The depression of pyrite in selective flotation by different reagent systems – A review

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ABSTRACT

Pyrite is a gangue mineral widely associated with valuable minerals. It is problematic to deal with in differential flotation because it easily reports to flotation concentrates. Pyrite may float due to natural or self-induced hydrophobicity or collector-induced hydrophobicity. Its flotation can also be enhanced by the activation of copper or lead ions emanating from other minerals. Depressants are generally required to selectively depress pyrite. In this article, a comprehensive review of the fundamental studies of depression mechanisms and effectiveness of commonly used reagent systems to depress pyrite is presented. It includes inorganic reagents (hydroxyl ions, oxygen conditioning, cyanide, sulfoxyl reagents, etc.), organic reagents such as polysaccharides (starch, dextrin, carboxymethyl cellulose etc.), polyacrylamides, wood-extracted biopolymers, diethylenetriamine and a combination of these methods. Overall, the action of pyrite depressants is either to desorb the collector or activator from pyrite surface, deactivate the activating ions, prevent collector adsorption on pyrite, or make the pyrite surface hydrophilic. The mechanisms of some non-xanthate collectors such as dithiophosphate, dithiophosphinate and thionocarbamate in rejecting pyrite were also briefly reviewed.

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1. Introduction

Pyrite (FeS$_2$, iron disulfide), is the most abundant sulfide mineral and commonly associated with valuable minerals such as sphalerite, chalcopyrite, galena, gold as well as coal (Wang and Forssberg, 1991; Wang, 1995; Dimitrijevic et al., 1996; Jiang et al., 1998). Pyrite has very low economic significance and is usually removed from the valuable components by flotation and processed as a waste material (Wang and Forssberg, 1991; Chandra and Gerson, 2009; Bulut et al., 2014). However, its presence has an impact on the handling and utilizing of the valuable components. In the differential flotation of multiple sulfide minerals, the misplacement of pyrite into concentrates dilute concentrate grades and reduce the economic value (Wang and Forssberg, 1991; Chandra and Gerson, 2009; Huang et al., 2013). It also has an adverse effect on the efficiency of pyro metallurgical processes (Ahmadi et al., 2012). Combustion of pyrite-bearing coal may lead to the release of sulfur dioxides causing acid rain (Cheng et al., 2013). Therefore, there are significant economic and environmental advantages to separate pyrite from valuable minerals at an early stage of processing.

Xanthate (ROCSS$^-$) is the most extensively used collector in the flotation of base metal sulfide minerals (Janetski et al., 1977; Wang and Forssberg, 1991). Adsorption of xanthate collectors on sulfide mineral surfaces has been considered as an electrochemical process, involving charge transfer in the chemisorption of xanthate ions (Eq. (1)), oxidation of xanthate to dixanthogen (Eq. (2)) and/or the formation of metal xanthate (Eq. (3)) (Ralston, 1991; Miller et al., 2002). Anodic oxidation in flotation is generally coupled with cathodic reduction of oxygen (Eq. (4)) (Miller et al., 2002; Guo et al., 2014).

$$X^- \rightarrow X_{ads} + e^- \tag{1}$$
$$2X^- \rightleftharpoons X_2 + 2e^- \tag{2}$$
$$MS + 2X^- \rightarrow MX_2 + S + 2e^- \tag{3}$$
$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{4}$$

In Eqs. (1)–(4) X^-, X_{ads}, X_2, MS and MX$_2$ represent xanthate ions, the adsorbed xanthate, dixanthogen, sulfide mineral and metal xanthate, respectively. S represents elemental sulfur or polysulfide.

Traditional theories consider that dixanthogen is the predominant species responsible for the hydrophobicity of pyrite, which has been confirmed by means of IR spectroscopy, UV and cyclic voltammetry techniques (Fuerstenau et al., 1968; Majima and Takeda, 1968; Janetski et al., 1977; Richardon and Walker, 1985; Miller et al., 2002). Dixanthogen is only formed if the mineral surface reaches a mixed potential higher than the X^-/X_2 equilibrium value (Allison et al., 1972). The reversible potential for the X^-/X_2 couple can be computed from the Nernst equation Eq. (5) (Miller et al., 2002; Guo et al., 2015). Some researchers have suggested that for pyrite, the coupled cathodic reaction may also be due to the reduction of ferric hydroxide to ferrous ions via Eq. (6) (López Valdivieso et al., 2005; Guo et al., 2014). The standard half-cell potential E^0 for the amyl xanthate/di-amyl dixanthogen couple is −0.158 V vs. SHE, and becomes progressively more positive with decreasing the length of hydrocarbon chain in xanthate molecules (Winter and Woods, 1973). The formation of ferric xanthate is also reported to contribute to pyrite flotation (Taggart et al., 1934; Leppinen, 1990; Wang and Forssberg, 1991).

$$E = E^0 - 0.059 \log[X^-] \tag{5}$$
$$2Fe(OH)_3(s) + 6H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 6H_2O \tag{6}$$
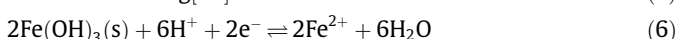
Fuerstenau et al. (2007) studied the flotation of pyrite at different pH conditions with various xanthate concentrations, and the results are shown in Fig. 1. At low xanthate concentrations, pyrite
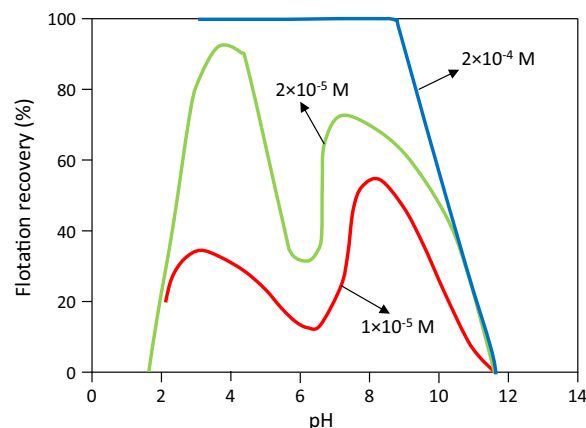

Fig. 1. Flotation recovery of pyrite as a function of pH with various additions of ethyl xanthate adapted from Fuerstenau et al. (2007).

flotation presents two maximums at around pH 4 and 8 with depression around pH 7. The high flotation yield at pH 4 is due to the formation of sulfur-rich products and dixanthogen (Leppinen, 1990; Wang and Forssberg, 1991; López Valdivieso et al., 2005). The yield at pH 8 has been explained to be due to the formation of iron hydroxide-xanthate complexes on pyrite surface (Fornasiero and Ralston, 1992). The depression of pyrite around pH 7 has been explained to be due to a high density of ferric hydroxide on pyrite, which, however, disappears with the increase of xanthate concentration. This has been interpreted to be due to the reduction of ferric hydroxides to ferrous species resulting from the oxidation of xanthate to dixanthogen (López Valdivieso et al., 2005). Depression of pyrite observed below pH 2 is due to decomposition of xanthate, while the depression above pH 11 is due to the thermodynamic instability of dixanthogen and the formation of ferric hydroxide islands on pyrite surface (Leppinen, 1990; Fuerstenau et al., 2007). While it is clear that flotation or depression depends upon the balance of hydrophobic and hydrophilic species on the surface, the finding above indicate that several ionic equilibria can modify pyrite surfaces only by a change in pH (He et al., 2005; López Valdivieso et al., 2005). In real ore systems, many ionic species can modify the surface properties of pyrite and change its flotation behavior.

In alkaline solutions, the separation of pyrite from other base metal sulfides (Pb/Cu/Zn) is difficult due to the inadvertent activation of pyrite by metallic species such as Cu^{2+} and Pb^{2+}, either dissolved from complex sulfide minerals due to galvanic interactions or present as contaminants in process water (Ekmekçi and Demirel, 1997; Zhang et al., 1997; Boulton et al., 2001b; Dichmann and Finch, 2001; He et al., 2005; Pecina et al., 2006; Barker et al., 2014; Owusu et al., 2014). Copper activation of pyrite is an electrochemical process that involves a single fast step of Cu^{2+} adsorption onto the reactive sulfur surface sites. During adsorption Cu^{2+} is reduced to Cu^+ to form Cu(I)-sulfide species accompanied by the oxidation of the surrounding S atoms (Weisener and Gerson, 2000a,b; Chandra et al., 2012; Peng et al., 2012). At alkaline pH above 8.5, copper hydroxide may precipitate over the Cu(I) activated surface (Weisener and Gerson, 2000a). The activation of pyrite by Pb^{2+} follows a different mechanism which does not involve an electrochemical process. It occurs via the precipitation of lead complexes such as hydroxides or carbonates (Finkelstein, 1997). The formation of lead complexes depends upon pH. Copper or lead species adsorbing/precipitating onto pyrite surface have significant chemical affinity for xanthate collectors and this interaction enhances pyrite flotation (Leppinen, 1990; Pecina et al., 2006; Chandra et al., 2012; Barker et al., 2014).