



The sulfide precipitation behaviour of Cu and Au from their aqueous alkaline glycinate and cyanide complexes



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ABSTRACT

Recently, a novel leach process for treating gold-copper ores and concentrates by glycine in the presence of starved cyanide in solutions were investigated where the Cu species are present as cuprous cyanide and cupric glycinate. Often Cu-levels in these gold ores are insufficient to economically justify solvent extraction with electrowinning, and sulfide precipitation is often preferred. This research reports the precipitation behaviour of Cu and Au from glycine-cyanide solutions by adding NaHS. Contrary to conventional cyanide-only systems, where all the copper is present as cuprous cyanide and alkaline precipitation of copper by sulfide addition is not feasible, the synergistic lixiviant system leads to a cupric-dominant system where copper can be precipitated. As the leach solution mainly contains glycine(Gly), cyanide(CN⁻) and copper in alkaline environment, the effect of glycine concentration [Gly], [HS⁻]:[Cu_T] and [CN⁻]:[Cu_T] molar concentration ratios, pH, temperature and reaction time on the Cu and Au precipitation have been studied, where [Cu_T] = [Cu⁺] + [Cu²⁺]. The results show that CuS precipitation (covellite) increased slightly with moderately elevated temperature, but decreased significantly with increasing [CN⁻]:[Cu_T] molar ratio. CuS precipitation was found to be insensitive to [HS⁻]:[Cu_T] molar ratio, glycine concentrations, pH and reaction time. Pre-oxidation of cuprous Cu⁺ to cupric Cu²⁺ was carried out using H₂O₂ to confirm the effect of oxidation state on copper precipitation. The kinetics of pre-oxidation was fast and above 95% of Cu⁺ were oxidized to Cu²⁺ in 5 min. The optimal [H₂O₂]:[Cu⁺] molar ratio was found to be 5:1 and 4:1 at [CN⁻]:[Cu_T] molar ratio of 2:1 and 1:1 respectively, implying significant reagent consumption to complete the reaction. With pre-oxidation and oxygen removal by nitrogen gas stripping, a Cu recovery as high as 96.5% was achieved with the addition of 1.4 mol of sulfide per mole Cu_T for 5 min at [Cu]:[CN⁻]:[Gly] molar ratio of 1:2:3 and pH 10.5. No Au co-precipitation was observed after precipitation for most of tested conditions. This study showed that a high level of Cu and Au separation can be obtained by sulphide precipitation with H₂O₂ pre-oxidation from CN-starved glycine solutions and allowing Au to be subsequently removed by activated carbon.

1. Introduction

Due to the decrease in high grade and free milling gold resources, a great proportion of gold deposits in the 21st century are now processing complex gold ores that contain soluble copper minerals. One of the options to recover the dissolved copper from the leachate is to precipitate the copper using sulfide such as sodium sulfide (Na₂S), sodium hydrosulphide (NaHS), or hydrogen sulfide (H₂S). Sulfide precipitation plays an important part in hydrometallurgical processes with the several merits over hydroxide precipitation, including lower solubility of precipitate, higher selectivity for metal removal, faster reaction rates, better settling properties and the copper can be easily recovered by smelting [12].

In the process of extracting gold from gold-copper ores by traditional cyanidation, copper can also be recovered as a by-product, and cyanide can be recycled by processes such as Metallgesellschaft Natural Resources (MNR) [19] or the Sulfurisation-Acidification-Recycle-Thickening (SART) process [1,10,11]. SART process is a relatively advanced technology compared with the MNR process in terms of safety and equipment size that includes thickening and recycling stages instead of only using filtration to separate the solid precipitates [10,11]. These two processes are based on the protonation of cyanide by adding acid to achieve low pH, releasing cyanide in copper cyanide complexes through reactions Eq. (1)–(4) [5]:



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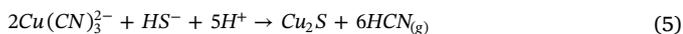
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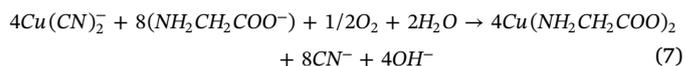
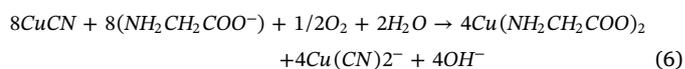
After acidification, adding bisulfide (HS^-) ion to the copper cyanide solutions leads to the copper precipitation as chalcocite as shown in Eq. (5) [10]. A recent study have cast doubt upon the existence of free “ S^{2-} ” in aqueous solutions based off the recent analytical and instrumental chemistry using a new Raman spectra [14]. This does not particularly influence our analysis, although previous sulfide precipitation papers may have used the free sulfide anion. For the SART system, the following reaction can therefore be proposed (historically this would have been written as free sulfide (S^{2-})) and



During the reaction, toxic hydrogen cyanide (HCN) gas is generated where an effective gas extraction and scrubbing system is required, giving rise to higher capital and operational costs. HCN and water are soluble in each other in all proportions and HCN has a strong water affinity, making it quite hard (high gas flows required with its associated blower costs and relatively large equipment) to effectively strip HCN from aqueous solutions for reabsorption into caustic solutions. Also, the use of sulfuric acid during acidification can lead to the formation of scale when lime is used for pH modification [5]. That is due to the reaction between sulfate and calcium to form gypsum which should be removed periodically.

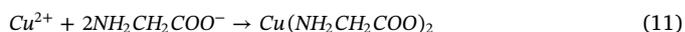
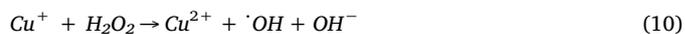
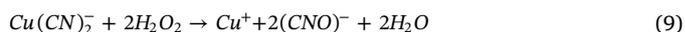
Recently, a new process using glycine as an alternative lixiviant in alkaline medium for gold and copper extraction has been invented and published [7,9,15,17,16,22,24,25]. Glycine has many advantages for its non-toxicity, ease of handling, non-volatility, cost-efficacy, and high stability over a wide range of pH- E_h and non-reactivity towards most ubiquitous gangue minerals. It was found that gold foils can be dissolved in alkaline glycine condition at a moderately elevated temperature in the presence of oxidants such as hydrogen peroxide and activated carbon can be an effective adsorbent for gold removal from the alkaline glycine solutions. [7,17,26,27]. Tanda et al. [23] has shown how copper can be removed from is alkaline glycinate leachates using solvent extraction, and Tauetsile et al. [28,29] has studied the adsorption of gold and copper from glycinate-cyanide solutions.

In a cyanide-starved glycine system with cyanide (11 mM) and glycine (13 mM), the gold dissolution rate was about 6.5 higher than that in the conventional cyanidation with the same amount of cyanide (11 mM) [16]. At the end of the leaching, the amount of cyanide is too small and is not measurable by traditional titration with silver nitrate. Thus all of the cyanide complex with Cu to form cuprous cyanide (with higher forms of complexation when more cyanide is present). Also, it was indicated that a glycine-cyanide synergistic (GCS) leaching process has a better gold, silver and copper recovery and faster dissolution rates compared to traditional cyanidation; in the presence of glycine, the cyanide consumption can be reduced by at least 75% [18] with commensurate savings in cyanide detoxification, whereas glycine can predominantly be recycled. It was reported that 99.5% gold extraction and 95.5% copper extraction were obtained when treating gold-copper gravity concentrate at ambient temperature in a solution with 800 ppm NaCN and 5 g/L glycine [18]. The authors have shown that in the GCS system, the copper minerals were complexed with cyanide and form different cuprous cyanide species (CuCN , $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$), depending on the cyanide to copper ratio in solution. The CuCN , and $\text{Cu}(\text{CN})_2^-$ can be oxidized to cupric glycinate in the presence of glycine and oxidants, thus reducing the levels of WAD cyanide and releasing more free cyanide to leach and complex with gold. Additionally, most of the copper present are in form of cupric glycinate at the end of the leaching, although a low level of copper cyanide species may remain; the reactions are indicated in Eqs. (6) and (7).



A study carried out by Eksteen et al. [8,9] pointed out that copper can be effectively precipitated as fast settling, coarse grained, covellite from cyanide-free cupric glycinate leachates by adding NaHS powder. Their results showed that 99.1% of copper can be precipitated at a bisulde (HS^-) to total copper (Cu_T) molar ratio of 1:1 in a cyanide-free system, where total the molar concentration total copper equates to the sum of the cupric and cuprous molar concentrations, i.e., $[\text{Cu}_T] = [\text{Cu}^+] + [\text{Cu}^{2+}]$. The study was conducted on a leachate derived from chalcopyrite using glycine as the only lixiviant at pH of 11. The XRD pattern data indicated that the copper sulphide precipitate is pure covellite (CuS).

However, alkaline cyanide systems behave quite different to their alkaline glycinate counterparts. A study carried out by Simons [20] illustrated that zero copper recovery was obtained by adding Na_2S from a solution containing 2000 mg/L copper with a $[\text{CN}^-]:[\text{Cu}_T]$ ratio of 3:1 and $[\text{HS}^-]:[\text{Cu}_T]$ ratio of 0.5:1 at pH 10. Tauetsile et al. [26,27] illustrated that the dicyanocuprate $[\text{Cu}(\text{CN})_2^-]$ complex has a higher affinity to adsorb onto activated carbon than the cupric glycinate equivalent (both having two moles of ligand coordinated with the copper). It is, therefore, proposed to oxidize the cuprous ions to cupric ions by the use of an oxidant such as hydrogen peroxide (H_2O_2) before precipitation: H_2O_2 is particularly favorable as it does not introduce any additional pollutant. According to Chen et al. [3], copper cyanide species ($\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_2^-$) can be destroyed progressively by H_2O_2 as own in Eqs. (8)–(10). During the reactions, cyanide was oxidized to cyanate and consequently Cu^+ was released and then oxidized to Cu^{2+} by H_2O_2 through a Fenton-like reaction. In the presence of glycine, Cu^{2+} will be complexed with glycine to form cupric glycinate instead of $\text{Cu}(\text{OH})_2$ in alkaline conditions, as shown in Eq. (11).



In terms of gold, it is expected that the precipitation will not occur, although some literature focused on SART process demonstrates that a small amount of gold ranging from about 1.5% to 30% was precipitated at different acidic pH values from 2.5 to 6 [20,13,6]. As for an alkaline glycine system, a gold loss of 16% and 24% was also reported after precipitation by adding NaHS from a leachate containing 784 mg/L $[\text{Cu}_T]$ and 0.241 mg/L gold at $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio of 1:1 and 1.1:1 [21]. It is suggested by Simons [20] that the gold loss might be attributed to the adsorption of copper precipitates instead of precipitation of gold as a sulfide due to the slight recovery of gold. Nevertheless, the behaviour of gold from cyanide-starved solutions by sulfide precipitation remains unknown.

The main aim of this study is to evaluate the behavior of copper and gold during sulfide precipitation in a synthetic glycine-cyanide solutions. The effects of pre-oxidation of Cu^+ to Cu^{2+} using hydrogen peroxide as an oxidant were also evaluated. For the precipitation tests without pre-oxidation, parameters which may affect the precipitation process were investigated, including $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio, $[\text{Gly}]:[\text{Cu}_T]$ molar ratio, $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio, reaction time, pH and temperature. Regarding the pre-oxidation tests, the kinetics of the oxidation with different $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio at different $[\text{CN}^-]:[\text{Cu}_T]$ molar ratios were investigated. The effects of different parameters, including dissolved oxygen, $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio, reaction

time and gold concentration on the copper precipitation with pre-oxidation were also studied. Free glycine analysis before and after oxidation and precipitation by titration was also performed to establish if the oxidation led to any measurable glycine destruction.

2. Experimental design

2.1. Synthetic solutions

All tests in this study were conducted using synthetic solutions, and analytical grade reagents and deionized water were used throughout the tests. A stock cyanide-starved glycine solution containing gold and copper was first prepared. Gold powders (99.998%, spherical, –200 mesh, Alfar Aesar – Thermo Fisher Scientific) were dissolved in deionized water contained glycine (> 99%, Sigma-Aldrich) and CuCN (95%, Ajax, Finechem). The pH of the solutions were buffered at pH 10 using sodium hydroxide (NaOH), and then the pH was adjusted to 10.5 using Ca(OH)₂ (Chem-Supply Pty Ltd) with a pH meter (Model AQUA-PH Meter). The solution was agitated with a magnetic stirrer and Teflon magnetic stirrer bars at 350 rpm. The solution was filtered with a Supor® 0.45 µm membrane disc filter (Pall Corporation) prior to the tests. A standard solution of glycine in the presence of starved cyanide containing 300 mg/L Cu_T, 1 mg/L Au at [Cu_T]:[CN⁻]:[Gly] molar ratio of 1:1:3 was obtained by diluting the stock solution accordingly.

2.2. Pre-oxidation

Pre-oxidation tests were performed in a 500 ml beaker agitated with a magnetic stirrer at 350 rpm. Various concentrations of hydrogen peroxide (30% w/v, Rowe Scientific) were added based on the Cu⁺ concentration which was determined by the differences between [Cu²⁺] and [Cu_T] using a UV-Vis and an atomic adsorption spectrometer (AAS, Agilent 55B AAS model), respectively. Samples were taken by a 10 ml syringe up to 4 h and the DO level was measured by a Syland M6000 DO meter.

2.3. Precipitation

Small-scale batch precipitation tests were conducted in a 200 ml beaker equipped with magnetic stirring facilities. A fresh high concentration of NaHS (0.5 g/ml) solution was used to avoid the effect of solution volume changes. The NaHS solution was added in relation to the moles of total copper in the leach solution. The precipitates were filtered by a vacuum filter and a Supor® 0.45 µm membrane disc filter paper (Pall Corporation). The solution samples before and after precipitation were analyzed for copper and gold by AAS tests to calculate the recovery of copper and gold. A UV-Vis spectrum was used to measure the concentration of Cu²⁺. The concentration of Cu⁺ in solutions was calculated by the differences between the total copper and the cupric ions. Zeta potential (E_h) was measured before and after precipitation using an Ionode platinum electrode with a Ag/AgCl reference. Free glycine concentration was measured by an acid-based titration method.

3. Results and discussions

3.1. Precipitation without pre-oxidation

3.1.1. Effects of [HS⁻]:[Cu_T] molar ratio

For a typical SART process, stoichiometric sulfide dosage values varied between 95 and 120% were used to achieve copper recovery higher than 85% [10]. The effects of different [HS⁻]:[Cu_T] molar ratio ranging from 1:1 to 3:1 on the metals precipitation from a solution containing 300 mg/L Cu_T, 1 mg/L Au, in the presence of glycine and cyanide [Cu_T]:[CN⁻]:[Gly] = 1:1:3) were investigated and the results are shown in Table 1. It is clear from Table 1 that the copper removals

Table 1

Metals removal and Cu²⁺ concentration after precipitation as different [HS⁻]:[Cu_T]. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] molar ratio = 1:1:3, pH = 10.5 and 5 min reaction time.

[HS ⁻]:[Cu _T]	[Cu ²⁺] after precipitation	pH after precipitation	Cu _T removal	Au Removal
	mg/l		%	%
1:1	30	10.41	62.8	0.0
1:1.1	0	10.23	68.1	0.0
1.3:1	0	10.20	69.1	0.0
1.6:1	0	10.31	68.0	0.0
2:1	0	10.34	66.1	0.0
3:1	0	10.35	68.3	0.0

peaked at 69.1% with [HS⁻]:[Cu_T] molar ratio of 1.3:1, and a decrease of copper removal was observed with the increasing [HS⁻]:[Cu_T] molar ratio. It is illustrated that the excess amount of sulfide tend to re-dissolve the copper precipitates by forming soluble copper polysulphide species in solutions [12,30], thus lowering the copper removal. No Cu²⁺ was present after the precipitation at [HS⁻]:[Cu_T] molar ratio ranging from 1.1:1 to 3:1. The remaining copper in solutions was cuprous cyanide which cannot be further precipitated with the increasing [HS⁻]:[Cu_T] molar ratio. A [HS⁻]:[Cu_T] molar ratio of 1:1 could not precipitate all the cupric ions that around 30 mg/L of Cu²⁺ remained in the filtrate.

The pH values after bisulfide precipitation were shown in Table 1, it can be seen that the pH bottomed at a [HS⁻]:[Cu_T] ratio of 1.3:1 and then increased slightly with the increasing sulfide additions. It is proposed that bisulfide in solutions was first consumed by the cupric ions to produce covellite (CuS) and hydrogen ions (H⁺) that decreased the pH, as shown in Eq. (12) [4].



The remaining HS⁻ in aqueous solutions underwent hydrolysis (equilibria shown in Eq. (13) [2], producing hydrogen sulfide (H₂S) and hydroxide (OH⁻) that increased the solution pH.



The change of pH indicated that a complete precipitation of Cu²⁺ was achieved at a [HS⁻]:[Cu_T] molar ratio of 1.3:1 and the excess sulfide addition influenced the equilibrium (Eq. (13)) that produced more OH⁻ and increased the solution pH.

Redox potential (E_h), usually used as an indicator for sulphide dosage, was also measured after the precipitation. As can be seen in Fig. 1, the results show that a more reducing E_h were observed with the increasing [HS⁻]:[Cu_T] molar ratio. This indicates that an E_h range from –200 to –300 mV (relative to a Ag/AgCl electrode) is optimum for the precipitation. It can also be seen from Table 1, no gold precipitation was observed, despite the presence of excess bisulphide. This implies that it is possible to achieve a high level of gold and copper separation if most of the copper can be precipitated.

3.1.2. Effects of reaction time

The effects of reaction time were also evaluated and the results are shown in Fig. 2. It is obvious that the reaction rate of the precipitation was fast, as 69.1% copper removal was achieved in 5 min, followed by a minor increase up to 72.8% at 30 min. The copper precipitation decreased slightly at 60 min, which might be owing to the re-dissolution of the copper sulfide precipitates in the presence of glycine. Similar experimental data were also obtained from the Telfer SART plant where a re-dissolution of copper sulfide precipitates (i.e. Cu₂S) was observed due to the prolonged residence time during the thickening process [20]. Moreover, it is noted that a small portion of gold (2.2%) were co-precipitated at 60 min, which agrees with the previous studies that report a small portion of gold loss occur during SART process [20,13,6]. It was

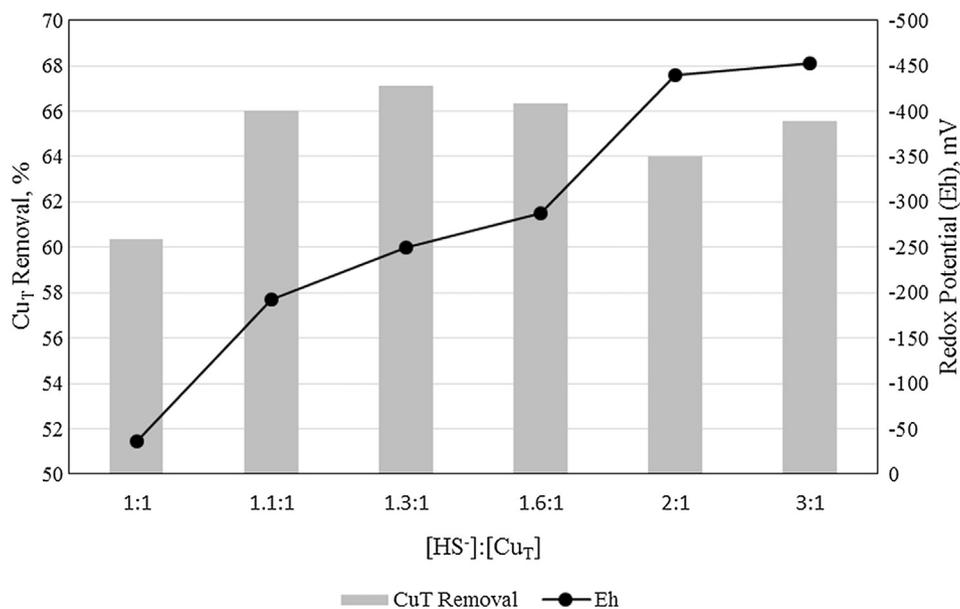


Fig. 1. Copper removal and Eh as a function of [HS⁻]:[Cu_T]. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] molar ratio = 1:1:3, pH = 10.5 and 5 mins reaction time.

also observed that the particle settling was being faster and larger particles were retained on the filter paper with time. This may be ascribed to the effects of aging that involves recrystallization of non-equilibrium shapes of primary particles to more compact shapes [31].

3.1.3. Effects of [Gly]:[CuT] molar ratio

An increase of [Gly]:[Cu_T] molar ratio up to (2.2:1) is favorable to higher gold and copper extractions during the GCS leaching process, further increase of the glycine concentration in the system have no evident effects on gold and copper extractions [18]. To evaluate the effects of glycine concentration on the metals precipitation, tests were performed at different [Gly]:[Cu_T] molar ratio ranged from 3:1 to 8:1. As can be observed from Table 2, there is no obvious variation in terms of metals removal (no gold precipitation). In addition, with the increasing [Gly]:[Cu_T] molar ratio, there are no noticeable changes in

Table 2

Metals removal and initial Cu²⁺ concentration at different [Gly]: [Cu_T] molar ratio. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [CN⁻]:[Cu_T] = 1:1, pH = 10.5, [HS⁻]:[Cu_T] = 1.3:1 and 5 min reaction time.

[Gly]:[Cu _T]	Initial [Cu ²⁺] mg/L	Cu _T removal %	Au removal %
3:1	200	68.8	0.0
4:1	202	69.4	0.0
6:1	202	69.4	0.0
8:1	203	69.9	0.0

Cu²⁺ concentration in solutions after 4 h mixing. A reasonable explanation is that the transformation from cuprous cyanide to cupric glycinate is a slow redox reaction where sufficient oxidants are

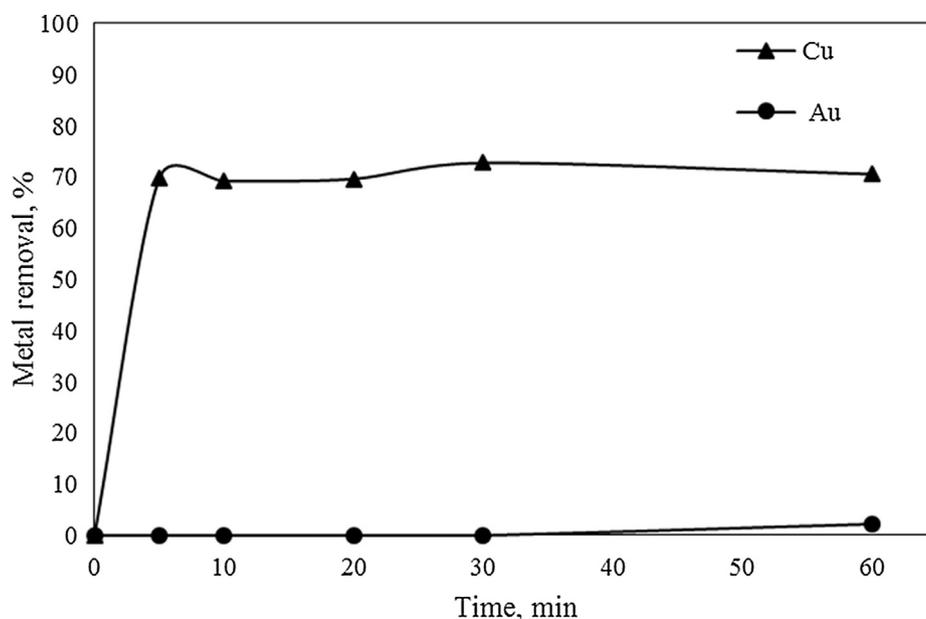


Fig. 2. Copper and gold removal as a function of reaction time. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] molar ratio = 1:1:3, pH = 10.5 and [HS⁻]:[Cu_T] = 1.3:1.

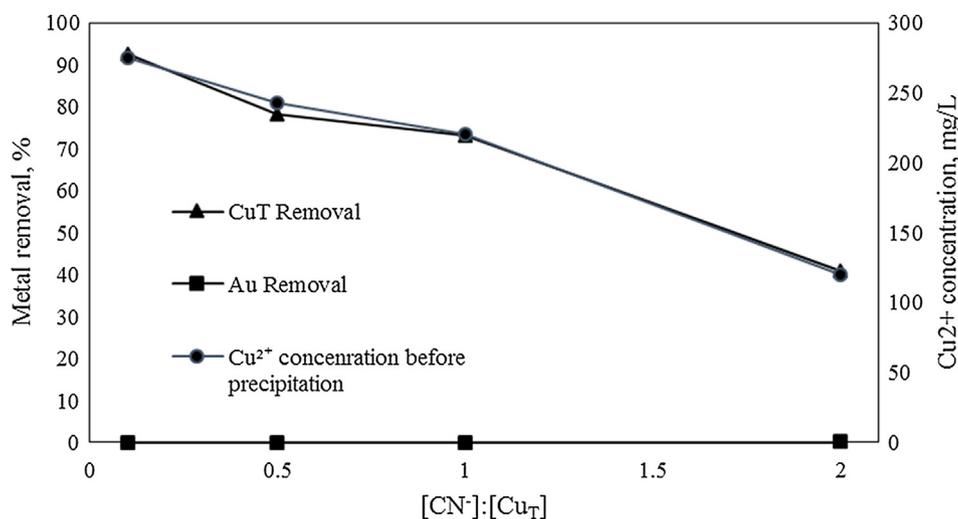


Fig. 3. Metal removal and Cu^{2+} concentration at different levels of $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio. Other conditions: 300 mg/L Cu_T , 1 mg/L Au, $[\text{Gly}]:[\text{Cu}_T] = 3:1$, pH = 10.5, $[\text{HS}^-]:[\text{Cu}_T] = 1.3:1$ and 5 min reaction time.

required. Also, this phenomenon demonstrates that the dissolutions of copper sulfide precipitates were insignificant in the presence of excess amount of free glycine.

3.1.4. Effects of $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio

Precipitation tests at four levels of $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio and fixed glycine concentration ($[\text{Gly}]:[\text{Cu}_T]$ molar ratio of 3:1) were carried out to investigate the effects of cyanide concentration on the copper and gold removal. Solid CuCN was dissolved in glycine solutions and then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powders were added accordingly to achieve the required total copper concentration (i.e. 300 mg/L) and low $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio (0.1:1 and 0.5:1). In order to obtain high $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio, CuCN and sodium cyanide (NaCN) were added stoichiometrically to achieve the target cyanide concentration (i.e. $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio of 2:1). It can be observed from Fig. 3, the effect of $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio is significant on copper precipitation that copper removal decreased dramatically as the $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio increased, 92.7% of copper removal was achieved at $[\text{CN}^-]:[\text{Cu}_T]$ ratio of 0.1:1, while only 40.8% of copper removal was obtained at $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio of 2:1. The concentrations of Cu^{2+} at different $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio are also indicated in Fig. 3, it appears that the initial Cu^{2+} concentration in solutions were determined by the $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio, indicating the $[\text{Cu}^{2+}]$ to $[\text{Cu}_T]$ ratio determines the copper removal. Again it confirmed that the remaining copper in form of cuprous cyanide cannot precipitate by using sulfide in alkaline conditions. During the precipitation, no gold precipitation was observed even at low $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio.

3.1.5. Effects of pH

Previous studies revealed that a pH range from 10.5 to 11 is optimal for gold extraction in a glycine-cyanide synergistic system [18]. The effects of pH were investigated in the range from 8 to 12; results are shown in Table 3. It can be seen that increasing the pH from 8 to 12 has marginal effects on the copper removal which ranges between 65.3% and 69%. Again, no gold precipitation was observed at different pH conditions. This phenomenon implies that no pH adjustment may be required at the end of the leaching where pH usually declines. Moreover, it is interesting to notice that the pH increased at pH 8 and 9 while pH decreased at pH 10.5 and 12 after precipitation. A more likely explanation is the different extent of hydrolysis of HS^- (shown in Eq. (13)) at different pH that more OH^- was generated at lower pH (i.e. pH 8 and 9), while the equilibrium may move backward in the presence of higher concentration of OH^- at higher pH values. This phenomenon can be beneficial if filtrates with low pH are recycled during the process

Table 3

Metals removal and pH before and after precipitation. Experimental conditions: 300 mg/L Cu_T , 1 mg/L Au, $[\text{Cu}_T]:[\text{CN}^-]:[\text{Gly}]$ molar ratio = 1:1:3, $[\text{HS}^-]:[\text{Cu}_T] = 1.3:1$, 5 min reaction time.

pH before precipitation	pH After precipitation	Cu removal	Au removal
8.10	9.50	%	%
9.04	9.58	65.3	0.0
10.55	10.38	69.0	0.0
12.00	11.79	67.6	0.0
		68.8	0.0

as fewer pH modifiers will be required to reach the optimal pH for leaching.

3.1.6. Effects of temperature

To evaluate the effects of temperature on the performance of precipitation, three levels of temperature (25, 35 and 55 °C) were selected in a solution containing 300 mg/L Cu_T , 1 mg/L Au, $[\text{Cu}_T]:[\text{CN}^-]:[\text{Gly}]$ molar ratio of 1:1:3. A hot plate equipped with a temperature probe was used to heat the solutions to the target temperature before and during the precipitation tests. As can be seen from Table 4, it can be observed that elevated temperature appears to increase the copper removal by around 10% from 25 to 55 °C. The changes in concentrations of Cu^{2+} after heating were marginal, indicating a portion of Cu^+ precipitated with the increasing temperature. This observation contradicts to some works for SART process, showing elevated temperature has an insignificant effect on copper recovery [13]. Also, it can be seen that gold remained stable in the solutions even at higher levels of temperature.

3.2. Pre-oxidation of Cu^+ to Cu^{2+}

It was obvious that the NaHS and glycine concentrations, pH and

Table 4

Metal removal and Cu^{2+} after heating for 4 h at different temperature. Experimental conditions 300 mg/L Cu_T , 1 mg/L Au, $[\text{Cu}_T]:[\text{CN}^-]:[\text{Gly}] = 1:1:3$, pH = 10.5, $[\text{HS}^-]:[\text{Cu}_T] = 1.3:1$ and 5 min reaction time.

Temperature	Cu_T removal	Au removal	Cu^{2+} after heating for 4 h
°C	%	%	mg/L
25	65.8	0.0	204
35	69.2	0.0	205
55	75.9	0.0	208

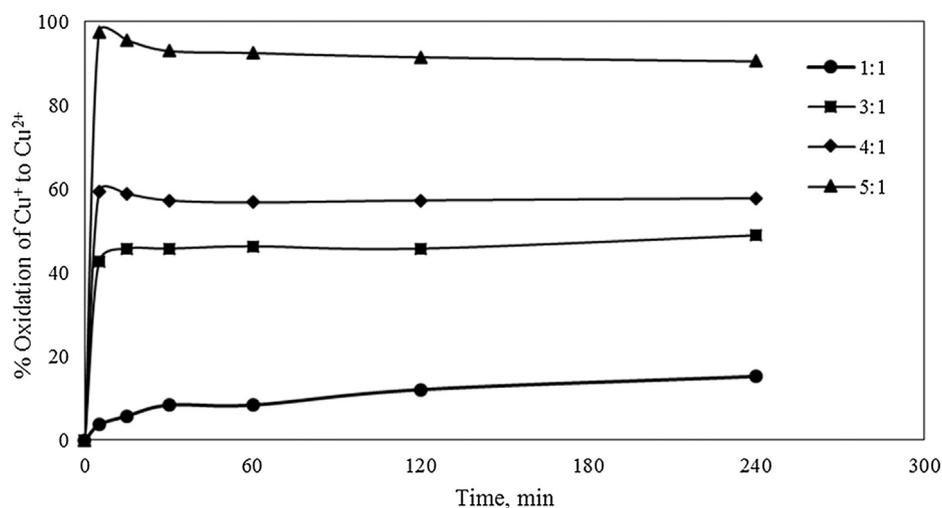


Fig. 4. Cu^+ oxidation to Cu^{2+} as a function of time at different $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio. Experimental conditions: 300 mg/L Cu_T , 1 mg/L Au, $[\text{Cu}_T]:[\text{CN}^-]:[\text{Gly}] = 1:2:3$, pH = 10.5 and room temperature.

time have minor effects on the copper and gold removal. It appears that the precipitation of copper is dominated by the $[\text{Cu}^{2+}]/[\text{Cu}^+]$ ratio in solutions. Therefore, it is essential to oxidize the Cu^+ to Cu^{2+} before the precipitation to achieve maximum copper removal.

In order to evaluate the effects of pre-oxidation on precipitation using H_2O_2 as the oxidant, a $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio of 2:1 was selected for the pre-oxidation tests. The other conditions were as follows: 300 mg/L Cu_T (100 mg/L Cu^{2+}), 1 mg/L Au, $[\text{Cu}_T]:[\text{Gly}]$ molar ratio of 3:1, pH 10.5 and room temperature. The amount of H_2O_2 was added stoichiometrically according to the amount of Cu^+ present in solutions.

3.2.1. Pre-oxidation at different $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio

Pre-oxidation at four levels of $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio were investigated. As it can be observed from Fig. 4, the level of oxidation was enhanced by the increasing $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio; 97.49% of Cu^+ was oxidized to Cu^{2+} in 5 min. Also, it appears that the levels of oxidation decreased slightly over time at higher $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio (i.e. 5:1 and 4:1), but increased gradually at lower level of $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio (i.e. 1:1 and 3:1). Based on the above observations, 5 mins of pre-oxidation with a $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio of 5:1 was chosen as optimal conditions for oxidizing Cu^+ to Cu^{2+} when the $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio is 2:1.

3.2.2. Effects of $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio on H_2O_2 dosage

The formation of cuprous cyanide species (i.e. CuCN , $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$) in solutions are dependent on the $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio that can affect the dosage of H_2O_2 for the oxidation from Cu^+ to Cu^{2+} . As can be seen Fig. 5, a $\text{H}_2\text{O}_2:\text{Cu}^+$ molar ratio of 4:1 was adequate when $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio is 1:1, where around 96% of Cu^+ were oxidized to Cu^{2+} in 5 min. Further increase in $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio to 5:1 only enhanced the oxidation Cu^+ to Cu^{2+} by about 2%. This observation reveals that the optimal $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio is determined by the $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio that lower $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio may require lower $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio to reach complete oxidation of Cu^+ to Cu^{2+} .

3.3. Precipitation after pre-oxidation

3.3.1. Effects of dissolved oxygen

As reported by Chen et al. [3] that the decomposition of H_2O_2 to O_2 occurred after the oxidation of Cu^+ to Cu^{2+} using a $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ ratio of 12:1 and the DO concentration reached the peak after 15 min at 45 ppm and then dramatically decreased to 12.5 ppm in 10 min. The concentrations of dissolved oxygen (DO) were measured during the pre-

oxidation and Fig. 6 shows the relationships between the DO concentration and the reaction time. It is clear that at any $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratio, the DO concentration reached the peak at 5 min, followed by a significant decline, the DO concentration kept constant after 60 min. It appears that the H_2O_2 decomposition occurred in 5 min of reaction, implying the rate oxidation of Cu^+ to Cu^{2+} completed in 5 min.

Precipitation tests were undertaken to investigate the effects of different initial DO concentrations at 22, 4.5 and 0 ppm. Solutions with 4.5 and 0 ppm DO were obtained by injecting nitrogen gas for 15 min and 30 mins, respectively, after 5 min of pre-oxidation. The results are shown in Fig. 7, it can be seen that the copper removals levelled off at about 94% from 0 to 4.5 ppm, and then decreased to 86.9% at 22 ppm DO. After the precipitation, almost most of the copper left in the solution was in the form of Cu^{2+} and the concentration of Cu^{2+} increased by the increasing DO concentration. A reasonable explanation is that a small portion of HS^- in solutions were oxidized by the high level of DO or by any H_2O_2 left in solutions thus negatively affecting on the Cu removal. It is, therefore, recommended to inject nitrogen gas to remove most of dissolved oxygen before starting the precipitation.

It should be noted no gold precipitation was detected at all levels of DO concentration and no cyanide can be detected by titration after the precipitation which suggests that the copper cyanide species may be oxidized to cyanate as indicated in Eqs. (8) and (9).

3.3.2. Effects of $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio

It was observed that around 10% of copper as Cu^{2+} remained unreacted after precipitation by adding NaHS with a $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio of 1.3:1, implying the dosage of NaHS might not be sufficient as HS^- can be oxidized by any H_2O_2 left in the system. The effects of four levels of $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio on precipitation were evaluated in a pre-oxidized solution at a zero DO level. Table 5 shows that the copper removals were enhanced by the increasing $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio up to 1.4:1 at 96.5%. However, a subsequent reduction in copper removal was observed at a $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio of 1.6:1. Again, this observation can be explained by the formation of soluble copper polysulfide species as the re-dissolution of copper precipitates. Also, in such conditions, no gold precipitation was observed. Based on the results, a $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio of 1.4:1 was selected to evaluate the other effects on copper and gold removal.

3.3.3. Effects of contact time during precipitation

The effects of extended precipitation time after the pre-oxidation were investigated at conditions of 0 ppm DO and $[\text{HS}^-]:[\text{Cu}_T]$ molar

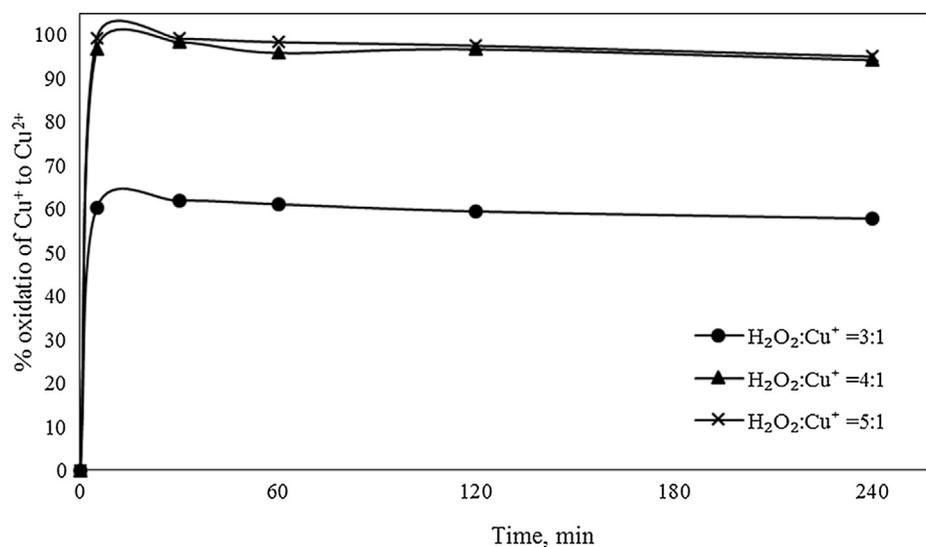


Fig. 5. Cu⁺ oxidation to Cu²⁺ as a function of time at different [H₂O₂]:[Cu⁺] molar ratio. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] = 1:1:3, pH = 10.5 and room temperature.

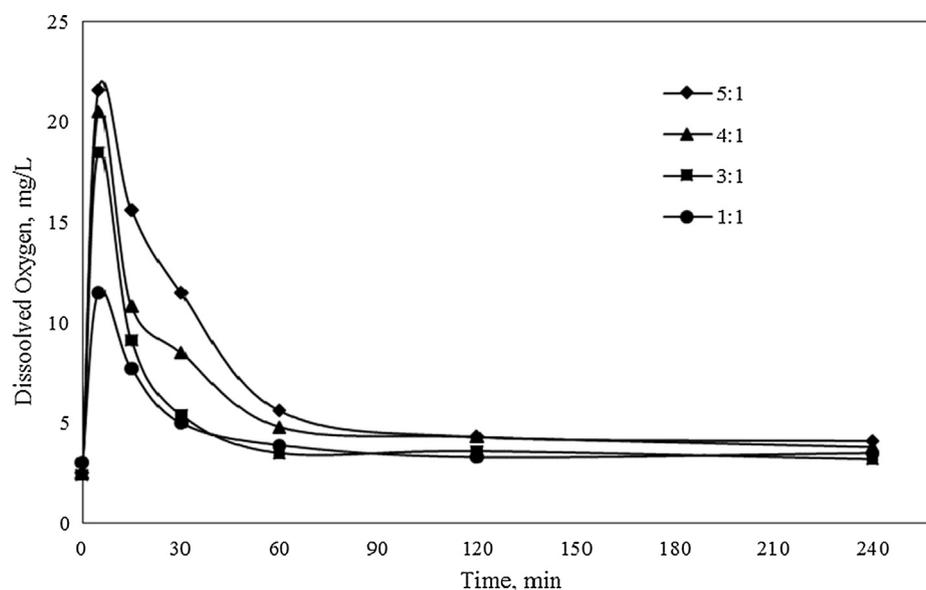


Fig. 6. DO concentration as a function of time at different [H₂O₂]:[Cu⁺] molar ratio. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] = 1:2:3, and pH = 10.5.

ratio of 1.4:1. As has been shown in Fig. 8, the copper removal declines gradually with the time from 96.5% at 5 min to 89.8% at 60 min, indicating the precipitation completed at 5 min. Similar to the results of precipitation without pre-oxidation, gold precipitation was observed at 60 min, but with larger amount of precipitation. This implied that the co-precipitation of gold may occur at an extended reaction time through adsorption onto the CuS particles. In order to achieve a maximum gold/copper separation and prevent any gold precipitation, a short reaction time (i.e. 5 min) was considered as the optimal reaction time.

3.3.4. Effects of pre-oxidation on gold precipitation

Precipitation tests were conducted to evaluate the effects of pre-oxidation and precipitation on metals recovery at higher gold concentration. The conditions of pre-oxidation and precipitation were as follows: 5 min of pre-oxidation using [H₂O₂]:[Cu⁺] molar ratio of 5:1 and 5 min of precipitation at 0 ppm DO and [HS⁻]:[Cu_T] molar ratio of 1.4:1. As indicated in Table 6, no gold precipitation was monitored at

any gold concentration level with or without pre-oxidation. And it is obvious that effects of initial gold concentration is negligible on the copper removal and it is clear that the copper removal increased significantly from 40.8% without pre-oxidation to 96.1% with pre-oxidation.

Followed copper precipitation, gold can be recovered by the conventional active carbon adsorption. Studies done by Tauetsile et al. [28,29] revealed that in the glycine-cyanide system, activated carbon could adsorb gold effectively at a wide range of pH from 9 to 12 and carbon has a higher selectivity of gold over copper in the presence of low concentration of free cyanide. The gold adsorption on carbon can be a feasible option to recover gold after the pre-oxidation and precipitation processes as cyanide oxidised by H₂O₂ and any copper left in solution is present in the cupric form Cu²⁺ which has less affinity to activated carbon.

3.3.5. Free glycine analysis by titration

An acid-based glycine titration method developed using a Metrohm

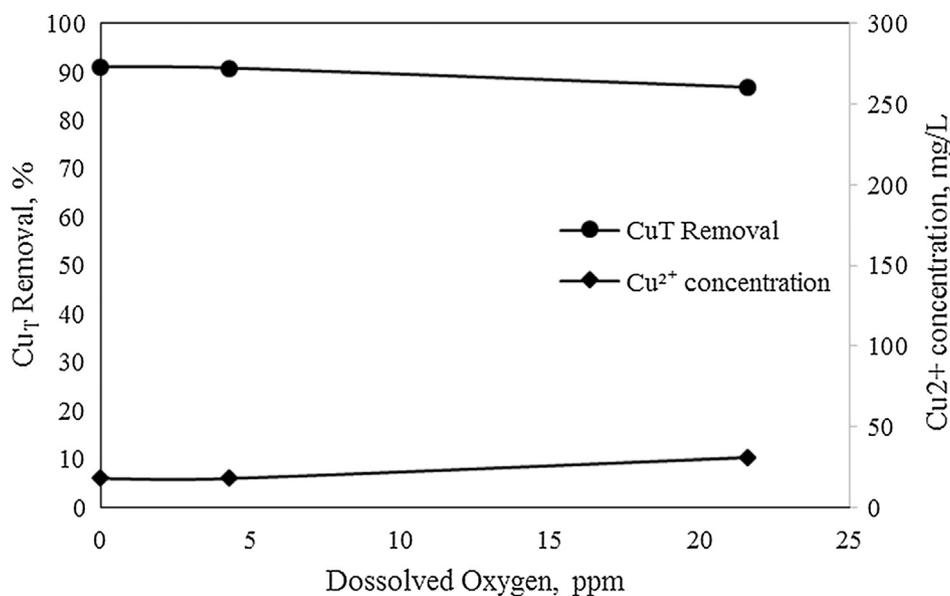


Fig. 7. Cu removal and Cu²⁺ concentration after precipitation as a function of DO concentration. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] = 1:2:3, and pH = 10.5, [HS⁻]:[Cu_T] = 1.3:1, 5 min reaction time.

Table 5

Cu and Au removal at different [HS⁻]:[Cu_T] molar ratio. Experimental conditions: 300 mg/L Cu_T, 1 mg/L Au, [Cu_T]:[CN⁻]:[Gly] = 1:2:3, and pH = 10.5, 0 ppm Do, 5 min reaction time.

[HS ⁻]:[Cu _T]	Cu _T removal	Au removal	[Cu ²⁺] after precipitation
	%	%	mg/L
1:1	71.2	0	86
1.3:1	91.1	0	27
1.4:1	96.5	0	12
1.6:1	91.4	0	26

716 DMS Titrimo was undertaken to investigate the effects of pre-oxidation on the free glycine concentration. Solutions from the tests for evaluating the effects of [HS⁻]:[Cu_T] molar ratio after pre-oxidation and precipitation were selected for free glycine titration, the conditions can be seen in Table 5. The results of experimental and theoretical free

Table 6

Gold and copper removal at different concentrations of gold with or without pre-oxidation.

Initial [Au] mg/L	Cu _T removal %	Au removal %
4 (With pre-oxidation)	96.1	0.0
1 (With pre-oxidation)	96.4	0.0
4 (Without pre-oxidation)	40.8	0.0

glycine concentration (assuming no glycine oxidation) are shown in Table 7. The free glycine concentration of the original solution was 0.965 g/L as around 0.1 g/L Cu²⁺ were complexed with glycine. The free glycine concentration reduced to 0.657 g/L after the pre-oxidation. This reduction is mainly because the cuprous cyanide was oxidized and Cu²⁺ were released and then complexed with glycine in solutions, resulting in a decline of free glycine concentration (but not in glycine

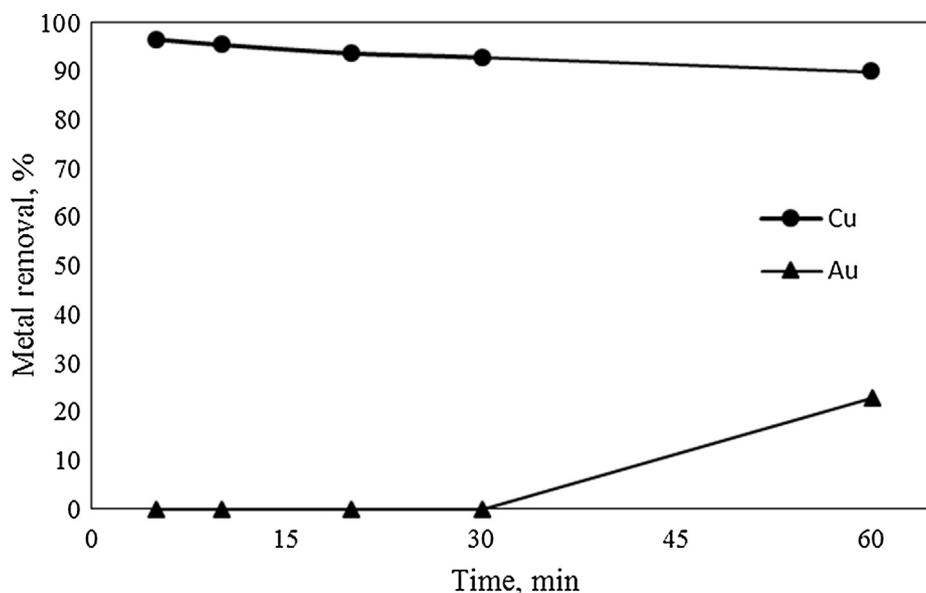


Fig. 8. Cu and Au removal as a function of time after the H₂O₂ pre-oxidation for 5 min, at 0 ppm DO, [Cu_T]:[CN⁻]:[Gly] = 1:2:3, [HS⁻]:[Cu_T] molar ratio of 1.4:1, 5 min of precipitation.

Table 7
Experimental and theoretical glycine concentration of different solutions.

Solutions	Experimental glycine concentration g/L	Theoretical glycine concentration g/L
Before pre-oxidation ($[\text{Cu}_T]:[\text{CN}^-]:[\text{Gly}] = 1:2:3$)	0.965	0.949
After pre-oxidation ($[\text{H}_2\text{O}_2]:[\text{Cu}^+] = 5:1$)	0.657	0.749
After precipitation ($[\text{HS}^-]:[\text{Cu}_T] = 1:1$)	0.878	0.963
After precipitation ($[\text{HS}^-]:[\text{Cu}_T] = 1.3:1$)	0.953	1.022
After precipitation ($[\text{HS}^-]:[\text{Cu}_T] = 1.4:1$)	0.986	1.037
After precipitation ($[\text{HS}^-]:[\text{Cu}_T] = 1.6:1$)	0.958	1.023
After precipitation ($[\text{HS}^-]:[\text{Cu}_T] = 1.6:1$, without pre-oxidation)	1.007	1.049

destruction) to form the cupric glycinate complex. It can be observed that the free glycine concentration increased after precipitation as the cupric glycinate were precipitated by bisulfide, thus glycine was released. However, it can also be seen that there are around 0.1–0.05 g/L differences between the experimental and theoretical results, which might be attributed to analytical errors or a small portion of glycine oxidation. Therefore, it can be concluded that the effect of H_2O_2 on free glycine concentration is insignificant.

4. Conclusion

The behaviour of copper precipitation derived from bisulfide (HS^-) addition to glycine-starved cyanide solutions has been studied at different conditions and the effects of pre-oxidation using H_2O_2 as the oxidant has also been evaluated. From the results that have been shown, the following can be concluded:

- The effects of $[\text{HS}^-]:[\text{Cu}_T]$, $[\text{Gly}]:[\text{Cu}_T]$, pH and time are insignificant on the copper precipitation
- A noticeable improvement in copper removal was observed when temperature was raised to 55 °C.
- Copper removal is dominantly controlled by $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio (which impacts the $[\text{Cu}^+]:[\text{Cu}^{2+}]$ molar ratio) in solutions and higher copper removal as CuS precipitate can be achieved in the presence of higher amount of Cu^{2+} .
- All gold tend to remain in solutions, but a small portion of gold precipitated at 60 min of contacting time which may be ascribed to surface adsorption of gold onto CuS.
- When the $[\text{CN}^-]:[\text{Cu}_T]$ molar ratio was 1:1 and 2:1, the optimal $[\text{H}_2\text{O}_2]:[\text{Cu}^+]$ molar ratios for pre-oxidation of Cu^{2+} to Cu^+ were 4:1 and 5:1, respectively.
- Copper redissolution can be decreased slightly by decreasing the DO concentration by nitrogen gas injection.
- There are no observable effects of pre-oxidation on the behavior of gold and the results confirmed that gold remained in solutions at different initial gold concentrations.
- Copper removal increased significantly after pre-oxidation, confirming that cupric glycinate participates in the precipitation reaction.
- The total glycine remained constant, within experimental error, during pre-oxidation.
- A high level of copper precipitation can be achieved after pre-oxidation and sulphide precipitation at the conditions of low concentration of DO, 5 min of reaction time and $[\text{HS}^-]:[\text{Cu}_T]$ molar ratio of 1.4:1 where the copper removal reached to ~96.5% without any gold precipitation.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.02.056>.

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