



Enhancing the kinetics of chalcopyrite leaching in the Galvanox™ process

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ABSTRACT

Pyrite is an effective catalyst for the atmospheric leaching of chalcopyrite in iron sulfate media via the Galvanox™ process. However, not all pyrite samples have the same catalytic effect on the process. Techniques to enhance the catalytic properties of pyrite were investigated. Specifically, the effects of pyrite treated with silver (enhanced pyrite) on the kinetics of chalcopyrite leaching were examined with the aim of improving the Galvanox™ process. It has been shown that by pretreating natural pyrite samples with miniscule amounts of silver ions, the rate of chalcopyrite leaching increases dramatically. As little as 50 ppm silver on pyrite, or about 50 g silver (about 1.5 troy ounces) per tonne of pyrite, is sufficient to ensure rapid chalcopyrite leaching kinetics in the Galvanox™ process, regardless of the source of the pyrite. With this new process, the catalytic properties of pyrite are improved such that all pyrite samples accelerate the rate of copper extraction from chalcopyrite significantly.

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1. Introduction

Chalcopyrite is the most important source of copper in the world (Dutrizac, 1978), and accounts for 70% of the world's known copper reserves (Wang, 2005). Extensive research in the field of hydrometallurgy has been conducted to develop an efficient process to extract copper from chalcopyrite. As a result, there are various hydrometallurgical processes for copper recovery. These processes can be categorized according to lixiviant type, such as sulfate, chloride, ammonia, and nitrate. Among these processes, it has been found that ferric sulfate leaching has several advantages, including simplicity of leaching chemistry, low capital and operating cost, and convenient copper recovery by solvent extraction and electrowinning.

In spite of these advantages, copper recovery from chalcopyrite leaching in ferric sulfate is typically low. The reasons for this have not been clearly established. Initial reaction rates have been noted to decline rapidly with time, leading many investigators to conclude that a passivating layer forms on the mineral surface (Hackl et al., 1995). Formation of the passive layer on the surface of the mineral hinders further copper dissolution. In spite of extensive research, the nature of this passive layer remains unclear. However, there are three main hypotheses to explain the structure of this impermeable layer. One theory suggests the formation of the sulfur layer as an impermeable layer which prevents the diffusion of reactants to the chalcopyrite core (McMillan et al., 1982). Another suggests the formation of a copper-rich polysulfide layer which develops on the surface as a result of solid-state changes to the mineral during leaching (Hackl et al., 1995). Yet another

suggests that the passivating layer consists of iron salts (Pinches et al., 1976).

Recently, it has been found that the addition of pyrite to the leach slurry in ferric sulfate media increases copper recovery significantly (Dixon et al., 2008). This process, known as Galvanox™, runs under atmospheric pressure and temperature, which eliminates the high cost of an autoclave, required for high-temperature, high-pressure processes. Also, since the operating temperature is low, and the chemical conditions mild, the near-quantitative yield of elemental sulfur is observed. This decreases both oxygen consumption and the necessity to neutralize large quantities of sulfuric acid. Complete copper recovery in Galvanox™ can be achieved at a considerably higher rate than other ferric sulfate leaching processes.

Recent studies on the Galvanox™ process have indicated that pyrite samples from different sources can influence the rate of chalcopyrite leaching differently. Some pyrite samples accelerate the leaching rate significantly, while others have less effect on the process. Furthermore, a strong correlation has been noted between the level of silver occurring in the pyrite samples and their effectiveness as catalysts for chalcopyrite leaching.

With the new process described in this paper, the catalytic properties of pyrite are improved such that all pyrite samples accelerate the rate of copper extraction from chalcopyrite significantly. To enhance the catalytic properties of pyrite, ground samples of natural pyrite are pretreated with miniscule amounts of silver ion by soaking the ground pyrite in a dilute solution of soluble silver salt such as silver nitrate before introducing the pyrite into the leaching reactor. Even at room temperature, the finely divided pyrite typically adsorbs all of the silver from solution in just a few minutes. As little as 50 ppm Ag on pyrite, or 50 g Ag (about 1.5 troy ounces) per tonne of pyrite, is sufficient to ensure rapid chalcopyrite leaching kinetics in the Galvanox™ process.

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The ability of silver to catalyze copper dissolution from chalcopyrite in both chemical and biological leaching systems is well known. Chalcopyrite can be chemically activated with silver ions to improve its leachability under acid oxidizing conditions. Several authors have demonstrated the ability of silver to catalyze copper dissolution from chalcopyrite in both chemical and biological leaching systems (Banerjee et al., 1990; Miller and Portillo, 1979; Price et al., 1986).

According to various authors, the dissolution of metals from mineral sulfides can be accelerated by the addition of soluble foreign ions. These ions alter the electrochemical behaviour of the sulfide after they become fixed onto its surface (Barriga et al., 1987; Ballester et al., 1990).

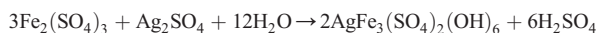
Initially it was shown by Snell and Fords (1976) that copper extraction from chalcopyrite increased in ferric sulfate solution by addition of silver as a soluble silver salt. In this work, it was claimed that the solid residue contained over 90% of the silver. To recover the silver, it was proposed to separate the elemental sulfur from the solid residue by aromatic liquid extraction to produce a tailings with less than 2% elemental sulfur and then to dissolve the silver using oxygen in a leaching solution containing 80% sulfuric acid. This reaction occurs at temperatures between 95 and 110 °C (Snell and Fords, 1976).

Recently, Carranza et al. (1997) have developed a process for copper recovery from chalcopyrite which is known as BRISA. This process is comprised of two steps; chalcopyrite leaching in ferric sulfate solution, and biooxidation of ferrous to ferric using mesophilic bacteria. Silver may be recovered from the leach residue by acidic brine leaching (Romero et al., 1998). Leaching was performed at 70 °C and pH 1.25 and 2 mg Ag/g concentrate. The concentrate contained 8.9% copper (i.e., 22.5 mg Ag/g Cu). Copper recovery of 95% was obtained after 8 hours. Palencia et al. (1998) have shown that all silver added as a catalyst remains in the leached residue as Ag₂S and Ag⁰. Furthermore, due to the acidity, temperature and ferric sulfate concentration in the BRISA process, silver is also precipitated as argentojarosite. Formation of this phase under similar conditions was also confirmed by Dutrizac and Jambor (1987), who state that silver is preferentially incorporated into jarosite precipitated from sulfate media.

There are two fundamental problems with silver catalyzed leaching in both chemical and biological systems which inhibits commercial use of the process:

1. Silver availability

The catalytic effect of silver is increased by increasing the ferric concentration in the leaching solution (Miller et al., 1981). However, higher ferric concentrations favour the precipitation of argentojarosite:



Formation of jarosite increases with increasing temperature, ferric concentration, and pH. Silver precipitation is rapid, and is completed before ferric precipitation (Bolorunduro et al., 2003) which leads to the zoning of the silver-rich jarosite in the core of the jarosite. In order to extract silver from jarosite, the leaching solution has to diffuse through the core of jarosite. Hence, formation of argentojarosite limits the availability of silver ion in solution (Munoz et al., 2007). Furthermore, once formed, it is difficult and expensive to redissolve this precipitate in order to recover the contained silver.

Silver which does not form argentojarosite typically reports to the leach residue as silver sulfide (e.g., argentite, Ag₂S) intimately associated with elemental sulfur. This silver can generally be recovered, but at the expense of several additional and rather inconvenient process steps, including melting sulfur with steam and filtering at 140 °C, leaching the desulfurized residue in hot hydrochloric/sulfuric

acid solution, and cementing metallic silver on copper powder (Palencia et al., 1998).

2. Silver toxicity

Solubility of silver in bioleaching experiments is low due to the bioaccumulation of silver ions within the cell membranes of microorganisms. In addition, silver ions are toxic to most microorganisms. Silver toxicity has been attributed to a competing mechanism between silver and ferrous ions for active sites on bacterial cell walls (Munoz et al., 2007). The accumulation of silver sulfide on ferrooxidant cells has been also observed (Pooley, 1982). It has been reported that biooxidant growth is inhibited in the presence of even minor amounts of silver (Hoffman and Hendrix, 1976).

Given these two weaknesses, and in spite of broad research, no commercial process has been developed which uses silver successfully as a catalyst to recover copper from chalcopyrite.

However, in our process, a high concentration of ferric is not required to facilitate the catalytic effect of silver. Indeed, one of the key parameters to achieve successful chalcopyrite leaching in this process is to maintain the solution potential at or below a certain level, not only to prevent chalcopyrite passivation but also to inhibit the oxidation of pyrite in order to minimize the loss of adsorbed silver into the leach solution. Such a low solution potential could not be maintained unless the net rate of the reactions which consume ferric were significantly higher than the net rate of the reactions which produce ferric. At low concentrations of ferric, the formation of argentojarosite is avoided completely. Furthermore, the silver remains largely with the pyrite, and little if any silver sulfide reports to the residue. Hence, silver is recycled back to the leach process simply by recycling the pyrite, which has been successfully demonstrated in continuous mode in pilot-scale Galvanox™ tests (Dixon et al., 2007).

2. Experimental

Batch leaching experiments are conducted in a sealed 2-L jacketed glass reactor. The temperature is maintained at 80 °C with a circulating water bath. The reactor is equipped with three baffles made of 316 stainless steel and a six-bladed Rushton turbine impeller with a motor and speed controller manufactured by Applikon Dependable Instruments (ADI). Impeller speed is maintained at 1200 rpm.

Each reactor is connected to a multi-channel digital controller (ADI 1030 Bio-controller). A pH probe, a redox potential probe and a thermocouple are connected to the controller and inserted into the reactor. The outputs of these probes are recorded to the computer from the controller. In each experiment, the solution potential is set at specific point. The controller is also equipped with two analogue outputs. When the solution potential falls below the set point, an

Table 1
XRD analysis of copper concentrate and pyrite samples.

Mineral	Ideal formula	Copper conc (%)	Pyrite #1 (%)	Pyrite #2 (%)	Pyrite #3 (%)
Pyrite	FeS ₂	15.9	97.6	70.8	95.6
Chalcopyrite	CuFeS ₂	78	—	4.0	—
Quartz	SiO ₂	1	0.6	1.9	1.3
Biotite	K(Mg,Fe ²⁺) ₃ AlSi ₃ O ₁₀ (OH) ₂	1.8	—	—	0.9
Dolomite	CaMg(CO ₃) ₂	1.1	—	12.2	—
Plagioclase	NaAlSi ₃ O ₈ –CaAl ₂ Si ₂ O ₈	2.2	—	—	—
Anhydrite	CaSO ₄	—	1.8	—	—
Gypsum	CaSO ₄ ·2H ₂ O	—	—	3.4	0.6
Calcite	CaCO ₃	—	—	—	1.6
Pyrrhotite	Fe _{1–x} S	—	—	2.1	—
Clinocllore	(Mg,Fe ²⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	—	—	2.2	—
Muscovite	KAl ₂ AlSi ₃ O ₁₀ (OH) ₂	—	—	3.4	—

Table 2
Elemental analysis of copper concentrate and pyrite samples.

Element	Copper conc	Pyrite #1	Pyrite #2	Pyrite #3
Cu	27.00%	0.13%	1.8%	9 ppm
Fe	31.14%	45.43%	38.02%	44.94%
S	36.70%	52.62%	45.3%	51.36%
Mg	0.27%	0.04%	1.88%	< 0.01%
Co	0.16%	—	68 ppm	—
Pb	—	0.14%	48 ppm	< 2 ppm
As	130 ppm	—	49 ppm	10 ppm
Ag	15.5 ppm	21 ppm	2 ppm	< 0.5 ppm
Ca	0.47%	0.56%	4.05%	0.69%
Al	0.51%	0.02%	0.41%	0.18%
Zn	0.01%	—	441 ppm	71 ppm
Si	1.14%	0.28%	1.18%	1.2%

analogue signal is sent to a digital gas mass flow meter (Aalborg GFCS), upon which oxygen from a cylinder flows into the reactor through a sparger until the potential set point is reached. The rate of oxygen flow decreases as the potential becomes closer to the set point. Each reactor is also equipped with a condenser, which allows excess oxygen to exit while condensing the associated water vapor and returning it to the reactor.

Pyrite is pretreated with silver according to the following procedure: 500 mL of solution containing the desired amount of

silver, added as silver nitrate solution, is prepared. The solution is well mixed using a magnetic stirrer. 50 g of ground pyrite are added and allowed to react with the silver until no silver is detected in the solution. The behaviour of silver is studied by following the silver concentration in the aqueous phase before and after addition of pyrite at various time intervals. The silver content is determined by atomic absorption spectroscopy. Pulp density is held at 10% to ensure a high degree of mixing by the magnetic stirrer in the glass beaker. After treating the pyrite with silver ions, the solid residue is filtered and rinsed several times with water to wash any unadsorbed silver off of the pyrite surfaces.

The leach reactor is filled with 1.5 L of solution with the required concentration of sulfuric acid, corresponding to 150% of the stoichiometric requirement based on the following overall leach reaction:



The reactor is then sealed and the condenser, stirring motor and oxygen tube are installed. Before adding the concentrate, the solution is heated to the desired temperature using a recirculating water bath. Ferrous and ferric salts are added after reaching the desired temperature, and the agitation speed is set to 1200 rpm. Before starting the leach test, the pH probe is calibrated using buffer solutions at pH 1 and pH 4. The redox potential probe is also placed in a standard solution ** (470 mV vs Ag/AgCl at 25 °C) to ensure that it is working properly. Then, concentrate and pyrite are added to the reactor. Slurry samples of approximately 2 mL are taken periodically for analysis. Samples are filtered and assayed for copper content by atomic absorption spectroscopy. At the end of each test, all contents of the reactor are emptied to a flask and filtered. The solid residue is collected for analysis by multiacid digestion and induction coupled plasma (ICP) spectroscopy. The dried residue is weighed, then coned and quartered to obtain a representative sample for analysis. Solid assays are conducted by a local commercial laboratory (International Plasma Laboratory (IPL), Richmond, BC).

3. Results and discussion

A copper concentrate containing 27% copper and three pyrite samples containing 97.6%, 70.8, and 95.6% pyrite from three different sources were used. Mineralogical and elemental compositions of the concentrate and pyrite samples are summarized in Tables 1 and 2, respectively.

The first test was conducted to observe the rate of copper extraction in ferric sulfate solution at 470 mV in the absence of added pyrite. Fig. 1

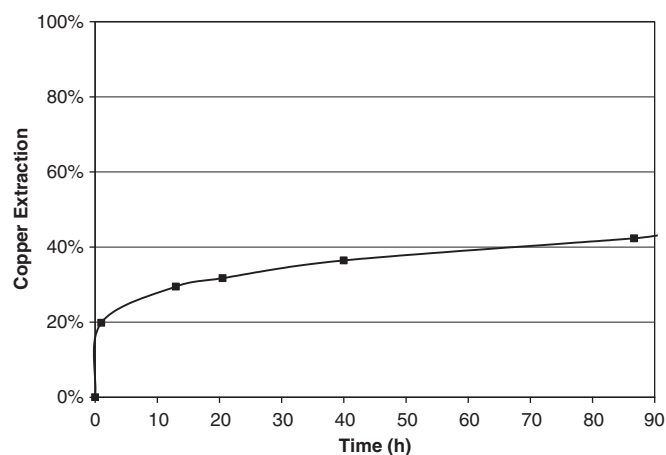


Fig. 1. Chalcopyrite leaching in ferric sulfate media at a potential set point of 470 mV and 80 °C.

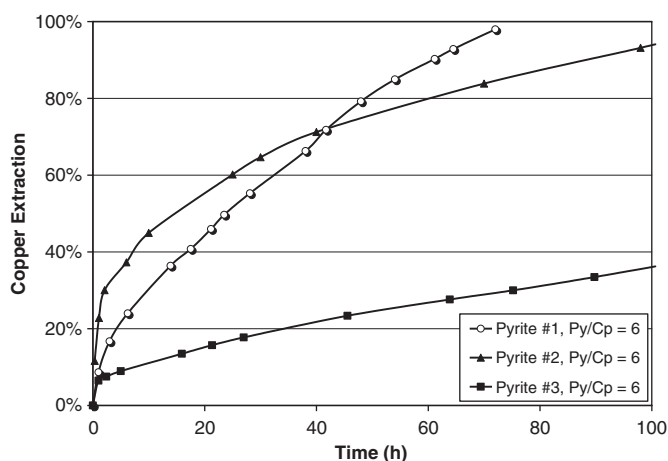


Fig. 2. Effect of pyrite addition on copper extraction using plain pyrite at a potential set point of 470 mV and 80 °C.

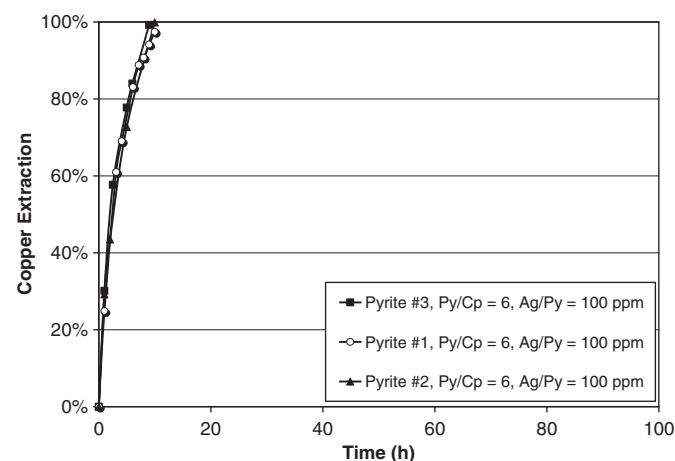


Fig. 3. Effect of silver-enhanced pyrite at a silver-to-pyrite ratio of 100 ppm, a potential set point of 470 mV, and 80 °C.

indicates very slow kinetics and incomplete copper extraction under these conditions.

Initially, pyrite samples from various sources were examined in order to obtain a broader understanding of their catalytic properties. The first series of tests were conducted to investigate the effect of adding pyrite from three different sources. The results are shown in Fig. 2. Then, these tests were repeated, but with the addition of silver at a silver-to-pyrite ratio of 100 ppm. The results are shown in Fig. 3 and show a dramatic increase in copper leaching kinetics.

The results shown in Fig. 3 also indicate that, in spite of major differences in the catalytic properties of natural pyrite from different sources, all silver-enhanced pyrite samples have an identical catalytic effect on chalcopyrite leaching. Given this similarity, all further results presented later are based only on pyrite #1.

A Malvern Mastersizer was used in order to obtain particle size distributions of the samples. Figs. 4 and 5 present the particle size distributions of concentrate and pyrite, respectively. Fig. 4 shows that the concentrate as received was not ground ultrafine ($P_{80} = 46 \mu\text{m}$). The pyrite particles were considerably larger, as shown in Fig. 5 ($P_{80} = 274 \mu\text{m}$).

A large number of leaching experiments have been conducted in order to develop an understanding of the effects of several variables on the kinetics of copper extraction from chalcopyrite using silver-enhanced pyrite. Selected results are shown later. All redox potentials are reported vs the KCl-saturated Ag/AgCl reference electrode.

Five variables were systematically investigated in this study to determine their effect on the rate of chalcopyrite leaching:

1. Mass ratio of silver-enhanced pyrite to chalcopyrite
2. Silver concentration of pyrite
3. Redox potential
4. Pyrite recycle
5. Pulp density

In addition, several tests were conducted in order to compare silver-enhanced pyrite-catalyzed leaching with conventional silver catalyzed leaching.

Two tests were conducted to observe the effect of adding pyrite #1 to chalcopyrite at two different ratios. For both tests the solution potentials were set at 470 mV. The pyrite residues were collected and recycled to subsequent tests. The results are shown in Fig. 6. While this pyrite did facilitate the complete recovery of copper from the chalcopyrite, the necessary leach times were very long (75 h or more), and the required pyrite-to-chalcopyrite ratios were high. Samples of this same pyrite material were used in all subsequent tests reported.

4. Effect of the mass ratio of silver-enhanced pyrite to chalcopyrite

In order to determine the effect of silver-enhanced pyrite addition, leaching experiments were performed at pyrite-to-chalcopyrite mass ratios of 2, 4, and 6. Each of these three ratios was tested at 100 ppm silver on pyrite. Fig. 7 shows the effects of addition of silver-enhanced pyrite on the kinetics of chalcopyrite leaching at a constant silver-to-pyrite ratio.

Fig. 7 clearly shows the significant effect of silver-enhanced pyrite on the kinetics of chalcopyrite leaching. For these tests, known amounts of pyrite were soaked in solution containing specific quantities of dissolved silver to make up 100 ppm of silver on pyrite, or 100 g Ag (roughly 3.3 troy ounces) per tonne of FeS_2 . At the highest pyrite-to-chalcopyrite ratio of 6:1, leaching is complete within roughly 10 h.

It is important to note that, for instance, at a silver-to-pyrite ratio of 100 ppm, by increasing the mass ratio of pyrite to chalcopyrite, the amount of silver used for that test in proportion to the amount of copper present also increases. Hence, increasing the ratio of pyrite to chalcopyrite may not be the only reason for the improved leaching rates in these tests. Fig. 8 presents the results for a total amount of

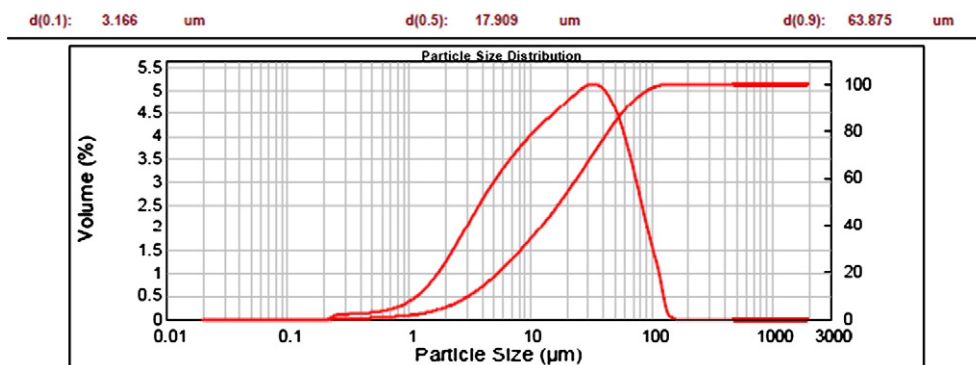


Fig. 4. Particle size distribution of copper concentrate.

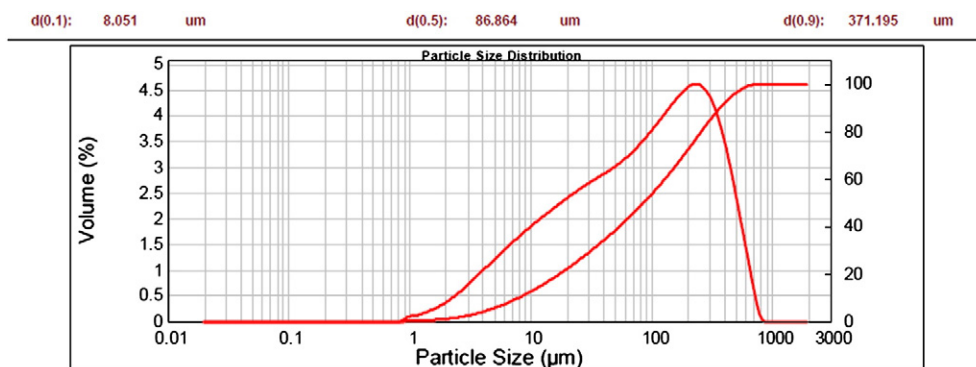


Fig. 5. Particle size distribution of pyrite.

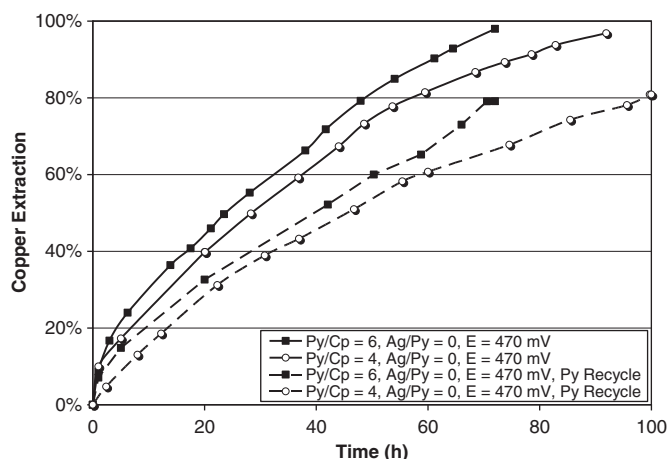


Fig. 6. Effect of pyrite addition on copper extraction using plain pyrite and the recycled plain pyrite at a potential set point of 470 mV and 80 °C.

5 mg silver. In one of the tests, the ratio of pyrite to chalcopyrite is twice the other, whereas the ratio of silver to pyrite is half. Fig. 8 shows that although the total amounts of silver in both cases are equal, the leaching rate is measurably faster at a higher pyrite-to-chalcopyrite ratio. This confirms the beneficial role of pyrite in the process.

5. Effect of silver concentration on pyrite

In order to delineate the effect of silver-to-pyrite ratio, this parameter was varied at fixed ratios of pyrite to chalcopyrite. Silver-to-pyrite ratios of 50, 100, and 200 ppm were tested at a pyrite-to-chalcopyrite ratio of 6. Results are shown in Fig. 9. Increasing the concentration of silver increases the rate of copper extraction significantly. At a silver-to-pyrite ratio of 200 ppm, leaching is complete in about 5 h.

6. Effect of solution potential

Previously, Dixon et al. (2008) have shown that increasing the solution potential set point from 425 to 470 mV accelerates chalcopyrite leaching rates in the presence of pyrite. Hence, the first series of experiments were conducted at a potential set point of 470 mV. In order to inhibit the oxidation of pyrite and the attendant loss of adsorbed silver, it was subsequently decided to decrease the solution potential set point.

Fig. 10 shows the effect of varying the solution potential set point. This figure clearly indicates that copper extraction was faster at 440 and

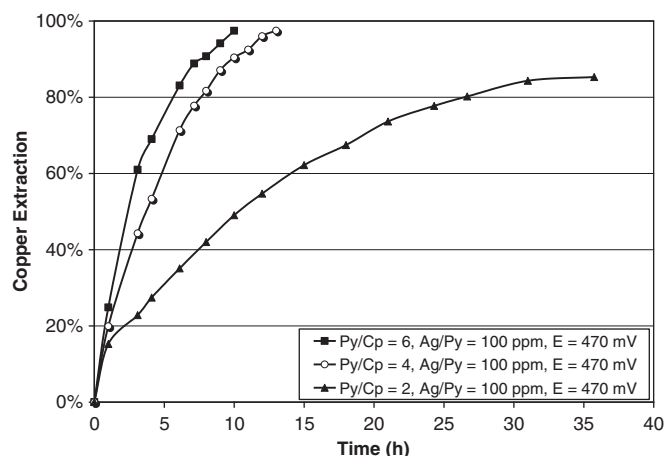


Fig. 7. Effect of silver-enhanced pyrite at various pyrite-to-chalcopyrite ratios, a silver-to-pyrite ratio of 100 ppm, a potential set point of 470 mV, and 80 °C.

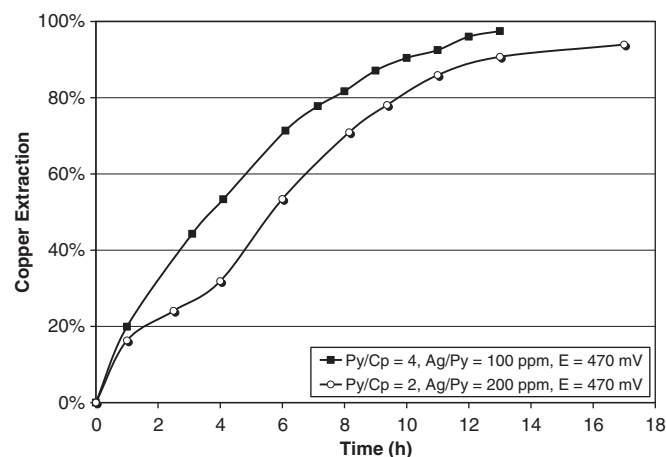


Fig. 8. Effect of pyrite and silver concentrations at 5 mg Ag total, a potential set point of 470 mV, and 80 °C.

450 mV than at 470 mV. However, dropping the solution potential to 420 mV gave a much slower rate. The rest potential of pyrite is roughly 455 mV vs Ag/AgCl (Abraitis et al., 2003). According to this graph, the fastest rate was achieved at 450 mV. This faster rate at lower potential can probably be attributed to a decrease in pyrite oxidation and, therefore, in the loss of adsorbed silver to solution. At significantly higher potentials, too much pyrite is oxidized and too much silver is lost. At lower potentials, the anodic decomposition of chalcopyrite is retarded, as also observed in conventional Galvanox™ leaching.

In Fig. 11, the rates of leaching at two different solution potential set points are compared. In each of these tests, the ratio of pyrite to chalcopyrite was 2. Only selected results are presented here. This figure shows the significant improvement in chalcopyrite leaching at lower solution potential. At 450 mV and a silver-to-pyrite ratio of 50 ppm, leaching was complete after 23 h whereas at 470 mV, only 88% copper extraction was achieved after 66 h.

It is also interesting to note that at a solution potential set point of 470 mV and a silver-to-pyrite ratio of 100 ppm, only 85% extraction was achieved after 36 h. Hence, although the amount of silver was reduced to half of the other test, due to the lower potential the leaching occurred at a much faster rate.

7. Effect of pyrite recycle

The feasibility of recycling pyrite for treating subsequent charges of concentrate was also examined. In each of the tests, upon

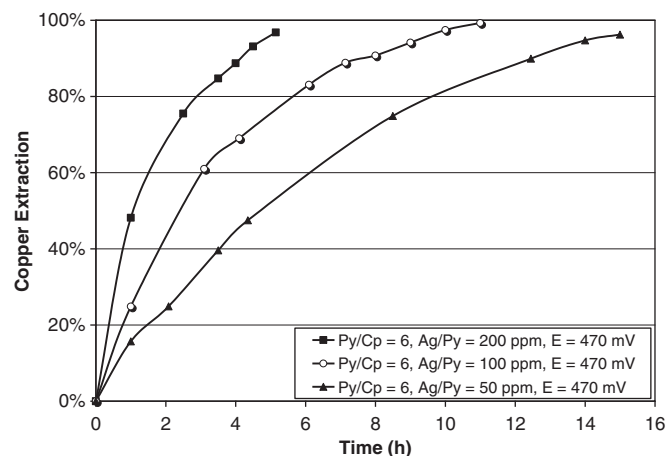


Fig. 9. Effect of silver-to-pyrite ratio at a constant pyrite-to-chalcopyrite ratio of 6, a potential set point of 470 mV, and 80 °C.

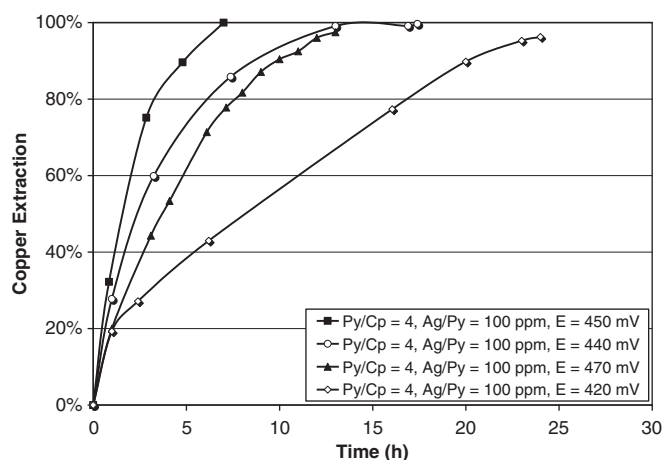


Fig. 10. Effect of potential at a constant pyrite-to-chalcopyrite ratio of 4, a constant silver-to-pyrite ratio of 100 ppm (1.23 g Ag per kg of contained Cu), at a pulp density of 4.3% (w/v), and 80 °C.

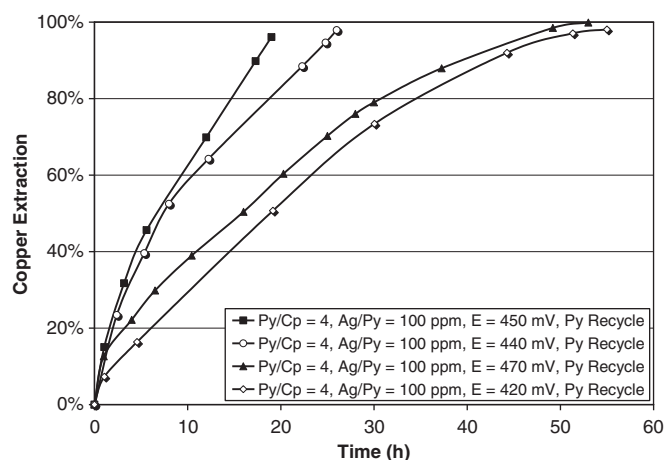


Fig. 12. Effect of potential with recycled pyrite at a constant pyrite-to-chalcopyrite ratio of 4, a constant silver-to-pyrite ratio of 100 ppm (1.23 g Ag per kg of contained Cu), at a pulp density of 4.3% (w/v), and 80 °C.

completion of the first test, the supernatant solution was decanted from the reactor while retaining the residue. Then, new solution containing the desired amounts of sulfuric acid was added. This new solution was heated to 80 °C and then the required amounts of ferric and ferrous sulfate and a new charge of fresh concentrate were added.

Fig. 12 shows the results of recycling pyrite from the tests that were presented in Fig. 10. The recycle tests follow the same trend as the initial tests. Similarly, the fastest and slowest copper extraction was observed at 450 and 420 mV, respectively. This indicates that the silver-enhanced pyrite retains its catalytic properties. However, it should be noted that the leach times are all longer in the recycle tests, by roughly a factor of two. Solid assay results confirm that the recycled pyrite contained less adsorbed silver than the freshly enhanced pyrite.

8. Effect of pulp density

While it has been demonstrated that recycled pyrite is an effective catalyst, it has also been noted that some of the adsorbed silver, and with it some of the catalytic effectiveness, is lost upon recycle. However, it was also determined that the concentration of silver dissolved in the leach solution at the end of each test was always about the same, and probably represented a solubility limit for silver under the prevailing conditions. Furthermore, this amount corresponded roughly to the amount lost from the recycled pyrite based on

solid assay results. Hence, it was hypothesized that increasing the concentration of pyrite in the reactor would decrease the relative loss of adsorbed silver to solution.

Fig. 13 shows the effect of increasing the pulp density on the rate of chalcopyrite leaching. Previous tests were run with 10 g of copper concentrate per L of solution whereas Fig. 13 shows the results of three tests run with 70 g of copper concentrate per L of solution, or 105 g total. In the first test, 175 g of fresh silver-enhanced pyrite with a silver-to-pyrite ratio of 100 ppm were added to give a pyrite-to-chalcopyrite ratio of 2:1. In the second and third tests, solid residues from the previous tests were recycled with fresh charges of copper concentrate, plus an additional 10% of the original charge, or 17.5 g, of fresh silver-enhanced pyrite. As shown in Fig. 13, leaching with recycled residue occurs just as rapidly as leaching with freshly enhanced pyrite, and there is no loss of catalytic ability even after recycling the pyrite a second time. In fact, the second recycle test gave slightly faster leaching than the others, suggesting that the 10% makeup of silver-enhanced pyrite was more than adequate to ensure optimum catalytic effectiveness. In any case, the addition of 10% silver-enhanced pyrite to each recycle test corresponds to the addition of just 60 mg of silver per kg of contained copper.

The pulp density in these tests was 18.7% (w/v) and the net increase in copper concentration in each test was roughly 19 g/L ($\Delta\text{Cu} = 19 \text{ g/L}$). In commercial practice, following leaching and solid

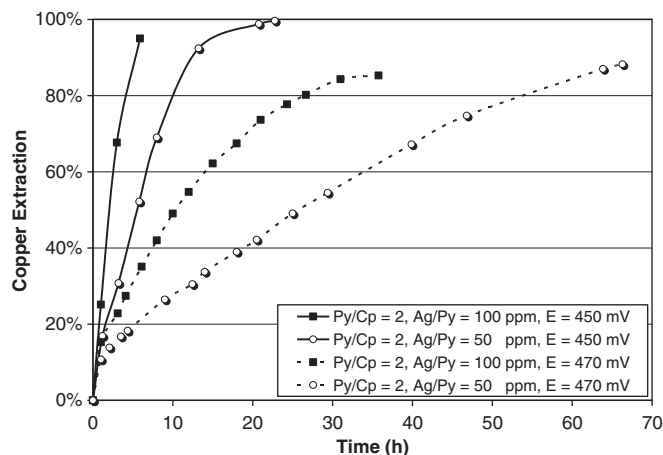


Fig. 11. Comparison of two different solution potential set points (450 and 470 mV) and silver-to-pyrite ratios (50 and 100 ppm) at a constant pyrite-to-chalcopyrite ratio of 2, and 80 °C.

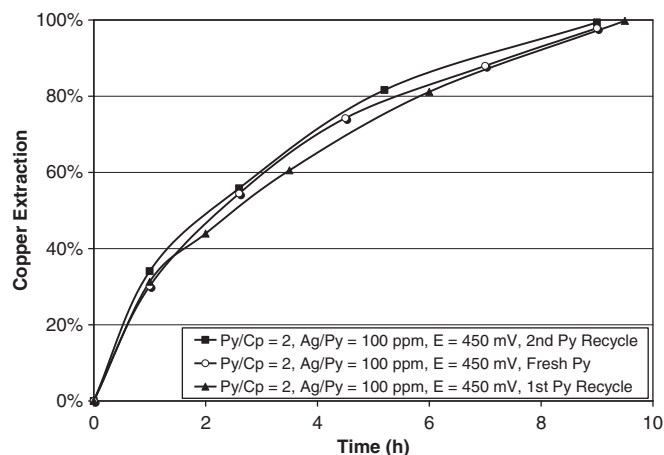


Fig. 13. Effect of higher pulp density at a constant pyrite-to-chalcopyrite ratio of 2, an initial silver-to-pyrite ratio of 100 ppm, a potential set point of 450 mV, at a pulp density of 18.7% (w/v) and 80 °C.

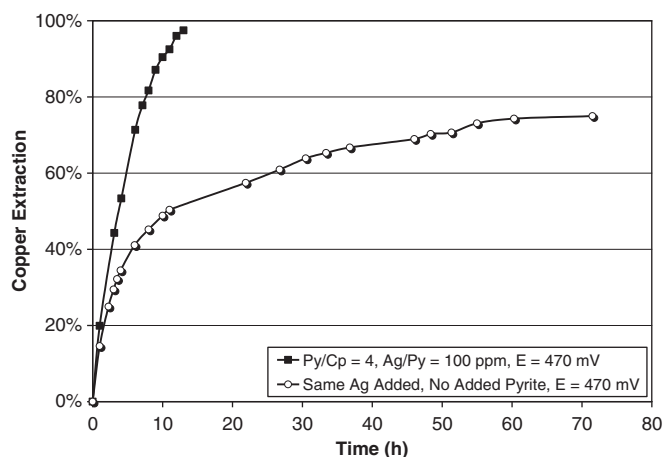


Fig. 14. Comparison between conventional silver-catalyzed leaching and leaching with silver-enhanced pyrite at 1.23 g Ag per kg of contained Cu, a potential set point of 470 mV, and 80 °C.

liquid separation, the pregnant leach solution (PLS) would be introduced to conventional solvent extraction, where each mole of copper removed from the aqueous solution would be replaced with one mole of sulfuric acid. In high copper tenor solutions, a significant amount of acid is produced which can affect the loading behaviour of the organic extractant by shifting the equilibrium toward stripping. Hence, in this process, the main factor limiting pulp density in the leach circuit is the capacity of the subsequent solvent extraction circuit.

9. Comparison between conventional silver-catalyzed leaching and leaching with silver-enhanced pyrite

A review of the literature indicates that several researchers have demonstrated the ability of silver to accelerate the leaching of copper from chalcopyrite. Furthermore, in several studies, it has been shown that silver has a much stronger affinity to interact with chalcopyrite than with pyrite. It has also been stated that, in the presence of ferric ions, adsorbed silver is oxidized and dissolved from the surface of pyrite. From this, one might conclude that adding silver to pyrite initially and then introducing this pyrite into the reactor would give similar results as adding silver to the chalcopyrite directly.

In order to test this hypothesis, two leaching experiments were conducted under identical conditions. In one test, silver-enhanced

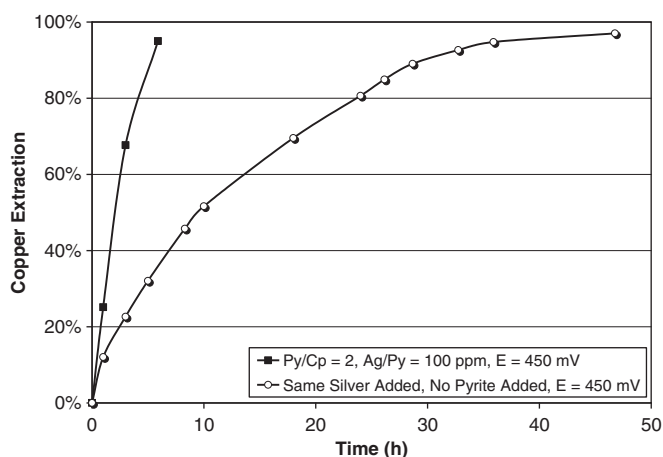


Fig. 15. Comparison between conventional silver-catalyzed leaching and leaching with silver-enhanced pyrite with 0.65 g Ag per kg of contained Cu, and at a potential set point of 450 mV, and 80 °C.

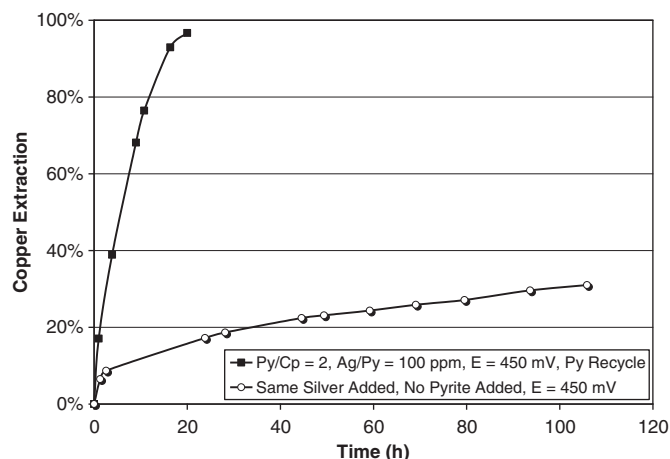


Fig. 16. Comparison between leaching with recycled residue from a conventional silver-catalyzed leaching test and with recycled silver-enhanced pyrite, both with 0.65 g of Ag added initially per kg of contained Cu, and at a potential set point of 450 mV, and 80 °C.

pyrite was added. In the other test, the same amount of silver was added directly to the chalcopyrite with no pyrite present. As shown in Fig. 14, the presence of pyrite is a critical factor for achieving rapid and complete copper extraction in both tests were similar, the rate declined sharply after just a few hours in the test without pyrite, and complete copper extraction was not achieved even after 70 h of leaching. However, in the presence of the silver-enhanced pyrite, leaching was very rapid for the duration of the test, and complete copper extraction was achieved within about 12 h.

Since faster leaching was observed at a lower redox potential, the tests shown in Fig. 14 were repeated at 450 mV, and the results are shown in Fig. 15. These results confirm the beneficial effect of lower solution potential, and also confirm the dramatic increase in both the rate and the extent of copper extraction in the presence of pyrite. It also bears noting that these tests were conducted with only half the amount of silver of the previous tests, but the results were significantly better, even in the absence of pyrite. This further confirms the benefit of operating at a lower redox potential.

The two tests shown in Fig. 15 were repeated with recycled solid residues to confirm that silver-enhanced pyrite retains its effectiveness as a catalyst upon recycle, and to determine whether the solid residues from the test in the absence of pyrite retained any similar catalytic ability. As shown in Fig. 16, copper extraction in the presence of the recycled pyrite was rapid and complete within about 20 h.

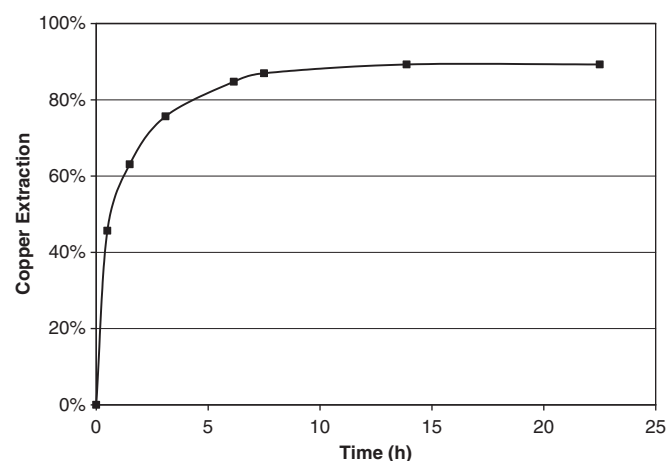


Fig. 17. Typical results of the BRISA process with 22.2 g Ag per kg of contained Cu, initial Fe^{3+} concentration of 24 g/L, at a pulp density of 2% (w/v) and 70 °C.

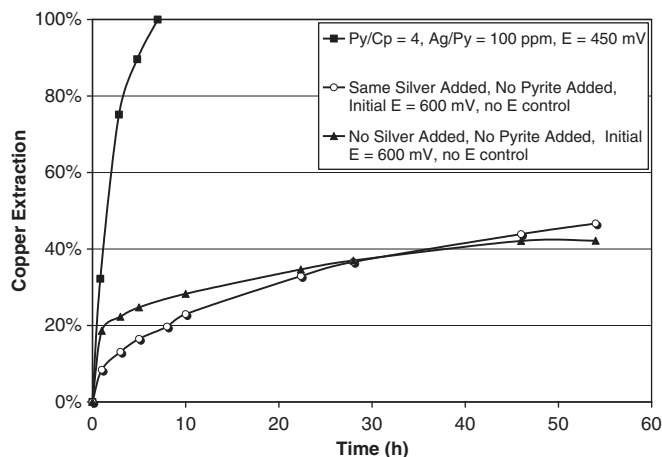


Fig. 18. Comparison between high-potential silver-catalyzed leaching and silver-enhanced pyrite-catalyzed leaching, both with 1.23 g Ag per kg of contained Cu, at 80 °C.

However, the residue without pyrite retained little or no catalytic ability. Any silver remaining in this residue was probably in the form of tiny Ag_2S particles embedded in elemental sulfur, as it is unlikely that argentiojarosite would have formed to a significant extent at a redox potential of only 450 mV. Even so, the results shown in Fig. 16 indicate that silver used in conventional silver catalyzed leaching cannot be recycled directly, but must first be recovered in soluble form. Dutrizac (1994) also showed that the dissolution of Ag_2S in ferric sulfate media at less than 110 °C is negligible. As mentioned earlier, recovering silver in a soluble form is a complicated undertaking which can only be achieved at significant expense.

Tests were also conducted to compare the addition of silver-enhanced pyrite with the BRISA process, which is based on conventional silver-catalyzed leaching and which has been the subject of several recent publications (Carranza et al., 1997; Romero et al., 1998; Romero et al., 2003). The first test was run under conditions identical to those recommended for the BRISA process, including the proposed amount of added silver. The results, shown in Fig. 17, agree very closely with the work of Romero et al. (2003). Leaching kinetics are reasonably rapid, but complete copper extraction is not achieved. This confirms similar results reported in Romero et al. (2003), which also showed incomplete copper extraction from every test. It bears noting that the amount of silver used in the BRISA process is nearly 40 times higher than the initial amount of silver used to enhance pyrite in our process.

This experiment was repeated with the same amount of silver required for silver-enhanced pyrite in our process. Fig. 18 compares the results of high-potential silver-catalyzed leaching and low-potential silver-enhanced pyrite, both using the same amount of silver. The main difference between these low-silver tests and the conventional silver-catalyzed tests shown in Figs. 15 and 18 is that the latter were initiated at a much higher redox potential (roughly 600 mV). For comparison purposes, another test was also run under conditions identical to the BRISA process, but without added silver. Obviously, at the very low levels of silver addition used in our process, high-potential silver-catalyzed leaching gives very similar results to leaching chalcopyrite with no catalyst present at all. The higher redox potential corresponds to the high ratios of ferric to ferrous recommended in Romero et al. (2003). Obviously, this practice is antithetical to rapid oxidation of chalcopyrite, for the reasons alluded to earlier.

10. Conclusions

A new process is reported here whereby pyrite, pretreated with miniscule amounts of soluble silver, is used as a catalyst for atmospheric

leaching of chalcopyrite in iron sulfate media. In this new process, which is an improvement on the Galvanox™ process, the catalytic properties of pyrite are improved such that all pyrite samples accelerate the rate of copper extraction from chalcopyrite significantly. The effects of several variables such as the mass ratio of pyrite to chalcopyrite, the ratio of silver to pyrite, solution potential, and pulp density were evaluated in order to discover the optimized conditions for this process and to render it economically feasible. It was found that the addition of as little as 60 mg of silver per kg of copper is sufficient to ensure the complete copper extraction within 10 h of leaching. It was also found that recycled pyrite is equally as effective as freshly enhanced pyrite as a catalyst, which adds significantly to the commercial attractiveness of the process.

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