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The effect of surface oxidation of copper sulfide minerals on clay slime coating in flotation

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ABSTRACT

The industry is well aware of the difficulty in treating copper ores in the presence of clay minerals. In this study, the effect of bentonite on the flotation of chalcopyrite (a primary copper sulfide mineral) and chalcocite (a secondary copper sulfide mineral) was investigated in terms of surface coating. Based on the flotation of copper ores containing both chalcopyrite and chalcocite, the flotation of chalcopyrite and chalcocite single minerals in the presence and absence of bentonite, and the zeta potential measurement of chalcopyrite, chalcocite and bentonite, it was found that the oxidation of chalcopyrite and chalcocite had a different effect on their interaction with bentonite. Under the normal grinding and flotation condition, significant oxidation occurred on the surface of chalcocite which was electrostatically attractive to bentonite resulting in bentonite slime coating and the depressed flotation of chalcocite. The reduction of oxidation on chalcocite could mitigate bentonite slime coating due to electrostatic repulsion between unoxidized chalcocite and bentonite. Unlike chalcocite, chalcopyrite with and without surface oxidation exhibited an electrostatic repulsion to bentonite. Its flotation was less affected by bentonite slimes.

1. Introduction

Copper orebodies are formed when geothermal solutions (superheated under pressure) bring copper dissolved from deep underground to cool near surface environments where the copper and associated metals precipitate as minerals in veins and disseminations within the rock (Sillitoe and Petersen, 1996). Copper is usually deposited as copper sulfide minerals or in some environments as native copper metal. The most common copper minerals in the primary hydrothermal zone are chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). During millions of years the mineral deposit may be exposed to oxygen by airpenetration, or by oxygen rich water flowing over it. This oxidation alters the mineralogy, replacing the copper and iron sulfides with carbonates and oxides as the sulfur is oxidized to soluble sulfate and carried away in acid solution (Sillitoe and Petersen, 1996). The most common copper minerals in the oxidized zone are azurite ($Cu_3(CO_3)_2(OH)_2$), cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$) and tenorite (CuO), etc. Beneath the oxidized zone, some dissolved copper is precipitated as secondary or supergene copper minerals. This enriches the sulfides, making a secondary enrichment, or transitional zone. The secondary enrichment replaces iron in the minerals with more copper, further enriching the ore (Sillitoe and Petersen, 1996). The most common copper minerals in the secondary enrichment zone are chalcocite (Cu_2S) and covellite (CuS). To recover primary and secondary copper sulfide minerals from ores, froth flotation which exploits the difference in surface wettability is normally used to separate them from other gangue minerals. Extensive studies have been conducted to understand their oxidation and flotation behavior.

Like other sulfide minerals, the surface of copper sulfide minerals is reactive and starts to oxidize as soon as they are in contact with air. Mild oxidation results in a surface that is rich in polysulfides with some metal hydroxides present at the surface, due to the dissolution of metal ions from the surface and near surface layers, as observed in ambient air, acidic and alkaline conditions by X-ray Photoelectron Spectroscopy (XPS) (Buckley and Woods, 1983, 1984). Extensive oxidation results in high quantities of metal hydroxides on the mineral surface (Senior and Trahar, 1991). The oxidation of chalcopyrite is slow in general. A number of studies shows that a small amount of copper ions are dissolved from chalcopyrite even with oxygen purging (Fairthorne et al., 1997; Lascelles and Finch, 2002). Electrochemical studies indicate that the initial product of chalcopyrite oxidation may be chalcocite or covellite (Arce and Gonzalez, 2002; Lazaro et al., 1995). The oxidation of secondary copper sulfides are faster than chalcopyrite. By EDTA extraction, Lascelles and Finch (2002) found that chalcocite produced about 50 times more copper ions than chalcopyrite at the same size fraction (150/212 μm). Fullston et al. (1999) measured the zeta potential of the copper sulfide minerals including chalcocite, covellite, chalcopyrite, bornite, enargite and tennantite as a function of pH and the oxidation condition. They found that

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the change in zeta potential was governed by a copper hydroxide layer covering a metal-deficient sulfur-rich surface and with the extent of this copper hydroxide coverage increasing with the oxidation condition. They also demonstrated that among these copper sulfide minerals examined, chalcopyrite was the most electrochemically noble while chalcocite was the most electrochemically active in terms of surface oxidation.

The flotation of copper sulfide minerals is intimately associated with their surface oxidation. The collectorless flotation of copper sulfide minerals is attributed to polysulfides on the surface as a result of mild surface oxidation (Lekki and Drzymala, 1990; Ekmekçi and Demirel, 1997). Metal hydroxides on the mineral surface decrease the flotation of copper sulfide minerals even in the presence of collector (Senior and Trahar, 1991). Barzyk et al. (1981) identified that chalcocite surface oxidation had a strong effect on both xanthate adsorption and chalcocite floatability, and the most oxidized chalcocite sample required 100 times more collector consumption to obtain the same flotation results than the least oxidized sample. There is a strong relationship between Cu recovery and the electrochemical potential in flotation. High chalcopyrite, bornite or chalcocite flotation recovery may be obtained at well controlled electrochemical potentials (Tolley et al., 1996).

The flotation of copper sulfide minerals is complicated by the presence of clay minerals. The industry is well aware of the difficulty in treating weathered copper ores containing clay minerals. Currently, the only way to treat this type of ores is to blend them at a small proportion with normal ores. Limited studies have been conducted to understand the role of clay minerals in copper flotation. Clay minerals are anisotropic and hydrated phyllosilicates with unit cells comprising a layer of one alumina octahedral sheet and either one (such as kaolinite) or two (such as smectite) silica tetrahedral sheets (Brigatti et al., 2006). A single particle may comprise several layers stacked on top of one another. Due to isomorphous substitution (e.g., Al(III) replacing Si(IV) in the SiO_2 layer), the basal faces carry a constant negative charge which is pH independent (Luckham and Rossi, 1999; Zhao et al., 2008). At the edges of the layers, the tetrahedral silica sheets and the octahedral alumina sheets have broken primary bonds. The electrical charge of the edge, arising from hydrolysis reactions from broken Al–O and Si–O bonds, is pH dependent. The edges of clay particles are positively charged in the neutral and acid pH ranges depending on the type of clay minerals (Swartzen-Allen and Egon, 1974). The anisotropic charges on edges and basal faces allow clay slime coating on the surface of a range of minerals. It has been well documented that clay slime coating occurs on galena, coal and bitumen surfaces through the electrostatic attraction, reduces surface hydrophobicity and then depresses the flotation significantly (Gaudin et al., 1960; Arnold and Aplan, 1986; Liu et al., 2005a,b).

It is generally observed that when clay minerals are placed in a solution where the pH and/or charged ions, reagents or other minerals (e.g., iron oxides) promote clay particle aggregation, these structures result in high viscosity (Luckham and Rossi, 1999). There is also evidence that the propensity towards high viscosity is markedly enhanced as particle size decreases (Tu et al., 2005). Clay minerals are naturally fine-grained with particles of colloidal size (Schoonheydt and Johnston, 2006; Kotlyar et al., 1996). Therefore, a relatively low concentration of clay minerals, in the range of 5–12 wt.% may be sufficient to cause high viscosity (Tu et al., 2005). The effect of viscosity itself, potentially caused by clay mineral aggregate structures, on mineral flotation has not been adequately examined (Schubert, 2008).

In this paper, the effect of clay slime coating on the flotation of primary (chalcopyrite) and secondary (chalcocite) copper sulfide minerals is explored. The effect of viscosity itself, caused by clay mineral aggregate structures, on the flotation of copper sulfide minerals was reported previously (Peng et al., 2010).

2. Experimental

2.1. Materials and reagents

An underground copper ore and an open pit copper ore were crushed to a size of −2.36 mm before grinding and flotation. The mineral composition of the two ores analyzed by X-ray Diffraction (XRD) is shown in Table 1. The two ores contain both chalcopyrite and chalcocite. The main copper mineral in the underground ore is chalcopyrite, 85% of the copper minerals. The main copper mineral in the open pit ore is chalcocite, 67% of the copper minerals. Another distinct difference in the two ores is the clay mineral (bentonite) in the open pit ore. About 0.5 ppm gold is also associated with the ores, but gold flotation is not considered in this paper.

Chalcopyrite, chalcocite and bentonite single minerals were obtained from Ward's Natural Science Establishment (US). All of them have more than 98% purity analyzed by XRD. Peroxide and dithionite (AR grade) were used to adjust the oxidation state of chalcopyrite and chalcocite during grinding. High quality of nitrogen and oxygen gases was used to adjust the Eh in the flotation of chalcopyrite and chalcocite. Potassium amyl xanthate (PAX) and IF56, industrial grade, were used as collector and frother, respectively in copper flotation. De-ionized water was used throughout the study.

2.2. Mineral grinding and flotation

One kilo-gram crushed copper ore sample was ground in a laboratory stainless steel rod mill with stainless steel rods at 40% solids to obtain 80 wt.% particles passing 75 μm. The mill discharge was transferred to a 2.5 L Agitair flotation cell using an agitation speed of 750 rpm and conditioned with 100–300 g/t collector and 20 g/t frother. In the plant, 50 g/t collector was used to float both copper and gold with recycled water in rougher and scavenger flotation. In the laboratory, 100 g/t collector was usually used without recycled water to match the flotation performance in the plant. Lime was used to control pH 9.0 at the end of grinding and during flotation. In flotation, four concentrates were collected after cumulative times of 0.5, 2.0, 4.0 and 8.0 min. Eh and pH were measured in the end of grinding and during flotation. Eh values were converted to the SHE standard.

The chalcopyrite or chalcocite single mineral (100 g) with and without 5 g bentonite was combined with 0.15 dm^3 of de-ionized water and ground in the stainless steel rod mill with stainless steel rods to obtain 80 wt.% particles passing 75 μm. Flotation of the single minerals was conducted in a 1.5 L Agitair flotation cell using an agitation speed of 500 rpm with 100 g/t collector and 150 g/t frother. The frother concentration required in the flotation of single minerals in this study was much higher than that in the flotation of ore samples probably due to the greater amount of hydrophobic particles to be laden by froth. This is consistent with previous studies where the flotation of galena, chalcopyrite and pyrite single minerals was conducted (Peng et al., 2003a,b; Peng and Grano, 2010). Other conditions were the same in single mineral flotation and copper ore flotation.

2.3. Chemical analysis of copper products

The head samples of the two copper ores and their flotation products were assayed for total copper and cyanide soluble copper by inductively coupled plasma – optical emission spectroscopy (ICP–OES) using standard methods. The total copper digestion method used aqua regia while the cyanide soluble copper digestion used cyanide. Since chalcocite is soluble in cyanide solutions as a secondary copper sulfide mineral but chalcopyrite is insoluble in cyanide solutions as a primary copper sulfide mineral (Scheffel,