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Glycine Leaching of Sarcheshmeh Chalcopyrite Concentrate at High Pulp Densities in a Stirred Tank Reactor

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Abstract

The simplest amino acid, glycine has recently been reported as a safe and environmentally benign reagent for the extraction of copper from both oxide and sulfide minerals. In the current study, leaching of a chalcopyrite concentrate from the Sarcheshmeh Copper Mine (Kerman, Iran) was conducted in stirred tank reactors in the presence of a glycine medium. The effect of some critical leaching parameters including glycine concentration (0.4 - 2 M), temperature (30 - 90 °C), stirring rate (250 - 750 rpm), pH (9 - 12), oxygen flowrate (0.5 - 2 L/min) and pulp density (1 - 20%) was investigated on copper recovery from the chalcopyrite concentrate. Results show that an increase in temperature from 30 to 60 °C enhanced the copper extraction, whereas at conditions > 60 °C a decrease in copper extraction was

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observed, probably as a result of the conversion of glycine to glycinate and decrease in oxygen solubility. Moreover, prolonged leaching times at higher pH levels (10.5 and 12) led to a decrease in the extraction of copper, primarily due to the chemical precipitation of copper sulfide and crystallization of copper glycinate. By increasing the pulp density from 1 to 20%, copper extraction declined significantly primarily as a consequence of the partial dissolved copper precipitation at higher copper concentrations. SEM/WDX analyses were subsequently used in order to evaluate the leach residues. Further investigation determined that the activation energy of the glycine leaching of concentrate was 37.4 KJ/mol, thus the kinetics were controlled by diffusion of the reagents through the product layer. From these results, it is evident that due to the high initial rate of glycine leaching and the precipitation of copper-bearing phases (i.e. copper glycinate and covellite) at high pulp densities, glycine leaching processes are recommended for the treatment of low grade chalcopyrite concentrates, ores or tailings.

Keywords: Glycine; Leaching; Kinetics; Chalcopyrite concentrate.

1. Introduction

Chalcopyrite is the most important copper sulfide mineral as it comprises more than 70% of current global copper reserves (Dreisinger, 2006; Li et al., 2013). Chalcopyritic ores are conventionally processed pyrometallurgically through production of a high-grade flotation concentrate, followed by smelting and refining steps (due to their fast reaction kinetics) that results in an LME (London Metal Exchange) grade copper. Nevertheless, this route has several environmental, economic and technical disadvantages, especially when used to treat low grade and highly complex ores. Over the last three decades, numerous investigations have aimed at the discovery of a feasible hydrometallurgical route to treat such complex

resources. The main challenge of this route is the slow leaching rate of chalcopyrite that occurs with a broad range of treatments such as sulfate, nitrate, chloride and ammonia media even under atmospheric or high-pressure conditions (Castellón et al., 2020; Hernández et al., 2019; Sokić et al., 2009; Thao et al., 2020; Turan et al., 2015; Watling, 2013; Yoo et al., 2010).

Hydrometallurgical methods often inherit their own environmental implications related to the acid consumption or the production of contaminated wastes. Consequently, growing levels of research have recently been devoted to find alternative methods for copper extraction from chalcopyrite concentrates. Use of glycine as an alternative reagent for copper leaching from oxide and sulfide copper ores has been the subject of increasing investigations over the last few years (Eksteen et al., 2016; Eksteen et al., 2017; Eksteen et al., 2018; Oraby and Eksteen, 2014, 2015a, b; Oraby et al., 2017; Tanda et al., 2017a; Tanda et al., 2017b). Glycine is the simplest amino acid with the chemical formula H₂N-CH₂-COOH, it is also a non-toxic, non-volatile and non-flammable reagent. Moreover, glycine is readily available commercially at a relatively low price and is widely used in both in agriculture and the food industry (Eksteen et al., 2017; Tanda et al., 2017; Tanda et al., 2017; Tanda et al., 2017a). Additionally, as an amino acid, glycine exhibits zwitterionic properties and can be found in different forms within an aqueous solution depending on the medium pH. Zwitterion, $^+H_3NCH_2COO^-$ (HL), is the major glycine species, which can gain or lose a proton to form glycinium cation (H₃NCH₂COOH⁺) or glycinate anion (H₂NCH₂COO⁻) (O'Connor et al., 2018b).

The dissolution of chalcopyrite in glycine solutions has been proposed to occur according to the following reactions (Eksteen et al., 2017; Kwon et al., 2005; O'Connor et al., 2018a; Song and Zhang, 2008):

$$CuFeS_{2}(s) + 2(NH_{2}CH_{2}COO)^{-}(aq) + 19OH^{-}(aq) \rightarrow Cu(NH_{2}CH_{2}COO)_{2}(aq) + Fe(OH)_{3}(s) + 2SO_{4}^{-2}(aq) + 8H_{2}O(l) + 17e^{-}$$
(1)

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$
⁽²⁾

$$Fe(OH)_3 (s) \rightarrow FeO(OH) (s) + H_2O (l)$$
(3)

$$CuFeS_{2}(s) + 2NH_{2}CH_{2}COO^{-}(aq) + 4.25O_{2}(aq) + 2OH^{-}(aq) \rightarrow Cu(NH_{2}CH_{2}COO)_{2}(aq) + FeO(OH)(s) + 2SO_{4}^{2-}(aq) + 0.5H_{2}O(l)$$
(4)

Furthermore, the related copper complexation mechanism in glycine solution can be described by (Eksteen et al., 2017):

$$Cu2+(aq) + 2(N+H3CH2COO-)(aq) \rightarrow Cu(NH2CH2COO)2(aq) + 2H+(aq)$$
(5)

It has been previously reported that during the electrochemical analyses of chalcopyrite-paste electrode in alkaline glycine solutions, passivation behavior was not observed (O'Connor et al., 2018a). Tanda et al. (2017a) found that copper oxide minerals can be readily leached with alkaline glycine solutions. A synergistic lixiviant mixture of glycine and cyanide was also used to recover both gold and copper from gold-copper ores and concentrates (Oraby et al., 2017). Copper has also been successfully leached from a chalcopyrite flotation concentrate in glycine solutions (Eksteen et al., 2017). More recently, the kinetics of chalcopyrite leaching at relatively low pulp densities have captured significant attention. Tanda et al. (2019) reported that iron-oxy-hydroxides was found on the leach residue and the diffusion of the reagents from the product layer was the dominant rate-limiting step. Shin et al.(2019) also found that during the glycine leaching of chalcopyrite concentrate at room temperature, copper sulfate and copper sulfide phases were precipitated.

Nevertheless, the ability of glycine leaching to extract copper from chalcopyrite concentrates at high pulp densities (> 6% (w/v)) and temperatures (above 0 C) has not yet been investigated. Such parameters are industrially critical for the leaching of ores and concentrates in stirred tank reactors, from both an economic and technical point of view. Thus, a comprehensive investigation to appraise the applicability of such process is necessary. Consequently, the research work outlined here is conducted in order to elucidate the effects of key material and process parameters, such as pulp density, grinding, temperature, reagent concentration and pH on the process efficiency, and leaching kinetics for the chalcopyrite concentrate of Sarcheshmeh Copper Mine.

2. Materials and methods

2.1. Materials

A representative sample of chalcopyrite flotation concentrate was obtained from the Sarcheshmeh Copper Mine (Kerman, Iran). Analysis of the sample by X-ray diffractometry (XRD) (by XMD50 using XPowder software) found that chalcopyrite (70%) and pyrite (9%) were the main phases present within the concentrate. The analyses of the sample with X-ray fluorescence (XRF) showed that the concentrate was composed of 38.3% Fe₂O₃, 30.5% S, 1.6% Al₂O₃, 0.4% CaO, 0.1% Mo and 4.8% SiO₂. Acid digestion of the sample and analyzing the solution with atomic absorbance spectrophotometry (AAS), exhibited that the concentrate contains 24.2% copper. All the reagents used were of analytical grade and deionized water was used throughout the experiments. For the re-grinding of the concentrate, the original sample with d₈₀ of 75µm was ground in a ball mill with a slurry pulp density of 50% (400 g concentrate for each batch), rotation speed of 70 rpm, Calgon addition of 1% (as a grinding aid) with 3200 g steel balls (ball diameters = 6.5 - 15 mm) for 5 hours. The slurry was then filtered and oven-dried at 5 °C for 12 hours. A laser particle size analyzer (Malvern Mastersizer 3000, Malvern, UK) was used to characterize the particle size of the sample and the results indicated that the size of the re-ground concentrate reached 11 µm (d₈₀).

2.2. Leaching experiments

In order to investigate the ability of glycine to dissolve copper from the chalcopyrite concentrate, leaching experiments were conducted to evaluate the effects of several critical parameters including glycine concentration, pH, temperature, stirring rate, pulp density, oxygen flowrate and re-grinding under the conditions outlined in Table 1. All experiments were performed with 500 mL of slurry in a 1000 mL glass reactor equipped with a pitch bladed mechanical stirrer (Fig. 1). The leaching vessel was placed inside a thermostatic bath and purged with oxygen for 24 hours and the various leaching conditions used are described in Table 1. A total of 19 experimental runs were performed to evaluate the effect of glycine concentration, temperature, pulp density, pH, stirring rate and oxygen flowrate on the efficiency of copper leaching from the concentrate. For experiments related to the effect of pulp density, the levels of reagents (glycine concentration and oxygen flowrate) were set proportional to the solid content to keep the molar ratio of solid to reagent at a constant value. During the tests, several samples were taken and filtered by Whatman no. 41 filter papers (pore size = $0.45 \mu m$) and the filtrate was diluted in 2% nitric acid prior to analysis by atomic adsorption spectroscopy (AAS; Model Thermo Scientific ICE 3000 Series) to ascertain the copper and iron concentrations. In addition, leaching solution samples after 6 hours at different pulp densities were also analyzed by ICP-OES to determine the presence of any dissolved impurities. In order to identify the nature of the leach residues, the remaining solids after the leaching process were washed with deionized water, filtered, dried and analyzed by scanning electron microscopy (SEM) (Model XL-30 Phillips) equipped with a WDX (Wavelength dispersive X-ray) (Model WDX-3PC) analyzer.

Furthermore, the pH of solutions was measured by a pH meter (Model VWR), and it was adjusted during the experiments with 10 M NaOH. Redox potential was recorded with a combined electrode Pt and Ag/AgCl connected to a voltmeter (Model WAVETEK).

2.3. Kinetic model

Modeling reaction kinetics is an important step for a better understanding of the leaching mechanism. Leaching of minerals is a heterogeneous process in which a liquid or gas reacts with solid in an aqueous solution. In order to study the reaction kinetics of the glycine leaching of the chalcopyrite concentrate, shrinking core and shrinking particle models were considered to describe the physical phenomena. In the shrinking core model, the reaction occurs at the surface of particle and then the reaction zone moves into the unreacted core and a product layer is generated during the process. The leaching rate of this model can be controlled either by the diffusion of reagent through the liquid film (Eq. 6), or through the product layer (Eq. 7), or by chemical reaction at the solid surface (Eq. 8) (Levenspiel, 1999):

$$X = k_l t \tag{6}$$

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_d t$$
⁽⁷⁾

$$1 - (1 - X)^{\frac{1}{3}} = k_r t \tag{8}$$

where X is fraction reacted, k_l , k_d and k_r are the kinetic constants and t is the leaching time.

While in the shrinking particle model, the particle shrinks during the leaching process without the formation of a product layer (Levenspiel, 1999). The rate can be controlled by either film diffusion (Eq. 9) or chemical reaction at the surface (Eq. 8).

$$1 - (1 - X)^{\frac{2}{3}} = k_f t \tag{9}$$

where k_f is the kinetic constant.

The activation energy (Eq. 10) could be determined based on the following Arrhenius equation (Levenspiel, 1999):

$$k = k_0 \exp\left(-\frac{Ea}{RT}\right) \tag{10}$$

Where Ea is activation energy (kJ/mol), T is temperature (K), R is gas constant (8.3145 J/K. mol), k is a reaction rate constant (1/hour) and k_0 is the frequency factor (1/hour).

3. Results and discussion

3.1. Effect of critical parameters on leaching efficiency

3.1.1. Glycine concentration

The extraction of copper as a function of time at different glycine concentrations is shown in Fig. 2A. As can be seen, copper extraction increases during the first 6 hours as glycine concentration is changed from 45% at 0.4 M to 70% at 2 M glycine concentration. After 6 hours, the extraction is observed to decrease at all concentration levels due to the precipitation of copper precipitates on the particle surfaces. O'Connor et al. (2018a, b) reported that copper could be precipitated as copper oxides such as CuO and Cu₂O, whereas iron could be precipitated as iron oxy-hydroxides that form on the surface of the minerals in glycine media . Moreover, Khezri et al. (2020) reported that covellite (CuS) and maghemite (γ -Fe₂O₃) could be detected in washed leach residue by XRD analysis. Besides, blue crystals of copper glycinate have also been found to formed in the final leaching solutions and on unwashed residues.

It is proposed that a part of dissolved copper can be precipitated as chalcocite (Cu_2S) according to Eq. 11 (Fernández-Reyes and García-Meza, 2018). This phase is then leached rapidly with glycine in the presence of oxygen to produce covellite and copper glycinate due to the fast kinetics (Eq. 12). Similarly, covellite is also leached in the presence of glycine according to Eq. 13 (Tanda et al., 2018).

$$2Cu^{2+} (aq) + HS^{-} (aq) + OH^{-} (aq) \to Cu_2S (s) + H_2O (l)^{+} 2e^{-}$$
(11)

$$Cu_{2}S(s) + 2NH_{2}CH_{2}COOH(aq) + 0.5O_{2}(aq) \xrightarrow{Fast} Cu(NH_{2}CH_{2}COO)_{2}(aq) + CuS(s) + H_{2}O(l)$$
(12)

CuS (s) + 2NH₂CH₂COOH (aq)+ 2O₂ (aq) + 2OH⁻ (aq) \xrightarrow{slow} Cu(NH₂CH₂COO)₂ (aq) + SO₄²⁻ (aq) + 2H₂O (l) (13)

The presence of covellite on the surface of leaching residues confirms that the reaction rate of Eq. 13 is slow. This copper sulfide phase may act as a passive-like layer on the surface of chalcopyrite. It was reported that covellite leaches slowly in the glycine media (Tanda et al., 2018). Covellite leaching could be the rate-limiting-step in the glycine leaching of chalcopyrite, thereby decreasing the overall rate of copper dissolution. In addition, the other phase distinguished in the leach residue was maghemite, which is proposed to be precipitated from the goethite via Eq. 14 (Popescu et al., 2010).

$$2\text{FeO(OH)}(s) \rightarrow \text{Fe}_2\text{O}_3(s) + \text{H}_2\text{O}(l)$$
(14)

In Fig. 3A, the variation of pH during the leaching process is portrayed at varying glycine concentrations ranging from 0.4 to 2 M. It can be observed that during the concentrate dissolution, the pH decreases in all the conditions investigated. This decrease in pH indicates the dissolution of copper in the glycine medium takes place and results in the reduction in OH⁻ ion concentration as indicated in Eq. 4. This decrease in OH⁻ was offset by the periodic addition of 10 M NaOH in order to re-establish pH to the initial level (when the difference of measured and initial pH was higher than 0.3 unit). With the leaching time, the drop in pH was found to be higher at increased glycine concentrations, which is mainly due to increased levels of copper dissolution that consumes OH⁻ ions. Fig. 3B represents the variation of redox potential during the process. For all leaching experiments, the redox potential initially decreases followed by an increase with the reaction times. This behavior is possibly because of the release of reductive ions, such as glycinate (N₂CH₂COO⁻) and HS⁻, while the later

increase may be due to the oxidation of these reductive species by the injected oxygen or the consumption of HS⁻ to form copper sulfide (Eq. 11). Furthermore, it can also be observed that an increase in glycine concentration results in a more significant decrease in the redox potential (Fig. 3B) probably as a consequence of more reductive species being generated.

3.1.2. Temperature

Fig. 2B shows the extraction of copper as a function of time at different temperatures and a fixed glycine concentration of 0.7 M. The results portrayed that the maximum copper extraction of 51% was achieved at a temperature of 60 C after 6 hours, whereas the minimum extraction was 2.9% occurred at 90 °C at 6 hours. It is expected that the chemical reactions of copper precipitation (such as covelite formation) proceed faster at higher temperatures. O'Connor et al. (2018b) reported that by increasing the temperature (up to 60 C), the concentration of glycinate increases, however at higher temperatures, the copper glycinate stability region is decreased, which is not desirable for copper leaching. It is also worth noting that the concentration of oxygen in the solution decreases when temperature is increased at atmospheric pressure, as can be predicted by the Henry's law (Mackay and Shiu, 1981). From the results it can be concluded that conducting the process at 60 C is recommended to optimize the copper extraction, which is in accordance with the previously published studies (Eksteen et al., 2016; Eksteen et al., 2017; Tanda et al., 2017a).

3.1.3. Pulp density

Extraction of copper as a function of time at different pulp densities are shown in Fig. 2C. The maximum copper extraction (91.1%) was observed at 6 hours leaching time and the pulp density of 1% for the re-ground concentrate ($d_{80} = 11 \mu m$), a level which is around 50% higher than that obtained at the concentrate with the original size ($d_{80} = 75 \mu m$). In contrast, when the pulp density was increased from 5 to 20%, the copper extraction at 6 hours

decreased from 51 to 11%. A decline in the extraction observed after 6 hours at pulp densities higher than 5% could be related to the partial removal of dissolved copper as precipitates such as copper sulfides or copper glycinate crystals. The ICP analysis of the leaching solutions after 6 hours at pulp densities of 5, 10, 15 and 20% indicated that their sulfur dosages were 4.3, 8.1, 8.6 and 9.2 g/L, respectively. This increase in the concentration of sulfur in the leach solution with increasing pulp density results from the higher sulfur content within the solid sample, although the concentrations of iron were less than 0.1 g/L. In this case, the iron concentration before 12 hours was found to be negligible, while at 12 and 24 hours, it had increased 0.97 and 1.48 g/L, respectively. The highest pH reduction (Fig. 4A) was found at 5 and 10% pulp densities, which correlated with high copper concentrations in the solution (Fig. 2C). The same behavior was also demonstrated with the lowest level of redox potential found with the 20% pulp density (Fig. 4B) that demonstrated the minimum copper extraction. The redox potentials at the pulp densities of 15 and 20% were found to be relatively lower than those at lower pulp densities. This low level of redox potential could be attributed to the higher viscosity of the slurry at these high pulp densities, which decreases the diffusion of oxygen in the liquid phase, - and increases the concentrations of reductive species (such as HS⁻ and glycinate).

3.1.4. pH

The effect of pH on the extraction of copper was presented in Fig. 2D. As can be seen during the first few hours, the copper extraction at the pHs of 10.5 and 12 was higher than that at the pH of 9, probably as a result of the higher concentrations of ionic glycinate at the higher pH levels as previously reported by O'Connor et al. (2018b). Moreover, the level of copper extraction was found to decrease after 3 hours for the test conducted at the initial pH of 12, whereas a similar decrease was only noted after 12 hours when the initial pH of 10.5. As previously mentioned, this decrease in extraction could be attributed to the formation of

copper sulfide precipitate and copper glycinate crystals. In contrast, for the test performed with an initial pH of 9, the extraction progressively increased throughout the experiment, which indicates that copper precipitation was not significant at low pH levels. During the first 3 hours, copper extraction at pH 9 was significantly lower than those at pH 10.5 and 12. O'Connor et al ((2018b) reported that at pH 9, the dissolution rate of chalcopyrite is limited by the concentration of glycinate, whereas at the pH higher than 10, it is limited by the formation of oxide species on the mineral surface and that pH > 11, surface inactivation depends on the concentration of glycine.

3.1.5. Stirring rate

As the rate of stirring in a tank affects the diffusion rate of the reagents to the mineral surface, the influence of stirring rate (from 250 to 750 rpm) on the leaching rate of the concentrate was performed and the extraction of copper as a function of time is displayed in Fig. 2E. It can be seen that the maximum extraction (51%, 6 hours) was obtained with a stirring rate of 500 rpm, while the minimum extraction (44%, 6 hours) was achieved at 250 rpm. This enhancement of extraction with the increase in stirring rate from 250 to 500 rpm could be related to the enhancement of the oxygen dissolution in the liquid phase. Fig. 5B portrays that the lowest redox potential was obtained at 250 rpm as a result of the lower distribution efficiency of the oxygen bubbles within the solution. On the other hand, the reason for the observed decrease in the copper extraction with 750 rpm results from an increased rate of copper precipitate formation. The highest drop in pH (Fig. 5A) occurred at 500 rpm and this can be related to the maximum level of copper extraction.

3.1.6. Oxygen flowrate

The effect of oxygen as a key reagent during the glycine leaching of copper from copperbearing minerals is displayed in Fig. 2F. It can be seen that by increasing the oxygen flowrate to the slurry, copper extraction increases during the first 6 hours, however, prolongation of the extraction process leads to a decline (6 hours for 0.5 and 1 L/min oxygen flowrate). Maximum copper extraction (68%) was achieved with an oxygen flow rate of 2 L/min oxygen and its decline commenced only after 12 hours primarily as a result of the lower levels of covellite formation under higher oxidation conditions. During the first three hours of the experiment, there is sufficient oxygen to commence the leaching process, thus the extraction values are similar in all cases. After that, copper extraction increased with increasing oxygen flowrate. The extraction of copper in all experiments initially increases with time, whereas after a certain duration (3 hours for 0.5 L/min and 12 hours for 2 L/min) it shows a continuous decrease. This decline can be attributed to the partial removal of dissolved copper as covellite or copper glycinate crystals.

3.1.7. Re-grinding

Fig. 2G represents the extraction of copper achieved from the flotation concentrate with and without an additional re-grinding operation. As can be observed, copper extraction was significantly increased by re-grinding of the concentrate from the d_{80} of 75 µm to the d_{80} of 11 µm. Copper extraction for the concentrate and the re-ground concentrate were respectively 22.6% and 51.0% at 6 hours. After 6 hours, the extraction decreased in the re-ground sample, whilst in the case of original concentrate extraction slightly increased to reach 31.5% after 24 hours. The initial increase for the re-ground sample could be related to its higher specific surface area and the high dependency of the leaching rate to the surface area. However, the reason for the subsequent decrease in extraction for the re-ground sample is attributed to its high concentration of dissolved copper, which leads to the crystallization of copper glycinate. In addition, the lower redox potential of the re-ground sample (Fig. 6B) at first few hours favors the formation of copper sulfide minerals, such as covellite and our previous research has shown the presence of copper glycinate and covellite in the solid leach residues (Khezri

et al., 2020). In addition, the pH reduction (Fig. 6A) in the re-ground sample was more significant than that in the original concentrate ($d_{80} = 75 \ \mu m$).

3.2. Characterization of leaching residues

In order to investigate the characteristics of the leach residues, the resultant washed solids were analyzed with SEM/WDX. Fig. 7 displays the SEM and the WDX maps of the residue obtained from the final slurry of the concentrate leaching at 10% (w/v) pulp density, 1.4 M glycine concentration, an initial pH of 10.5, 1.5 L/min oxygen flowrate and 500 rpm stirring rate at 60 °C. According to Fig. 7, in the area marked by the rectangular box, the relative content of iron and copper is high, whilst sulfur is somewhat lower. This may indicate a partial dissolution of the chalcopyrite and partial precipitation of the iron and copper ions. In the diamond-shaped area, the content of iron and copper are both high and the sulfur significantly lower, suggesting chalcopyrite dissolution followed by precipitation of iron and copper on the surface of the particles. In the circle, the content of iron and sulfur was determined to be at high levels, whereas copper was at a low level, which implies non-dissolution of pyrite or the precipitation of maghemite (Eq. 14). In the oval, the content of iron and copper was found to be high and sulfur to be low indicating dissolution of the chalcopyrite, and precipitation of iron and copper. The high ratio of copper to iron could be related to the precipitation of copper as secondary minerals. From these analyses it can be concluded that the dissolution occurs and is followed by copper and iron precipitation. Our previous work has demonstrated that maghemite and covellite could be precipitated during glycine leaching of chalcopyrite concentrate (Khezri et al., 2020). These results explain the decrease in copper extraction after 6 hours presented in Fig. 2C.

Fig. 8 illustrates the SEM picture and WDX maps of the residue obtained from the concentrate leached at 20% (w/v) pulp density, 2.8 M glycine concentration, an initial pH of

10.5, 3 L/min oxygen flowrate and 500 rpm. The contents of iron and copper are high and the associated sulfur is low at the rectangular and circle regions, which indicates chalcopyrite dissolution followed by iron and copper precipitation. In the diamond area, the content of iron, copper and sulfur are all relatively high, implying that precipitation of copper sulfide and iron oxide has occurred.

3.3. Kinetics of leaching

The kinetic data obtained from the glycine leaching of the concentrate ($d_{80} = 11 \mu m$) at various temperatures ranging from 30 to 90 °C (presented in Fig. 2B) were fitted with different models (Fig. 9). The formulas of the kinetic models, the equation related to the line of best fit and the thermodynamic data are presented in Table 2.

It can be seen that the model of the diffusion from a boundary fluid film (C and D in Table 2) and chemical control (B in Table 2) did not well fit with the data at different temperatures, while the model related to the diffusion of the reagents from the product layer (A in Table 2) was in a good agreement with the results (e cept for 90 C) and therefore, it can be concluded that this model best reflects the leaching process at temperature of 30 to 60 C. The best fit model was employed to deduce the activation energy of the glycine leaching of the concentrate to be 37.42 kJ/mol through the Arrhenius plot (Fig. 10). This value is relatively lower than those reported in the literature for other chalcopyrite leaching systems. Dutrizac (1981) investigated the kinetics of chalcopyrite leaching in both ferric sulfate and ferric chloride media. He reported that the activation energy was 42 and 75 kJ/mol for the chloride and sulfate systems, respectively. Yévenes et al. (2010) calculated the activation energy of about 72 kJ/mol for chalcopyrite concentrate and reported that the rate-determining step is chemical reaction. Veloso et al. (2016) reported that activation energy for chalcopyrite leaching in both ferric sulfate and cupric sulfate in the presence of sodium chloride was about 66 kJ/mol. However, the rate constant in the cupric medium was 1.5 times larger than that

obtained in the ferric medium. Recently, the activation energies for glycine leaching of chalcopyrite was found to be 72 and 30 kJ/mol for the 20–38 and <10 μ m size fractions, respectively (Tanda et al., 2019). A low level of activation energy (<40 kJ/mol) indicates that the process is influenced by the mass transfer of the reagents through the liquid film or product layer, while a high level of activation energy indicates that the process is greatly dependent on temperature and is controlled by chemical reaction at the solid surface (Levenspiel, 1999). The relatively low value of activation energy in the current work confirms that the leaching process is controlled by the diffusion of reagent through the product layer.

4. Industrial evaluation

Previous investigations for the glycine leaching of chalcopyrite was conducted at relatively low pulp densities. Shin et al. (2019) investigated the glycine leaching of a chalcopyrite concentrate with a d_{80} of 40 µm and in the presence of peroxide hydrogen at 6% pulp density. Maximum copper extraction was found to be around 45% during 170 hours (with changing the lixiviant during the process). Tanda et al. (2019) also evaluated the effect of several critical parameters on the glycine leaching of chalcopyrite at 0.75% pulp density. The extraction curves were progressively increased during the process. This behavior was also observed in the current study for the tests conducted at 1% pulp density. However, at higher pulp densities (5-20%), a significant decrease in copper extraction was found after a few hours, which was contributed to the formation of copper glycinate crystals and covellite. This new finding indicates that this selective and environmentally-friendly process has a major limitation in the tank leaching of high-grade chalcopyrite concentrates at relatively high pulp densities. However, the proposed strategy can be highly attractive for the treating of lowgrade chalcopyrite or copper/gold ores in heaps. Oraby and Eksteen (2014) conducted successfully the selective leaching of copper from a copper-gold gravity concentrate in glycine solutions. Furthermore, application in the vat/tank leaching also presents an opportunity for target metal extraction. Glycine leaching could also be a good processing option for in situ leaching of base metals which can significantly decrease its environmental concerns.

5. Conclusions

The atmospheric leaching of Sarcheshmeh chalcopyrite concentrate was investigated in a 1-L stirred tank reactor in glycine medium and the following results were obtained:

- Results showed that the leaching of concentrate is significantly accelerated by increasing the concentration of the glycine and decreasing the particle size. The maximum copper extraction (> 90 %) was found at a 1% pulp density of the reground concentrate. Increasing the temperature led to an enhancement of the leaching rate up to 60 °C followed by a decrease in the extraction at higher temperatures. This decrease at 90 °C could be related to the lower conversion degree of glycine to glycinate, decreasing the dissolution of oxygen in the solution and the higher precipitation rate of copper sulfide.
- The extraction of copper from the concentrate declined by prolonging the process at higher levels of pH (10.5 and 12) especially at higher pulp densities (i.e. 15 and 20%, w/v), due to the removal of a part of dissolved copper as copper glycinate crystals and covellite precipitate. Covellite is a refractory phase in glycine leaching which may cause a passivating behavior during the leaching process.
- The leaching of concentrate was investigated at different temperatures and the results were correlated with various rate equations. It was found that the diffusion of the

reagents through the product layer was supposed to be the rate-limiting step and the activation energy of the dissolution reaction was 37.42 KJ/mol.

Glycine is a selective, environmentally-friendly and strong reagent for the leaching of chalcopyrite. However, at high pulp densities of high grade concentrates, copper precipitates are formed and significantly decrease copper extraction. Thus, the reagent portrays a high industrial potential to treat low grade chalcopyrite concentrates, ores and tailings.

Acknowledgments

The authors gratefully acknowledge the financial support from National Copper Industries Company (Iran) especially Mrs. Torabi, and the Hydrometallurgy and Corrosion Group of Aalto University (Finland) for providing equipment and materials. Mr. Petteri Halli and Dr. Jari Aromaa for their assistance with the experiments. This research also made use of the Academy of Finland's Raw Materials Infrastructure (RAMI) that is based in Aalto University.

References

Castellón, C.I., Hernández, P.C., Velásquez-Yévenes, L., Taboada, M.E., An Alternative Process for Leaching Chalcopyrite Concentrate in Nitrate-Acid-Seawater Media with Oxidant Recovery. Metals, 2020, **10(4)**, 518.

Dreisinger, D., Copper leaching from primary sulfides: Options for biological and chemical extraction of copper. Hydrometallurgy, 2006, **83(1-4)**, 10-20.

Dutrizac, J., The dissolution of chalcopyrite in ferric sulfate and ferric chloride media. Metallurgical Transactions B, 1981, **12(2)**, 371-378.

Eksteen, J., Oraby, E., Tanda, B., An alkaline glycine-based process for copper recovery and iron rejection from chalcopyrite. Proceedings of the IMPC, 2016.

Eksteen, J., Oraby, E., Tanda, B., A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Minerals Engineering, 2017, **108**, 53-66.

Eksteen, J., Oraby, E., Tanda, B., Tauetsile, P., Bezuidenhout, G., Newton, T., Trask, F., Bryan, I., Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores. Canadian Metallurgical Quarterly, 2018, **57(4)**, 390-398.

Fernández-Reyes, J.S., García-Meza, J.V., Bioelectrochemical system for the biooxidation of a chalcopyrite concentrate by acidophilic bacteria coupled to energy current generation and cathodic copper recovery. Biotechnology letters, 2018, **40(1)**, 63-73.

Hernández, P.C., Dupont, J., Herreros, O.O., Jimenez, Y.P., Torres, C.M., Accelerating copper leaching from sulfide ores in acid-nitrate-chloride media using agglomeration and curing as pretreatment. Minerals, 2019, **9(4)**, 250.

Khezri, M., Rezai, B., Abdollahzadeh, A. A., Wilson, B. P., Molaeinasab, M,. Lundström, M., Investigation into the Effect of Mechanical Activation on the Leaching of Chalcopyrite in a Glycine Medium. Under review in Hydrometallurgy.

Kwon, S.-K., Kimijima, K.i., Kanie, K., Muramatsu, A., Suzuki, S., Matsubara, E., Waseda, Y., Inhibition of conversion process from Fe (OH) 3 to β -FeOOH and α -Fe2O3 by the addition of silicate ions. ISIJ international, 2005, **45(1)**, 77-81.

Levenspiel, O., Chemical reaction engineering. Industrial & engineering chemistry research, 1999, **38(11)**, 4140-4143.

Li, Y., Kawashima, N., Li, J., Chandra, A., Gerson, A.R., A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. Advances in colloid and interface science, 2013, **197**, 1-32.

Mackay, D., Shiu, W.Y., A critical review of Henry's law constants for chemicals of environmental interest. Journal of physical and chemical reference data, 1981, **10(4)**, 1175-1199.

O'Connor, G., Lepkova, K., Eksteen, J., Oraby, E., Electrochemical behaviour and surface analysis of chalcopyrite in alkaline glycine solutions. Hydrometallurgy, 2018a, **182**, 32-43.

O'Connor, G., Lepkova, K., Eksteen, J., Oraby, E., Electrochemical behaviour of copper in alkaline glycine solutions. Hydrometallurgy, 2018b, **181**, 221-229.

Oraby, E., Eksteen, J., The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy, 2014, **150**, 14-19.

Oraby, E., Eksteen, J., Gold leaching in cyanide-starved copper solutions in the presence of glycine. Hydrometallurgy, 2015a, **156**, 81-88.

Oraby, E., Eksteen, J., The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy, 2015b, **152**, 199-203.

Oraby, E., Eksteen, J., Tanda, B., Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy, 2017, **169**, 339-345.

Popescu, M., Piticescu, R., Vasile, E., Taloi, D., Petriceanu, M., Stoiciu, M., Badilita, V., The influence of synthesis parameters on FeO (OH)/Fe2O3 formation by hydrothermal techniques. Zeitschrift für Naturforschung B, 2010, **65(8)**, 1024-1032.

Shin, D., Ahn, J., Lee, J., Kinetic study of copper leaching from chalcopyrite concentrate in alkaline glycine solution. Hydrometallurgy, 2019, **183**, 71-78.

Sokić, M.D., Marković, B., Živković, D., Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid. Hydrometallurgy, 2009, **95(3-4)**, 273-279.

Song, C., Zhang, J., 2008. Electrocatalytic oxygen reduction reaction, In *PEM fuel cell electrocatalysts and catalyst layers*. Springer, pp. 89-134.

Tanda, B., Eksteen, J., Oraby, E., An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy, 2017a, **167**, 153-162.

Tanda, B., Eksteen, J., Oraby, E., Kinetics of chalcocite leaching in oxygenated alkaline glycine solutions. Hydrometallurgy, 2018, **178**, 264-273.

Tanda, B., Eksteen, J., Oraby, E., O'Connor, G., The kinetics of chalcopyrite leaching in alkaline glycine/glycinate solutions. Minerals Engineering, 2019, **135**, 118-128.

Tanda, B., Oraby, E., Eksteen, J., Recovery of copper from alkaline glycine leach solution using solvent extraction. Separation and Purification Technology, 2017b, **187**, 389-396.

Thao, N.T., Tsuji, S., Jeon, S., Park, I., Tabelin, C.B., Ito, M., Hiroyoshi, N., Redox potentialdependent chalcopyrite leaching in acidic ferric chloride solutions: Leaching experiments. Hydrometallurgy, 2020, 105299.

Turan, M.D., Arslanoğlu, H., Altundoğan, H.S., Optimization of the leaching conditions of chalcopyrite concentrate using ammonium persulfate in an autoclave system. Journal of the Taiwan Institute of Chemical Engineers, 2015, **50**, 49-55.

Veloso, T.C., Peixoto, J.J., Pereira, M.S., Leao, V.A., Kinetics of chalcopyrite leaching in either ferric sulphate or cupric sulphate media in the presence of NaCl. International Journal of Mineral Processing, 2016, **148**, 147-154.

Watling, H., Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate–chloride and sulfate–nitrate process options. Hydrometallurgy, 2013, **140**, 163-180.

Yévenes, L.V., Miki, H., Nicol, M., The dissolution of chalcopyrite in chloride solutions: Part 2: Effect of various parameters on the rate. Hydrometallurgy, 2010, **103(1-4)**, 80-85.

Yoo, K., Kim, S.-k., Lee, J.-c., Ito, M., Tsunekawa, M., Hiroyoshi, N., Effect of chloride ions on leaching rate of chalcopyrite. Minerals Engineering, 2010, **23(6)**, 471-477.

Dear Professors Wills,

Thank you for the opportunity to revise our manuscript, entitled "*Glycine Leaching of Sarcheshmeh Chalcopyrite Concentrate at High Pulp Densities in a Stirred Tank Reactor*" manuscript No: MINE-D-19-01067. We appreciate the careful review and constructive suggestions. We have carefully reviewed the comments and have revised the manuscript accordingly. It is our belief that the manuscript is substantially improved after making the suggested edits. Following this letter are the reviewers' comments. Our responses are given in a point-by-point manner below. Changes in the manuscript are marked as track changes. For easier reading, an accepted change file was also submitted (editions as yellow color).

We hope that this improved manuscript is acceptable for publication in Minerals Engineering and look forward to hearing from you.

Sincerely yours,

Bahram Rezai

Reviewer #2: Reviewer: Overall view

The manuscript reads well after the improvements suggested. The authors should be commended for the hard work put into restructuring the entire manuscript. As a reviewer I am happy that most of the comments were acknowledged and addressed. I believe that the standard has improved significantly in the current version.

Several subtle mistakes are highlighted in the marked-up manuscript that is attached herewith. The Figure (Figure 1 in particular) quality can be further improved for sure, please look into my suggestion. Make sure the manuscript is proof-read thoroughly before the next submission. Response: Thank you so much for your delicate and very helpful comments and suggestions.

The quality of figures especially Figure1 and d_{80} for other figures were improved in the revised manuscript.

I am happy with the technical aspects of the paper and a bit of restructuring is proposed for a better presentation of the key elements (the Kinetics Section). The inclusion of a small discussion (right after the Kinetics results) is noteworthy and make sure a separate section is assigned for that. I strongly believe the manuscript quality will elevate significantly subsequent to such an addition.

Response: Thank you so much for your helpful suggestion. Section 2.3: (Kinetic model) was added to the Materials and methods section and some sentences of the section 3.3 were moved to this new section as follows:

"2.3. Kinetic model

Modeling reaction kinetics is an important step for a better understanding of the leaching mechanism. Leaching of minerals is a heterogeneous process in which a liquid or gas reacts with solid in an aqueous solution. In order to study the reaction kinetics of the glycine leaching of the

chalcopyrite concentrate, shrinking core and shrinking particle models were considered to describe the physical phenomena. In the shrinking core model, the reaction occurs at the surface of particle and then the reaction zone moves into the unreacted core and a product layer is generated during the process. The leaching rate of this model can be controlled either by the diffusion of reagent through the liquid film (Eq. 6), or through the product layer (Eq. 7), or by chemical reaction at the solid surface (Eq. 8) (Levenspiel, 1999):

$$X = k_l t \tag{6}$$

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_d t$$
⁽⁷⁾

$$1 - (1 - X)^{\frac{1}{3}} = k_r t \tag{8}$$

where X is fraction reacted, kl, kd and kr are the kinetic constants and t is the leaching time. While in the shrinking particle model, the particle shrinks during the leaching process without the formation of a product layer (Levenspiel, 1999). The rate can be controlled by either film diffusion (Eq. 9) or chemical reaction at the surface (Eq. 8).

$$1 - (1 - X)^{\frac{2}{3}} = k_f t \tag{9}$$

where kf is the kinetic constant.

The activation energy (Eq. 10) could be determined based on the following Arrhenius equation (Levenspiel, 1999):

$$k = k_0 \exp\left(-\frac{Ea}{RT}\right) \tag{10}$$

Where Ea is activation energy (kJ/mol), T is temperature (K), R is gas constant (8.3145 J/K. mol), k is a reaction rate constant (1/hour) and k0 is the frequency factor (1/hour)."

The section 3.3 (Kinetics of leaching) was edited as follows:

"3.3. Kinetics of leaching

" The kinetic data obtained from the glycine leaching of the concentrate ($d80 = 11\mu m$) at various temperatures ranging from 30 to 90 °C (presented in Fig. 2B) were fitted with different models (Fig. 9). The formulas of the kinetic models, the equation related to the line of best fit and the thermodynamic data are presented in Table 2.

It can be seen that the model of the diffusion from a boundary fluid film (C and D in Table 2) and chemical control (B in Table 2) did not well fit with the data at different temperatures, while the model related to the diffusion of the reagents from the product layer (in Ta le 2) was in a good agreement with the results (e cept for 90 C) and therefore, it can be concluded that this model best reflects the leaching process at temperature of 30 to 0 C. The best fit model was employed to deduce the activation energy of the glycine leaching of the concentrate to be 37.42 kJ/mol through the Arrhenius plot (Fig. 10). This value is relatively lower than those reported in the literature for other chalcopyrite leaching systems. Dutrizac (1981) investigated the kinetics of chalcopyrite leaching in both ferric sulfate and ferric chloride media. He reported that the activation energy was 42 and 75 kJ/mol for the chloride and sulfate systems, respectively. Yévenes et al. (2010) calculated the activation energy of about 72 kJ/mol for chalcopyrite concentrate and reported that the rate-determining step is chemical reaction. Veloso et al. (2016) reported that activation energy for chalcopyrite leaching in both ferric sulfate and cupric sulfate in the presence of sodium chloride was about 66 kJ/mol. However, the rate constant in the cupric medium was 1.5 times larger than that obtained in the ferric medium. Recently, the activation energies for glycine leaching of chalcopyrite was found to be 72 and 30 kJ/mol for the 20–38 and <10 µm size fractions, respectively (Tanda et al., 2019). low level of activation energy (<40 kJ/mol) indicates that the process is influenced by the mass transfer of the reagents through the

liquid film or product layer, while a high level of activation energy indicates that the process is greatly dependent on temperature and is controlled by chemical reaction at the solid surface (Levenspiel, 1999). The relatively low value of activation energy in the current work confirms that the leaching process is controlled by the diffusion of reagent through the product layer. "

Section 4 (Industrial evaluation) was added in the revised manuscript as follows:

"4. Industrial evaluation

"Previous investigations for the glycine leaching of chalcopyrite was conducted at relatively low pulp densities. Shin et al. (2019) investigated the glycine leaching of a chalcopyrite concentrate with a d80 of 40 µm and in the presence of peroxide hydrogen at 6% pulp density. Maximum copper extraction was found to be around 45% during 170 hours (with changing the lixiviant during the process). Tanda et al. (2019) also evaluated the effect of several critical parameters on the glycine leaching of chalcopyrite at 0.75% pulp density. The extraction curves were progressively increased during the process. This behavior was also observed in the current study for the tests conducted at 1% pulp density. However, at higher pulp densities (5-20%), a significant decrease in copper extraction was found after a few hours, which was contributed to the formation of copper glycinate crystals and covellite. This new finding indicates that this selective and environmentally-friendly process has a major limitation in the tank leaching of high-grade chalcopyrite concentrates at relatively high pulp densities. However, at higher pulp densities (5-20%), a significant decrease in copper extraction was found after a few hours, which was contributed to the formation of copper glycinate crystals and covellite. This new finding indicates that this selective and environmentally-friendly process has a major limitation in the tank leaching of high-grade chalcopyrite concentrates at relatively high pulp densities. However, the proposed strategy can be highly attractive for the treating of low-grade chalcopyrite or copper/gold ores in heaps. Oraby and Eksteen (2014) conducted successfully the selective leaching of copper from a copper-gold gravity concentrate in glycine solutions. Furthermore, application in the vat/tank leaching also presents an opportunity for target metal extraction. Glycine leaching could also be a good processing option for in situ leaching of base metals which can significantly decrease its environmental concerns."

I would prefer a chronological order for the in-text citations.

Response: Thank you for your comment. The references have been cited according to the format of Minerals Engineering by Endnote toolbar.

Other suggestions and comments were carefully considered and edited in the revised manuscript.

Many thanks and best regards for very delicate and helpful comments.

Highlights

- Glycine leaching of a chalcopyrite concentrate was studied at high pulp densities.
- Copper extractions were declined at high levels of pulp density and temperature.
- The process was controlled by the diffusion of reagents through the product layer.
- The activation energy of glycine leaching for the copper concentrate was 37.4 KJ/mol.

Glycine Leaching of Sarcheshmeh Chalcopyrite Concentrate at High Pulp Densities in a Stirred Tank Reactor

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Abstract

The simplest amino acid, glycine has recently been reported as a safe and environmentally benign reagent for the extraction of copper from both oxide and sulfide minerals. In the current study, leaching of a chalcopyrite concentrate from the Sarcheshmeh Copper Mine (Kerman, Iran) was conducted in stirred tank reactors in the presence of a glycine medium. The effect of some critical leaching parameters including glycine concentration (0.4 - 2 M), temperature (30 - 90 °C), stirring rate (250 - 750 rpm), pH (9 - 12), oxygen flowrate (0.5 - 2 L/min) and pulp density (1 - 20%) was investigated on copper recovery from the chalcopyrite concentrate. Results show that an increase in temperature from 30 to 60 °C enhanced the copper extraction, whereas at conditions > 60 °C a decrease in copper extraction was

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observed, probably as a result of the conversion of glycine to glycinate and decrease in oxygen solubility. Moreover, prolonged leaching times at higher pH levels (10.5 and 12) led to a decrease in the extraction of copper, <u>primarilymainly</u> due to the chemical precipitation of copper sulfide and crystallization of copper glycinate. By increasing the pulp density from 1 to 20%, copper extraction declined significantly primarily as a consequence of the partial dissolved copper precipitation at higher copper concentrations. SEM/WDX analyses were also subsequently used in order to evaluate the leach residues. Further investigation determined that the activation energy of the glycine leaching of concentrate was 37.4 KJ/mol, <u>thusand that</u> the kinetics were controlled by diffusion of the reagents through the product layer. From <u>these</u> results, it is evident that due to the high initial rate of glycine leaching and the precipitation of copper-bearing phases (i.e. copper glycinate and covellite) at high pulp densities, glycine leaching processes are recommended for the treatment of low grade chalcopyrite concentrates, ores or tailings.

Keywords: Glycine; Leaching; Kinetics; Chalcopyrite concentrate.

1. Introduction

Chalcopyrite is the most important copper sulfide mineral as it comprises more than 70% of current global copper reserves (Dreisinger, 2006; Li et al., 2013). Chalcopyritic ores are conventionally processed pyrometallurgically through production of a high-grade flotation concentrate, followed by smelting and refining steps (due to their fast reaction kinetics) that results in an LME (London Metal Exchange) grade copper. Nevertheless, this route has several environmental, economic and technical disadvantages, especially when used to treat low grade and <u>highly</u> complex ores. Over the last three decades, numerous investigations have aimed at the discovery of a feasible hydrometallurgical route to treat such complex

resources. The main challenge of this route is the slow leaching rate of chalcopyrite that occurs with a broad range of treatments such as sulfate, nitrate, chloride and ammonia media even under atmospheric or high-pressure conditions (Castellón et al., 2020; Hernández et al., 2019; Sokić et al., 2009; Thao et al., 2020; Turan et al., 2015; Watling, 2013; Yoo et al., 2010).

The treatment of sulfide concentrates is possible by hydrometallurgical methods, but the slow leaching kinetics of chalcopyrite requires the addition of strongly oxidizing reagents, as well as utilization of high temperature or high pressure conditions that increase capital and operational costs (Eksteen et al., 2017). Moreover, hydrometallurgical-Hydrometallurgical methods often inherit their own environmental implications related to the acid consumption or the production of contaminated wastes. Consequently, growing levels of research have recently been devoted to find alternative methods for copper extraction from chalcopyrite concentrates. Use of glycine as an alternative reagent for copper leaching from oxide and sulfide copper ores has been the subject of increasing investigations over the last few years (Eksteen et al., 2016; Eksteen et al., 2017; Eksteen et al., 2018; Oraby and Eksteen, 2014, 2015a, b; Oraby et al., 2017; Tanda et al., 2017a; Tanda et al., 2017b). Glycine is the simplest amino acid with the chemical formula H₂N-CH₂-COOH, it is also a non-toxic, non-volatile and non-flammable reagent. Moreover, glycine is readily available commercially at a relatively low price and is widely used in both in agriculture and the food industry (Eksteen et al., 2017; Tanda et al., 2017a). Additionally, as an amino acid, glycine exhibits zwitterionic properties and can be found in different forms within an aqueous solution depending on the medium pH. Zwitterion, ⁺H₃NCH₂COO⁻ (HL), is the major glycine species, which can gain or lose a proton to form glycinium cation ($H_3NCH_2COOH^+$) or glycinate anion ($H_2NCH_2COO^-$) (O'Connor et al., 2018b).

The dissolution of chalcopyrite in glycine solutions has been proposed to occur according to the following reactions (Eksteen et al., 2017; Kwon et al., 2005; O'Connor et al., 2018a; Song and Zhang, 2008):

 $CuFeS_{2}(\underline{s}) + 2(NH_{2}CH_{2}COO)^{-}(\underline{aq}) + 19OH^{-}(\underline{aq}) \rightarrow Cu(NH_{2}CH_{2}COO)_{2}(\underline{aq}) + Fe(OH)_{3}(\underline{s}) + 2SO_{4}^{-2}(\underline{aq}) + 8H_{2}O(\underline{l}) + 17e^{-}$

$$O_2(\underline{g}) + 2H_2O(\underline{l}) + 4e^- \rightarrow 4OH^-(\underline{aq})$$
⁽²⁾

$$Fe(OH)_{3}(\underline{s}) \rightarrow FeO(OH)(\underline{s}) + H_2O(\underline{l})$$
(3)

$$CuFeS_{2}(\underline{s}) + 2NH_{2}CH_{2}COO^{-}(\underline{aq}) + 4.25O_{2}(\underline{aq}) + 2OH^{-}(\underline{aq}) \rightarrow Cu(NH_{2}CH_{2}COO)_{2}(\underline{aq}) + FeO(OH)(\underline{s}) + 2SO_{4}^{2-}(\underline{aq}) + 0.5H_{2}O(I)$$
(4)

Furthermore, the related copper complexation mechanism in glycine solution can be described by (Eksteen et al., 2017):

$$\operatorname{Cu}^{2+}(\operatorname{aq}) + 2(\operatorname{N}^{+}\operatorname{H_3CH_2COO^{-}})(\operatorname{aq}) \to \operatorname{Cu}(\operatorname{NH_2CH_2COO})_2(\operatorname{aq}) + 2\operatorname{H}^{+}(\operatorname{aq})$$
(5)

It has been previously reported that during <u>the</u> electrochemical analyses of chalcopyrite-paste electrode in alkaline glycine solutions, passivation behavior was not observed (O'Connor et al., 2018a). Tanda et al. (2017a) found that copper oxide minerals can be readily leached with alkaline glycine solutions. A synergistic lixiviant mixture of glycine and cyanide was also used to recover both gold and copper from gold-copper ores and concentrates (Oraby et al., 2017). Copper has also been successfully leached from a chalcopyrite flotation concentrate in glycine solutions (Eksteen et al., 2017). More recently, the kinetics of chalcopyrite leaching at relatively low pulp densities <u>have captured significant attention</u> was investigated. Tanda et al. (2019) reported that iron-oxy-hydroxides was found on the leach residue and the diffusion of the reagents from the product layer was the dominant rate-limiting step. - In another recent

work, Shin et al.(2019) <u>also</u> found that during the glycine leaching of chalcopyrite concentrate at room temperature, copper sulfate and copper sulfide phases were precipitated.

Nevertheless, the ability of glycine leaching to extract copper from chalcopyrite concentrates at high pulp densities (> 6% (w/v)) and temperatures (above 0 C) has not yet been investigated. Such parameters are industrially critical for the leaching of ores and concentrates in stirred tank reactors, from both an economic and technical point of view. Thus, a comprehensive investigation to <u>appraise the applicability of such process elarify the</u> process applicability is <u>necessary</u>required. Consequently, the research work outlined here was <u>is</u> conducted in order to elucidate the effects of key material and process parameters, such as pulp density, grinding, temperature, reagent concentration and pH on the process efficiency, and leaching kinetics for the chalcopyrite concentrate of Sarcheshmeh Copper Mine.

2. Materials and methods

2.1. Materials

A representative sample of chalcopyrite flotation concentrate was obtained from the Sarcheshmeh Copper Mine (Kerman, Iran). Analysis of the samples by X-ray diffractometry (XRD) (by XMD50 using XPowder software) found that chalcopyrite (70%) and pyrite (9%) were the main phases present within the concentrate. The analyses of the sample with X-ray fluorescence (XRF) showed that the concentrate <u>was composed omprised</u> 38.3% Fe₂O₃, 30.5% S, 1.6% Al₂O₃, 0.4% CaO, 0.1% Mo and 4.8% SiO₂. Acid digestion of the sample and analyzing the solution with atomic absorbance spectrophotometry (AAS), <u>exhibitedshowed</u> that the concentrate contains 24.2% copper. All the reagents used were of analytical grade and deionized water was used throughout the experiments. For the re-grinding of the concentrate, the original sample with d_{80} of 75µm was ground in a ball mill with a slurry pulp

density of 50% (400 g concentrate for each batch), rotation speed of 70 rpm, Calgon addition of 1% (as a grinding aid) with 3200 g steel balls (ball diameters = 6.5 - 15 mm) for 5 hours. The slurry was then filtered and oven-dried at 5 °C for 12 hours. A laser particle size analyzer (Malvern Mastersizer 3000, Malvern, UK) was used to characterize the particle size of the sample and the results indicated that the size of the re-ground concentrate reached 11 μ m (d₈₀).

2.2. Leaching experiments

In order to investigate the ability of glycine to dissolve copper from the chalcopyrite concentrate, leaching experiments were conducted to evaluate the effects of several critical parameters including glycine concentration, pH, temperature, stirring rate, pulp density, oxygen flowrate and re-grinding under the conditions outlined in Table 1. All experiments were performed with 500 mL of slurry in a 1000 mL glass reactor equipped with a pitch bladed mechanical stirrer (Fig. 1). The leaching vessel was placed inside a thermostatic bath and purged with oxygen for 24 hours and the various leaching conditions used are described in Table 1. A total of 19 experimental runs were performed to evaluate the effect of glycine concentration, temperature, pulp density, pH, stirring rate and oxygen flowrate on the efficiency of copper leaching from the concentrate. For experiments related to the effect of pulp density, the levels of reagents (glycine concentration and oxygen flowrate) were set proportional to the solid content to keep the molar ratio of solid to reagent at a constant value. During the tests, several samples were taken and filtered by Whatman no. 41 filter papers (pore size = $0.45 \,\mu$ m) and the filtrate was diluted in 2% nitric acid prior to analysis by atomic adsorption spectroscopy (AAS; Model Thermo Scientific ICE 3000 Series) to ascertain the copper and iron concentrations. In addition, leaching solution samples after 6 hours at different pulp densities were also analyzed by ICP-OES to determine the presence of any

 dissolved impurities. In order to identify the nature of the leach residues, the remaining solids after <u>the leaching processwas complete</u> were washed with deionized water, filtered, dried and analyzed by scanning electron microscopy (SEM) (Model XL-30 Phillips) equipped with a WDX (Wavelength dispersive X-ray) (Model WDX-3PC) analyzer.

The<u>Furthermore, the</u> pH of solutions was measured by a pH meter (Model VWR), and- It-it was adjusted during the experiments with 10 M NaOH. ORP (oxidation reduction potential) Redox potential was recorded with a combined electrode Pt and Ag/AgCl connected to a voltmeter (Model WAVETEK).

2.3. Kinetic model

Modeling reaction kinetics is an important step for a better understanding of the leaching mechanism. Leaching of minerals is a heterogeneous process in which a liquid or gas reacts with solid in an aqueous solution. In order to study the reaction kinetics of the glycine leaching of the chalcopyrite concentrate, shrinking core and shrinking particle models were considered to describe the physical phenomena. In the shrinking core model, the reaction occurs at the surface of particle and then the reaction zone moves into the unreacted core and a product layer is generated during the process. The leaching rate of this model can be controlled either by the diffusion of reagent through the liquid film (Eq. 6), or through the product layer (Eq. 7), or by chemical reaction at the solid surface (Eq. 8) (Levenspiel, 1999):

X =	$k_l t_{\perp}$	5)
	•	

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_d t$$
(7)

$$1 - (1 - X)^{\frac{1}{3}} = k_r t \tag{8}$$

where X is fraction reacted, k_l , k_d and k_r are the kinetic constants and t is the leaching time.

<u>While in the shrinking particle model, the particle shrinks during the leaching process without</u> <u>the formation of a product layer (Levenspiel, 1999). The rate can be controlled by either film</u> diffusion (Eq. 9) or chemical reaction at the surface (Eq. 8).

$$1 - (1 - X)^{\frac{2}{3}} = k_f t$$
(9)

where k_{f} is the kinetic constant.

The activation energy (Eq. 10) could be determined based on the following Arrhenius equation (Levenspiel, 1999):

$$k = k_0 \exp\left(-\frac{Ea}{RT}\right)$$

<u>(10)</u>

Where Ea is activation energy (kJ/mol), T is temperature (K), R is gas constant (8.3145 J/K. mol), k is a reaction rate constant (1/hour) and k_0 is the frequency factor (1/hour).

3. Results and discussion

3.1. Effect of critical parameters on leaching efficiency

3.1.1. Glycine concentration

The extraction of copper as a function of time at different glycine concentrations is shown in Fig. 2A. As can be seen, copper extraction increases during the first 6 hours as glycine concentration is changed from 45% at 0.4 M to 70% at 2 M glycine concentration. After 6 hours, the extraction is observed to decrease at all concentration levels due to the precipitation of copper precipitates on the particle surfaces. O'Connor et al. (2018a, b) reported that copper could be precipitated as copper oxides such as CuO and Cu₂O, whereas iron could be precipitated as iron oxy-hydroxides that form on the surface of the minerals in glycine media. Moreover, Khezri et al. (2020) reported that covellite (CuS) and maghemite

 $(\gamma$ -Fe₂O₃) could be detected detected in washed leach residue by XRD analysis. Besides, blue crystals of copper glycinate have also been found to formed in the final leaching solutions and on unwashed residues.

It is proposed that a part of dissolved copper can be precipitated as chalcocite (Cu₂S) according to Eq. 6–<u>11</u> (Fernández-Reyes and García-Meza, 2018). This secondary phase is then leached rapidlyfast leached with glycine in the presence of oxygen to produce covellite and copper glycinate <u>due to the fast kinetics</u> (Eq. 7<u>12</u>). Similarly, covellite is also leached in the presence of glycine according to Eq. 8–<u>13</u> (Tanda et al., 2018).

$$2\mathrm{Cu}^{2+}(\underline{\mathrm{aq}}) + \mathrm{HS}^{-}(\underline{\mathrm{aq}}) + \mathrm{OH}^{-}(\underline{\mathrm{aq}}) \to \mathrm{Cu}_{2}\mathrm{S}(\underline{\mathrm{s}}) + \mathrm{H}_{2}\mathrm{O}(\underline{\mathrm{l}})^{+}2\mathrm{e}^{-}$$

$$(\underline{\mathbf{611}})$$

$$Cu_{2}S(s) + 2NH_{2}CH_{2}COOH(\underline{aq}) + 0.5O_{2}(\underline{aq}) \xrightarrow{Fast} Cu(NH_{2}CH_{2}COO)_{2}(\underline{aq}) + CuS(\underline{s}) + H_{2}O$$
(1)
(712)

CuS (s) + 2NH₂CH₂COOH (aq)+ 2O₂ (aq) + 2OH⁻ (aq)
$$\xrightarrow{Slow}$$
 Cu(NH₂CH₂COO)₂ (aq) + SO₄²⁻
(aq) _____+ 2H₂O (1)
(§13)

The presence of covellite on the surface of leaching residues confirms that the reaction rate of Eq. 8-13 is slow. This secondary copper sulfide phase may act as a passive-like layer on the surface of chalcopyrite. It was reported that covellite leaches slowly in the glycine media (Tanda et al., 2018). Covellite leaching could be the rate-limiting-step in the glycine leaching of chalcopyrite, thereby decreasing the overall rate of copper dissolution. In addition, the other secondary phase distinguished in the leach residue was maghemite, which is proposed to be precipitated from the goethite via Eq. 9-14 (Popescu et al., 2010).

 $2FeO(OH) (s) \rightarrow Fe_2O_3 (s) + H_2O (l)$ (914)

In Fig. 3A, the variation of pH during the leaching process is portrayed at varying glycine concentrationsshown in various glycine solutions _ranging from 0.4 to 2 M. It can be observed that during the concentrate dissolution, the pH decreases in all the conditions investigated. This decrease in pH indicates the dissolution of copper in the glycine medium takes place and results in the reduction in OH⁻ ion concentration as <u>indicatedshown</u> in Eq. 4. This decrease in OH was offset by the periodic addition of 10 M NaOH in order to reestablish pH to the initial level (when the difference of measured and initial pH was higher than 0.3 unit). With increasing the leaching time, the drop in pH was found to be higher at increased glycine concentrations, which is mainly due to increased levels of copper dissolution that consumes OH⁻ ions. Fig. 3B shows-represents the variation of redox potential during the process. For all of leaching experimentstests, the redox potential initially decreases followed by an before being seen to increase with prolonged the reaction times. This behavior is possibly because of the release of reductive ions, such as glycinate (N₂CH₂COO⁻) and HS⁻, while the later increase may be due to the oxidation of these reductive species by the injected oxygen or the consumption of HS^- to form copper sulfide (Eq. 611). Furthermore, it can also be observed that an increase in glycine concentration results in a more significant decrease in the in more significant decreases of the redox potential (Fig. 3B) probably as a consequence of more reductive species being generated.

3.1.2. Temperature

Fig. 2B shows the extraction of copper as a function of time at different temperatures and a fixed glycine concentration of 0.7 M. The results portrayed that the maximum copper extraction of 51% was achieved at a temperature of 60 C after 6 hours, whereas the minimum extraction was 2.9% occurred at 90 °C at 6 hours!. It is expected that the chemical reactions of copper precipitation —(such as covelite formation—) proceed faster at the higherst temperatures. O'Connor et al. (2018b) reported that by increasing the temperature (up to

 60 C), the concentration of glycinate increases, however at higher temperatures, the copper glycinate stability region is decreased, which is not desirable for copper leaching. It is also worth noting that the concentration of oxygen in the solution decreases when temperature is increased at atmospheric pressure, as can be predicted by the Henry's law (Mackay and Shiu, 1981). From the results it can be concluded that conducting the process at 60 C is recommended to optimize the copper extraction, which is in accordance with the previously published <u>studies</u> (Eksteen et al., 2016; Eksteen et al., 2017; Tanda et al., 2017a).

3.1.3. Pulp density

Extraction of copper as a function of time at different pulp densities are shown in Fig. 2C. The maximum copper extraction (91.1%) was observed found at 6 hours leaching time and the pulp density of 1% for the re-ground concentrate ($d_{80} = 11 \mu m$), a level which is around 50% higher than that obtained at the concentrate with the original size ($d_{80} = 75 \mu m$). In contrast, when the pulp density was increased from 5 to 20%, the copper extraction at 6 hours decreased from 51 to 11%. A decline in the extraction observed after 6 hours at pulp densities higher than 5% could be related to the partial removal of dissolved copper as precipitates such as copper sulfides or copper glycinate crystals. The ICP analysis of the leaching solutions after 6 hours at pulp densities of 5, 10, 15 and 20% indicated that their sulfur dosages were 4.3, 8.1, 8.6 and 9.2 g/L, respectively. This increase in the concentration of sulfur in the leach solution with increasing pulp density results from the higher sulfur content within the solid sample, although the concentrations of iron were less than 0.1 g/L. In this case, the iron concentration before 12 hours was found to be negligible, while at 12 and 24 hours, it had increased 0.97 and 1.48 g/L, respectively. The highest pH reduction (Fig. 4A) was found at 5 and 10% pulp densities, which correlated with high copper concentrations in the solution (Fig. 2C). The same behavior was also demonstrated with the lowest level of redox potential found with the 20% pulp density (Fig. 4B) that demonstrated the minimum

 copper extraction. The redox potentials at the pulp densities of 15 and 20% were found to be relatively lower than those at lower pulp densities. This low level <u>of redox potential</u> could be attributed to the higher viscosity of the slurry at these high pulp densities₂— which decreases the diffusion of oxygen in the liquid phase₂ – and <u>the higher increases the</u> concentrations of reductive species (such as HS⁻ and glycinate).

3.1.4. pH

The <u>effect of pH on the</u> extraction of copper as a function of time was shownwas presented at different levels of pHin (Fig. 2D). As can be seen during the first few hours, the copper extraction at the pHs of 10.5 and 12 was higher than that at the pH of 9, probably as a result of the higher concentrations of ionic glycinate at the higher pH levels as previously reported by O'Connor et al. (2018b). Moreover, the level of copper extraction was found to decrease after 3 hours for the test conducted at the initial pH of 12, whereas a similar decrease was only noted after 12 hours when the initial pH of 10.5. As previously mentioned, this decrease in extraction could be attributed to the formation of copper sulfide precipitate and copper glycinate crystals. In contrast, for the test performed with an initial pH of 9, the extraction was not significant at low pH levels. During the first 3 hours, copper extraction at pH 9 was significantly lower than those at pH 10.5 and 12. O'Connor et al ((2018b) reported that at pH 9, the dissolution rate of chalcopyrite is limited by the concentration of glycinate, whereas at the pH higher than 10, it is limited by the formation of oxide species on the mineral surface and that pH > 11, surface inactivation depends on the concentration of glycine.

3.1.5. Stirring rate

As the rate of stirring in a tank affects the diffusion rate of the reagents to the mineral surface, the influence of stirring rate (from 250 to 750 rpm) on the leaching rate of the concentrate

was performed and the extraction of copper as a function of time is displayed in Fig. 2E. It can be seen that the maximum extraction (51%, 6 hours) was obtained with a stirring rate of 500 rpm, while the minimum extraction (44%, 6 hours) was achieved at 250 rpm. This enhancement of extraction with the increase in stirring rate from 250 to 500 rpm could be related to the enhancement of the oxygen dissolution in the liquid phase. Fig. 5B portrays that the lowest redox potential was obtained at 250 rpm as a result of the lower distribution efficiency of the oxygen bubbles within the solution. On the other hand, the reason for the observed decrease in the copper extraction with 750 rpm results from an increased rate of copper precipitate formation. The highest drop in pH (Fig. 5A) occurred at 500 rpm and this can be related to the maximum level of copper extraction. Fig. 5B shows that the lowest redox potential was obtained at 250 rpm as a result of the lower distribution efficiency of the oxygen bubbles within the solution.

3.1.6. Oxygen flowrate

The effect of oxygen as a key reagent during the glycine leaching of copper from copperbearing minerals is displayed in Fig. 2F. It can be seen that by increasing the oxygen flowrate to the slurry, copper extraction increases during the first 6 hours, however, prolongation of the extraction process leads to a decline (6 hours for 0.5 and 1 L/min oxygen flowrate). Maximum copper extraction (68%) was achieved with an oxygen flow rate of 2 L/min oxygen and its decline commenced only after 12 hours primarily as a result of the lower levels of covellite formation under higher oxidation conditions. During the first few-three hours of the experiment, there is sufficient oxygen to commence the leaching process, thus the extraction values are similar in all cases. during this period (first 3 hours) and overall e <u>After that</u>, copper extraction increased with increasing oxygen flowrate. The extraction <u>of</u> copper_in all experiments initially increases with time, whereas after a certain duration —(3 hours for 0.5 L/min and 12 hours for 2 L/min)— the copper extractionit shows a continuous decrease. This decline that can be attributed to the partial removal of dissolved copper as covellite or copper glycinate crystals.

3.1.7. Re-grinding

Fig. 2G represents the extraction of copper achieved from the flotation concentrate with and without an additional re-grinding operation. As can be observed, copper extraction was significantly increased by re-grinding of the concentrate from the d_{80} of 75 µm (d_{80}) to the d_{80} of 11 µm. Copper extraction for the concentrate and the re-ground concentrate were respectively 22.6% and 51.0% at 6 hours. After 6 hours, the extraction decreased in the re-ground sample, whilst in the case of original concentrate extraction slightly increased to reach 31.5% after 24 hours. The initial increase for the re-ground sample could be related to its higher specific surface area and the high dependency of the leaching rate to the surface area. However, the reason for the subsequent decrease in extraction for the re-ground sample (Fig. 6B) at first few hours favors the formation of copper sulfide minerals, such as covellite and our previous research has shown the presence of copper glycinate and covellite in the solid leach residues (Khezri et al., 2020). It can also be seen In addition, the pH reduction (Fig. 6A) in the re-ground sample was more significant than that in the original concentrate ($d_{80} = 75$ µm).

3.2. Characterization of leaching residues

In order to investigate the characteristics of the leach residues, the resultant washed solids were analyzed with SEM/WDX. Fig. 7 shows displays the SEM and the WDX maps of the residue obtained from the final slurry of the concentrate leaching at 10% (w/v) pulp density, 1.4 M glycine concentration, an initial pH of 10.5, 1.5 L/min oxygen flowrate and 500 rpm stirring rate at 60 °C.

According to Fig. 7, in the area marked by the rectangular box, the relative content of iron and copper is high, whilst sulfur is somewhat lower₂, which-<u>This</u> may indicate a partial dissolution of the chalcopyrite and partial precipitation of the iron and copper ions—with the level of copper precipitation higher than iron. In the diamond-shaped area, the content of iron and copper are both high and the sulfur significantly lower, suggesting chalcopyrite dissolution followed by precipitation of iron and copper on the surface of the particles. In the circle, the content of iron and sulfur was determined to be at high levels, whereas copper was at a low level, which implies non-dissolution of pyrite or the precipitation of maghemite (Eq. 914). In the oval, the content of iron and copper was found to be high and sulfur to be low indicating dissolution of the chalcopyrite, and precipitation of iron and copper. The high ratio of copper to iron could be related to the precipitation of copper as secondary minerals. From these analyses it can be concluded that the dissolution occurs and is followed by copper and iron precipitation. Our previous work has demonstrated that maghemite and covellite could be precipitated during glycine leaching of chalcopyrite concentrate (Khezri et al., 2020). These results explain the decrease in copper extraction after 6 hours presented in Fig. 2C.

Fig. 8 <u>illustrates</u> the SEM picture and WDX maps of the residue obtained from the concentrate leached at 20% (w/v) pulp density, 2.8 M glycine concentration, an initial pH of 10.5, 3 L/min oxygen flowrate and 500 rpm. The contents of iron and copper are high and the associated sulfur is low at the rectangular and circle regions, which indicates chalcopyrite dissolution followed by iron and copper precipitation. In the diamond area, the content of iron, copper and sulfur are all relatively high, implying that precipitation of copper sulfide and iron oxide has occurred.

3.3. Kinetics of leaching

Modeling reaction kinetics is an important step for a better understanding of the leaching mechanism. Leaching of minerals is a heterogeneous process in which a liquid or gas reacts with solid in an aqueous solution. In order to study the reaction kinetics of the glycine leaching of the chalcopyrite concentrate, shrinking core and shrinking particle models were considered to describe the physical phenomena. In the shrinking core model, the reaction occurs at the surface of particle and then the reaction zone moves into the unreacted core and a product layer is generated during the process. While in the shrinking particle model the particle shrinks during the leaching process without the formation of a product layer (Levenspiel, 1999).

The kinetic data obtained from the glycine leaching of <u>the</u> concentrate ($d_{80} = 11\mu m$) at various temperatures ranging from 30 to 90 °C —(presented in Fig. 2B—) were fitted with different models (Fig. 9). The formulas of the kinetic models, the equation related to the line of best fit and the thermodynamic data are presented in Table 2.

It can be seen that the model of the diffusion from a boundary fluid film (C and D in Table 2) and chemical control (B in Table 2) did not well fit with the data at different temperatures, while the model related to the diffusion of the reagents from the product layer (A in Table 2) was in a good agreement with the results (except for 90 C) and therefore, it can be concluded that this model best reflects the leaching process at temperature of 30 to 60 C. By taking this model into account, The best fit model was employed to deduce the activation energy of the glycine leaching of the concentrate to be 37.42 kJ/mol through the Arrhenius plot (Fig. 10). This value is relatively lower than those reported in the literature for other chalcopyrite leaching in both ferric sulfate and ferric chloride media. He reported that the activation energy was 42 and 75 kJ/mol for the chloride and sulfate systems, respectively. Yévenes et al. (2010) calculated the rate-determining step is chemical reaction. Veloso et al. (2016) reported that activation energy for chalcopyrite leaching in both ferric sulfate and cupric sulfate and cupric sulfate in the presence of sodium

chloride was about 66 kJ/mol. However, the rate constant in the cupric medium was 1.5 times larger than that obtained in the ferric medium. Recently, the activation energies for glycine leaching of chalcopyrite was found to be 72 and 30 kJ/mol for the 20–38 and <10 µm size fractions, respectively (Tanda et al., 2019). A low level of activation energy (<40 kJ/mol) indicates that the process is influenced by the mass transfer of the reagents through the liquid film or product layer, while a high level of activation energy indicates that the process is greatly dependent on temperature and is controlled by chemical reaction at the solid surface (Levenspiel, 1999). The relatively low value of activation energy in the current work confirms that the leaching process is controlled by the diffusion of reagent through the product layer.

the Arrhenius curve shown in Fig. 10 was plotted and the activation energy was calculated to be 37.42 kJ/mol. The activation energy (Eq.10) was determined based on the following Arrhenius equation (Levenspiel, 1999):

 $\mathbf{k} = \mathbf{k}_0 \mathbf{e}^{-\mathbf{E}\mathbf{a}/\mathbf{R}\mathbf{T}}$

Where Ea is activation energy (kJ/mol), T is temperature (K), R is gas constant (8.3145 J/K. mol), k is a reaction rate constant (1/hour) and k_0 is the frequency factor (1/hour).

(10)

<u>4. Industrial evaluation</u>

Previous investigations for the glycine leaching of chalcopyrite was conducted at relatively low pulp densities. Shin et al. (2019) investigated the glycine leaching of a chalcopyrite concentrate with a d_{80} of 40 µm and in the presence of peroxide hydrogen at 6% pulp density. Maximum copper extraction was found to be around 45% during 170 hours (with changing the lixiviant during the process). Tanda et al. (2019) also evaluated the effect of several critical parameters on the glycine leaching of chalcopyrite at 0.75% pulp density. The extraction curves were progressively increased during the process. This behavior was also observed in the current study for the tests conducted at 1% pulp density. However, at higher pulp densities (5-20%), a significant decrease in copper extraction was found after a few hours, which was contributed to the formation of copper glycinate crystals and covellite. This new finding indicates that this selective and environmentally-friendly process has a major limitation in the tank leaching of high-grade chalcopyrite concentrates at relatively high pulp densities. However, the proposed strategy can be highly attractive the high potential of the process is for the treating of low-grade chalcopyrite or copper/gold ores in heaps. <u>Oraby and</u> Eksteen (2014) conducted successfully the selective leaching of copper from a copper-gold gravity concentrate in glycine solutions. (2014)Furthermore, application in the vat/tank leaching also presents an opportunity for target metal extraction. Glycine leaching could also be a good processing option for in situ leaching of base metals which can significantly decrease its environmental concerns. The other application could be the vat or tank leaching of low-grade and pyritic chalcopyrite concentrates. These lean and complex deposits are an important copper resource in future.

5. Conclusions

The atmospheric leaching of Sarcheshmeh chalcopyrite concentrate was investigated in a 1-L stirred tank reactor in glycine medium and the following results were obtained:

- Results showed that the leaching of concentrate is significantly accelerated by increasing the concentration of the glycine and decreasing the particle size. The maximum copper extraction (> 90 %) was found at a 1% pulp density of the reground concentrate. Increasing the temperature led to an enhancement of the leaching rate up to 60 °C followed by a decrease in the extraction at higher temperatures. This decrease at 90 °C could be related to the lower conversion degree of glycine to

glycinate, decreasing the dissolution of oxygen in the solution and the higher precipitation rate of copper sulfide.

- The extraction of copper from the concentrate declined by prolonging the process at higher levels of pH (10.5 and 12) especially at higher pulp densities (i.e. 15 and 20%, w/v), due to the removal of a part of dissolved copper as copper glycinate crystals and covellite precipitate. Covellite is a refractory phase in glycine leaching which may cause a passivating behavior during the leaching process.
- The leaching of concentrate was investigated at different temperatures and the results were correlated with various rate equations. It was found that the diffusion of the reagents through the product layer was supposed to be the rate-limiting step and the activation energy of the dissolution reaction was 37.42 KJ/mol.

Glycine is a selective, environmentally-friendly and strong reagent for the leaching of chalcopyrite. However, at high pulp densities of high grade concentrates, copper precipitates are formed and significantly decrease copper extraction. <u>Thus, the reagent portraysSo, this</u> reagent has a high industrial potential to treat low grade chalcopyrite concentrates, ores and tailings.

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References

Castellón, C.I., Hernández, P.C., Velásquez-Yévenes, L., Taboada, M.E., An Alternative Process for Leaching Chalcopyrite Concentrate in Nitrate-Acid-Seawater Media with Oxidant Recovery. Metals, 2020, **10(4)**, 518.

Dreisinger, D., Copper leaching from primary sulfides: Options for biological and chemical extraction of copper. Hydrometallurgy, 2006, **83(1-4)**, 10-20.

Dutrizac, J., The dissolution of chalcopyrite in ferric sulfate and ferric chloride media. Metallurgical Transactions B, 1981, **12(2)**, 371-378.

Eksteen, J., Oraby, E., Tanda, B., An alkaline glycine-based process for copper recovery and iron rejection from chalcopyrite. Proceedings of the IMPC, 2016.

Eksteen, J., Oraby, E., Tanda, B., A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Minerals Engineering, 2017, **108**, 53-66.

Eksteen, J., Oraby, E., Tanda, B., Tauetsile, P., Bezuidenhout, G., Newton, T., Trask, F., Bryan, I., Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores. Canadian Metallurgical Quarterly, 2018, **57(4)**, 390-398.

Fernández-Reyes, J.S., García-Meza, J.V., Bioelectrochemical system for the biooxidation of a chalcopyrite concentrate by acidophilic bacteria coupled to energy current generation and cathodic copper recovery. Biotechnology letters, 2018, **40(1)**, 63-73.

Hernández, P.C., Dupont, J., Herreros, O.O., Jimenez, Y.P., Torres, C.M., Accelerating copper leaching from sulfide ores in acid-nitrate-chloride media using agglomeration and curing as pretreatment. Minerals, 2019, **9(4)**, 250.

Khezri, M., Rezai, B., Abdollahzadeh, A. A., Wilson, B. P., Molaeinasab, M., Lundström, M., Investigation into the Effect of Mechanical Activation on the Leaching of Chalcopyrite in a Glycine Medium. Under review in Hydrometallurgy.

Kwon, S.-K., Kimijima, K.i., Kanie, K., Muramatsu, A., Suzuki, S., Matsubara, E., Waseda, Y., Inhibition of conversion process from Fe (OH) 3 to β -FeOOH and α -Fe2O3 by the addition of silicate ions. ISIJ international, 2005, **45(1)**, 77-81.

Levenspiel, O., Chemical reaction engineering. Industrial & engineering chemistry research, 1999, **38(11)**, 4140-4143.

Li, Y., Kawashima, N., Li, J., Chandra, A., Gerson, A.R., A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. Advances in colloid and interface science, 2013, **197**, 1-32.

Mackay, D., Shiu, W.Y., A critical review of Henry's law constants for chemicals of environmental interest. Journal of physical and chemical reference data, 1981, **10(4)**, 1175-1199.

O'Connor, G., Lepkova, K., Eksteen, J., Oraby, E., Electrochemical behaviour and surface analysis of chalcopyrite in alkaline glycine solutions. Hydrometallurgy, 2018a, **182**, 32-43.

O'Connor, G., Lepkova, K., Eksteen, J., Oraby, E., Electrochemical behaviour of copper in alkaline glycine solutions. Hydrometallurgy, 2018b, **181**, 221-229.

Oraby, E., Eksteen, J., The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy, 2014, **150**, 14-19.

Oraby, E., Eksteen, J., Gold leaching in cyanide-starved copper solutions in the presence of glycine. Hydrometallurgy, 2015a, **156**, 81-88.

Oraby, E., Eksteen, J., The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy, 2015b, **152**, 199-203.

- Oraby, E., Eksteen, J., Tanda, B., Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy, 2017, **169**, 339-345.
- Popescu, M., Piticescu, R., Vasile, E., Taloi, D., Petriceanu, M., Stoiciu, M., Badilita, V., The influence of synthesis parameters on FeO (OH)/Fe2O3 formation by hydrothermal techniques. Zeitschrift für Naturforschung B, 2010, **65(8)**, 1024-1032.
- Shin, D., Ahn, J., Lee, J., Kinetic study of copper leaching from chalcopyrite concentrate in alkaline glycine solution. Hydrometallurgy, 2019, **183**, 71-78.
- Sokić, M.D., Marković, B., Živković, D., Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid. Hydrometallurgy, 2009, **95(3-4)**, 273-279.
- Song, C., Zhang, J., 2008. Electrocatalytic oxygen reduction reaction, In *PEM fuel cell electrocatalysts and catalyst layers*. Springer, pp. 89-134.
- Tanda, B., Eksteen, J., Oraby, E., An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy, 2017a, **167**, 153-162.
- Tanda, B., Eksteen, J., Oraby, E., Kinetics of chalcocite leaching in oxygenated alkaline glycine solutions. Hydrometallurgy, 2018, **178**, 264-273.
- Tanda, B., Eksteen, J., Oraby, E., O'Connor, G., The kinetics of chalcopyrite leaching in alkaline glycine/glycinate solutions. Minerals Engineering, 2019, **135**, 118-128.
- Tanda, B., Oraby, E., Eksteen, J., Recovery of copper from alkaline glycine leach solution using solvent extraction. Separation and Purification Technology, 2017b, **187**, 389-396.
- Thao, N.T., Tsuji, S., Jeon, S., Park, I., Tabelin, C.B., Ito, M., Hiroyoshi, N., Redox potentialdependent chalcopyrite leaching in acidic ferric chloride solutions: Leaching experiments. Hydrometallurgy, 2020, 105299.
- Turan, M.D., Arslanoğlu, H., Altundoğan, H.S., Optimization of the leaching conditions of chalcopyrite concentrate using ammonium persulfate in an autoclave system. Journal of the Taiwan Institute of Chemical Engineers, 2015, **50**, 49-55.
- Veloso, T.C., Peixoto, J.J., Pereira, M.S., Leao, V.A., Kinetics of chalcopyrite leaching in either ferric sulphate or cupric sulphate media in the presence of NaCl. International Journal of Mineral Processing, 2016, **148**, 147-154.
- Watling, H., Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate–chloride and sulfate–nitrate process options. Hydrometallurgy, 2013, **140**, 163-180.
- Yévenes, L.V., Miki, H., Nicol, M., The dissolution of chalcopyrite in chloride solutions: Part 2: Effect of various parameters on the rate. Hydrometallurgy, 2010, **103(1-4)**, 80-85.
- Yoo, K., Kim, S.-k., Lee, J.-c., Ito, M., Tsunekawa, M., Hiroyoshi, N., Effect of chloride ions on leaching rate of chalcopyrite. Minerals Engineering, 2010, **23(6)**, 471-477.

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Fig. 1. Schematic representation of the leaching set up in the stirred tank reactor.



Fig. 2. Extraction of copper from the chalcopyrite concentrate ($d_{80} = 11 \mu m$) at pulp density of 5%, glycine concentration of 0.7 M, an initial pH of 10.5, oxygen flowrate of 1 L/min, stirring rate of 500 rpm and temperature of C (except for the test of investigated parameter). A: Glycine concentration, B: Temperature, C: Pulp density, D: pH, E: Stirring rate, F: Oxygen flowrate, G: Re-grinding (See Table 1).



Fig. 3. Variation of pH (A) and redox potential (B) during leaching of the chalcopyrite concentrate at a pulp density of 5%, temperature of 60 °C, oxygen flowrate of 1 L/min, initial solution pH of 10.5 and different glycine concentrations.



Fig. 4. Variation of pH (A) and redox potential (B) during leaching of the chalcopyrite concentrate at temperature of 60 °C, glycine concentration from 0.7 to 2.8 M, oxygen flowrate from 1 to 3 L/min, pulp density from 5 to 20% and an initial solution pH of 10.5.



Fig. 5. Variation of pH (A) and redox potential (B) during leaching of the chalcopyrite concentrate at pulp density of 5%, temperature of 60 °C, oxygen flowrate of 1 L/min, glycine concentration of 0.7 M, an initial solution pH of 10.5 and different stirring rates.



Fig. 6. Variation of pH (A) and redox potential (B) during leaching of the chalcopyrite concentrate at the d₈₀s of 11 and 75 μm, pulp density of 5%, temperature of 60 °C, oxygen flowrate of 1 L/min, glycine concentration of 0.7 M and an initial solution pH of 10.5.



Fig. 7. SEM (A) and WDX maps of concentrate leaching residues with d_{80} of 11 µm at 1 % (w/v) pulp density, 60 ° C, 1.4 M glycine concentration, an initial pH of 10.5, 1.5 L/min oxygen flowrate and 500 rpm stirring rate (Fig. 2C). B: Sulfur, C: Iron and D: Copper.



Fig. 8. SEM (A) and WDX maps of concentrate leaching residues with d₈₀ of 11 μm at 20% (w/v) pulp density, 60 ° C, 2.8 M glycine concentration, an initial pH of 10.5, 3 L/min oxygen flowrate and 500 rpm stirring rate (Fig. 2C). B: Sulfur, C: Iron, D: Copper.



Fig. 9. Plot of different model fits of conversion vs. time at various temperatures in glycine environment based on Fig. 2B.



Fig. 10. Plot of the reaction rate versus reciprocal of the temperature (Arrhenius curve) for concentrate in the glycine medium is based on Fig. 9, assuming control of the product layer diffusion.

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Run	Glycine concentration (M)	Temperature C)	Pulp density (%)	рН	Stirring rate (rpm)	Oxygen flowrate (L/min)
1	0.4	60	1 (75 µm)	10.5	500	1
2	0.4	60	1	10.5	500	1
3-16*	0.4 <u>0.7</u> 1 2	30 45 <u>60</u> 90	5*	9 <u>10.5</u> 12	250 <u>500</u> 750	0.5 <u>1</u> 2
17	1.4	60	10	10.5	500	1.5
18	2.1	60	15	10.5	500	2
19	2.8	60	20	10.5	500	3

Table 1: Parameters and their investigated ranges for the leaching experiments of the copper concentrate $(d_{80} = 11 \ \mu m, except run 1)$.

* Each parameter was investigated at its different levels, while other parameters were fixed as denoted by the underlined level.

Temperature	С	С	С	С
Model				
$1-2/3X-(1-X)^{(2/3)}$	y = 0.0017t	y = 0.003t	y = 0.0065t	y = 1E-04t
(A)	$R^2 = 0.9636$	$R^2 = 0.994$	$R^2 = 0.9934$	$R^2 = -0.639$
1-(1-X) ^(1/3)	y = 0.0189t	y = 0.026t	y = 0.0393t	y = 0.0041t
(B)	$R^2 = 0.9303$	$R^2 = 0.917$	$R^2 = 0.8791$	$R^2 = -0.725$
1-(1-X) ^(2/3)	y = 0.036t	y = 0.0486t	y = 0.0711t	y = 0.008t
(C)	$R^2 = 0.9184$	$R^2 = 0.8988$	$R^2 = 0.8483$	$R^2 = -0.726$
X	y = 0.0515t	y = 0.0684t	y = 0.0969t	y = 0.0119t
(D)	$R^2 = 0.9053$	$R^2 = 0.879$	$R^2 = 0.8148$	$R^2 = -0.727$

Table 2: Lines of best fit for model curve vs. time at various temperatures and thermodynamic data for concentrate in glycine environments.

Graphical abstract



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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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