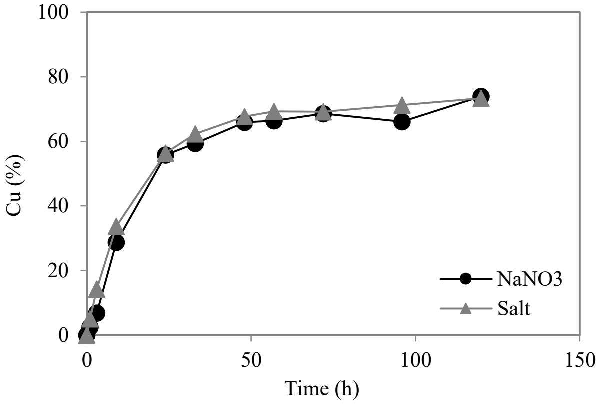

Fig. 7 Copper extraction (%) vs. time (h) in function of nitrate source: analytical $NaNO_3$ or industrial salt. (Experimental conditions: leaching by stirring, 45 ° C, $[H_2SO_4] = [NaNO_3] = 0.5$ M, seawater as solvent, 100 g of ore/1000 mL solution, 5 days of leaching, particle size under 150 μm, low grade ore 1.6% Cu)

Figure 8 shows the copper extraction over the time when a pretreatment and repose in solution were used in a concentrate sample. It can be seen that both treatments have a positive response to copper extraction, compared to the untreated system. By projecting the extraction curve of the test without pretreatment, the same extraction percentages could be achieved as the samples with pre-conditioning, but raising the costs, because the leaching process has been continuous. Case different from when there is a resting time where the expense would occur in a physical place where the solid treated leave for a certain time.

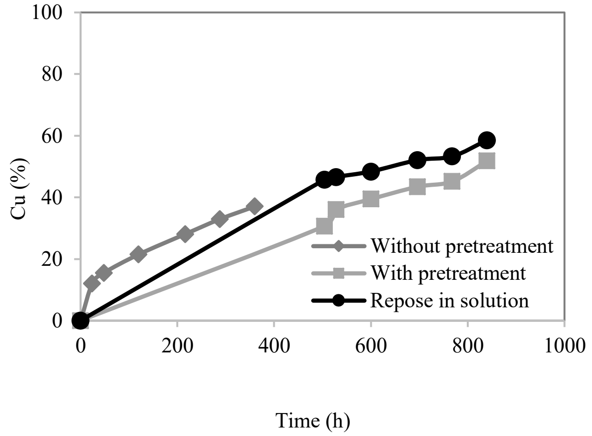

Fig. 8 Copper extraction (%) vs. time (h) in function of pretreatment: without pretreatment (only leaching), with pretreatment and repose in solution. (Experimental conditions: leaching by stirring, 25 ° C, $[H_2SO_4] = [NaNO_3] = 0.7$ M, seawater as solvent, 50 g concentrate/500 mL solution ,15

days of leaching, particle size under 150 μm, concentrate copper grade 12.9% Cu)

IV. CONCLUSIONS

The acid-nitrate-chloride system for leaching chalcopyrite has been studied as alternative to leach chalcopyrite ore using seawater or brine and salts of caliche industry. The results have shown that:

- This system produces satisfactory copper extractions, above 60% at atmospheric pressure and temperatures of 45 ° C.
- Chloride ions are beneficial to chalcopyrite leaching, but in samples with gangues presence, the use of seawater or brines (36 g/L) is enough to obtain satisfactoriness results of copper extractions at studied conditions in this research.
- Industrial salts and brine solutions (seawater and discard of reverse osmosis) have been used with satisfactory results. They could be alternatives of raw materials in the leaching process of chalcopyrite dissolution.
- A conditioning stage (pretreatment) was essential to accelerate the dissolution kinetics of copper in the systems studied because the majority of copper extraction is achieved in this step.
- A pretreatment step could be beneficious alternative to industrial scale due to the reduction of the energy consumption by a decrease of the irrigation time in heap leaching.

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