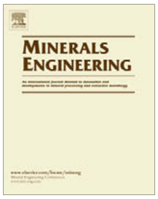
Minerals Engineering 22 (2009) 469–476

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng



Cyanide and copper cyanide recovery by activated carbon

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ARTICLE INFO

Article history:
Received 8 September 2008
Accepted 15 December 2008
Available online 1 February 2009

Keywords:
Gold ores
Activated carbon
Cyanidation
Hydrometallurgy

ABSTRACT

A process is proposed to recover the cyanide and copper cyanides following the leaching and recovery of gold from copper-containing gold ores. Metallic copper is dissolved into the tailings stream to convert the residual free cyanide to copper cyanides and to concurrently reduce the overall cyanide-to-copper ratio to facilitate copper and cyanide recovery by activated carbon. Metallic copper readily dissolves in both free cyanide and $Cu(CN)_3^{2-}$ solutions to achieve a final cyanide-to-copper ratio below 3. The theoretical critical CN^- and $Cu(CN)_3^{2-}$ concentration for copper dissolution in air saturated solutions are 2.9 and 2.7 mM, respectively, matching well with the measured values of 3 mM. The copper dissolution rate decreases proportionately with concentration below these critical concentrations. The increase in pH due to oxygen reduction during copper dissolution may cause copper to precipitate as $Cu(OH)_2$. The pH of precipitation decreases with increasing copper concentration and with decreasing cyanide-to-copper ratio. However, precipitation is not observed in the presence of carbon due to the simultaneous adsorption of copper onto carbon, which reduces the solution copper concentration.

1. Introduction

Cyanidation is the dominant means of recovering gold from its ores. In recovering gold from copper-containing gold ores by cyanidation, some copper minerals readily dissolve in cyanide. These can have a detrimental effect on the process efficiency and economics due to high cyanide consumption, reduced gold leach rates and poor gold recovery (Coderre and Dixon, 1999; Tran et al., 1997; Deschenes and Prudhomme, 1997; Nguyen et al., 1997; Sceresini and Richardson, 1991; Sceresini and Staunton, 1991; Muir et al., 1989). There are also increasing restrictions on the discharge of cyanide and copper cyanide complexes to tailings dams due to environmental concerns; copper cyanides are more difficult than free cyanide to be destroyed naturally, although they are less toxic than the equivalent free cyanide. Destruction of the cyanide and copper cyanides before discharge to tailings is uneconomical for high copper concentrations. Therefore, various processes have been developed or investigated to economically treat copper-containing gold ores by either reducing the cyanide consumption or recovering and recycling the cyanide (Adams, 2005).

1.1. Copper-containing gold ores processing technologies

One approach of treating copper-containing gold ores is the Sceresini process (Fleming and Nicol, 1984; Sceresini and Richardson, 1991; Sceresini and Staunton, 1991; Parson et al., 1993; Nugent, 1991) in which gold leaching is conducted with low free cyanide, where the copper cyanide complexes are also considered to contribute to gold dissolution. The copper cyanide complexes can be recovered along with the gold by a conventional carbon adsorption process. However, the recovery of gold has generally been found to be poor.

Technologies have been proposed to selectively leach gold over copper rather than recovering the copper afterwards. There have been a number of studies of the applicability of the copper/ammonia/cyanide process for the treatment of copper-containing ores (Costello et al., 1992; Muir et al., 1989, 1991). It has been shown that the addition of ammonia to the cyanide solution results in a lower cyanide consumption and an increased selectivity of gold leaching over copper. However, the rate of gold leaching in this system is apparently slower than that with free cyanide and the use of ammonia has its own occupational health and environmental concerns. Other selective approaches include leaching with Br_2 by the K-process (Sehic, 1988) and leaching with thiourea (Chen et al., 1980; Deschenes et al., 1994; Bilston et al., 1984), though neither of these processes have been adopted commercially.

1.2. Cyanide and copper recovery/recycle

Acidification–volatilisation–reneutralisation (AVR) (Riveros et al., 1993) is one process used commercially. It is an extremely simple and elegant process: alkaline cyanide leach solution is acidified to produce hydrogen cyanide, which is removed by volatilisation in a stream of air, and the gaseous hydrogen cyanide is re-adsorbed back into an alkaline solution.

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doi:10.1016/j.mineng.2008.12.007

Recently the sulfidisation–acidification-recycle-thickening (SART) process has been implemented to recover both copper and cyanide (Barter et al., 2001). This process involves a solid/liquid separation step to obtain a clarified copper cyanide solution, to which water soluble sulfide compounds (NaSH or Na_2S) are added and the solution acidified to pH < 5 by the addition of sulfuric acid. Copper cyanide complexes are converted to a copper sulfide precipitate and free cyanide to aqueous HCN. The copper sulfide precipitate is recovered by thickening, and the aqueous hydrogen cyanide neutralised and recycled.

Several issues remain with AVR and SART technologies: (1) the entire solution in the tailings stream needs to be treated on a continuous basis, unless another method (e.g. ion exchange) is used to produce a clarified copper–cyanide stream; (2) the process requires acidification and then neutralisation of the clarified tailings stream; (3) the copper product (CuCN for AVR and Cu_2S for SART) is difficult to recover and handle, and on sale of the product only provides a financial return of approximately 60% of the value of the contained copper; and (4) HCN volatilisation to low residual dissolved levels is difficult and energy intensive.

The recovery of copper cyanide using ion exchange resins has received considerable attention in recent times due to their strong affinity for metal cyanide complexes (Silva et al., 2003; Leao and Ciminelli, 2002; Lukey et al., 1999, 2000; Fernando et al., 2002; Whittle, 1992; Bachiller et al., 2004; Leao et al., 2001). However, effective elution and recovery of the copper and cyanide has proven to be difficult.

Direct electrowinning of copper from the waste stream has also been proposed (Lemos et al., 2006; Dutra et al., 2008; Lu et al., 2002). This technology, however, often suffers from low current efficiency and high energy consumption due to the low copper concentration and high cyanide-to-copper ratio. Moreover, the cyanide is destroyed at the anode.

1.3. Potential cyanide and copper recovery process

Clearly, there is opportunity to develop a process that allows for the ease of gold recovery from copper-containing gold ores in which the copper is subsequently recovered (preferably in metallic form) and cyanide recycled. To potentially recover the copper and cyanide using activated carbon, it is proposed to complex the cyanide by the dissolution of metallic copper and concurrently convert $Cu(CN)_4^{3-}$ and the majority of $Cu(CN)_3^{2-}$ to the readily absorbed $Cu(CN)_2^-$ complex. The copper can then be recovered by a carbon adsorption and desorption process, followed potentially by a low-pH copper electrowinning and cyanide recycling stage (Dai, 2005; Breuer et al., 2005). This paper presents a detailed study of the kinetics and mechanism of copper dissolution in cyanide and copper cyanide solutions, and its integration with copper cyanide recovery by activated carbon.

2. Experimental methods

All experiments were carried out using solutions prepared from analytical grade reagents and deionised water. Unless stated otherwise, experiments were conducted in air saturated solutions at an initial pH of 10.5 and ambient temperature.

Copper leach rates were measured using a rotating electrochemical quartz crystal microbalance (REQCM), which is described elsewhere (Jeffrey et al., 2000), at a rotation rate of 300 rpm. Prior to each experiment, copper was electroplated onto the quartz electrode at 75 A m^{-2} from a solution containing 0.75 M cupric sulfate and 0.25 M sulfuric acid. 50 mM sodium perchlorate was used as the electrolyte when conducting electrochemical studies. All potentials were measured relative to the saturated calomel electrode (+0.242 V vs. SHE), but are reported relative to the SHE. Linear sweep voltammetry was carried out using a PAR362 potentiostat at a scan rate of 1 mV s^{-1}. A platinum wire was used as the counter electrode.

Copper powder dissolution experiments were conducted in a 500 mL beaker. Unless otherwise specified, 250 mL of a solution containing 4 mM copper powder (~0.1 mm from Hopkin & Williams Ltd.) and cyanide (CN:Cu = 4) was used. The agitation speed was kept constant at 300 rpm using an overhead stirrer. Metallic copper powder was added to the solution to start the experiment, and 5 mL samples were taken at various time intervals and filtered for copper analysis by ICP. For the simultaneous copper dissolution and adsorption onto carbon investigations, activated carbon was contained in a stainless-steel mesh basket immersed in the solution. The copper loading onto activated carbon was calculated from a mass balance of the copper added less that in the samples taken and remaining in solution.

For investigation of copper precipitation conditions, synthetic copper cyanide solutions of various copper concentrations and cyanide-to-copper ratios were prepared by dissolving copper cyanide powder in a cyanide solution. 35 mL of solution was titrated with 0.2 M NaOH (or lower concentrations depending on the composition of copper cyanide solution) at a rate of 0.02 mL min^{-1} using a Metrohm 776 Dosimat. The pH of the solution was measured by a TPS WP-90 pH meter, whilst the presence of precipitate was monitored by a NEP 160 turbidity meter. All the data was logged using a DataTaker and subsequently transferred onto a PC for further processing.

3. Results and discussion

3.1. Dissolution and electrochemistry of copper in cyanide solutions

The following reactions may occur during copper dissolution in cyanide and/or copper cyanide solutions. The standard potential for the anodic reactions were calculated using the standard free energy of formation obtained from the NBS tables in Stabcal for each of these species (CN^-: 172.4 kJ mol^{-1}, $Cu(CN)_2^-$: 257.8 kJ mol^{-1}, $Cu(CN)_3^{2-}$: 403.8 kJ mol^{-1}) (Huang and Young, 1996).

Anodic reactions:

$$Cu + 3CN^- \rightarrow Cu(CN)_3^{2-} + e^- \quad (E^0 = -1175 \text{ mV}) \tag{1}$$

$$Cu + 2CN^- \rightarrow Cu(CN)_2^- + e^- \quad (E^0 = -902 \text{ mV}) \tag{2}$$

$$Cu + 2CuCN_3^{2-} \rightarrow 3Cu(CN)_2^- + e^- \quad (E^0 = -354 \text{ mV}) \tag{3}$$

Cathodic reactions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (E^0 = 401 \text{ mV}) \tag{4}$$

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (E^0 = -146 \text{ mV}) \tag{5}$$

3.1.1. Copper dissolution in free cyanide

Fig. 1 shows the measured (REQCM) copper leach rates as a function of free cyanide concentration (square data points). It is clear that a steady increase in the leach rate with cyanide concentration can be observed for cyanide concentrations less than 3 mM. The leach rate approaches a limiting plateau above 3 mM cyanide.

The copper dissolution in cyanide solutions involves two solution phase reactants, oxygen and cyanide. The maximum rate of copper dissolution can thus be limited by either the flux of cyanide or oxygen. The cyanide concentration at which the cyanide limiting rate is equal to the oxygen limiting rate is defined as the critical cyanide concentration, $[CN^-]_{crit}$. The method for calculating the reaction limiting rates and $[CN^-]_{crit}$ can be found elsewhere (Zheng et al., 1995). The $[CN^-]_{crit}$ calculated based on the stoichiometry of Reactions (1) and (4) (i.e. the formation of $Cu(CN)_3^{2-}$) was 2.9 mM,