

Acidic sulphate leaching of chalcopyrite concentrates in presence of pyrite

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ABSTRACT

Copper concentrates with mineralogy dominated by chalcopyrite have slow leaching kinetics at atmospheric pressure in sulphate media because of the formation of passivation layer on its surface during the leaching. To enhance the leaching rate of the copper concentrate, pyrite was added to act as a catalyst. Pyrite and copper sulphide minerals then form a galvanic cell which increases both the copper leaching rate and yield. Effect of parameters such as solution redox potential, temperature, initial acid concentration, solids content, total initial iron concentration and pyrite to copper sulphide minerals mass ratio were investigated. Mineralogical analyses by XRD were performed on selected leach residues and the feed materials. A copper recovery higher than 80% in 24 h was achieved at a redox potential of 410 mV vs Ag, AgCl, a temperature of 85 °C, 15 g/L of initial acid concentration, a solid content of 7.8% (w/v), a total initial iron concentration 5 g/L and pyrite to copper sulphide minerals mass ratio 2:1. XRD patterns on leach residues showed that candidates for surface passivation, i.e. jarosite and elemental sulphur, were formed at high total initial iron concentrations.

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1. Introduction

Presently, the smelting/converting technology is the preferred route to produce copper from sulphide concentrates containing chalcopyrite as the main copper sulphide and sulphides of deleterious minor elements such as arsenic, antimony, and bismuth (Padilla et al., 2010).

The world production of refined copper, estimated by the Australian Bureau of Agricultural and Resource Economics (ABARE), for the years 2008–2009 was 19.987 Mt and around 20% of that was produced by hydrometallurgical methods (Helle et al., 2010).

Chalcopyrite (CuFeS_2), with valence +1, +3 and –2 for Cu, Fe and S, respectively, is the most abundant copper sulphide mineral and also it is the most refractory copper mineral regarding chemical as well as bioleaching (Sandström et al., 2005). In order to accelerate the dissolution of chalcopyrite, various leaching methods have been proposed from laboratory studies. There are different options to enhance chalcopyrite leaching in sulphate media; among these are: autoclave leaching at high pressure and temperature, use of microorganisms, ultra fine grinding, and the addition of silver ions or chloride ions (McDonald and Muir, 2007; Carranza et al., 2004; Dreisinger, 2006). In nature, most metal sulphide minerals have semiconductor properties. The mineral, or the region, with the highest rest potential will act as the cathode of the galvanic cell and is protected whereas that with the lowest rest potential will

serve as anode, and its rate of dissolution will be increased (Nicol, 1975; Mehta and Murr, 1982; Natarajan and Iwasaki, 1983; Liu et al., 2007; Tshilombo, 2004). Galvanic effects, occurring between conducting and semiconducting minerals in aqueous systems, play an important role in the aqueous processing of ores and minerals, such as in flotation and leaching. For semiconductive minerals, such as sulphides, direct contact of different minerals with dissimilar rest potentials initiates the galvanic effect. These interactions occur between sulphides, involving the flow of electrons from grains with a higher potential to grains with lower potentials, modifying the Fermi level of both minerals (Cruz et al., 2005; Holmes and Crundwell, 1995). Mehta and Murr (1983) experimentally studied the galvanic interactions between a series of sulphide minerals, including the pyrite–chalcopyrite couple. The experimental results revealed that the galvanic interactions between pyrite and chalcopyrite significantly affected leaching and extraction of chalcopyrite from a mixed-ore slurry of pyrite and chalcopyrite. The presence of pyrite in the slurry led to a 2–15 times increase in the rate of dissolution of chalcopyrite. The rest potential of certain sulphide minerals are given in Table 1.

Pyrite and chalcopyrite, the most common and exploitable sulphide minerals, usually occur together and in contact with each other. Due to the companionship of pyrite with chalcopyrite in nature the co-treatment of these minerals might be advantages from an economic point of view. A novel process for chalcopyrite leaching, Galvanox™, based on a galvanically-assisted leaching has been introduced (Dixon et al., 2008). In this process primary copper concentrates are leached under atmospheric pressure in a ferric-ferrous sulphate medium in the presence of pyrite.

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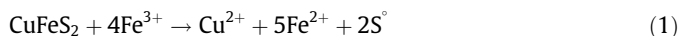
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Table 1

Rest potential of some sulphide minerals (Mehta and Murr, 1983).

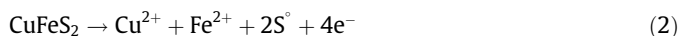
Mineral	Chemical formula	Rest potential (V vs SHE)
Pyrite	FeS ₂	0.63
Chalcopyrite	CuFeS ₂	0.52
Chalcocite	Cu ₂ S	0.44
Covellite	CuS	0.42
Galena	PbS	0.28
Sphalerite	ZnS	−0.24

The dissolution reaction of chalcopyrite with ferric ions is written as



Chalcopyrite dissolution in sulphate media with ferric sulphate is an electrochemical reaction, therefore it can be written as anodic and cathodic half-cell reactions as Eqs. (2) and (3) (Mikhin et al., 2004; Misra and Fuerstenau, 2005; Watling, 2006; Liu et al., 2007).

Anodic half-cell reaction: chalcopyrite oxidation



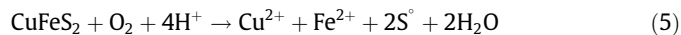
Cathodic half-cell reaction: reduction of ferric ions



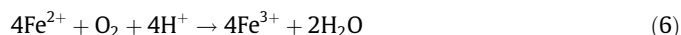
According to Fig. 1a, in the absence of pyrite both the anodic and cathodic half-cell reactions take place on the chalcopyrite surface. Dixon et al. (2009) claim that the slow dissolution rate of chalcopyrite is because of a slow cathodic half-cell reaction at the surface of chalcopyrite. That means that if the rate of the cathodic half-cell reaction could be increased, the dissolution rate of chalcopyrite would be increased. In the presence of pyrite, the cathodic reaction on the pyrite surface is fast which in turn gives faster dissolution rate of chalcopyrite (Tshilombo, 2004). According to Fig. 1b both the cathodic reaction and the anodic reaction takes place at the surfaces of pyrite and chalcopyrite, respectively.

Instead of ferric ions oxygen can be the active oxidant. In this case oxygen is reduced on the pyrite surface (Eq. (4)). Direct oxida-

tion of chalcopyrite by oxygen according to Eq. (5) is, according to Liu et al., (2007) negligible in comparison to Eq. (1).

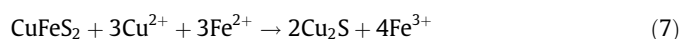


In galvanic leaching of chalcopyrite in the presence of pyrite, ferric ions are consumed but are during the process regenerated by oxidation with oxygen blowing according to Eq. (6) (Holmes and Crundwell, 2000).

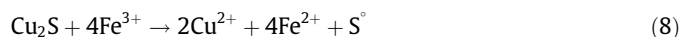


However, when the sum reaction of Eqs. (1) and (6) are considered, Eq. (5) is derived, which thus is the reaction which represents the complete chalcopyrite oxidation. From Eq. (5) it can be seen that oxidation of chalcopyrite under conditions where elemental sulphur is formed, is an acid consuming reaction.

The redox potential is important for effective leaching of chalcopyrite and in contrast to most other metal sulphides it has been found that chalcopyrite leaches better at relatively low redox potential (Sandström et al., 2005). Already in 1985, Kametani and Aoki (1985) established the effect of solution redox potential on chalcopyrite leaching in mixed solutions of ferrous and ferric sulphate. The authors reported that there is a critical potential at which the leaching rate is maximum and that the rate decreases above and below this potential, the optimum redox potential was found to be in the range 400–430 mV vs SCE. Hiroyoshi et al. (2000, 2001, 2004, 2008) found that copper extraction during oxidative leaching of chalcopyrite by ferric ion or by dissolved oxygen in sulphuric acid solution is a function of the ferrous, ferric, cupric ions and acid sulphuric concentrations. They proposed a model consisting of a two-step reaction where conversion of chalcopyrite is first achieved



The newly formed chalcocite is easier to leach than chalcopyrite (Sandström et al., 2005; Aleksandar et al., 1982) and is oxidized by ferric ions



when Eqs. (7) and (8) are summed Eq. (1) for ferric leaching of chalcopyrite is derived.

In this study, the galvanic effect between pyrite and chalcopyrite was used. To enhance chalcopyrite leaching the effect of parameters such as the solution redox potential, temperature, initial acid concentration, solids content, total initial iron concentration and mass ratio of pyrite to copper sulphide minerals were investigated. To study changes in mineralogy, XRD diffractograms were taken on selected residues and the feed materials.

2. Material and methods

2.1. Material, analytical and instrumentation techniques

Copper concentrate and pyrite samples from Sarcheshmeh copper mine in Iran were used in the experiments. Mineralogical and chemical analyses of samples were investigated by optical microscopy and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Quadrupole Mass Spectrometry (ICP-QMS)/Sector Field Mass Spectrometry (ICP-SFMS) respectively. The copper concentrate was used without further preparation whereas the pyrite sample was first crushed with a roller crusher and then ground in a rod mill. Size distribution analysis by CILAS 1064 Liquid showed that particle size of copper concentrate was 90% less than 33.4 micron and for pyrite it was 90% less than 27 µm.

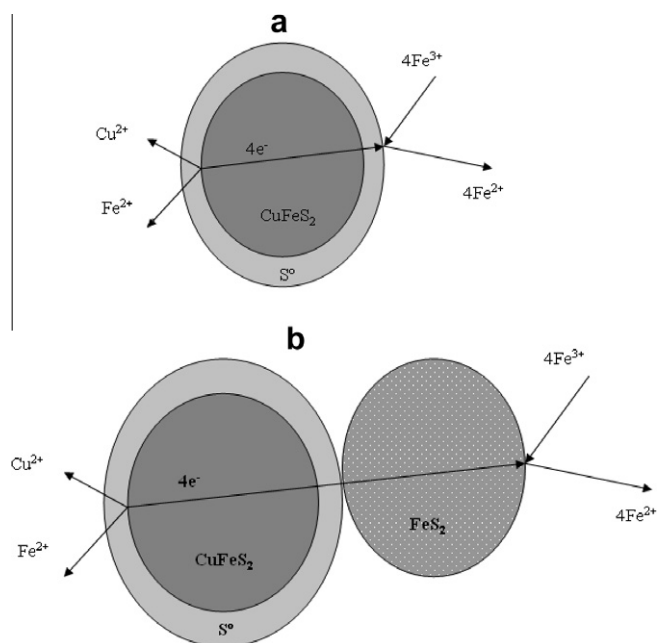


Fig. 1. Chalcopyrite leaching by ferric ions (a) without pyrite (b) with pyrite.

In the leaching experiments, sulphuric acid with purity of approximately 98%, ferrous hepta hydrate sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 6.76 \text{H}_2\text{O}$ with high purity were used. All chemicals used was from Merck Company. Deionised water was used for leaching experiments. Oxygen and nitrogen with high purity were used for control of redox potential in the leaching reactor. Copper and total iron was analyzed by AAS (Perkin Elmer Instruments, Analyst 100). A platinum electrode with a Ag, AgCl reference electrode was used for redox measurements, while a Lange LDO™/sc100 was used for the measurement of dissolved oxygen in the reactor. All reported redox potentials in this article are relative to the Ag, AgCl reference electrode. X-ray diffraction (XRD) was performed using a Siemens D5000 automatic diffractometer provided with a continuous scanning device. Cu K α radiation of 40 kV and 30 mA and a sample rotation of 30 rpm were used. Diffraction patterns were measured in the range from 10° to 90° in 0.02°/step by counting 2 s/step and crystalline phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

2.2. Experimental procedure

Leaching experiments were performed in a 2.5 L glass reactor with a working volume of 1 L. An airtight lid with a condenser was used to minimize the evaporation from the reactor. Homogeneous mixing of the pulp was achieved by agitation with a propeller stirrer at a rotation speed of 400 rpm. To avoid vortex formation two baffles were mounted perpendicular to the vessel wall.

Initial redox potential was controlled by adjusting the ferric to ferrous ion ratio. Oxygen or nitrogen gas was injected continuously inside the reactor for controlling the redox potential. The redox potential of leaching reactor was controlled manually within ± 15 mV. At desired time intervals, 5 ml solution was withdrawn for analysis of copper and iron. Solution lost by sampling and evaporation was compensated by addition of deionised water.

3. Results and discussion

3.1. Mineralogical and chemical analysis of the pyrite and copper concentrate samples

Chemical and mineralogical analysis of the copper concentrate and pyrite samples are shown in Tables 2 and 3, respectively. The mineralogical analysis is calculated based on the chemical analysis and knowledge from optical microscopy of the mineralogical phases present in the samples. As seen in Table 3 the major copper mineral in the copper concentrate is chalcopyrite with minor amounts chalcocite and covellite. Apart from its presence in chalcopyrite and pyrite smaller amounts of iron were by optical microscopy also seen in hematite and magnetite. The pyrite sample was relatively pure with a pyrite content of approximately 90–95% with the remaining mainly as gangue minerals.

3.2. Effect of solution redox potential

In Fig. 2 the rate of copper recovery at different redox potentials at 85 °C, initial acid concentration of 15 g/L, solid content of 7.8% (w/v), total initial iron concentration of 5 g/L and pyrite to copper

Table 3

Calculated mineralogical content of the copper concentrate.

Cu_2S	CuS	CuFeS_2	FeS_2	MoS_2	ZnS
6.3	2.7	47.7	15.8	0.1	0.8

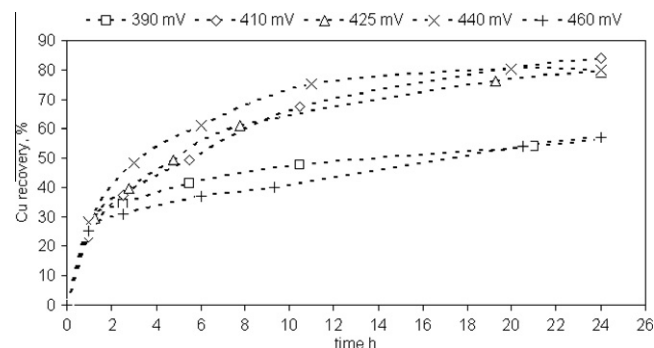


Fig. 2. Copper recovery as a function of solution redox potential.

sulphide minerals mass ratio of 4 is shown. It is evident that there is a redox potential window in the range, 410–440 mV in which the copper recovery is decent. This is in close agreement with the results from a number of studies where it has been seen that the optimum redox potential for good copper recoveries varies relatively much in the range between 400 mV and 480 mV vs Ag, AgCl (Hiroyoshi et al., 2000, 2001, 2004, 2008; Sandström et al., 2005; Dixon and Tshilombo, 2005; Dixon et al., 2008; Koleini et al., 2010). This relative big difference in optimum conditions is concentrate dependent and the reasons for this might be differences in crystal orientation, impurity content or slight variations in mineral stoichiometry (Tshilombo, 2004).

When the optimum redox potential is exceeded the passivation gradually increases and becomes severe at redox potentials above 550 mV vs Ag, AgCl (Dixon and Tshilombo, 2005; Tshilombo, 2004). On the other hand oxidation of pyrite starts to be significant at redox potentials above 500 mV vs Ag, AgCl (Ou et al., 2007; Tshilombo, 2004). This is of course an unwanted reaction, since pyrite is needed to achieve the galvanic interaction but also due to the costs associated with first the consumption of oxidation agent during leaching and later its removal by precipitation in the down stream processing. Therefore, a redox potential below 500 mV (vs Ag, AgCl) is the best option since it minimizes both passivation of chalcopyrite as well as oxidation of pyrite.

In Fig. 3 the XRD patterns of feed and leach residues from the experiments with solution redox potentials of 410 and 460 mV are shown. The feed is a mix of the pyrite sample and the copper sulphide minerals at a mass ratio of 4:1 and the major phases found were pyrite and chalcopyrite together with quartz as the gangue material. Chalcocite and covellite were not detected by XRD due to their small concentrations in the feed. The diffractogram of the leach residue obtained after leaching at 410 mV shows that most of the chalcopyrite has been leached at this redox potential whereas the leach residue pattern from the experiment at 460 mV confirms the low recovery of copper. In addition, traces of elemental sulphur were found in the residue from the high redox potential (460 mV) experiment.

Table 2

Chemical composition of the copper concentrate and pyrite (%).

Component	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Zn	Cu	Fe	S	Mo
Copper concentrate	16.0	5.1	0.94	1.0	0.24	0.742	23.2	25.1	26.5	0.049
Pyrite	1.95	1.0	0.07	0.3	0.03	0.010	0.035	44.1	45.7	0.000

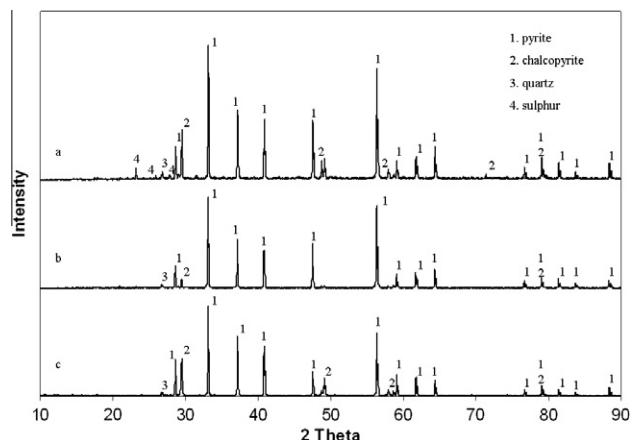


Fig. 3. XRD pattern of (a) leach residue at 460 mV, (b) leach residue at 410 mV and (c) feed.

3.3. Influence of temperature

In Fig. 4 the temperature dependence on copper recovery at the temperatures 48 °C, 68 °C and 85 °C is illustrated with the other leaching conditions constant, i.e. solution redox potential 410 mV, initial acid concentration 15 g/L, solid content 7.8% (w/v), total initial iron concentration of 5 g/L and pyrite to copper sulphide minerals mass ratio of 4. The copper recovery was significantly elevated and increased from 20% at 48 °C up to 84% at 85 °C. It has been shown in previous studies that leaching of chalcopyrite is controlled by the chemical reaction at the surface with an activation energy around 70–90 kJ/mol (Dutrizac et al., 1969; Dutrizac, 1981; Munoz-Castillo et al., 1979; Koleini et al., 2010). Such high activation energy implies that leaching rate and recovery is highly temperature dependent and it has earlier been shown by Berry et al. (1978) that a twofold increase in reaction rate was obtained for each 10 °C rise in temperature. Similar results on temperature dependence were seen in a recent study on the effect of galvanic interaction between chalcopyrite and pyrite (Koleini et al., 2010). The XRD diffractogram of the leach residue from the experiment at 48 °C confirms that a substantial amount of chalcopyrite still remains in the residue (Fig. 5).

3.4. Dependence of initial acid concentration

The influence of initial acid concentration on copper recovery was investigated at various initial acid concentration (7.5, 15 and 30 g/L), solution redox potential 410 mV, temperature of 85 °C,

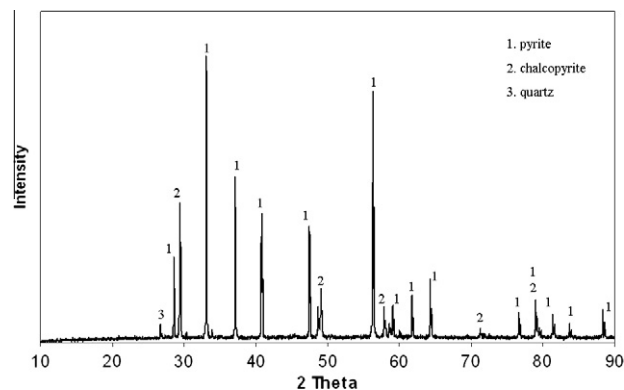


Fig. 5. XRD pattern of leach residue from the experiment at 48 °C.

solid content of 7.8% (w/v), total initial iron concentration of 5 g/L and pyrite to copper sulphide minerals mass ratio of 4 is shown in Fig. 6. It can be seen that the initial acid concentration has no or little effect on the copper recovery under the conditions used in these experiments. However, as discussed previously, leaching of chalcopyrite is an acid consuming process and enough acid for the reaction has to be provided. In the experiments with the lowest initial acid concentration, pH at the start was around 0.8 and when pH was checked after the experiments it was usually in the range of 1.4–1.6, but in some experiments with good copper recoveries pH was as high as 1.8–1.9. These high pH values are at the limit where ferric iron starts to hydrolyse and might precipitate as jarosite. The main role of acid is to prevent hydrolysis of ferric ions and in general an acid concentration of at least 0.1 M is sufficient to avoid this (Dutrizac et al., 1969; Dutrizac, 1981). Dixon et al. (2008) showed in a galvanically assisted copper concentrate leaching study that only stoichiometric amount of acid is required and that further increase in acid concentration had little effect on leaching. Antonijevic and Bogdanovic (2004) showed that at low pH values passivation occurs by the formation of an iron deficient solid phase at the surface. Interestingly, it was shown in a thermodynamic study calculated on a solution containing 0.09 M Fe^{3+} and 0.2 M SO_4^{2-} that the main specie responsible for chalcopyrite oxidation was the ferric sulphate complex ($\text{Fe}(\text{SO}_4)_2^+$) and not the ferric ion itself (Córdoba et al., 2008). Tshilombo (2004) claimed that at high initial acid concentration, the recovery of copper is higher because of an increased galvanic effect and non-oxidative dissolution of chalcopyrite. However, in the present research no dependence on the acid concentration was observed. One of the reasons can be the difficulties in controlling the redox potential. In our previous work on pure chalcopyrite leaching in the presence of pyrite, the

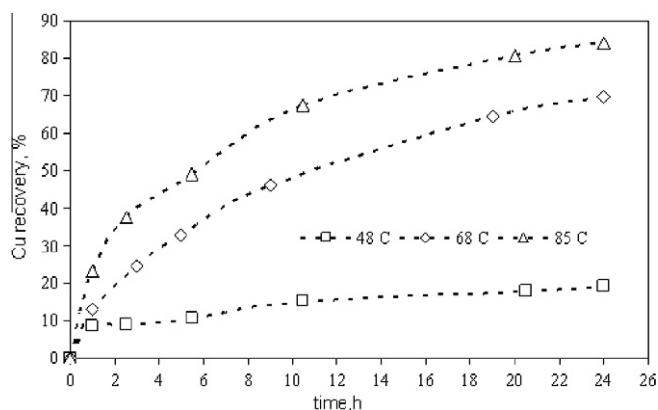


Fig. 4. Copper recovery as a function of temperature.

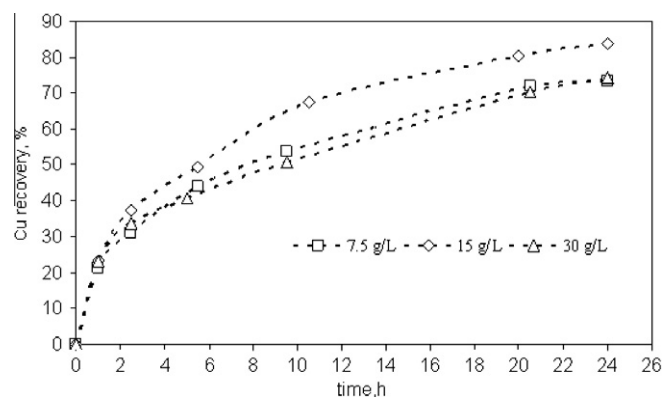


Fig. 6. Effect of initial acid concentration on copper recovery.

control of redox potential was more convenient, probably because of lower solid content and by using pure chalcopyrite and pyrite minerals, therefore increasing the initial acid concentration had positive effect on chalcopyrite leaching (Koleini et al., 2010).

3.5. Effect of solid content

Fig. 7 shows the effect of solid content on copper recovery with varying solid content (2.5%, 7.8% and 14.5% (w/v)) at solution redox potential 410 mV, temperature of 85 °C, 15 g/L initial acid concentration, total initial iron concentration of 5 g/L and pyrite to copper sulphide minerals mass ratio of 4. It is evident that solid content has little effect on copper concentrate leaching. However, at the higher solid content (14.5%) the copper recovery is somewhat lower.

3.6. Influence of initial iron concentration

In Fig. 8 the results of leaching at various total initial iron concentration (2.5, 5 and 10 g/L) at solution redox potential of 410 mV, temperature of 85 °C, initial acid concentration of 15 g/L, solid content of 7.8% and a mass ratio pyrite to copper sulphide minerals of 4 are shown.

As can be seen in Fig. 8 initial iron concentrations of 2.5 and 5 g/L give similar copper recoveries whereas the recovery is considerably decreased when the initial iron concentration is increased to 10 g/L. In Fig. 9 the XRD pattern of the residue after leaching with an initial iron concentration of 10 g/L is shown. Apart from the phases seen in the feed material, i.e. chalcopyrite, pyrite and

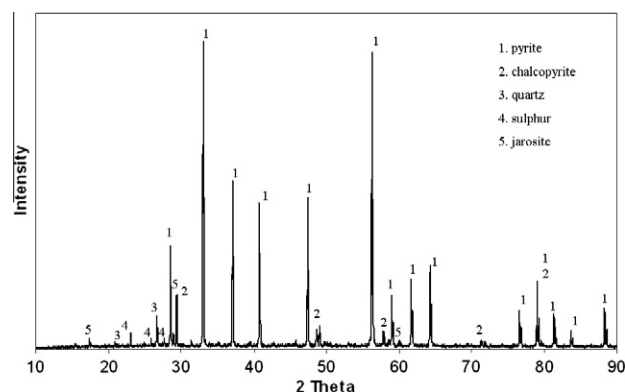


Fig. 9. XRD diffractogram of leach residue at 10 g/L total initial iron concentration.

quartz, new crystalline phases of jarosite and sulphur were formed, which both have been discussed as candidates causing chalcopyrite passivation. In a study where chalcopyrite was leached both chemically in ferric sulphate media and bioleached at low and high redox potential it was, with aid of XPS measurements, concluded that jarosite was responsible for passivation (Sandström et al., 2005). Chemical leaching at low redox potentials (420 mV vs Ag, AgCl) gave the best copper recovery despite the formation of huge amounts of elemental sulphur. In another study by Córdoba et al. (2008) it was also concluded that jarosite is responsible for the passivation and that a high redox should be avoided at the onset of leaching since that provoked rapid passivation. In a critical review Klauber (2008) suggested a model for chalcopyrite dissolution where in the initial stages a thin layer of elemental sulphur is formed on the surface through which ions and electrons have to diffuse. At a later stage jarosite formation at the surface come into play and which is the cause for the true hindered dissolution of chalcopyrite.

3.7. Effect of pyrite to copper sulphide minerals mass ratio

Four different mass ratios of pyrite to copper sulphide minerals 0, 1, 2 and 4 were investigated under the following conditions; solution redox potential 410 mV, temperature 85 °C, 15 g/L initial acid concentration, solid content of 7.8% and total initial iron concentration of 5 g/L. When no extra pyrite was added the leaching was quickly passivated after the initial fast dissolution of mainly chalcocite and covellite and after 24 h a copper recovery of 43% was obtained, Fig. 10. The copper recovery gradually increased as the pyrite to copper minerals ratio was increased up to a ratio of 2 resulting in a copper recovery of 84%, i.e. a doubling of the recovery. However, when the ratio was increased up to 4, no further increase in the copper recovery was obtained. This is in agreement with

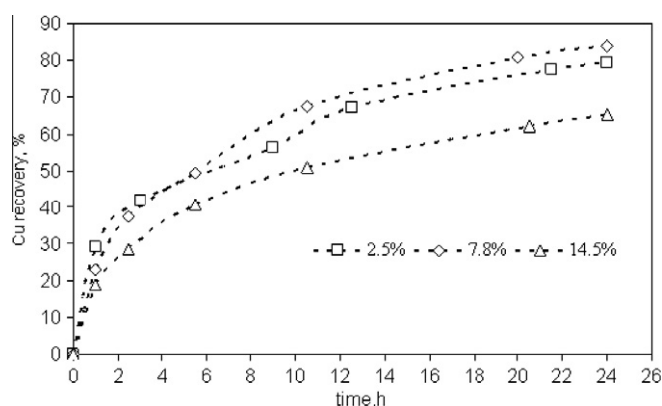


Fig. 7. Copper recovery as a function of solid content in the leach.

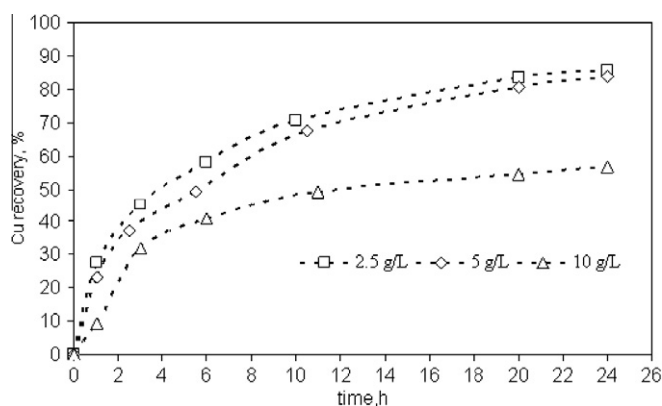


Fig. 8. Effect of total initial iron concentration on copper recovery.

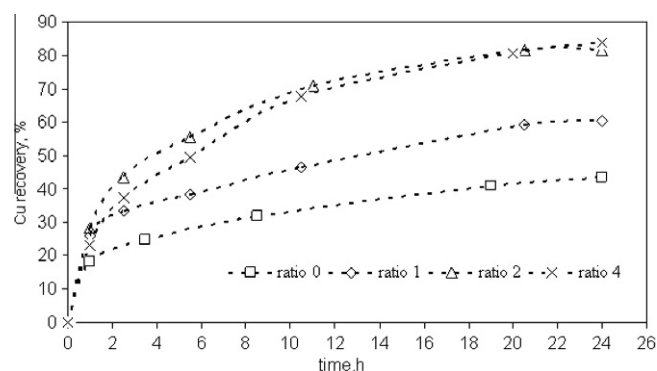


Fig. 10. Copper recovery as a function of pyrite to copper sulphide minerals mass ratio.

other studies where it was observed that as the amount of pyrite in contact with another mineral increases, the leaching rate of this mineral increases up to a certain level above which further pyrite additions did not improve the leaching (Dixon and Tshilombo, 2005; Mehta and Murr, 1983; Holmes and Crundwell, 1995). Koleini et al. (2010) found an optimum ratio of pyrite to chalcopyrite of 4. The diversity in the optimum ratios in different investigations is due to the dissimilarity in the mineralogy of the concentrates. The employed material in the present investigation contains chalcocite and covellite compared to the pure chalcopyrite that was used in the study by Koleini et al. (2010).

4. Conclusions

The obtained results confirms that pyrite addition has a major catalytic effect on the chalcopyrite leaching due to the formation of a galvanic cell between the minerals which is caused by their difference in rest potential. A mass ratio of 2 for pyrite to copper sulphide minerals was found to be the optimum ratio to obtain the maximum copper recovery. Dissolution of chalcopyrite was shown to be highly temperature dependent which is consistent with the generally high activation energies (80–90 kJ/mol) reported in literature. The redox potential had a big influence on the rate of chalcopyrite leaching and the highest copper recoveries were seen in a small redox potential window around 410–440 mV. Higher redox potentials and also total iron concentrations above 5 g/L resulted in low copper recovery due to passivation of the chalcopyrite surfaces. The initial acidity only had minor impact on the copper recovery, although working under suitable pH is vital to avoid hydrolysis of iron ions. A copper recovery higher than 80% in 24 h was achieved at a redox potential of 410 mV vs Ag, AgCl, a temperature of 85 °C, 15 g/L of initial acid concentration, a solid content of 7.8% (w/v), a total initial iron concentration 5 g/L and pyrite to copper sulphide minerals mass ratio 2:1. It can thus be concluded that ferric leaching of chalcopyrite in acidic sulphate media with additions of pyrite leaching is a promising hydrometallurgical method for copper recovery.

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