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# Gold dissolution and copper suppression during leaching of copper–gold gravity concentrates in caustic soda-low free cyanide solutions

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#### ABSTRACT

In the cyanidation process, copper-gold deposits containing significant amounts of cyanide soluble copper can lead to high cyanide consumption with low gold extraction. The significant levels of weak acid dissociable (WAD) cyanide must then be destroyed prior to tailings disposal. This increases the cost to the gold mining companies to cover both the extra cyanide consumption in the leaching stage and the additional cost for cyanide recovery/destruction. Therefore, in this study, a selective cyanide leaching process of gold over copper from copper-gold concentrate (also see Oraby and Eksteen, 2014) containing 490 g/t Au and 0.97% Cu present as metallic copper, oxides and sulfides has been investigated. To decrease the cyanide consumption, cyanide is added into the leach solutions to maintain a ratio of cyanide to total reactive copper (CN/Cu) below 2. At low CN/Cu ratio, increasing the pH of solution can lead to the precipitation of solubilized copper as CuO/Cu(OH)<sub>2</sub>, releasing cyanide ions for further both gold and copper dissolution. A comparison of leaching gold in cyanide-caustic, cyanide-ammonia and conventional cyanidation processes has been made. Higher gold extraction and lower copper concentration in the final leach was achieved in the cyanide-caustic system than in either the cyanide-ammonia or conventional cyanidation processes. The effects of the caustic soda (pH) concentration or cyanide concentration on gold extraction and copper suppression have also been studied. The results show that at high pH (>12), the gold dissolution rate increases significantly in solutions containing caustic soda and cyanide at zero, or very low free cyanide concentration.

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#### 1. Introduction

The high cyanide consumption during the hydrometallurgical processing of high copper–gold ores or concentrates often makes the conventional cyanidation uneconomic. Cyanide consumption can be up to 2.3 kg of NaCN for every kilogram of Cu leached (Stewart and Kappes, 2012). The requirement in most cases is to remove WAD cyanide prior to final tailings disposal, usually by chemical oxidation which also adds to the cost of cyanidation. Alternatively other capital and operating cost intensive processes such as AVR and SART are added to recover the copper and cyanide (Muir et al., 1993; Nguyen et al., 1997). Currently many gold mines are facing the problem of treating gold ores containing significant amounts of reactive copper. Alternative process options include the recovery of copper and the recycle of cyanide to the leaching stage, using a variety of processes and technologies which were recently reviewed by Dai et al. (2012) such as AVR and SART,

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http://dx.doi.org/10.1016/j.mineng.2015.08.006 0892-6875/© 2015 Elsevier Ltd. All rights reserved. electrowinning and adsorption of copper cyanides on either activated carbon or ion exchange resins. However, these processes are rarely economic. La Brooy (1992) reported that 0.5% soluble copper was the critical level for direct cyanidation in oxide ores, while the critical level is 1% for sulfide ores.

For economic cyanidation applications, the preferred treatment of copper–gold resources is to selectively leach gold over copper rather than leaching both gold and copper followed by cyanide and copper recovery. One of these applications is the cyanide–ammonia process to leach gold over copper from oxidized ores which has been applied for over a century in the treatment of different gold–copper ores (Muir, 2011). The cyanide–ammonia system to leach gold over copper from oxidized ores has been studied using different gold–copper ores (Drok and Ritchie, 1997; Costello et al., 1992; Muir et al., 1995; La Brooy et al., 1991). However, the treatment of sulfide ores gave poor gold recovery and required higher reagent concentrations (Muir, 2011). It was also found that, due to the loss of volatile ammonia, a significant loss of gold and cyanide was observed due to the precipitation of gold as AuCN-CuCN (Muir et al., 1991; Dai et al., 2005). In addition, there are some environmen-



tal concerns of using ammonia due to its volatility and toxicity. The threshold limiting value (TLV) for ammonia is 17 mg/m<sup>3</sup> (25 ppm) according to the National Institute of Occupational Safety and Health (NOISH, 1992; Rubo et al., 2000), which is close to that of HCN (11 mg/m<sup>3</sup>) according to the American Conference of Governmental Industrial Hygienists (ACGIH, 1986).

Some earlier studies focused on the concept of leaching coppergold ores in cyanide deficient copper solutions. It was reported by Hedley and Kentro (1945) that gold could be dissolved by copper cyanide complexes. Copper-cyanide species (e.g.  $Cu(CN)_3^{2-})$  can enhance gold dissolution in the cyanidation process under the specific leaching conditions of zero or low free cyanide concentration by release of one or more of the associated cyanide ions (Muir et al., 1989; Van Deventer and Rees, 1999). However, the outcomes of other studies show that gold leaching occurred in air-saturated  $Cu(CN)_3^{2-}$  solutions at a much slower rate than in free cyanide solutions (Breuer et al., 2005; Nugent, 1991).

At zero or low free cyanide concentration, low CN/Cu ratio and high pH, the precipitation of copper as  $Cu(OH)_2$  occurs as shown in Eq. (1) (Vukcevic, 1997). The released cyanide ions (Eq. (1)) can then be involved in further copper and gold dissolution as shown in Eqs. (2) and (3) respectively.

$$4Cu(CN)_{2}^{-} + O_{2} + 4OH^{-} + 2H_{2}O \rightarrow 4Cu(OH)_{2} \downarrow + 8CN^{-}$$
(1)

$$4Cu + 12CN^{-} + O_2 + 2H_2O \rightarrow 4Cu(CN)_3^{2-} + 4OH^{-}$$
(2)

$$4Au + 8CN^{-} + O_2 + 2H_2O \rightarrow 4Au(CN)_2^{-} + 4OH^{-}$$
(3)

The precipitation of Cu(OH)<sub>2</sub> at low cyanide/copper ratio and high pH was also observed by Dai and Breuer (2009). These authors also found that the pH at which the copper starts to precipitate decreases with decreasing cyanide/copper ratio and increasing copper concentration. The increase in hydroxide ions enhances the precipitation of copper at low free cyanide concentration. Vukcevic (1997) concluded that the precipitation of copper as CuO, Cu<sub>2</sub>O or Cu(OH)<sub>2</sub> occurs as a parallel process to gold dissolution. Moreover, the presence of copper oxides enhances the copper precipitation. However, in the cyanide leaching of copper minerals, Cu(I) cyanide complexes can be formed which can then be involved in gold dissolution. In the cyanidation process small amounts of hydroxide ions from the reduction of oxygen can be released in the leach solution as shown in Eqs. (4) and (5).

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

$$O_2 + 2H_2O + 2e^- \to H_2O_2 + 2OH^- \tag{5}$$

However, the additional contribution of these hydroxyl ions is insignificant given the low levels of dissolved oxygen available.

From the past research studies that deal with the treatment of gold–copper resources, it is known that the gold dissolution and copper suppression can be enhanced under one or both of the following leaching conditions:

- By leaching at low cyanide/reactive copper molar ratio, most of the cyanide will be involved in copper dissolution and mainly forms Cu(CN)<sub>2</sub><sup>-</sup> and some Cu(CN)<sub>3</sub><sup>-2</sup> with no free cyanide left in the leach solution.
- By leaching at high pH (>12.5) using caustic soda, copper precipitates as Cu<sub>2</sub>O/CuO/Cu(OH)<sub>2</sub> and releases cyanide ions. In the presence of copper sulfide minerals, leaching gold at high pH is performed by adding caustic soda instead of lime. Adding lime at pH > 11 can decrease the gold dissolution due to the formation of passivating films of gypsum on the gold surface (Kudryk and Kellogg, 1954).

Therefore, taking advantage of the cyanide ions released from copper precipitation at low cyanide/copper ratio and high pH using caustic soda as a pH modifier, the proposed work aims to optimize and enhance the leaching of gold from copper–gold resources containing high reactive copper contents. The research work also aims to reduce both cyanide consumption and copper concentration in the final leach solutions to avoid having to employ either the cyanide destruction or cyanide–copper recovery processes.

#### 2. Experimental

All experiments were carried out using solutions prepared from analytical grade reagents and deionised water. The feed material for these experiments was a high copper-gold gravity concentrate (Falcon centrifugal concentrator product) diluted with silica powder (100%  $-75 \,\mu\text{m}$ ). The particle size of the concentrate used in the leaching experiments was  $100\% - 150 \,\mu\text{m}$  and  $80\% - 106 \,\mu\text{m}$ . The mineralogical composition of the diluted gravity concentrate was determined by the quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) technique at CSIRO, Waterford, WA. The cyanide and sulfur speciation in the leach solution at various leach times was also carried out at CSIRO, Waterford, WA using High Performance Liquid Chromatography (HPLC). Leaching solution pH was initially adjusted using sodium hydroxide. Unless specified, the cyanide addition was 0.8 g/L NaCN (16.3 mM CN<sup>-</sup>). Leaching of gold-copper concentrate at 28.5% pulp density was conducted in a 2.5 L Winchester bottle using a bottle roller at a speed of 150 rpm, at room temperature. Bottles are left open to allow for atmospheric oxygen transfer, to ensure sufficient oxygen for leaching. At specified times, 25 mL samples of the leach slurry were filtered using a membrane filter (pore size  $0.45 \,\mu$ m) and the solids returned to the leach. The clear solution was analyzed for gold and copper using Atomic Absorption Spectrophotometry (AAS). S, Si, Pb, Fe, As, Zn and Ni were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The gold content of the feed and residues was determined by fire assay at SGS Australia laboratory in Western Australia.

#### 3. Results and discussion

#### 3.1. Gold and copper dissolution

Preliminary experiments were conducted to evaluate the leaching of gold from a feed containing 490 g/t Au and 0.94% Cu as metallic copper, oxides and sulfides. The mineralogical composition of the feed was analyzed by QEMSCAN and the results are shown in Table 1. The total amount of the reactive copper in the treated concentrate can be estimated by reference to the solubility of different copper minerals in cyanide solution shown in Table 2. From the data shown in Tables 1 and 2, the percentage of the

Table 1

The mineralogical analysis of copper and gangue minerals of the studied copper-gold gravity concentrate.

Mineral	Wt, %	Mineral	Wt, %
Chalcocite/digenite	0.4	Arsenopyrite	0.00
Cu-metal	0.3	Quartz	87.1
Cuprite	0.2	Feldspar	1.3
Chalcopyrite	0.2	Calcite	<0.1
Bornite	0.1	Dolomite	0.00
Covellite	<0.1	Ankerite/dolomite	0.2
Exotic complex Cu-sulfides	<0.1	Rutile/anatase/ilmenite	0.1
Cu boundaries	0.1	Hematite	0.2
Pyrite	7.1	Goethite	0.7
Pyrrhotite	0.1	Others	1.8

Minerals and Assays in bold are copper-containing minerals.

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