Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide

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The presence of cyanide soluble copper in the cyanidation of gold-copper ores and concentrates significantly increases the cyanide consumption in order to achieve sufficient gold recovery. In addition, cyanide recovery or cyanide detoxification/destruction processes are also required which adds extra cost to the process. This research introduces a leaching approach to extract gold, silver and copper from gold-copper ores and concentrates using a synergistic lixiviant leaching process using glycine in the presence of low concentrations of cyanide. The effects of glycine and cyanide concentrations on gold, silver and copper leaching kinetics and recovery were studied. It is shown that, in the presence of glycine, gold, silver and copper extraction increase significantly in solutions containing copper-cyanide species at a very low, or zero, free cyanide concentration. It has also been shown that the gold dissolution rate in glycine-cyanide system is almost three times higher than the gold dissolution rate in the conventional cyanidation. Kinetic studies were conducted to evaluate the effects of glycine concentration, pH, and CN/Cu ratio on the dissolution of gold and silver. It has also been shown that the gold dissolution rate increases by increasing the glycine concentration up to 2.0 g/L (Gly:Cu molar ratio of 2:2:1) and any further glycine addition has no significant effect on the dissolution of gold. It is shown that the presence of glycine in solutions containing copper (I)-cyanide species can significantly enhance the dissolution of precious and base metals. The proposed leaching approach significantly reduces the cyanide consumption by at least 75% and most of the copper is present as cupric glycinate in the final leach solution. In addition, gold, silver and copper extraction was higher than the conventional cyanidation process utilising similar cyanide dosages for all the gold-copper sources studied.

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1. Introduction

To extract precious metals from gold-copper ores and concentrates, the presence of copper minerals has detrimental effects on gold extraction unless high cyanide should be added to keep CN:Cu molar ratio above 4. For every 1% of reactive copper present about 30 kg/t NaCN was reported to be consumed (Muir, 2011). Stewart and Kappes (2012) also reported cyanide consumption can reach up to 2.3 kg/kg Cu recovered. The presence of copper minerals also has a negative effect on the extraction of gold (Muir et al., 1993; Nguyen et al., 1997; Jiang et al., 2001). In addition to lower gold recovery, additional costs are incurred to either recover the copper and/or cyanide, or to destruct/detox cyanide and WAD cyanide species in the final tail solutions (Mudder and Botz, 2001; Sceresini, 2005). Table 1 shows the effect of glycine soluble copper on cyanide consumption and gold recovery from Jiang et al. (2001) research study. High cyanide consumption and low gold recovery were observed at higher reactive copper contents of different ores. Therefore, finding an alternative process of leaching such problematic ores is essential to make these ores more feasible by decreasing the consumption of cyanide whilst maintaining gold recovery.

It is well known that cyanide soluble copper dissolves in cyanide solutions to form toxic copper-cyanide complexes such as Cu(CN)2−, Cu(CN)32−, Cu(CN)33−. A number of studies have been published to treat gold-copper ores by either adding ammonia to the conventional cyanidation process, or recycling cyanide after the leaching stage (La Brooy et al., 1991; Muir et al., 1991 and 1993; Costello et al., 1992; Jeffrey et al., 2002; Gonen et al., 2004; Adams et al., 2008; Xie and Dreisinger, 2009a and b; Alonso-González et al., 2009 and 2013). However, there are some issues regarding the environmental considerations of toxic and volatile ammonia which need attention. Threshold limit values (TLV’s) established by the American Conference of Governmental Industrial Hygienists for ammonia is 25 ppm (ACGIH, 1994). In addition, there are also increasing public and environmental concerns and restrictions on the discharge of cyanide and copper-cyanide complexes to tailings dams. Moreover, destruction of the WAD cyanide after leaching is sometimes uneconomical especially in the presence of high...
copper concentrations (Dai and Breuer, 2009; Smith and Mudder, 1991). The formation of strong (therefore non-WAD) cyanide complexes, such as ferrocyanide, from copper-iron minerals leads to further reduction in the potential to recover cyanide.

Recently the authors have developed and patented the use of amino acids and particularly glycine, as an alternative lixiviant to cyanide in the gold industry (Oraby and Eksteen, 2014a and b; Oraby and Eksteen, 2015a; Eksteen and Oraby, 2015). In addition, the authors have found that a mixture of glycine and copper-WAD cyanide has significantly improved the gold extraction from clear solutions using pure gold disc (Oraby and Eksteen, 2015b). The authors have concluded the major roles of glycine in copper-cyanide solutions to be one or more of the following roles: (i) glycine complexes with both cupric and cuprous ions (Aksu and Doyle, 2001) as shown in Eqs. (1), (2) and (3);

\[
\begin{align*}
\text{Cu}^{2+} + 2(\text{NH}_3\text{CH}_2\text{COO}^-) &\rightleftharpoons \text{Cu}(\text{NH}_3\text{CH}_2\text{COO})_2^+, \quad \log K = 8.6 \quad (1) \\
\text{Cu}^{2+} + 2(\text{NH}_3\text{CH}_2\text{COO}^-) &\rightleftharpoons \text{Cu}(\text{NH}_3\text{CH}_2\text{COO})_2^-, \quad \log K = 15.6 \quad (2) \\
\text{Cu}^+ + 2(\text{NH}_3\text{CH}_2\text{COO}^-) &\rightleftharpoons \text{Cu}(\text{NH}_3\text{CH}_2\text{COO})_2^-, \quad \log K = 10.1 \quad (3)
\end{align*}
\]

(ii) glycine presents cupric glycinate as an additional oxidant with higher availability and solubility in leach solutions; (iii) glycine dissolves the passivation layers of CuCN, AuCN, AuCN–CuCN and Cu(OH)\(_2\) on gold and copper surfaces; (iv) glycine increases the copper dissolution and breaking the copper sulfide matrixes and released fine particles of gold locked in copper sulfides; and (v) glycine acts as an additional lixiviant for gold dissolution as shown in Eq. (4) (Eksteen and Oraby, 2015).

\[
4\text{Au} + 8\text{NH}_3\text{CH}_2\text{COOH} + 4\text{NaOH} + 0_2 \rightarrow 4\text{Na[Au(NH}_3\text{CH}_2\text{COO})_2] + 6\text{H}_2\text{O} \quad (4)
\]

Glycine is a non-toxic, non-volatile, and low cost reagent which is produced in large industrial quantities for use in several industries. It can be easily produced industrially or derived as a by-product from different micro-organisms (González-López et al., 2005). Glycine and its copper and precious metals complexes are stable over a wide pH, Eh and temperature range. Other than losses in leach residues during solid/liquid separation, the glycine is recovered and recycled for leaching.

Therefore, the main aim of this work is to study and evaluate the application of the glycine-cyanide synergistic (GCS) process on gold extraction from gold-copper ores and concentrates. The main principle of the process is to utilise glycine to regenerate cyanide ions from copper-WAD cyanide in the presence of very low or zero free cyanide in the leach solutions. The proposed process aims to introduce several advantages in treating gold-copper ores and concentrates, such as (1) low cyanide consumption compared to the conventional cyanidation; (2) high gold, silver and copper extraction; (3) leaching conducted at a very low or no free cyanide in the leach solutions; (4) most of the copper in the final leach solution present as cupric glycinate; and (5) replacing the use of high cyanide with much safer and environmentally benign reagents.

2. Experimental

2.1. Samples preparation

Three samples of different gold-copper sources have been used and tested to conduct this research and the description of these samples are:

- Cu-Au-Ag gravity concentrate with complex copper mineralogy
- Cu-Au ore (oxide Au ore with nuisance Cu)
- Cu-Au ore (porphyry sulfide ore with low grade Au and recoverable levels of Cu).

These materials are discussed below.

2.1.1. Gold-copper gravity concentrate

The concentrate was produced from a centrifugal gravity separator at a gold-copper plant in Western Australia. The gravity concentrate sample was then ground to 100% passing 75 μm. The mineralogical compositions of the gravity concentrate was analyzed by an integrated automated mineralogy technique providing quantitative analysis of minerals using quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN). The concentrate was diluted using silica flour sized at 100% passing 75 μm to have average contents of 44.5 ppm Au, 4.5 ppm Ag, and 0.08% Cu. To calculate the final gold, silver and copper extractions, the final leach residues were analyzed for gold and silver by fire assay and for copper by X-ray Fluorescence (XRF).

2.1.2. Gold-copper oxides and sulfides samples

The gold-copper oxides and gold-copper sulfides samples were provided from two different Western Australian mining companies. The samples were then split and ground to 100% passing 75 μm. The mineralogical compositions of these two ores were analyzed by Quantitative X-ray Diffraction (XRD). Feed and residue samples were analyzed for gold by fire assay and for copper by X-ray Fluorescence (XRF) to calculate the final gold and copper extraction.

2.2. Leaching

All experiments were carried out using solutions prepared from analytical grade reagents and deionised water. Unless specified, all experiments are conducted using a bottle roller, and the ore or concentrate sample and glycine-cyanide solution were placed in a 2.5 L Winchester bottle. After pH adjustment to 10.5–11.0, the slurry was agitated by rolling the bottle on a bottle roll at 150 rpm. Bottles are vented through a 5 mm hole in the lid to allow for oxygen transfer. At different sampling times, solution samples of the leach solution were obtained after filtration using a 0.45 μm filter paper. The solids were returned back to the leach bottle. The filtrate were analyzed for gold, silver and copper by using atomic absorption spectrometry (AAS).

3. Results and discussions

The mineralogical analysis of the three tested samples by XRD are shown in Table 2.

Table 3 shows the elemental analysis of these samples. The gold-copper concentrate prior to 50 times silica flour dilution has 3.75% Cu distributed amongst a range of reactive copper minerals, such as chalcocite, cuprite and native copper. The gold–copper oxides ore contains 12.9 ppm Au and 0.04% copper. The gold–copper sulfides ore mainly contains chalcocytite as a copper mineral and it contains low gold grade of 0.77 ppm gold and 0.15% copper.
3.1. GCS versus cyanidation

Preliminary experiments were conducted to evaluate the leaching of gold-copper ores/concentrate by the GCS and conventional cyanidation processes. This was done using three different gold-copper sources covering gold-copper concentrates, gold-copper oxides and gold-copper sulfides ores. The following sections cover the gold and copper extraction from ores and gold, silver and copper extraction form a concentrate.

3.2. Gold-copper ores: gold-copper oxides

The gold extraction from leaching gold-copper oxides ore, containing 12.9 ppm gold and 0.04% copper, has been studied. The copper in such ore is present at nuisance levels, meaning that copper presence adds additional cost for treatment without bringing any additional revenue.

Gold extraction from the gold-copper oxides by GCS and direct cyanidation processes is shown in Fig. 1. The results presented in Fig. 1 show that at a 300 ppm sodium cyanide concentration, representing 1000 ppm (CN:Cu molar ratio 3.2:1), gold extraction only reaches 47.9%. This can be attributed to most of the cyanide being consumed by dissolving and complexing copper as shown in Eqs. (5) and (6) (Breuer et al., 2005). The slow gold leaching in both GCS and cyanidation processes can be referred to the coarse gravity gold present, hence the leaching of larger gold particles.

\[
2CuO + 5CN^{-} + H_2O \rightarrow 2Cu(CN)_2^{-} + OCN^{-} + 2OH^{-} \quad (5)
\]

\[
Cu_2S + 6CN^{-} \rightarrow 2Cu(CN)_4^{2-} + S^{2-} \quad (6)
\]

Eq. (5) is given for tenorite. Cuprite (Cu$_2$O) dissolution in the presence of cyanide and oxygen follows a pathway in which tenorite is formed as an intermediate product prior to further dissolution as per Eq. (5) above, as discussed by Breuer et al. (2005).

Fig. 2 confirms that most of cyanide in the conventional cyanidation process ends up as copper cyanide complexes and it can be seen that about 75.0% copper (282 mg/L Cu) was dissolved in 1000 ppm NaCN solutions.

In GCS process, most of the dissolved copper were complexed by glycine which leads to be more available cyanide to leach and complex gold. According to Eq. (7), at a starved cyanide concentration, CuCN is formed as an intermediate product prior to further dissolution as per Eq. (5) above.

\[
Cu(CN)_2^{-} \rightarrow CuCN + CN^{-} \quad (7)
\]

Gold and copper extraction from gold-copper sulfides ore, containing 0.77 ppm Au and 0.15% porphyry Cu (mainly present as chalcocite), has been calculated and presented in Figs. 3 and 4 respectively.
Fig. 3 shows that by adding 2 g/L glycine at similar cyanide concentration (450 ppm NaCN), gold extraction increased from 29.2% to 38.9%.

Fig. 4 shows that about a twofold improvement in copper extraction (21.9% Cu) was observed in the presence of 5 g/L glycine, when compared to only cyanidation (11.2% Cu). The higher copper dissolution in the presence of glycine may explain the increasing of gold extraction during GCS leach due to the increased available cyanide to leach gold whilst glycine complexing more copper.

Gold extraction from gold-copper oxides at 300 ppm NaCN and 5 g/L glycine was 45.0% after 24 h (Fig. 1) which is much higher than gold extraction from gold-copper sulfides (30.1% after 24 h at 450 ppm NaCN and 5 g/L glycine). This can be happen particularly when the sulfide is chalcopyrite and the leaching takes place at room temperature. It should also be noted that oxygen mass transfer for chalcopyrite oxidisation is very limited in a conventional bottle roll. It should be noted that increased chalcopyrite leaching can be achieved at slightly elevated temperature and use of oxygen injection through a fritted sparger and better agitation. This will also enhance gold exposure and liberation.

3.4. Gold-copper concentrate

Gold extraction from gold-copper gravity concentrate which contains 47.5 ppm Au, 4.7 ppm Ag and 0.08% Cu by GCS and conventional cyanidation processes has been evaluated. Most of the copper minerals in the concentrate were in the form of cyanide soluble copper such as metallic copper, chalcocite, and cuprite with some chalcocypite present. The concentrate has been leached in solutions containing cyanide only and glycine-cyanide synergistic mixture (GCS) at pH 11.0. Gold extraction from the gold-copper concentrate by GCS and direct cyanidation processes at two cyanide levels is shown in Fig. 5.

It can be seen that at 800 ppm NaCN, gold extraction was only 31.0% as the cyanide addition was only at a molar ratio of 1.3:1 to copper present in the ore. Glycine addition to a similar concentration of cyanide (800 ppm) significantly increases gold extraction up to 99.5%. These findings show that using glycine cyanide synergistic (GCS) process to treat gold-copper deposits may present at least four merits, being (1) low cyanide consumption; (2) high metals recovery; (3) utilisation of low or zero free cyanide during leaching; and (4) most of the copper in the final leach solution is present as the cupric glycinate complex (Eq. (8)).

Fig. 6 shows the copper extraction from such a concentrate by GCS and cyanidation processes. The glycine-cyanide process dissolves more copper (95.5%) than the conventional cyanidation processes (88.1%).

Silver extraction was enhanced by adding glycine to cyanide solutions as shown in Fig. 7. In fact, similar silver extraction by GCS at 800 ppm NaCN and cyanidation at 2500 ppm NaCN was observed. For similar silver extraction, the GCS process provides a 70% saving in cyanide. In addition, copper in the final cyanidation leach solution is present as WAD cyanide which requires further treatment and destruction.

On the other hand, with the GCS process most of the copper in the final leach solution is present as cupric glycinate complex (shown in...
Fig. 8. Copper extraction from gold-copper concentrate by GCS and conventional cyanidation processes at leach conditions of 50% solid contents, 100%-75 μm, pH 11.0 and room temperature.

3.5. Parameter optimisation

3.5.1. Effect of glycine

It has been shown the presence of glycine in a starved cyanide leach solution enhances gold extraction from gold-copper sources. Glycine stabilises the cupric ion in the system which acts as a stronger oxidant for gold leaching (Oraby and Eksteen, 2015b). The effects of glycine addition (at a fixed cyanide initial concentration of 800 ppm as NaCN) on gold, silver and copper extraction from the gold-copper concentrate are shown in Figs. 9, 10 and 11 respectively.

Glycine concentration of 5 g/L gave the highest gold extraction. However, over a period of 48 h, the same gold extraction is achieved with 2 g/L, 5 g/L and 10 g/L glycine. In the case where no glycine recycling option is applied, this result allows glycine addition to be minimised with no major effects on the final gold extraction. The presence of glycine can enhance the gold dissolution in aqueous solutions as an additional lixiviant of dissolving gold besides cyanide due to its complexing action with gold (Brown and Smith, 1982; Eksteen and Oraby, 2015; Oraby and Eksteen, 2015a). Clearly, the addition of glycine to cyanide also enhances the silver and copper extraction (Figs. 10 and 11). Copper was more sensitive to glycine concentration, with higher concentrations yielding higher extractions (Fig. 11). However, increasing glycine concentration above 2 g/L does not effect on the silver extraction (Fig. 10). These results indicate that if copper is present as nuisance copper in the gold-copper ores/concentrates, low glycine concentrations (2 g/L) can achieve good gold and silver extraction. However, if copper is present in a percentage that allows economic recovery, it may be viable to increase copper extraction through higher glycine concentrations. The effect of glycine concentrations, based on molar ratio of

Fig. 9. Effect of initial glycine concentration on gold extraction from gold-copper concentrate by GCS process using 800 ppm NaCN, 50% solids, 100%-75 μm, pH 11.0 and room temperature.

Fig. 10. Effect of initial glycine concentration on silver extraction from gold-copper concentrate by GCS process using 800 ppm NaCN, 50% solids, 100%-75 μm, pH 11.0 and room temperature.
glycine to copper, on gold and copper extraction after 48 hours leaching time is shown in Fig. 12. The CN:Cu molar ratio was kept at 1.4:1, pH 11.0 and room temperature.

It can be seen that increasing glycine to copper molar ratio increases gold and copper extractions. Most of the gold (99.4%) and copper (88.2%) was extracted at Gly:Cu ratio of 2.2:1 (2 g/L glycine). Any further increase in the Gly:Cu ratio slowly increases copper extraction.

3.5.2. Effect of cyanide

To further investigate the effect of cyanide concentration on gold, silver and copper dissolutions, three levels of cyanide were added at a fixed initial glycine concentration of 10 g/L and pH 11.0. Gold, silver and copper extraction from these tests are shown in Figs. 13, 14 and 15 respectively.

It is not surprising to observe that the metals extraction increases when the initial cyanide concentration increases, due to higher WAD cyanide generation. This was also observed during gold leaching from pure gold disc electrode by glycine-cyanide mixtures (Oraby and Eksteen, 2015b). The cyanide addition to the GCS process should be added at such concentration that leaves the WAD cyanide in the final leach solution <50 mg/L WAD cyanide solutions to be discharged to the tailing for the protection of wildlife (Donato et al., 2007).

Fig. 16 shows gold and copper extraction at different CN:Cu molar ratios in the presence and absence of 10 g/L glycine. It is interesting to see that increasing the CN:Cu molar ratio from 0.72:1 to 2.2:1 in the absence of glycine significantly increases copper extraction from 23.8% to 73.3%. However, increasing the CN:Cu molar ratio up to 2.2:1 slightly improves gold extraction from 27.3% to 35.5%. On the other hand, in the presence of glycine (10 g/L) at CN/Cu ratio of 1.4:1 most of the gold (99.5%) and copper (97%) was extracted. These results clarify what is normally happening during conventional cyanidation; adding high levels of cyanide to complex most of the cyanide soluble copper at a Cu:CN molar ratio of 1:4 in order to achieve high gold recovery.

Fig. 11. Effect of initial glycine concentration on copper extraction from gold-copper concentrate by GCS process using 800 ppm NaCN, 50% solids, 100%-75 μm, pH 11.0 and room temperature.

Fig. 12. Effect of glycine:Cu molar ratio on gold and copper extraction from gold-copper concentrate at leach conditions of CN:Cu molar ratio of 1.4:1, 50% solid contents, 100%-75 μm, pH 11.0, 48 hours leaching time and room temperature.

Fig. 13. Effect of initial cyanide concentration on gold extraction from gold-copper concentrate by GCS process using 10 g/L glycine, 50% solids, 100%-75 μm, pH 11.0 and room temperature.

Fig. 14. Effect of initial cyanide concentration on silver extraction from gold-copper concentrate by GCS process using 10 g/L glycine, 50% solids, 100%-75 μm, pH 11.0 and room temperature.

Fig. 15. Effect of initial cyanide concentration on copper extraction from gold-copper concentrate by GCS process using 10 g/L glycine, 50% solids, 100%-75 μm, pH 11.0 and room temperature.
4. Conclusions

Leaching studies of different gold-copper sources has been conducted and a comparison between conventional cyanidation and glycine-cyanide synergistic leach process has been made. The effect of glycine/copper and cyanide/copper molar ratios on gold and copper leaching kinetics in synergistic leach process has also been studied. The synergistic leach process treats gold-copper deposits by breaking down the copper-cyanide complexes to give a zero, or a very low free cyanide concentration in the presence of glycine. The synergistic process was found to be very effective to treat complex copper-gold deposits with four significant advantages, being (1) low cyanide consumption; (2) high metals recovery; (3) zero or very low free cyanide during the leaching; and (4) copper complexed largely with glycine rather than cyanide in the final tailing solutions. Adding CN/Cu at 1:1 M ratio and Gly/Cu at 2.2:1 was enough to extract high recoveries of gold and silver. It was observed that copper is sensitive to glycine additions and more copper can be extracted with higher glycine additions. The glycine impacts on gold, silver and copper extraction in the presence of very low cyanide concentrations, through (1) glycine complexes with both cupric and cuprous ions; (2) glycine appears to dissolve the CuCN, formed at zero, or a very low free cyanide concentration and regenerate cyanide for further gold and copper dissolution; and (3) glycine acts as an additional lixiviant in the presence of cyanide for gold, silver and copper extraction.

References


