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Gold leaching in cyanide-starved copper solutions in the presence of glycine

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In the cyanidation of copper–gold ores, the presence of copper minerals can lead to soluble gold losses, the production of weak acid dissociable (WAD) cyanide, as well as a number of operational challenges in CIP/CIL circuits with regard to competitive adsorption, and subsequent difficulties associated with elution, electrowinning and smelting. In addition, copper minerals are significant cyanide consumers, leading to higher cost in ore treatment. This paper presents a process to enhance the dissolution of gold using copper–cyanide solutions in the presence of glycine where the solution is cyanide starved. The effect of glycine addition on gold leaching kinetics in copper–cyanide solutions under different leaching conditions was studied. The results show that, in the presence of glycine, gold dissolution rate increases significantly in solutions containing copper–cyanide species at a very low, or zero, free cyanide concentration. In the presence and absence of glycine, gold dissolution rates in solutions containing 10 mM $Cu(CN)_3^{2-}$ were 11.1 μmol/m^2·s and 0.65 μmol/m^2·s, respectively. It is shown that the average gold dissolution rate in a Cu–CN$^-$-glycine system is about 6.5 times higher than the gold dissolution rate in the conventional cyanidation, the presence of cyanide being similar in each system. Kinetic and electrochemical studies were conducted to evaluate the effects of glycine concentration, pH, CN/Cu ratio, and initial copper concentrations on the dissolution of gold. It has also been shown that the gold dissolution rate increases by increasing the glycine concentration up to 1 g/L and any further glycine addition has a negative effect on the dissolution of gold. Increasing leaching pH up to 12 enhances gold dissolution in the copper–cyanide–glycine solutions. However, increasing leaching pH to 13 has an adverse effect on the dissolution of gold.

1. Introduction

In the cyanidation of copper–gold ores to recover precious metals, the presence of copper minerals can cause a number of serious problems, which include, but are not limited to:

(1) Copper minerals consume about 30 kg/t NaCN for every 1% of reactive copper present (Muir, 2011) or about 2.3 kg of NaCN for every kilogram of Cu leached (Stewart and Kappes, 2012). The high cyanide consumption could render the conventional cyanidation of high copper–gold ores or concentrates uneconomic, unless other additional processes are added to recover either cyanide or both copper and cyanide.

(2) The presence of copper minerals has a negative effect on the extraction of gold; leading to various gold losses and challenges (Muir et al., 1993; Nguyen et al., 1997) such as:

- Native copper dilutes gold gravity concentrate or/and provides a reducing surface for gold cementation during the leaching;
- High free cyanide consumption leading to low gold recovery due to less free cyanide available;
- Competitive adsorption with gold leading to lower gold recovery; and
- Gold losses during electrowinning, smelting and refining.

(3) Additional processes are required to recover the copper and/or cyanide such as AVR (Acidification, Volatilization and Reneutralization) and SART (Sulphidization, Acidification, Recycling and Thickening), adsorption onto activated carbon or ion exchange resins, electrowinning and solvent extraction. Even then, the cyanide that deports to $Fe(CN)_6^{4-}$ and thiocyanate cannot be economically recovered (Dai et al., 2012; Estay et al., 2012).

(4) The presence of copper in the final tail solutions significantly contributes to weak acid dissociable (WAD) cyanide species which should be kept below 50 mg/L before the tail water is discharged to the environment (Botz and di Parodi, 1997; Donato et al., 2007; Mudder and Botz, 2001) and, consequently, requires additional cyanide detoxification/destruction processes.

In leaching gold from copper-containing gold ores by cyanidation, some copper minerals dissolve in cyanide solutions to form different

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soluble copper–cyanide complexes such as $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. The distribution of these complexes in the leach solution is normally a function of the cyanide concentration and pH (Dai et al., 2005). Recently, the recovery and re-use of the copper–cyanide complexes from the final leaching solution streams have received some attention. Therefore, research investigations have been conducted to economically treat copper containing gold ores by either reducing the cyanide consumption using a cyanide–ammonia system in the leaching stage (Costello et al., 1992; Jeffrey et al., 2002; La Brooy et al., 1991; Muir et al., 1991, 1993), or by recovering copper and recycling the cyanide after leaching (Adams et al., 2008; Alonso-Gonzalez et al., 2009; Alonso-González et al., 2013; Gonen et al., 2004; Xie and Dreisinger, 2009a,b).

A fundamental study by Jeffrey et al. (2002) has shown that the addition of ammonia to solutions containing cuprous cyanide species increases the dissolution of gold. The presence of copper(II) was also shown by the authors to increase the gold leach rate. However, there are some issues regarding the stability of the cyanide–ammonia system and the environmental considerations of ammonia which need attention as the threshold limiting value (TLV) for ammonia gas, in air, is 14 mg/m^3 (Gos and Rubo, 2000).

There are also increasing environmental concerns and restrictions on the discharge of cyanide and copper–cyanide complexes to tailing dams. It is well known that copper–cyanide species are more difficult to destroy naturally than free cyanide although they are less toxic than the free cyanide (Mudder and Botz, 2001). Destruction of the cyanide and copper cyanides before discharge is adding an additional cost to the gold production process and the treatment cost also increases in the presence of high copper concentrations (Dai and Breuer, 2009).

Some research studies have also focused on the concept of leaching copper–gold ores in cyanide deficient copper solutions. The outcomes of these studies show that gold leaching in air-saturated $Cu(CN)_3^{2-}$ solutions occurs at a much slower rate than that in solutions with significant free cyanide (Breuer et al., 2005; Nugent, 1991). The $Cu(CN)_3^{2-}$ species tend to predominate under gold leaching conditions, even though the $Cu(CN)_2^-$ species tend to predominantly adsorb on to carbon. As was reported by Fleming and Nicol (1984) and recently by Dai et al. (2010), the adsorption of copper cyanide species on carbon is following the order of $Cu(CN)_2^- > Cu(CN)_3^{2-} > Cu(CN)_4^{-3}$.

Therefore, the main aim of this work is to investigate the effect of adding glycine on the enhancement of gold dissolution in solutions containing different copper–cyanide species, based on earlier research by the authors looking at the solubility of copper minerals and gold in an alkaline glycine–peroxide system (Eksteen and Oraby, 2015; Oraby and Eksteen, 2014, 2015). Glycine is one of the simplest and cheapest amino acids among the available 20 amino acids; it can be easily produced industrially or derived as a by-product of different micro-organisms (González-lópez et al., 2005). The presence of glycine can also enhance the solubility of gold in aqueous solutions as the main lixiviant of dissolving gold due to its complexing action with gold (Brown and Smith, 1982; Aylmore, 2005; Eksteen and Oraby, 2015). Glycine also increases copper solubility at higher pH and lower potentials, and the stability constant (logβ) of glycine with copper, according to Aliyu and Na'aliya (2012), is 18.9. As shown in Fig. 1, after Aksu and Doyle (2001), the stability regions of CuO and Cu_2O in a copper–water–glycine system decrease by increasing the glycine concentration. Glycine also forms soluble complexes with both cupric [$Cu(H_3NCH_2COO)^{+2}$], $Cu(H_2NCH_2COO)^+$, $Cu(H_2NCH_2COO)_2$ and cuprous ions ($Cu(H_2NCH_2COO)^-{}_2$). These species are referred to in Fig. 1 as $CuHL^{2+}$, CuL^+, CuL_2 for Cu(II) and CuL_2^- for Cu(I). The large Eh–pH stability region of the neutral cupric ligand (CuL_2) should be noted (Fig. 1), as well as the transition points from ligand to oxide stability fields at pHs around 12.5, giving the pH ceiling for a practical interaction with glycine.

Therefore, considering the merits of copper–glycine species stability, this research work presents a potential process to treat copper–gold ores in the presence of glycine. The proposed work aims to significantly enhance the leaching of gold in copper–cyanide solutions containing low free cyanide by the addition of glycine.

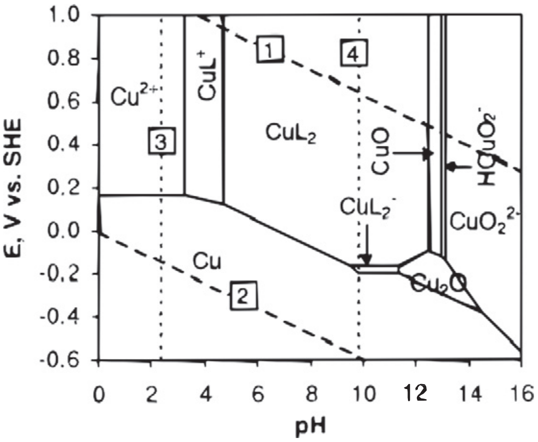

Fig. 1. Potential-pH diagram for the copper–water–glycine system at 25 °C and 1 atm, 0.01 M glycine and 10^{-6} M cupric nitrate (after Aksu and Doyle, 2001).

2. Experimental

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water. An analytical grade reagent (AR) of glycine has been used in all the conducted experiments. Copper–cyanide complexes were prepared by the complete dissolution of an analytical grade CuCN powder (5.5 mM Cu) in sodium cyanide solutions (5.5 mM CN^-). Leaching experiments were carried out using a pure gold rotating disc electrode. The gold disc was polished using a waterproof silicon carbide paper (FEPA # 2400) and 3-micron aluminium oxide powder prior to each experiment. The pure gold disc was made from pure gold foil (99.99% Au). All discs are 17 mm in diameter and have a surface area of 2.27 cm^2. Gold and copper in solutions were determined by atomic absorption spectrophotometry (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES).

The electrochemical experiments (linear sweep voltammetry) were conducted using a Pine WaveNow potentiostat. The reaction cell was a three-electrode system in which a platinum wire was used as a counter electrode. All potentials were measured relative to the Ag/AgCl electrode (+0.199 V vs. SHE), but reported relative to the standard hydrogen electrode (SHE). A gold disc electrode of 5 mm in diameter was used to evaluate the anodic reaction of gold in the copper–cyanide solutions, in the presence and absence of glycine. Linear sweep voltammetry experiments were performed at 22 °C, with a rotation rate of 400 rpm and a scan rate of 1 mV/s. The oxidation current (i) was measured as μA and reported as A/m^2 at different potential ranges.

3. Results and discussions

In the following sections, kinetic and electrochemical studies were conducted to evaluate and demonstrate the fundamental aspects of gold leaching in cuprous–cyanide solutions in the presence and absence of glycine under different leaching conditions. Gold dissolution rates and linear sweep voltammograms for the anodic gold dissolution have been conducted. The effects of glycine concentration, solution pH, initial copper concentration and glycine to copper molar ratio on gold dissolution rate and the anodic reaction of gold in copper–cyanide–glycine system are presented below. A comparison of using different complexing agents of copper such as glycine, ammonia and EDTA will also be presented in the following sections.