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# Cyanide chemistry and its effect on mineral flotation

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ABSTRACT

Cyanide has been widely used as a depressant in sulphide mineral flotation. It occasionally activates mineral flotation as well. In addition, cyanide species in the water from gold cyanidation process may be recycled to flotation circuits and have an inadvertent effect on mineral flotation. Therefore, the investigation on mineral flotation in the presence of cyanide with different speciation is of great importance. Even after decades of research, the mechanisms of cyanide depression and activation processes are not fully understood and effective ways to solve problems encountered in minerals flotation plants using cyanide-containing recycled water are not currently available. In this paper, a review of previous literature on the effect of free cyanide, weak acid dissociable (WAD) cyanide and strong acid dissociable (SAD) cyanide on the flotation of base metal and precious minerals is presented, with a particular focus on the underpinning mechanisms and process solutions. Ultimately, an overall picture of current status of studies in this area is provided and the future research associated with using cyanide in mineral flotation is suggested.

**Contents**

## 1. Introduction

Cyanide was introduced commercially over a century ago and since then it has been used in several types of industry and mining is one industrial activity that uses a significant amount of cyanide, about 20% of the total production (Logsdon et al., 1999). The cyanide

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species discussed in this paper can be broadly classified into three categories: free cyanide including hydrocyanic acid (HCN) and the cyanide anion ($CN^-$); weak acid dissociable (WAD) cyanide (cyanide complexes with Cd, Cu, Ni, Ag or Zn which dissociates under mildly acidic conditions to free cyanide); strong acid dissociable (SAD) cyanide (cyanide complexes with Fe, Co or Au which dissociates only under extreme acidic conditions). The thermodynamic stability constants for some of the metal cyanide complexes or compounds commonly existing in mineral processing plant water are summarized in Table 1. The stability constants of some metal xanthate complexes are also listed in Table 1 for further discussions.

Cyanide is among the most commonly used reagents for enhancing the separation efficiency of base metal sulphide minerals by flotation, particularly when the depression of iron and zinc sulphides is desired. At early stages, Sutherland and Wark (Sutherland and Wark, 1955; Wark, 1938) comprehensively reviewed the depression of many sulphide minerals by cyanide in the presence of several collectors of xanthate type, which has been regarded as a standard reference for industry application of cyanide in flotation for many decades. Their work was mainly on the basis of captive bubble contact tests, giving the theoretical possibility of mineral separations in flotation. However, many of these early studies have been of a phenomenological nature and the surface interaction of cyanide species with minerals and the influence of electrochemical environments of flotation have not been fully addressed. In fact, mineral separations by the use of cyanide are practically not easy and have relied entirely on empirical testing. It has been reported that cyanide activates, rather than depresses, mineral flotation under some conditions (Prestidge et al., 1993a; Rao et al., 2011; Seke and Pistorius, 2006). This paper reviews the action of cyanide species in flotation based on mineral type followed by ways to mitigate their depression effects. Thermodynamic and kinetic aspects are considered to develop a rational scheme for the interpretation of cyanide depression and activation.

## 2. Effect of cyanide on mineral flotation

### 2.1. The action of xanthate on sulphide minerals

Xanthate is commonly used as collector to float sulphide minerals, and the depression of cyanide occurs mainly by altering the action of xanthate on mineral surfaces. The adsorption of xanthate on pyrite has been studied extensively and various adsorption mechanisms have been proposed including surface specific interactions with the formation of iron xanthate complexes (Fuerstenau and Mishra, 1980; Wang and Forssberg, 1990b) and the oxidation of xanthate to dixanthogen on the pyrite surface (Allison et al., 1972; Majima and Takeda, 1968). Fuerstenau et al. (1968) reported that non-oxidised pyrite adsorbed xanthate ions through specific interactions while on oxidised pyrite the adsorption took place through the oxidation of xanthate to dixanthogen. Miller et al. (2002) found that dixanthogen was the dominant species on pyrite at low pH while at high pH ferric xanthate complexes were found to be prevalent. It was also presented by Leppinen (1990) using surface analyses that ferric ethyl xanthate ($Fe(EX)_3$) was the main species of monolayer coverage on pyrite when the xanthate concentration was low (less than $3 \times 10^{-5}$ M) while dixanthogen multilayers covered on this ferric ethyl xanthate at a higher xanthate concentration. It was confirmed that both ferric xanthate and dixanthogen were responsible for the surface hydrophobicity (Leppinen, 1990).

**Table 1**
Thermodynamic stability constants of various metal cyanide (Wang and Forssberg, 1990a) and metal xanthate species (Wang et al., 1989a).

| Species | log β or pKsp | Species | log β or pKsp |
|---|---|---|---|
| $Zn(CN)_2(s)$ | 15.5 | $Fe_2[Fe(CN)_6](s)$ | 14.1 |
| $Zn(CN)_3^-$ | 16.0 | $Cu_2[Fe(CN)_6](s)$ | 17 |
| $Zn(CN)_4^{2-}$ | 19.6 | $Cu_3[Fe(CN)_6]_2(s)$ | 24.5 |
| $CuCN(s)$ | 19.4 | $K_2Cu_3[Fe(CN)_6](s)$ | 34.3 |
| $Cu(CN)_2^-$ | 16.3 | $K_2Zn_3[Fe(CN)_6](s)$ | 38.5 |
| $Ag(CN)_2^-$ | 20.5 | $KCu_{10}[Fe(CN)_6]_7(s)$ | 74 |
| $Cu(CN)_3^{2-}$ | 21.6 | $Zn(EX)_2(s)$ | 8.3 |
| $Cu(CN)_4^{3-}$ | 23.1 | $CuEX(s)$ | 14.2 |
| $Ni(CN)_4^{2-}$ | 30.2 | $Ni(EX)_2(s)$ | 12.5 |
| $Fe(CN)_6^{4-}$ | 35.4 | $Fe(EX)_2(s)$ | 7.2 |
| $Au(CN)_2^-$ | 39.3 | $Fe(EX)_3(s)$ | 24.8 |
| $Fe(CN)_6^{3-}$ | 43.6 | $PbEX_2(s)$ | 16.7 |
| $Fe_4[Fe(CN)_6]_3(s)$ | 40.5 | | |

The formation of metal xanthate complexes on sulphide mineral surfaces has been regarded as an electrochemical process involving the charge transfer (Ralston, 1991). The anodic reactions occur as Eqs. (1) and (2) while the reduction of oxygen occurs on the cathode as Eq. (3).

$$X^- \rightarrow X_{ads} + e \tag{1}$$

$$MS + 2X^- \rightarrow MX_2 + S + 2e \tag{2}$$

$$1/2O_2 + H_2O + 2e \rightarrow 2OH^- \tag{3}$$

where MS, $MX_2$, $X^-$, and $X_{ads}$ represent the sulphide mineral, the metal xanthate, the xanthate ion, and the adsorbed xanthate, respectively. S represents elemental sulphur or polysulphide.

Dixanthogen forms through the anodic oxidation of xanthate ions at the pyrite surface via Eq. (4), coupled with the reduction of ferric hydroxide to ferrous ions via Eq. (5) (Haung and Miller, 1978; Janetski et al., 1977; Valdivieso et al., 2005).

$$2X^-_{ads} \rightarrow X_2 + 2e \tag{4}$$

$$2Fe(OH)_3(s) + 6H^+ + 2e \rightarrow 2Fe^{2+} + 6H_2O \tag{5}$$

### 2.2. Effect of cyanide on iron sulphide minerals flotation

Of all the sulphide minerals studied so far, the depression of pyrite by free cyanide is the best understood. Free cyanide at a concentration as low as 10 mg/L NaCN was found to significantly depress pyrite flotation using sodium isopropyl xanthate (SIPX) as collector (Wet et al., 1997). The addition of 200 mg/L NaCN at pH 11 resulted in a drop in sulphur recovery from 90% to less than 10% in pyrite flotation with 50 g/t SIPX (Wet et al., 1997). Using

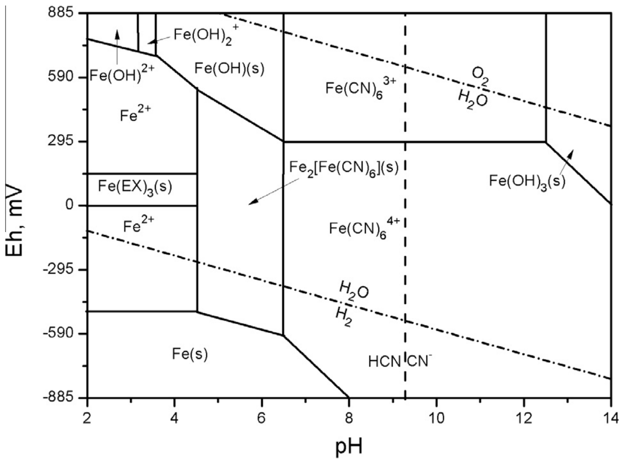

**Fig. 1.** Eh–pH stability diagram for Fe–EX–CN–$H_2O$ system ($[Fe] = [EX] = 1.0 \times 10^{-3}$ M, $[CN] = 5.0 \times 10^{-3}$ M) (Wang and Forssberg, 1996).