A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions

J.J. Eksteen,⇑ E.A. Oraby, B.C. Tanda

A conceptual flowsheet is proposed and the main processing steps are evaluated for the alkaline processing of chalcopyrite where glycine is the complexing agent. Glycine is utilised in an oxidising, alkaline environment to leach chalcopyrite at atmospheric pressure and mildly elevated temperatures. Process steps to recover copper and glycine from alkaline aqueous solutions were also investigated. The leaching of chalcopyrite flotation concentrate in glycine solutions was conducted at different leach conditions in a 1.25 L leach reactor with an agitated slurry and controlled dissolved oxygen (DO) concentration. In the presence of air, oxygen or hydrogen peroxide or a mixture thereof, glycine can dissolve copper from chalcopyrite at either ambient or elevated (40–60 °C) temperatures and atmospheric pressure. Increasing temperature, pH, glycine concentration and DO concentration all increase the rate and extent of copper extraction. The extraction of copper from “as-received” chalcopyrite flotation concentrate, at a particle size of 100% <45 µm, in solutions containing 0.4 M glycine at 60 °C with 25 ppm DO, was 40.1% after 24 h. If the chalcopyrite concentrate underwent an ultrafine grind to 100% <10 µm with prior alkaline atmospheric pre-oxidation, 92% of the copper is leached within 17 h at 60 °C, atmospheric pressure and 9% solids during a batch leach. Pyrite associated with the chalcopyrite remained unreacted during leaching of chalcopyrite and iron concentration in the final pregnant solution was found to be less than 20 mg/L. Copper recovery by sulfide precipitation from the leach solution as pure covellite was up to 99.1% at a Cu:S molar ratio of 1:1. Solvent extraction (SX) experiments with LIX 84-I demonstrated that copper can be extracted into the organic phase up to 99.4% in a single stage at an equilibrium pH range 8.8–10.0. It is shown that copper can be stripped from the organic phase in a single stage acidic strip using conventional acidic return electrolyte containing 180 g/L sulfuric acid. During copper recovery by precipitation as sulfide, or by solvent extraction, the glycine is made available for recycling and reuse as a barren leach solution, after treatment with lime.

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1. Introduction

1.1. Background to chalcopyrite leaching

The objective of this research was to evaluate a proposed conceptual flowsheet for the leaching of chalcopyrite using aqueous glycine in an alkaline environment with a suitable oxidant, and to identify potentially feasible routes for copper recovery from such a pregnant leach solution with concomitant reagent regeneration. The approach is based on earlier research by the authors (Oraby and Eksteen, 2014) that indicated that chalcopyrite from copper-gold gravity concentrates is solubilised in such a system. The scope of the research was to experimentally validate the key metal recovery steps of an integrated process, rather than a fundamental study of each process step, in order to serve as a reference and provide context for further research. Such an approach to chalcopyrite leaching is warranted due to the challenges associated with the treatment of chalcopyrite ores via conventional leaching approaches, as will be discussed below.

The persisting trend of decreasing grades of copper and copper-gold ores, the occurrence of finely disseminated chalcopyrite in gold-bearing pyrite and the presence of deleterious contaminants, limits the extent to which conventional milling and flotation processes can be used economically to produce clean flotation concentrates that are acceptable for smelting. A significant body of research has accumulated over the past two decades on the
extraction of copper from low grade copper or copper-gold deposits (Carranza et al., 2004; Dixon et al., 2007; Maley et al., 2009; Turan and Altundoğan, 2013a,b). The profitable extraction of copper from low-grade ores requires low-cost processing methods such as in situ or heap leaching (Watling, 2006). Copper (often with precious metals) is predominantly found as chalcopyrite in copper porphyries, iron-oxide-copper-gold (IOCG) and volcanic massive sulfide (VMS) deposits. This study will focus on chalcopyrite as it is the most abundant copper mineral and because of its known refractory nature to conventional acid leaching. The leaching of gold (and non-dissolution of pyrite) in oxidising, alkaline, glycine solutions has already been demonstrated by the authors (Eksteen and Oraby, 2015) who also observed that the presence of copper in solution enhances the gold leaching kinetics. In addition, significant increases in gold dissolution is observed when the gold is leached with glycine, copper and starvation amounts of cyanide.

About 70% of the world’s copper resources are present as chalcopyrite (Harmer et al., 2006). Many hydrometallurgical processes have been studied to extract copper from chalcopyrite. None of these processes has reached commercial-scale operation due to a diverse range of challenges such as (Wang, 2005): (1) the formation of a passivation layer on the chalcopyrite surfaces; (2) surplus production of sulfuric acid or elemental sulfur; (3) problems with purification of leaching solutions, (4) issues with recovery of precious metals from the leached residues; and (5) the need for stabilization of the final leaching residue for disposal, or (6) the high capital costs associated with pressure oxidative leach processes. The direct leaching of chalcopyrite flotation concentrates and the subsequent solvent extraction-electrowinning processes of copper cannot economically compete with the smelting of the same concentrates for concentrates that meet smelter quality specifications and where existing smelting capacity is available. Electrowinning is energy intensive whereas smelting utilises undiluted material and use the inherent fuel values of the sulfides for the smelting. It is therefore very hard to economically justify chalcopyrite concentrate leaching for concentrates that satisfy the smelter specifications (i.e. “clean” concentrates), particularly in an environment of existing available smelting capacity. However, to obtain high grade “clean” concentrates, the mill-and-float concentrator at the mine often have to reduce flotation mass pulls and suppress (gold bearing) pyrites, implying that a cyanide based tailings leach is often required to recover the gold with concomitant production of significant weak acid dissolvable cyanides.

Sulfide concentrates can be treated hydrometallurgically, but leaching of chalcopyrite is difficult and slow and requires strongly oxidising, high temperature or high pressure conditions (Lu et al., 2000; Hiroyoshi et al., 2001; McDonald and Muir, 2007; Yoo et al., 2010), with concomitant impacts on capital and operating costs.

In the field of hydrometallurgy, there are a many publications related to the recovery of copper from chalcopyrite in which different lixiviants such as chloride (Hirato et al., 1986; Liddicoat and Dreisinger, 2007; Al-Harashshe et al., 2008; Yoo et al., 2010; Miki and Nicol, 2011), sulfate (Munoz et al., 1979; Hirato et al., 1987; Córdoba et al., 2008; Nazari and Asselin, 2009), ammonia (Beckstead and Miller, 1977a and Beckstead and Miller, 1977b; Reilly and Scott, 1977; Turan and Altundoğan, 2013a,b; Nabizadeh and Aghazadeh, 2015) and nitric acid (Habashi, 1999) are used. The use of ammonia is problematic for numerous reasons such as its limitation in recovery and reuse, the limited E_pH stability fields of its metal complexes, its volatility (especially at elevated temperature), and numerous health and environmental concerns. As conventional alkaline leach options have been limited in technical and economic appeal, acid leaching (or acidic heap bioleaching) is the predominant hydrometallurgical route to deal with copper (and chalcopyrite) ores. While sulfuric acid is a relatively low cost commodity, acid leaching of copper minerals creates a number of challenges, and even more so when the ore or concentrate to be leached contains gold which may require alkaline cyanidation of the leach residues.

A few salient aspects of acid leaching are listed here to contrast it to leaching in the alkaline systems: (1) Gangue mineralisation may result in high acid consumption. (2) Acid leaching leads to the formation of elemental sulfur as a by-product which can significantly passivate copper extraction. (3) Depending on leach temperature and acid concentration, it can lead to significant iron co-dissolution and jarosite precipitation with concomitant expensive solid-liquid separation of the iron-rich residues. Cost effective iron removal remains one of the major challenges in acid-based non-ferrous hydrometallurgy. (4) If silver is present in the ore, the silver may be locked into an argento-jarosite crystal lattice. (5) Acid leaching interacts with a number of altered silicates to produce silica gels that causes severe operational problems, particularly in solvent extraction circuits. (6) In addition, many of these silicates can release fluoride or other halide ions in strong acidic environments. Fluorides are also problematic for smelters when these gangue minerals appear in flotation concentrates. (7) Acids mobilise magnesium, calcium, iron, manganese and aluminium ions, which accumulate and have to be managed, as they will influence solvent extraction, and can result in scaling of process equipment and unwanted precipitation throughout the process circuit. This may often lead to challenging water balance issues. (8) Should the copper deposit also contain gold, a significant neutralisation cost is incurred by switching from acidic leaching of copper to the alkaline cyanide leaching of gold. (9) Over and above the raw material costs, particularly if the acid has to be transported over large distances, significant neutralisation costs can be incurred in some instances. The main disadvantages of the alkaline cyanide leach system are: it is more expensive than sulfuric acid, ultrafine grinding may be required for high copper extraction and it is oxygen intensive as sulfur is fully oxidised to sulfate (rather than elemental sulfur). The precipitation of gypsum and iron hydroxide may form a surface coating on the copper surface if lime is used as a pH modifier.

Even where smelters with acid production facilities may be at hand to smelt sulfide flotation concentrates, acid production is limited by the overall regional market to absorb the excess acid. This is particularly problematic for inland smelters where copper production can be limited by the ability of the regional market to absorb excess sulfuric acid and large scale storage is a major environmental and safety risk.

Given these constraints related to acid leaching and the operability, health, safety and environmental constraints of other alkalineline routes (cyanide and ammonia leaching), other more benign alternatives were considered as candidates for leaching chalcopyrite in the alkaline pH region.

A conceptual process is proposed below which involves leaching copper from chalcopyrite in an alkaline glycine solution at room or elevated temperature (40–60 °C) using air, or oxygen, or hydrogen peroxide, or a mixture of these as an oxidant in the leach system. In recently published research work, the authors have developed a process using an alkaline glycine system to leach copper from a range of oxide (Tanda et al., 2017a) and sulfide minerals, as well as native copper (Oraby and Eksteen, 2014). Additionally, the authors have also shown that this leaching system is applicable to gold and silver (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015a). It has also been demonstrated by Oraby and Eksteen (2015b) that
should gold be extracted from the leach residue with cyanide in alkaline media, residual copper and glycine in solution enhances the rate of gold leaching. Oraby and Eksteen (2014) identified that chalcopyrite can be leached from copper-gold concentrates using glycine in an alkaline environment and hydrogen peroxide as oxidant. However, the authors did not present an integrated process with copper recovery from solution and reagent recycle, as will be done in this paper. In dealing with reagents such as glycine, reagent recovery and recycle becomes an important to minimise reagent costs.

1.2. Glycine as lixiviant

Glycine is the simplest and cheapest of the amino acids that constitute the building blocks of all proteins. It is produced in industrial bulk quantities and is used in the food, animal feed, pharmaceutical and metal plating industries. It is non-toxic and chemically and thermally stable over a wide pH and E° range. Its low cost and large scale production via many processing routes adds to its economic appeal as lixiviant. Due to its complexing action, glycine enhances the solubility of copper ions in aqueous solutions (Aksu and Doyle, 2001 and Aksu and Doyle, 2002). The stability constant (log K) of the copper(II) glycinate complex is 18.9 (Aliyu and Na’aliya, 2012). Glycine can exist in aqueous solutions in three different forms, namely \( \text{H}_2\text{NCH}_2\text{COOH} \) (cation), \( \text{H}_2\text{NCH}_2\text{COO}^- \) (anion), and \( \text{NH}_2\text{CH}_2\text{COO}^- \) (zwitterion). It forms a strong complex with both copper(II) and copper(I), although the cupric complex shows the larger stability domain (as shown in Eqs. (1)–(3) and their corresponding equilibrium ligand stabilities) and can enhance the solubility of copper ions in aqueous solutions due to its ability to chelate copper (Aksu and Doyle, 2001).

\[
\text{Cu}^{2+} + (\text{NH}_2\text{CH}_2\text{COO})^- \rightarrow \text{Cu(NH}_2\text{CH}_2\text{COO})^+ \; \log K = 8.6 \tag{1}
\]

\[
\text{Cu}^{2+} + 2(\text{NH}_2\text{CH}_2\text{COO})^- \rightarrow \text{Cu(NH}_2\text{CH}_2\text{COO})_2^- \; \log K = 15.0 \tag{2}
\]

\[
\text{Cu}^+ + 2(\text{NH}_2\text{CH}_2\text{COO})^- \rightarrow \text{Cu(NH}_2\text{CH}_2\text{COO})_2^+ \; \log K = 10.1 \tag{3}
\]

The complexing mechanism of copper in solutions containing glycine initially involves the formation of a copper complex through carboxyl group by an ion-exchange mechanism as shown in Eqs. (4) and (5) (Korobushkina et al., 1983; Aksu and Doyle, 2001). During metal-ligand complexation there is a competition through carboxyl group by an ion-exchange mechanism as shown in Eqs. (4) and (5) (Korobushkina et al., 1983; Aksu and Doyle, 2001). During metal-ligand complexation there is a competition between the metal and hydrogen ions and by increasing pH, a displacement between copper and hydrogen proton to make a stable copper-glycinate complex.

\[
(\text{N}^+\text{H}_2\text{CH}_2\text{COOH}) \rightarrow \text{N}^+\text{H}_2\text{CH}_2\text{COO}^- + \text{H}^+ \tag{4}
\]

\[
\text{Cu}^{2+} + 2(\text{N}^+\text{H}_2\text{CH}_2\text{COO}^-) \rightarrow \text{Cu(NH}_2\text{CH}_2\text{COO})_2^+ + 2\text{H}^+ \tag{5}
\]

Mixtures of glycine and hydrogen peroxide have shown promising copper chemical-mechanical planarization behaviour and it was found that the glycine-peroxide mixture can leach metallic copper from the exposed areas during the chemical-mechanical planarization (Hirabayashi et al., 1996; Doyle and Wang, 2003). It is clear from the literature that a significant opportunity exists to evaluate glycine as a new lixiviant for copper extraction from its minerals and other copper-bearing materials. If a glycine based process can be made feasible in an alkaline environment with minimum gangue co-dissolution/high selectivity, it would open up multiple opportunities to treat many sub-economic copper deposits.

1.3. A proposed integrated conceptual process for the leaching of chalcopyrite ores and concentrates

The research in this paper will evaluate the steps in an overall flowsheet of leaching-metal recovery-sulfur/contaminant removal-reagent recycle, whereby the most expensive reagents (glycine and caustic soda) are regenerated and recycled. Reagent losses are limited to mother liquor losses in leach and precipitation residues after dewatering. The high level process proposed below consists of the steps (Fig. 1) which include:

1. Reagent make-up;
2. Fine grinding of concentrate (optional);
3. Alkaline atmospheric pre-oxidation of concentrate (optional);
4. Leaching of pre-oxidised concentrate;
5. Leaching of “as-is” or unoxidised concentrate;
6. Solid-liquid separation;
7. Copper recovery form solution (as CuS by precipitation or through solvent extraction) and glycinate regeneration;
8. pH re-establishment and precipitation of impurities by lime addition (only sulfate shown below as predominant species) as shown in Eq. (9);
9. Solid-liquid separation of the residue after lime addition; and
10. Recycling of the clarified barren filtrate containing glycine back to the leach stage.

The key uncertainties in the reaction sequence above are the feasibility of the leaching reaction of chalcopyrite with alkaline glycine/glycinate (steps 4 and 5) and the copper recovery from alkaline glycinate solutions (step 7). These two steps are covered in the research presented in this article. For the other steps there is sufficient verification of their feasibility in the literature. Chalcopyrite leaching in an alkaline glycinate environment will be evaluated under ambient temperature conditions and at elevated temperature conditions. The regeneration of (sodium) glycinate (step 8, reaction 7) is similar to caustic regeneration in dual alkaline circuits where alkali hydroxides (such as caustic soda) are regenerated from sodium sulfate (and/or sulfite) using slaked lime. Industrial examples include the scrubbing of SO₂ and SO₃ from flue gases (flue gas desulfurization), whereby the resulting sodium sulfate solutions after a caustic scrubbing are regenerated using slaked lime (Bezuidenhout et al., 2012; Lunt et al., 2003).
In the experimental studies below multiple approaches were evaluated: (1) leaching at ambient temperature and atmospheric pressure, (2) leaching at atmospheric pressure and mildly elevated temperature in stirred vessels, (3) leaching of ultrafine ground concentrate after partial alkaline pre-oxidation at atmospheric pressure and mildly elevated temperature.

2. Experimental

The experiments were executed to evaluate the leaching of chalcopyrite with and without dissolved oxygen (feedback) control and the subsequent recovery of copper from solution.

2.1. Sample preparation and characterisation

All experiments were carried out using chalcopyrite concentrate samples of size 100% passing 45 μm, except when ultrafine ground, when the particle size was 100% passing 10 μm. The assay was determined by fused disc X-ray Fluorescence assay of the chalcopyrite concentrate, after loss on ignition (LOI). The sulfur was determined independently by LECO analysis. The assay is given in Table 1.

2.2. Leaching without oxygen control

All experiments were carried out using solutions prepared from analytical grade reagents and deionised water. Unless specified, all experiments were conducted at room temperature (23 °C) using magnetic stirrers with Teflon coated magnetic stirrer bars. In the beaker tests, 500 mL of 0.1 M glycine and dilute hydrogen peroxide was stirred at 300 rpm. In a typical experiment, 5 g of chalcopyrite concentrate was added to the 500 mL of glycine solution. At different times, samples of the leach solution were obtained using a syringe-membrane filter (pore size 0.45 μm). The filtrates were analysed for copper and iron by using atomic absorption spectrophotometry (AAS). The trace elements were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES). The final leach residues were analysed for copper by X-ray Fluorescence (XRF) to calculate the final copper extraction. Sulfur speciation of the final alkaline glycine leach solution was conducted as follows: sulfide by methylene blue colorimetric method and thiosulfate, sulfite, and sulfate using anion analysis by Ion Chromatography (IC).

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>Co</th>
<th>As</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay (%)</td>
<td>3.33</td>
<td>0.17</td>
<td>0.242</td>
<td>27.73</td>
<td>0.032</td>
<td>0.075</td>
<td>0.032</td>
</tr>
<tr>
<td>Element (%)</td>
<td>Mg</td>
<td>Mn</td>
<td>Ni</td>
<td>Cu</td>
<td>Pb</td>
<td>Zn</td>
<td>S (LECO)</td>
</tr>
<tr>
<td>Assay</td>
<td>1.39</td>
<td>0.023</td>
<td>0.001</td>
<td>24.5</td>
<td>0.136</td>
<td>0.81</td>
<td>31.55</td>
</tr>
</tbody>
</table>
2.3. Leaching with dissolved oxygen (DO) control

For the leach tests with dissolved oxygen (DO) control, the DO level in the leach pulp was controlled at 20 ppm. Leaching experiments were conducted at ambient temperature (23 °C) in a 1.25 L leach vessels with slurry agitated at a speed of 300 rpm using overhead stirrers. 10 g of concentrate were mixed with 600 mL of deionised water before glycine was added to the slurry. The pH of the solution was adjusted to pH 10.5 by the addition of sodium hydroxide. As shown in Fig. 2, the DO level of the leach solution was measured and controlled over the whole leaching time using a Syland DO meter, a mass flow controller, a multifunction data acquisition module (DAQ) and a laptop operating with the LabVIEW program.

2.4. Leaching of partially pre-oxidised ultrafine ground concentrate

The dissolved oxygen was measured and controlled as described in Section 2.2. All experiments were carried out using ultrafine chalcopyrite concentrate samples of size 100% passing 100 μm, or “As Is” concentrate, 100% passing 45 μm. All leaching experiments were conducted using solutions prepared from analytical grade reagents and deionised water. Unless specified, all experiments were conducted using a closed glass reactor fitted with a reflux condenser to prevent evaporation losses. In the atmospheric pre-oxidation tests, an alkaline 550 g slurry (pH 12) containing 50 g chalcopyrite concentrate was oxygenated by adding pure oxygen to the slurry at a flowrate of 75–100 mL/min. The pre-oxidation experiments were performed in glass reactor where the slurry stirred at 500 rpm and temperature was maintained at 60 °C under atmospheric pressure for 24 h, using sodium hydroxide as pH modifier. These conditions were selected and modified based on the chalcopyrite oxidation research studies by Yin et al. (2000) and Hakett et al., 1976. During the leaching experiments, 500 mL of slurry containing 40 g/L glycine at pH 11.0 was heated up to 60 °C oxygenated (0.75 mL/min O2) and stirred at 500 rpm for 24 h, using calcium hydroxide to establish the initial pH. This was also the reason for the high calcium content in the leach residue above (where it is present as gypsum). In a typical experiment, 5 g of chalcopyrite concentrate was added to the 500 mL of glycine solution. At different times, samples of the leach solution were obtained using a membrane filter. The filtrates were analysed for copper and iron by using atomic absorption spectrophotometry (AAS). The final leach residues were analysed for copper by X-ray Fluorescence (XRF) to calculate the final copper extraction. XRD analyses confirmed that the remaining copper was undissolved chalcopyrite and that the iron converted predominantly to goethite/limonite.

2.5. Copper recovery

The recovery of copper from solution was by either CuS precipitation or by solvent extraction followed by electrowinning. For the precipitation with NaSH, the required stoichiometric mass of dry NaSH powder was weighed and added to an agitated copper glycinate solution at 300 rpm, pH 11 and room temperature. The residual copper in solution was measured using AAS. The copper sulfide precipitate after NaSH precipitation has been assessed by XRD, Scanning Electron Microscopy (SEM) and particle size analysis at Commonwealth Scientific and Industrial Research Organisation (CSIRO) Australian Minerals Research Centre (AMRC), in Waterford, Western Australia.

For the solvent extraction of copper from its alkaline glycinate solution, the aqueous phase was mixed with 10% (v/v) LIX 84-I at 1:1 organic to aqueous (O/A) ratio, and room temperature for 10 min. LIX 84-I solvent extraction reagent is a water insoluble 2-hydroxy-5-nonylacetophenone oxime dissolved in a high flash point hydrocarbon diluent (kerosene). The solvent extraction and stripping were performed in conventional separatory funnels. In the following section, the results of the tests will be compared for the following conditions:

- An exploratory batch leaching of chalcopyrite concentrate at room temperature with a constant flow of oxygen (but no DO control) to evaluate the progression of the reaction chemistry.
- Batch leaching of chalcopyrite concentrate at room temperature to compare hydrogen peroxide and oxygen as oxidants.
- Batch leaching of chalcopyrite concentrate with controlled DO, where the factors of temperature, DO and glycine concentration are varied.
- A comparison of batch leaching of partially alkaline pre-oxidised, ultrafine ground concentrate to “as-is” concentrate at 60 °C and atmospheric pressure.
3. Results and discussion

3.1. Chalcopyrite leaching at room temperature and atmospheric pressure in alkaline glycine solutions in the absence of DO control

An exploratory test was performed to evaluate the progression of the chemistry of leaching of copper from 1% solids chalcopyrite concentrate slurry at room temperature using 0.1 M glycine and a constant oxygen flow rate sparged at 200 mL per minute. Cu leach of 52% after 580 h was observed. The copper dissolution data from leaching chalcopyrite in this system are shown in Fig. 3.

Although the chalcopyrite appeared to be slow leaching in glycine solution at ambient temperature, it is clear from the data shown in Fig. 3 that copper can be extracted from chalcopyrite at room temperature and atmospheric pressure with no indication of hydrolyses, re-precipitation and preg-robbing. Oxygen utilisation was not optimal as it was injected as fairly large bubbles from a tube rather than through a porous frit (sintered glass/metal). The leach solution pH and Eh were measured during the leaching period and are plotted in Fig. 4.

The pH was manually adjusted to pH 11 at several times during the leaching time and it was observed that pH continuously decreased as the leach proceeded. In oxygenated alkaline glycine solutions, chalcopyrite dissolves according to Eq. (4), showing how hydroxyl anions are consumed (with commensurate decrease

- Copper recovery through precipitation as sulfide.
- Copper recovery through solvent extraction.

### Table 2
Copper and other impurity concentrations in the final leach solution after 580 h.

<table>
<thead>
<tr>
<th>Concentration, mg/L</th>
<th>Cu</th>
<th>As</th>
<th>S</th>
<th>Fe</th>
<th>Si</th>
<th>Ni</th>
<th>Co</th>
<th>Pb</th>
<th>K</th>
<th>Mn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1523</td>
<td>3.46</td>
<td>423</td>
<td>19.0</td>
<td>2.76</td>
<td>0.47</td>
<td>2.35</td>
<td>4.30</td>
<td>4.81</td>
<td>0.61</td>
<td>1.15</td>
</tr>
</tbody>
</table>

![Fig. 3. Chalcopryte leaching in alkaline glycine solutions at leaching conditions: 0.1 M glycine, 200 mL/min O₂, room temperature, pH 9.8–11, 1% solids density.](image1)

![Fig. 4. Changes of pH and Eh during chalcopryte leaching in alkaline glycine solutions: 0.1 M glycine, 200 mL/min O₂, room temperature, pH 9.8–11.](image2)
in pH) and showing the iron and sulfur oxidation products, which were also verified experimentally. In the case of iron, an amorphous, which could not be detected by XRD but was readily in filterable iron oxy-hydroxide forms.

Aksu et al. (2003) have shown that most copper-glycinate species are found to be stable over a wide range of pH values up to pH 12 and beyond. The concentrations of copper and impurities in the final leach solutions were measured and are given in Table 3. It can be seen that most of the impurities in the final leach solution are at very low concentration, considering the extended leach times used. The particular advantage of leaching under alkaline conditions is that the iron in the final solution is less than 20 mg/L compared to Cu which is present at 1523 mg/L. The lower amounts of sulfur than copper in the final leach solution (Table 2) can be attributed to sulfur precipitation with soluble calcium as gypsum and/or SO$_2$ emission.

Most metal sulfides, when leached in (acidic) oxidising environments, produce sulfur species including, sulfide, bisulfide, sulfite, thiosulfate, sulfate and polythionate ions (Goldhaber, 1983; Schippers and Sand, 1999). The results of sulfur speciation (by ion chromatography and the methylene blue colorimetric method) as shown in Table 3 shows that about 90% of sulfides is oxidised to sulfate and the rest is sulfite and minor amounts of thiosulfate. The sulfide/bisulfide ion concentrations were less than the detection limit. The sulfite resulting from the sulfide and thiosulfate oxidation is oxidised further with dissolved oxygen to form sulfate (Hewitt et al., 2009). The presence of sulfate ions can lead to the precipitation of gypsum (as shown in Eq. (10)) which may form a surface coating on the copper minerals if slaked lime (Ca(OH)$_2$) is used as a pH modifier.

$$\text{Ca(OH)}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O(s)} + 2\text{NaOH(}aq)$$

To evaluate the effect of slaked lime as an alternative pH modifier, leaching of chalcopyrite in glycine solution was conducted using lime with copper extraction of 43% being obtained which is less than the 52% copper extraction in the glycine solution with caustic soda (for the same leach duration, i.e. after the 580 h of leaching). This may still be dealt with through surface refreshment using stirred grinding mills as an intermittent stage during the leach.

3.2. Glycine-hydrogen peroxide system

The effects of using hydrogen peroxide (peroxide) as an oxidant for chalcopyrite dissolution have been studied in solutions containing 0.1 M glycine and 2% peroxide at pH varying from 10.2 to 11.5. The pH was over shot to 11.5 during the addition of peroxide for very short time then decreases rapidly due to peroxide oxidation. The peroxide was added to the equivalent of 1% H$_2$O$_2$ (w/w) at the start of each test; then another 1% solution was added after 48 h. Sodium hydroxide was added periodically to the glycine-peroxide leach test to maintain pH in the target range. Recently, the authors have shown that most copper minerals (oxides and sulfides) were dissolved before gold in the glycine-peroxide system (Oraby and Eksteen, 2014). The effect of using peroxide as an oxidant compared to oxygen is shown in Fig. 4. Using peroxide enhances the initial leaching rate of copper, but a subsequent slight decrease in copper extraction rate was observed. Copper extraction enhancement due to the presence of peroxide can be ascribed to the formation of the highly oxidative hydroxide radicals (OH$^\circ$). According to Baba et al. (2012), a hydroxide radical reacts with sulfides to form elemental sulfur and then the elemental sulfur is oxidised to sulfate ions (Eqs. (11) and (12)).

$$2\text{HO} + 2\text{S}^2^- \rightarrow 2\text{S}^0 + \text{H}_2\text{O} + 0.5\text{O}_2 \quad \text{(11)}$$

$$2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{S}^2^- + 4\text{H}^+ \quad \text{(12)}$$

The results, depicted in Fig. 5, also show that the copper extraction rate using oxygen as an oxidant is slower than the rate in the presence of peroxide; however the more important observation here is that copper extraction continues nearly linearly in the glycine-oxygen system. Copper extraction of 29.5% was achieved after 120 h of leaching in glycine-peroxide system, but reached a comparative level of Cu extraction only after 172 h in a glycine-oxygen system.

![Fig. 5. Copper extraction in glycine-peroxide (2% H$_2$O$_2$) system and glycine-oxygen system (0.1 M glycine, 1% solid density, pH 10.2–11.5 for glycine-peroxide and pH 9.8–11.0 for glycine-oxygen).](image-url)
3.3. Glycine-controlled oxygen system

Leaching of chalcopyrite concentrate in glycine solutions under controlled oxygen addition was undertaken to investigate the effect of dissolved oxygen (DO) on extraction and leaching kinetics.

3.3.1. Effect of glycine concentration

Copper dissolution data from leaching chalcopyrite concentrate at different glycine concentrations are shown in Fig. 6. It can be seen that the increase of glycine concentration enhances the extent of copper dissolution and leach kinetics. However the maximum
copper extraction was 40.1% after 24 h at 0.4 M alkaline glycine, 60°C and DO level of 25 ppm. The average copper extraction rates were 1.168 mgCu/min and 1.38 mgCu/min in the presence of 0.1 M and 0.4 M glycine respectively.

3.3.2. Effect of temperature

Fig. 7 shows the effect of increased temperature on the kinetics of copper extraction from chalcopyrite. It can be seen that copper extraction was highly sensitive and increases significantly with increasing temperature. It was found that the pH of the solution decreased significantly from 11.5 to 9.71 after 24 h at higher temperature (60°C). The rapid decrease in leaching pH at high temperature aligns with the reaction given in Eq. (4) where 3 mol of hydroxyl anions are consumed in the reaction per mole of chalcopyrite leached. At room temperature, the leaching pH decreased at a slower rate from 11.5 to 10.9 after 24 h of leaching.

3.3.3. Effect of dissolved oxygen (DO)

As has been shown in Eq. (4), oxygen is required to complete the copper extraction from chalcopyrite and in order to evaluate the effect of oxygen level on copper extraction; chalcopyrite was leached in 0.2 M glycine at different controlled DO levels. Fig. 8 shows the copper extraction at no oxygen injection, and when the oxygen concentration is controlled to 15 and 25 ppm DO. It was observed that maintaining a DO level at or above 15 ppm significantly improved the extraction of copper. The results showed that oxygen needs to be maintained at 15 ppm or above to maintain high rates of copper extraction.

3.4. A comparison of the glycine leaching of an alkaline pre-oxidised ultrafine ground concentrate versus “as-is” concentrate

Table 4 gives the XRD analysis of the feed and the leach residues. The XRD analysis is not fully quantitative and the % Cu Extraction is best calculated from the assays of the leach solution (by AAS) and the assay of the feed (by XRF). The concentration of Cu in solution was 2.0 g/L after 24 h for the ultrafine ground material and 1.04 g/L for the “as-received” concentrate (not ground).

A pre-conditioned/oxidised chalcopyrite concentrate of size 100% – 45 μm was leached at pH 11.0. The copper extraction and pH changes are shown in Fig. 9. It can be seen that the rate of initial copper extraction, after pre-oxidation, is quite rapid after which there is a change in rate due to iron hydroxide precipitate on the chalcopyrite surface.

Copper extraction and pH changes during leaching a pre-oxidised ultra-fine ground chalcopyrite concentrate is shown in Fig. 10. It is clear that the copper leach rate is rapid (compared to the “as-is” flotation concentrate) as about 92% of copper was extracted in 17.5 h of leaching. The iron concentration was less

<table>
<thead>
<tr>
<th>Material</th>
<th>Chalcopyrite content (Q-XRD), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial flotation concentrate</td>
<td>73.5</td>
</tr>
<tr>
<td>Residue after leaching “as-is” concentrate</td>
<td>39.8</td>
</tr>
<tr>
<td>Residue after leaching finely ground of concentrate</td>
<td>6.0</td>
</tr>
</tbody>
</table>
than 13.0 mg/L in the pregnant leach solution after 24 h. The leach residue was confirmed to be predominantly iron hydroxide and was found to be easily filterable.

3.5. Copper and glycine recovery

The dissolved copper can be recovered from glycine solution by either sulfide precipitation, using hydrogen sulfide (H₂S), sodium hydrogen sulfide, (NaSH) or sodium sulfide (Na₂S), or by solvent extraction coupled with electrowinning.

3.5.1. Sulfide (NaSH) precipitation

For recovery by precipitation, sulfide ions were added (as NaSH powder) to the pregnant liquor in different Cu:S²⁻ molar ratios in order to recover copper from the glycine solution. A copper recovery from solution of 99.1% was obtained (as copper(II) sulfide/CuS) at a Cu:S²⁻ molar ratio of 1:1 with 10 min contact time. Table 5 shows the copper concentration in the leach solution before and after NaSH precipitation. The barren solution after NaSH precipitation containing 12.5 mg/L copper-glycinate was then used to leach copper from fresh chalcopyrite concentrate. XRD pattern data (Fig. 11) of the precipitate confirmed that the sulfide precipitate is pure covellite (CuS). A coarse particle size (for a sulfide precipitate) of the CuS precipitate was observed during the filtration which resulted in fast settling behaviour. The particle concentration in the leach before and after sulfide (NaSH) precipitation.

Table 5

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Cu, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before precipitation</td>
<td>1243.0</td>
</tr>
<tr>
<td>After precipitation Cu:S²⁻ 1:1</td>
<td>11.5</td>
</tr>
<tr>
<td>After precipitation Cu:S²⁻ 1:0.75</td>
<td>226.3</td>
</tr>
</tbody>
</table>

Fig. 11. XRD pattern of the copper sulfide (Covellite) precipitate.

Fig. 12. Chalcopyrite leaching in reused alkaline barren glycine solutions at controlled DO (20 ppm), room temperature and pH 10.5, 1% (w/w) solid density.
size distribution of the precipitate was confirmed by the particle size fraction analysis and the results show that $P_{80}$ of the precipitate was 67 $\mu$m.

3.5.2. Leach of chalcopyrite using recycled barren leach solution

The ability of the recycled barren solution to be re-used to leach copper from chalcopyrite has also been investigated. The barren solution after sulfide precipitation of copper was used after adjusting the solution pH to 11.0 with caustic soda to leach a fresh sample of chalcopyrite concentrate. The leach conditions were kept similar to the original leach solution. Results shown in Fig. 12 illustrate that the barren solution, without adding any new glycine addition, leaches copper from chalcopyrite at a similar rate to the fresh solution. For instance the copper extraction with barren solution after the first 100 h of chalcopyrite leaching at a DO of 20 ppm was around 24.5% whereas it was around 26% for the original fresh solution. The presence of any copper(II) in the barren solution after sulfide precipitation can be involved as an additional oxidant beside oxygen in leaching copper.

3.5.3. Solvent extraction (SX)

Depending on the nature of the contaminants and the concentration of copper in the pregnant leach solution, it may be preferable to recover the copper using solvent extraction instead of sulfide precipitation. For example, the application of SX may be required to generate a high enough copper concentration that may be suitable for a particular copper recovery processes, particularly if employing a heap leach process. SX experiments show that

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Table 6
Copper extraction from copper glycinate aqueous (Aq) solution using LIX 84I at 40 $^\circ$C and 1:1 organic/aqueous ratio.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Equilibrium pH</th>
<th>Cu (Aqueous, mg/L)</th>
<th>Extraction, (%)</th>
<th>Stripping, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>11.5</td>
<td>3596.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Raffinate 1</td>
<td>8.8</td>
<td>43.9</td>
<td>98.8</td>
<td>–</td>
</tr>
<tr>
<td>Raffinate 2</td>
<td>9.4</td>
<td>65.6</td>
<td>98.2</td>
<td>100</td>
</tr>
<tr>
<td>Raffinate 3</td>
<td>10.0</td>
<td>22.3</td>
<td>98.4</td>
<td>100</td>
</tr>
</tbody>
</table>

---

Fig. 13. Flowsheet for alkaline glycinate copper leaching and recovery by sulfide precipitation.
copper glycinate can be easily extracted from the alkaline aqueous medium using a 10% (v/v) LIX 84I as extractant and a 1:1 ratio of organic to aqueous phase ratio. A more detailed study of the copper solvent extraction and stripping is provided by the authors (Tanda et al., 2017b) using alternative extractants from an alkaline glycinate matrix. Copper extraction into the organic phase of up to 99.4% could be achieved, with higher copper extractions obtained at different equilibrium pH’s, depending on the initial copper concentration in the aqueous phase. The stripping of the organic phase with 180 g/L sulfuric acid solution showed that all the copper can be stripped back into the sulfuric acid aqueous phase. Table 6 shows the copper extraction from aqueous medium and the stripping of copper from organic medium.

3.6. Conceptual flowsheet of alkaline glycine leach process

A flowsheet of a conceptual copper leaching process can be constructed where chalcopyrite (or other copper sulfide and oxide minerals) can be leached in alkaline glycine systems, followed by solid-liquid separation and recovery of the copper from solution with restoration of the glycine to an alkaline pH in the range 9 < pH < 12.5. Fig. 13 shows the schematic diagram of this leaching process in alkaline glycine solutions where copper is recovered from solution as covellite (for smelting) using NaSH addition. The lime addition for sulfur removal (as sulfate) is also a polishing step to remove any solubilised silicate, phosphate, aluminate or carbonate as their calcium-based precipitates from the barren aqueous glycinate stream prior to recycling the barren solution. In Fig. 13, it was shown that the gypsum (and other calcium precipitates) is removed in a separate step (shown within a dotted boundary). This separate thickening/filtration process step can be eliminated as it would also be possible to recycle the gypsum slurry, without thickening, to the leach and filter the calcium based precipitates with the glycine ore/concentrate leach residue.

As technical grade glycine varies between USD 1500 and USD 2000 per tonne for bulk quantities (June 2016 prices), it is important to try and recover as much glycine/glycinate containing solution as possible to minimise reagent losses. This implies the disposal of filter cake rather than thickened leach residue to tailings. Glycine loss is therefore proportional to solution losses to leach residue (% moisture in filter cake) and concentration in the pregnant leach solution.

Alternatively, the copper can be removed from the solution using a solvent extraction-electrowinning circuit (SX-EW). Fig. 14 illustrates this option, where copper is removed as cathode copper from the SX-EW circuit and the organic phase (containing LIX 84-I, for example) can be stripped using an EW return (spent) electrolyte, i.e. typically containing 180 g/L sulfuric acid and 30 g/L Cu²⁺ (as sulfate). In addition, should the glycine leaching be accelerated through partial alkaline pre-oxidation and ultrafine

![Fig. 14. Flowsheet for alkaline glycinate based copper leaching and recovery by SX-EW.](image-url)
grinding be added, including gold recovery through carbon-in-column adsorption, a modified conceptual flowsheet shown in Fig. 15 can be proposed.

4. Conclusions

A novel integrated alkaline process for the extraction of copper from chalcopyrite has been proposed and the chemistry of the main steps in the process including reagent recirculation has been demonstrated. At ambient temperatures, copper extractions of up to 52% are achievable after 580 h in solutions of glycine and air as oxidant. Ambient temperature leaching is therefore only a potential option for the heap leaching of chalcopyrite bearing ores. However, mild heating of the leach pulp up to 60°C and operating under increased controlled DO levels, allows copper leaching in a multistage tank leach approach using alkaline glycinate solutions. Increasing the glycine concentration further accelerates copper extraction and leads to a higher extent and rate of copper extraction. Alternatively, concentrates may be ultrafine ground and partially preoxidised under alkaline atmospheric conditions, followed by alkaline glycine leaching, when leach extraction of around 92% may be achieved. Further optimising by refreshing the particle surfaces, improved oxygen mass transfer and agitation, and the use of caustic soda or soda ash (instead of slaked lime), and maintenance of pH and free glycine levels in a continuous leach may lead to further improvement in leach recoveries. The results have also shown that copper can be recovered as an iron-free precipitate from glycine solutions by either sulfide precipitation followed by smelting. This allows the production of a higher grade and reduced mass (per unit copper produced) smelttable concentrate. Alternatively and preferably, it was shown that copper may be easily recovered from glycinate solutions using conventional solvent extraction coupled with electrowinning. A technically feasible conceptual flowsheets for the extraction of copper from chalcopyrite have been proposed, which will serve as an important reference and basis for further research into the optimisation and modelling of the various process stages. Previous research by the authors (Oraby and Eksteen, 2014) indicated that this approach can be extended to other copper minerals such as oxides, native copper and other sulfides, whereby the flowsheet presented above may be used for a complex copper mineralisation while not leaching acid consuming gangue, pyrite or iron oxides and not solubilising iron to any significant extent.

Fig. 15. A high level process flow diagram for the glycine based leaching of chalcopyrite concentrate using glycine in an alkaline environment with concentrate ultrafine grinding, and gold recovery by carbon-in-column included (optional)).

References
