



The effect of zinc cyanide on the flotation of gold from pyritic ore



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ABSTRACT

In gold processing plants, the process water contains a considerable amount of weak acid dissociable (WAD) cyanide species. The cyanide-containing water recycled to flotation circuits has a deleterious effect on mineral flotation. Zinc cyanide can be a major constituent of the process water due to the cyanide leaching of zinc minerals and the zinc cementation applied to precipitate gold and silver. In the present study, the effect of zinc cyanide on the flotation of gold from a pyritic ore was evaluated and the competitive adsorption between zinc cyanide species and the collector, potassium amyl xanthate (PAX) or Aerophine promoter (3418A), on gold was studied by surface enhanced Raman spectroscopy (SERS). It was found that free cyanide did not depress the flotation of liberated gold, but zinc cyanide with a CN/Zn ratio of 2 did. The depression of gold flotation by zinc cyanide was due to the preferential adsorption of Zn(CN)₂ on gold surface over either 3418A or amyl xanthate in the solution, rendering gold surface hydrophilic.

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1. Introduction

The extraction of gold from ores involves gravity separation to recover coarse gold, and flotation to recover fine liberated gold and the gold associated with other sulfide minerals. The gold bearing concentrates or tailings can be leached in alkaline cyanide media, followed by the Merrill-Crowe process or carbon adsorption/electrowinning to remove gold from cyanide solutions. Gold precipitates are calcined and smelted to produce gold dore. For ores with high silver contents, the Merrill Crowe process where zinc dust is added to the clarified, de-aerated solution is often used to precipitate gold and silver. For instance, at Hidden Valley Mine, gold and silver in cyanide solutions are recovered in a Merrill-Crowe circuit after a Counter Current Decantation (CCD) circuit.

In gold processing plants, the remaining cyanide species in the final tailing are sent to detox circuits, producing the main source of process water which is recycled to the upstream circuits such as grinding and flotation (Adams, 2013). Despite cyanide destruction, the process water still contains a considerable amount of weak acid dissociable (WAD) cyanide species, of which copper cyanide and zinc cyanide species are most common. Soluble cuprous cyanide species originate from the extensive cyanide leaching of copper-bearing minerals such as chalcocite and chalcopyrite (Breuer et al., 2005). The existence of zinc cyanide species is due

to either the cyanide leaching of zinc sulfide minerals or the byproduct of zinc cementation process (Vilchis-Carbajal et al., 2000).

The process water containing cyanide species has a deleterious effect on mineral flotation. Free cyanide in the form of NaCN is the most commonly used depressant for sulfide minerals in flotation. Since Sutherland and Wark (1955) and Wark (1938) established the depression behavior of sulfide minerals by NaCN, the interactions between free cyanide and pyrite (Janetski et al., 1977; Prestidge et al., 1993; Wet et al., 1997), pyrrhotite (Prestidge et al., 1993), chalcocite (Castro and Larrondo, 1981), and sphalerite (Buckley et al., 1989; Prestidge et al., 1997) have been extensively investigated. The interactions of cuprous cyanide with sphalerite (Seke and Pistorius, 2006) and a pyritic gold ore (Guo et al., 2015) have also been studied recently. It has been found that Cu(CN)₂⁻ depresses pyrite flotation similarly as free cyanide by inhibiting surface electrochemical reactions and removing the surface layer of xanthate adsorption. On the other hand, cuprous cyanide species have little depression effect on the flotation of liberated gold (Guo et al., 2015). However, no research has been conducted to understand the interactions of zinc cyanide species with minerals under a flotation condition despite their existence in process water.

In this study, a pyritic gold ore was chosen to understand how zinc cyanide species affect gold flotation in line with the previous study (Guo et al., 2015) where the effect of copper cyanide species on gold flotation was studied. To explain gold flotation behavior in the presence of zinc cyanide species, the competitive adsorption

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between zinc cyanide species and thiol collectors on gold surface was studied.

2. Materials and methods

2.1. Materials

Zinc cyanide solutions were prepared by combining aqueous solutions of sodium cyanide (NaCN, 99.9%, Aldrich) and zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 99.9%, Aldrich) with a cyanide concentration of 2×10^{-3} M and a CN/Zn molar ratio of 2 or 4. Free cyanide (NaCN) was also tested for a comparison. Aerophine promoter 3418A (sodium diisobutylidithiophosphinate, NaDIBDTPI) was supplied from Cytec Industries Inc. as a 50% aqueous solution. PAX (potassium amyl xanthate) was also supplied from Cytec Industries Inc. and was used as received. Collector solutions were prepared using deionized water (resistivity > 18 M Ω cm). The ore sample from a primary sulfide deposit in Hidden Valley Mine, Papua New Guinea was tested. The chemical compositions and mineralogical liberation of this sample were detailed elsewhere (Guo et al., 2015). The Au, Fe, and S grade of the ore is 2.13 ppm, 3.87%, and 1.61%, respectively.

2.2. Grinding and flotation

The grinding and flotation procedure was detailed elsewhere (Guo et al., 2015). Free cyanide or zinc cyanide solution was added in milling pulp with 1 kg ore as the feed. The pH of the milling and flotation pulp was about 7 (the nature pH value). Four concentrates were collected at cumulative times of 1, 3, 5, and 10 min. 5×10^{-5} M Aerophine 3418A was added prior to flotation and 1×10^{-4} M PAX was added after the cumulative flotation time of 3 min. This reagent scheme is used in the flotation plant at Hidden Valley Mine. In this study, the flotation performance without the addition of 3418A was also tested.

2.3. Raman spectroscopy measurements

Raman spectroscopy measurements were conducted on Renishaw Raman spectrometer using 632.8 nm red excitation from a He–Ne laser. The scattered light was detected with a CCD detector cooled to -50°C with the spectral resolution of 2.7 cm^{-1} . The laser and scattered radiation were focused through the spectrometer objective lenses with a long working distance. Spectra were collected for 10 s with 20 accumulations. The grating was calibrated using the 520 cm^{-1} silicon band.

The gold electrode was prepared from gold of 99.99% purity. It consisted of a 0.1 cm radius disk imbedded in a 0.4 cm radius Teflon sheath, and mechanically polished successively with 1.0 and 0.3 μm alumina and rinsed with distilled water immediately before use. The electrode surface was electrochemically roughened by applying a succession of potential sweep oxidation and reduction cycles in 0.1 M KCl at 500 mV s^{-1} from 1.25 to -0.25 V (vs. Ag/AgCl/3 M KCl), with waiting times of 1.3 s at 1.25 V and 30 s at -0.25 V (Beltramo et al., 2004). Electrochemical roughening has been extensively applied to obtain enhanced Raman signal on gold electrode interacting with organic species (Gao and Weaver, 1985; Hope et al., 2000; Michota and Bukowska, 2003; Woods et al., 1998) and inorganic species (Beltramo et al., 2004; Gao et al., 1992; Fleischmann et al., 1985; Lowry, 1993; Tadayyoni and Weaver, 1986). This technique is an effective method providing molecular-level information on the adsorbed species involved (Tian et al., 2002).

In this study, the in-situ SERS experiments were carried out on the roughened electrode surface immersed in a drop of prepared

reagent solution in equilibrium with air and at the open circuit potential (OCP). The pH of the solution was modified to 7 using sodium hydroxide or hydrochloric acid. The OCP of gold electrode in solutions recorded for SERS measurements and in flotation pulp was about 0.310 V and 0.304 V (SHE), respectively, in the presence of 3418A, and decreased to about 0.200 V and 0.207 V (SHE), respectively, after the addition of PAX. The highly comparable OCP suggests that SERS measurement is indicative of the surface reaction on gold during flotation.

3. Results and discussion

3.1. Flotation

Fig. 1 shows the kinetic flotation of Au, Fe, and S with various reagent schemes. The base line flotation with the plant reagent scheme was repeated three times and the error bars were indicated in the figure. It can be seen that after 3 min flotation, 43.7% gold recovery was achieved in the absence of any collector, indicating some extent of collectorless flotation of gold from the ore. The Au displayed good floatability in the presence of PAX alone, reaching a recovery of 91.7% after 10 min flotation. The addition of 3418A prior to flotation promoted the flotation of gold, with a recovery of 86.1% after 3 min flotation in the presence of 3418A alone and a final recovery of 93.7% after 10 min flotation with additional PAX.

Since this is a pyrite-dominant ore, the flotation recoveries of Fe and S presented in Fig. 1 are indicative of the flotation performance of pyrite. It can be seen that the collector-less flotation of pyrite was poor in the first 3 min flotation without the addition of 3418A prior to flotation with only 2.1% Fe recovery and 2.7% S recovery. Pyrite did not respond well to 3418A with about 30% recovery after 3 min flotation when 3418A was added prior to flotation. PAX displayed a strong collecting power for pyrite. After PAX addition, 32.0% Fe recovery and 95.8% S recovery were achieved at the end of flotation. Fig. 1 shows that the addition of 3418A prior to flotation promoted the flotation of gold at the initial stage of flotation.

The flotation kinetics of Au, Fe, and S in the presence of free cyanide (NaCN) is also included in Fig. 1. In these tests, the total cyanide concentration was 2×10^{-3} M, and both 3418A and PAX were added. It is seen that 80.9% Au recovery was obtained after 3 min flotation and 81.7% was obtained at the end of flotation if free cyanide was present. The Fe and S recoveries decreased to 6.7% and 4.2%, respectively. This indicates a strong depressive effect of free cyanide on the flotation of pyrite but only a slight effect on the flotation of gold.

Fig. 2 shows Au, Fe and S flotation recoveries at the end of flotation as a function of NaCN concentration. Both 3418A and PAX were applied in the flotation. As can be seen, Fe and S recoveries decreased to 6.9% and 4.5%, respectively, at 4×10^{-4} M NaCN. Further increasing NaCN concentration to 2×10^{-3} M had little influence on the already low Fe and S recoveries. This indicates that pyrite flotation was completely depressed at 4×10^{-4} M NaCN. Au recovery shows a similar dependence on NaCN concentration. It decreased from 93.7% to 81.7% at 4×10^{-4} M NaCN. High NaCN concentrations at 1.2×10^{-3} M and 2×10^{-3} M did not further decrease gold recovery significantly. In the ore, 13.4% of the gold in the flotation concentrate in the absence of cyanide is associated with sulfide minerals, mainly auriferous pyrite (Guo et al., 2015). Clearly, the auriferous pyrite was depressed by free cyanide, while the flotation of liberated gold (free gold) was not affected by free cyanide.

The flotation kinetics of Au, Fe, and S in the presence of zinc cyanide with the CN/Zn molar ratio of 2 and 4 is shown in Fig. 3.

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