The selective leaching of copper from a gold–copper concentrate in glycine solutions

E.A. Oraby, J.J. Eksteen *

Western Australian School of Mines, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

The presence of copper minerals with gold is known to lead to many challenges during the cyanidation of gold ores, such as high consumption of cyanide with low gold extraction and undesirable impacts on gold recovery during the downstream processes. An alternative selective leaching process for copper minerals from copper–gold gravity concentrate (3.75% Cu, 11.6% Fe, 11.4%S and 0.213% Au) using alkaline glycine solutions was studied and evaluated. The lixiviant system containing glycine and peroxide showed that total copper dissolution of 98% was obtained in 48 h at ambient conditions and a pH of 10.5–11. The results show that 100% of chalcocite, cuprite, metallic copper, and about 80% of chalcopyrite in the concentrate were also dissolved. Pyrite remained intact during the leaching time and iron concentration in the final pregnant solution was found to be 12 mg/L when copper is solution is at 4745 mg/L, whilst the gold concentration was limited to 0.8 mg/L Au. QEMScan analysis indicated that unleached copper in the leach residue was mostly distributed amongst larger chalcopyrite grains and covellite. The effects of single versus two-stage leaching, pH, oxidant concentration, pulp density and glycine concentration on copper extraction rate and extent were explored.

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1. Introduction

Recently, many researchers have focused on the recovery of copper from ores and concentrates using hydrometallurgical solutions in order to replace the traditional pyrometallurgical processes. Currently, more than 20% of world copper production is produced by using hydro-metallurgical processes, particularly by acidic heap leach (or heap bioleach)–solvent extraction–electrowinning processes for low grade ores.

A review of the selective leaching of gold from oxidised copper–gold ores with ammonia–cyanide, and their plant control and operation has been published by Muir (2011). The application of cyanide–ammonia system to leach gold over copper from oxidised ores has been tested successfully using different gold–copper ores (Drok and Ritchie, 1997; La Brooy et al., 1991; Muir et al., 1989). However, this system in the treatment of transition or sulphidic ores gave poor gold recovery and required higher reagent concentrations (Muir, 2011). Moreover, both cyanide and ammonia have detrimental environmental effects.

Muir et al. (1989) reported that there are five methodologies for treating copper–gold ores: (1) float and produce a copper–gold con-centrate for smelting; (2) selectively mine and cyanide leach ore with <0.5% Cu as oxidised minerals and <1% as sulphidic minerals; (3) cyanide leaching and selectively absorbing gold using either activated carbon or ion-exchange resins; (4) cyanide leaching and

selectively recovering copper from solution; and (5) selectively leaching either copper or gold with alternative reagents. The decision as to which of these approaches to apply depends upon the relative amounts of copper and gold present, the mineralogy and process economics.

This paper presents a process of selectively leaching the reactive copper before gold, as it is well known that the presence of copper min-erals has detrimental effects on the cyanide leaching of gold resulting in a huge consumption of cyanide (La Brooy et al., 1994). Copper minerals consume about 30 kg/t NaCN for every 1% of reactive copper present, making conventional cyanidation of copper–gold ores or concentrates uneconomic (Muir, 2011). According to La Brooy (1992), the oxidised copper–gold ores are selectively mined to minimise the presence of re-active copper to below 0.5% and otherwise; sulphidic copper–gold ores are floated and gold is recovered as a by-product of copper smelting and refining. However, when copper is present in significant levels with gold in gravity concentrates, it can also lead to complexities with direct smelting of the concentrates.

There are a number of large copper–gold mines in Australia and the Asia-Pacific region. These plants produce copper–gold concentrates and ship them for copper smelting and gold recovery from anode slimes (e.g. Telfer, Mt Carlton, Boddington and Cadia Valley, etc.). However, the increase of pyrite content in the high grade copper ores results in the production of low grade copper concentrate. In addition, the pres-ence of arsenic limits the flotation mass pull of chalcopyrite rich concen-trates, so that a significant portion of the gold have to be recovered by gravity and leaching of the flotation tails. The transportation of the

* Corresponding author.
E-mail address: jacques.eksteen@curtin.edu.au (J.J. Eksteen).

low grade concentrate overseas is often uneconomical. Therefore, an alternative process would be useful for recovering both copper and gold from such a low-grade concentrate. Cyanide–ammonia leaching of Telfer flotation tailings has been carried out by Muir et al. (1991) for 24 h with 0.3 M NH_3/0.1 M $(NH_4)_2SO_4$. This process extracted 82% Cu and no gold, followed by subsequent cyanidation of the washed leach residue. The proposed process depends on copper selective leaching before gold in an alkaline glycine solution followed by washing and gold leaching either using the same process at elevated temperature (40–60 °C), as patented by the authors, or using a cyanidation process. Copper selective leaching will reduce the gold losses due to a cementation mechanism of gold in the presence of metallic copper as all of the metallic copper will dissolve in the pre-leaching stage. Nguyen et al. (1997a, 1997b) found that, at ambient conditions and pH 11, all gold in a solution containing 1000 mg/L NaCN and 0.5 g/L Cu had been cemented on copper in the first 2 h.

According to Stewart and Kappes (2012), the presence of reactive copper in high percentages in a gold ore has negative effects on the efficiency and economic viability of any gold project due to (1) high cyanide consumption in which copper will consume at least 2.3 kg of sodium cyanide for every kilogramme of copper leached; (2) copper competing with gold in the adsorption/stripping circuit, which can effectively reduce the gold loading capacity of the carbon, increasing the plant size and the cost of the adsorption circuit. In addition, the high level of copper in cyanide as weak acid dissociable (WAD) cyanide creates a problem that requires expensive processes such as sulfidisation, acidification, recycle and thickening (SART) to be operated to recover cyanide (Simons and Breuer, 2013), often in a dilute form which may create water balance problems with the plant. Alternatively a range of WAD cyanide destruction processes are to be implanted, each with significant concomitant costs.

The main aim of this work was therefore to investigate an environmentally benign hydrometallurgical process to selectively leach copper from copper–gold resources with mixed mineralisation. To this end, a gravity gold concentrate was selected with high levels of copper distributed amongst a range of sulphide and oxide minerals, as well as native copper. The gravity concentrate has sufficient gold to evaluate the effect of the lixiviant system on gold dissolution under the proposed leaching conditions.
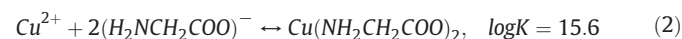
1.1. Background to copper–glycine leaching

Glycine is one of the simplest and cheapest amino acids, and is available in bulk. It has a number of attractive chemical and physical properties and it will be used as a main reagent in this research. Glycine has a number of advantages over many other copper lixiviants: it is an environmentally safe and stable reagent, yet it is enzymatically destructible and is easily metabolised in most living organisms. Due to its complexing action, glycine can also enhance the solubility of copper ions in aqueous solutions (Aksu and Doyle, 2001, 2002). Potentiometric

studies on complexes formed by essential metals (Cr, Mn, Fe, Co, Ni, Cu and Zn) and different amino acids have been conducted by Aliyu and Na'aliya (2012). The stability constant of glycine with copper according to Aliyu and Na'aliya (2012) is 18.9.

The complexing mechanism of copper in solutions containing glycine involves, initially, the formation of a hydroxyl copper complex by an ion-exchange mechanism.

Glycine can exist in aqueous solutions in three different forms, namely $^+H_3NCH_2COOH$ (cation), $^+H_3NCH_2COO^-$ (zwitterion), and $H_2NCH_2COO^-$ (anion). It also forms a strong complex with copper (II) as $Cu(H_2NCH_2COO)_2$ and with copper (I) as $Cu(H_2NCH_2COO)^-_2$ (Eqs. (1), (2) and (3)) and can enhance the solubility of copper ions in aqueous solutions due to its ability to chelate copper (Aksu and Doyle, 2001).

$$Cu^{2+} + (H_2NCH_2COO)^- \leftrightarrow Cu(NH_2CH_2COO)^+, \quad logK = 8.6 \quad (1)$$

$$Cu^{2+} + 2(H_2NCH_2COO)^- \leftrightarrow Cu(NH_2CH_2COO)_2, \quad logK = 15.6 \quad (2)$$

$$Cu^+ + 2(H_2NCH_2COO)^- \leftrightarrow Cu(NH_2CH_2COO)^-_2, \quad log K = 10.1 \quad (3)$$

A glycine–peroxide system is widely used as a polishing mixture in the chemical–mechanical planarization (CMP) technique. Mixtures of glycine and hydrogen peroxide have shown promising copper CMP behaviour and it was found that the glycine–peroxide mixture is successful to leach metallic copper from the exposed areas during the planarization (Aksu and Doyle, 2001; Ein-Eli et al., 2004; Hirabayashi et al., 1996).

As an example, the stoichiometry of cupric ions complexing in alkaline glycine solutions is described in Eq. (4).

$$Cu^{+2} + 2(NH_2CH_2COOH) + 2OH^- \rightarrow Cu(NH_2CH_2COO)_2 + 2H_2O \quad (4)$$
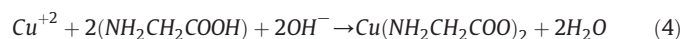
In a recent provisional patent, Oraby and Eksteen (2013) and recent research, Eksteen and Oraby (2014) and Oraby and Eksteen (2014), the authors developed a process using an alkaline amino acid–peroxide lixiviant system to leach gold, silver and their alloys at mildly elevated temperatures (40–60 °C) and dilute and concentrated concentrations. It was found that the elevated temperature (~60 °C) and hydrogen peroxide addition was crucial to obtain feasible leach rates of precious metals. This should be contrasted to the temperatures and hydrogen peroxide requirements as investigated for the alkaline copper–glycine system discussed below.

This study therefore addresses a persisting challenge in the copper and copper–gold processing, i.e. finding an appropriate lixiviant with lower environmental and safety risks for heap, dump, in-situ and vat leaching operations, which are slow leaching operations open to the surrounding environment. Alternatively, it may also be implemented in a counter-current decantation (CCD) circuit, allowing for sufficient residence time.

2. Experimental

2.1. Sample preparation

The concentrate was produced from the cyclone underflow feeding into a batch centrifugal gravity separator at a copper–gold plant in Western Australia. The gravity concentrate conveniently concentrates many non-sulphide minerals of copper, native copper, as well as sulphide minerals, with gold to provide a wide distribution of copper mineralogy. The gravity concentrate sample was then ground using a disc mill and screened using 150 and 106 μm screens. The +150 μm was recycled back to the mill. The particle size of the ground sample used

Table 1
Solubility of Cu minerals in 1 g/L NaCN solution (Hedley and Tabachnick, 1968).

Mineral	Formula	%copper dissolved[a]
Azurite	$2Cu(CO)_3 \cdot Cu(OH)_2$	94.5
Malachite	$2CuCO_3(OH)_2$	90.2
Chalcocite	Cu_2S	90.2
Covellite	CuS	95.6
Chalcopyrite	$CuFeS_2$	5.60
Native Copper	Cu	90.0
Cuprite	Cu_2O	85.5
Bornite	$FeS \cdot 2Cu_2S$	70.0
Enargite	Cu_3AsS_4	65.8
Tetrahedrite	$(Cu \cdot Fe \cdot Ag \cdot Zn) 12Sb_4S_{13}$	21.9
Chrysocolla	$CuSiO_3 \cdot (nH_2O)$	11.8

[a] Percent total copper dissolved at 23 °C in agitated tank for 24 h, ratio of solution to ore 10:1 (cited in Coderre and Dixon, 1999).