



## Effects of free cyanide and cuprous cyanide on the flotation of gold and silver bearing pyrite



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### ABSTRACT

At gold and silver mineral processing plants, cyanide species are always present in the process water recycled to flotation circuits, despite the cyanide destruction process. The effect of cyanide, in particular, cuprous cyanide on gold and silver flotation has not been well understood. In the present study, free cyanide and cuprous cyanide species were isolated and their effects on the flotation of a pyritic ore were evaluated. It was found that free cyanide depressed gold and silver flotation through their carrier, pyrite. Cuprous cyanide mainly in the form of  $\text{Cu}(\text{CN})_2^-$  depressed pyrite flotation similarly as free cyanide. Electrochemical studies including open circuit potential (OCP), cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques were carried out to understand the underpinning depression mechanism of cyanide species on pyrite flotation using xanthate as collector. It was found that all surface electrochemical reactions were inhibited by either free cyanide or cuprous cyanide. The surface layer as a result of xanthate adsorption on pyrite was completely removed in the presence of these cyanide species, which was suggested to contribute to the hydrophilic pyrite surface.

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### 1. Introduction

When gold and silver are associated with sulphide minerals, they are often recovered with these sulphide minerals by flotation with the flotation concentrate leached to recover the precious metals or smelted to recover the precious and base metals. At Hidden Valley (HV) Mine, gravity separation is used to recover the coarse gold, followed by a bulk flotation step to recover most of the gold and silver minerals. The flotation concentrate is then leached and the gold and silver in solution are removed by a Counter Current Decantation (CCD) circuit and then recovered in a Merrill Crowe circuit. The precipitate from the Merrill Crowe circuit is calcined and smelted to produce a dore. The flotation and CCD tailings are sent to a Carbon in Leach (CIL) circuit to recover these precious metals and the carbon elution solution is sent to a separate Merrill–Crowe circuit and the precipitate is also calcined and smelted to produce a dore. The remaining cyanide in the final tailing is sent to an Inco Detox and a Caro's Acid detox circuits, producing the main source of process water which is recycled to the upstream circuits such as grinding and flotation. At the time that this research was initiated, the Au and Ag recoveries were below the

values achieved in the feasibility study. A contributing factor was the process water containing cyanide species which may have a deleterious effect on gold and silver flotation despite cyanide destruction processes. This is a common problem encountered in precious mineral processing plants (Adams, 2013).

Cyanide is among the most commonly used flotation reagents to depress iron sulphides and enhance the separation efficiency of base metal sulphide flotation. At early stages, (Sutherland and Wark, 1955; Wark, 1938) reviewed the depression of various sulphide minerals by NaCN based on bubble contact tests. Then, several attempts have been made to explain the depression behaviour and the underpinning mechanism for pyrite (Grano et al., 1990; Hodgkinson et al., 1994; 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; Seke, 2005; Seke and Pistorius, 2006).

It has been proposed based on thermodynamic considerations (Elgillani and Fuerstenau, 1968; Wang and Forssberg, 1996) that cyanide preferentially adsorbs on pyrite surface as iron cyanide compounds, inhibiting the chemisorption and oxidation of xanthate. However, the existence of insoluble iron cyanide compounds on pyrite surface has not been well confirmed by experimental studies (Prestidge et al., 1993). No continuous surface layers are formed as a result of the interaction between pyrite and cyanide according to electrochemical impedance spectroscopy studies

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(Wet et al., 1997). It was also proposed that cyanide as a strong reducing agent significantly decreased the flotation pulp potential, thus inhibiting the oxidation of xanthate which is essential for the hydrophobic surface of pyrite (Kocabag and Guler, 2007; Ralston, 1991; Miller et al., 2006). Janetski et al. (1977) and Wet et al. (1997) showed that cyanide reduced the surface electrochemical activities, limiting both anodic and cathodic reactions on pyrite surface.

The above cyanide species are discussed on a basis of free cyanide including hydrocyanic acid (HCN) and the cyanide anion (CN<sup>-</sup>). On the other hand, weak acid dissociable (WAD) cyanide species (cyanide complexes with Cu, Zn, Ag, Cd, and Ni, which dissociates under mildly acidic conditions to free cyanide) are also commonly seen in the process water and copper cyanide species are of the most importance. Despite the large volume of research on cyanide–pyrite interactions, there has been little research on the interactions of copper cyanide species with pyrite. It was first suggested by Wark (1938) that the contact of pyrite with air bubbles was still possible at a CuSO<sub>4</sub>/NaCN ratio of approximately 3/1 under which the formation of cuprous dicyanide complex Cu(CN)<sub>2</sub><sup>-</sup> was favoured in addition to cyanate (OCN<sup>-</sup>), an oxidation product of cyanide. Copper cyanide speciation largely depends on cyanide concentration, cyanide to copper molar ratio, pH and salinity of the solution (Dai et al., 2012; Lu et al., 2002; Lukey et al., 1999). The interaction of various copper cyanide species with sulphide minerals needs to be examined in detail. In this study, the Hidden Valley Mine was taken as a case study to understand how free cyanide and cuprous cyanide affect gold and silver flotation.

## 2. Thermodynamic consideration

The cyanide anion in aqueous solution forms hydrocyanic acid according to the following dissociation reaction (Marsden and House, 2006).



The logarithmic exponent of the dissociation constant pKa of HCN at 25 °C is 9.21 (Lu et al., 2002). A pH value higher than 9.21 increases CN<sup>-</sup> concentration while a pH value lower than 9.21 promotes the presence of aqueous HCN in the solution. HCN is a volatile substance and the formation of aqueous HCN would promote its volatilisation, which is responsible for cyanide loss in many gold processing plants (Smith and Mudder, 1991). A significant portion of the cyanide in the tailing dam is volatilised to HCN as the pH decreases and decanted solution has more contact with air (Lotter, 2006). It is estimated that volatilisation rates from ore processing operations such as leaching are generally low, with only 1% of total cyanide being lost through HCN volatilisation at an operation pH of around 10 (Heath et al., 1998 and Adams, 1990).

The processing circuits where cyanide loss should be considered in the present paper include grinding and flotation. It is generally observed that in flotation circuits, the pulp pH is typically adjusted in the mildly alkaline range with little cyanide loss. However, the pH of the milling pulp drops significantly as a result of certain interactions including the hydrolysis of metal species to generate acid and carbon dioxide uptake from the air forming carbonic acid and oxidation of sulphur species in the sulphide minerals. Low pH may cause cyanide loss via HCN volatilisation during milling and probably change the cyanide speciation. In the present study, the HCN volatilisation rate from the flotation pulp with modified pH 10 is generally low as long as the cyanide is dosed after grinding circuit, while the majority of cyanide exists as CN<sup>-</sup> in the solution.

In copper cyanide system, the loss of cyanide is determined by both the dissociation of the copper cyanide complex and

subsequent volatilisation of the formed aqueous HCN. The rate of the first process was found to be dependent on the dissociation rates of the different cuprous cyanide complexes as shown from Eqs. (2)–(5).



The copper cyanide speciation under the present experimental conditions was modelled using a computer program Visual MINTEQ (version 3.0) (Gustafsson, 2012). In these modellings, copper(I) cyanide (CuCN) was specified as finite solid phase and was dissolved by CN<sup>-</sup> at 25 °C. The solubility product ( $K_{sp}$ ) of CuCN was defined at a value of  $10^{-19.5}$  with its reaction enthalpy  $\Delta H^\circ = -19$  kJ/mol. In this program, the corresponding equilibrium constants for Eqs. (3)–(5) were defined as  $10^{-23.9}$ ,  $10^{-29.2}$ ,  $10^{-30.7}$ , respectively and  $\Delta H^\circ$  values for those reactions were defined as  $-121$ ,  $-167.4$ ,  $-214.2$  kJ/mol, respectively. Parameters such as pulp potential Eh, pH and the molality of CuCN, CN<sup>-</sup> and the balanced Na<sup>+</sup> were considered to formulate the input data for the calculation. Cu<sup>+</sup>/Cu<sup>2+</sup> redox couple was specified with  $\log K = 2.69$  and  $\Delta H^\circ = 6.9$  kJ/mol. Oversaturated solids were allowed to precipitate. From this thermodynamic analysis it is possible to know the concentration of each cuprous cyanide species of interest.

The distribution of cyanide species as a function of pH at CN/Cu mole ratio of 3/1 is presented in Fig. 1. The initial cyanide concentration was fixed at 10 ppm and the calculation suggests that there is no influence on cyanide speciation when Eh ranges from 0 mV to 550 mV (SHE) which is consistent with the expected pulp potential in flotation. At pH 10, the dominant cyanide species is cuprous tricyanide Cu(CN)<sub>3</sub><sup>2-</sup> (accounting for 81% of the initial cyanide) while Cu(CN)<sub>2</sub><sup>-</sup> accounting for 13%. This agrees with the previous study on the copper cyanide system (Lu et al., 2002). It is noted from Fig. 1 that both HCN and Cu(CN)<sub>2</sub><sup>-</sup> become dominant in the solution when pH drops down to 7, which is commonly observed during the grinding process. This suggests that H<sup>+</sup> ions at low pH compete with Cu(CN)<sub>2</sub><sup>-</sup> to complex with CN<sup>-</sup> following Eq. (6).



Thermodynamic calculation for cyanide speciation at CN/Cu mole ratio of 2/1 is presented in Fig. 2. The initial cyanide concentration was fixed at 10 ppm and Eh at 300 mV (SHE). The only dominant

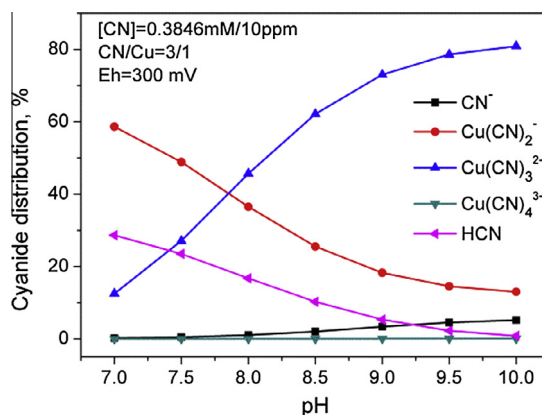


Fig. 1. Copper cyanide speciation at [CN]/[Cu] = 3/1, [CN] = 10 ppm, Eh = 300 mV (SHE), 25 °C.

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