



The galvanic interaction between chalcopyrite and pyrite in the presence of lignosulfonate-based biopolymers and its effects on flotation performance

Yufan Mu^a, Yongjun Peng^{a,*}, Rolf A. Lauten^b

^a School of Chemical Engineering, The University of Queensland, St. Lucia, Brisbane, QLD 4072, Australia

^b Pionera, P.O. Box 162, NO-1701 Sarpsborg, Norway

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ABSTRACT

Pyrite, a gangue mineral, is commonly associated with valuable base metal sulfide minerals and the separation of pyrite from these valuable sulfide minerals by flotation is difficult. In this study, a type of biopolymers, modified from lignosulfonates, was used to reject pyrite in chalcopyrite flotation based on the previous investigations. It was found that these biopolymers selectively depressed pyrite flotation with little effect on chalcopyrite flotation. The presence of pyrite decreased the depression effect of biopolymers on chalcopyrite flotation due to the preferential adsorption of biopolymers on copper-activated pyrite as revealed by the adsorption isotherms and ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) analyses. The presence of chalcopyrite increased the depression effect of biopolymers on the flotation of copper-activated pyrite due to enhanced oxidation of the copper activation product, Cu(I)S, on pyrite as a result of the galvanic interaction among Cu(I)S, pyrite and chalcopyrite.

1. Introduction

Pyrite (FeS_2) is normally a gangue mineral widely associated with valuable base metal sulfide minerals such as chalcopyrite (CuFeS_2), chalcocite (Cu_2S), galena (PbS) and sphalerite (ZnS) which are the major mineral sources for copper, lead and zinc. The economic extraction of metals requires selective separation of pyrite from these base metal sulfide minerals by flotation (Bulatovic, 2007). The separation of pyrite from these base metal sulfide minerals is difficult due to the galvanic interactions between these minerals, and the inadvertent activation of pyrite which may result from copper or lead ions added intentionally or dissolved from the associated minerals during grinding and flotation (Peng and Grano, 2010; Qin et al., 2015). In terms of pyrite associated with chalcopyrite, chalcopyrite serves as an anode, the oxidation and dissolution of which is accelerated with electrons flowing from chalcopyrite to pyrite, while pyrite acts as a cathode, on which oxygen is preferentially reduced (Cruz et al., 2005; Azizi et al., 2013). Copper ions originating from chalcopyrite attach onto pyrite surface and are reduced to cuprous ions. This reduction is accompanied by the oxidation of surrounding sulfur leading to the formation of cuprous sulfide which enhances the adsorption of collector xanthate on pyrite surface and therefore increase pyrite flotation (Finkelstein, 1997; Weisener and Gerson, 2000a, b; Pecina et al., 2006; Chandra and Gerson, 2009).

A substantial effort has been made to separate pyrite from other base metal sulfide minerals in the last decades by using selective collectors and depressants. Pyrite depressants are usually inorganics such as cyanide, sulfite, hydroxide, lime and oxygen, or a combination of them (Janetski et al., 1977; Boulton et al., 2001; Khmeleva et al., 2003; Mu et al., 2016b). However, these reagents are restricted due to environmental concerns, high pH values and operational costs, long conditioning time and extensive surface oxidation to realize their depression on pyrite flotation. Some organic depressants such as starch, dextrin, CMC and PAM polymers are also applied to depress pyrite flotation in recent years. They act through the adsorption on pyrite surface by forming a hydrophilic layer which inhibits collector adsorption (Mu et al., 2016b). However, these organic depressants usually lack of selectivity and may cause depression of all minerals present at high dosages. Therefore, it is of significant importance to develop an economic, effective and eco-friendly depressant for pyrite flotation.

A recent study has shown that several non-toxic, biodegradable polymers (DP-1775, DP-1777 and DP-1778), modified from lignosulfonates, are promising pyrite depressants (Mu et al., 2014; Mu et al., 2016a). Lignosulfonates are derived from lignin through sulfite pulping processes (Kai et al., 2016). They are highly cross-linked with carboxylic groups, hydroxyl groups and some terminal sulfonic groups in their aliphatic side chains (Ouyang et al., 2006). It has shown that these three biopolymers could depress the flotation of chalcopyrite and

* Corresponding author.

E-mail address: yongjun.peng@uq.edu.au (Y. Peng).

copper-activated pyrite in single mineral systems at pH 9.0 with potassium amyl xanthate (PAX) as a collector (Mu et al., 2014; Mu et al., 2016a). The depression action of the biopolymers on the flotation of copper-activated pyrite has been thoroughly investigated (Mu et al., 2016a). It was found that these biopolymers deactivated pyrite by combining with surface activating Cu(I) ions and then accelerated the oxidation of Cu(I). They also inhibited the further activation of pyrite by combining with solution copper species (Mu et al., 2016a). Liu et al. (2009) studied the effect of lignosulfonate calcium (LSC) on pyrite flotation in the presence of chalcocopyrite. They found that LSC improved the copper grade at pH 9–10 with butyl xanthate as a collector. In this system, a galvanic interaction occurs between chalcocopyrite and pyrite and the role of LSC in the flotation is unknown.

In the current study, the effect of the three lignosulfonate-based biopolymers (DP-1775, DP-1777 and DP-1778) on the flotation of chalcocopyrite and pyrite in single and mixed mineral systems was investigated. The adsorption isotherms, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and electrochemical studies were employed to understand how these biopolymers modified the surface properties of chalcocopyrite and pyrite upon galvanic contact and then influenced the flotation performance. Compared with the previous study (Mu et al., 2016a), the objective of this study was to investigate the galvanic interaction between chalcocopyrite and pyrite in the presence of lignosulfonate-based biopolymers and its effect on their flotation behavior.

2. Materials and methods

2.1. Materials and reagents

2.1.1. Materials

Chalcocopyrite and pyrite were purchased from GEOdiscoveries, Australia. The chemical compositions of chalcocopyrite and pyrite, analysed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), are shown in Table 1. The analyses revealed 85 wt% purity for chalcocopyrite with quartz, lime and sphalerite as the main impurities and 97 wt% purity for pyrite with quartz as the main impurity. These samples were crushed using a roll crusher and then screened to collect the $-3.2 + 0.6$ mm particle size fraction. The processed samples were then sealed in polyethylene bags and stored in a fridge to avoid further oxidation.

2.1.2. Reagents

Potassium amyl xanthate (PAX) and NASCOL 442 were used as collector and frother, respectively, in flotation. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, AR grade) was used to introduce copper ions to activate pyrite. The pH was adjusted by the addition of AR grade NaOH solution. Brisbane tap water was used in grinding and flotation.

The biopolymers used in this study were DP-1775, DP-1777 and DP-1778 supplied from Pionera, Norway. Some physiochemical properties of these biopolymers are listed in Table 2. DP-1775 has the highest molecular weight and lowest content of anionic functional groups. DP-1777 has a lower molecular weight and a higher content of functional groups than DP-1775. DP-1778 has the lowest molecular weight among the three biopolymers with special counter-ion Ca^{2+} and a large proportion of carboxylic group (14.5 wt%).

Table 1
Chemical compositions of chalcocopyrite and pyrite samples.

Minerals	Species present (wt%)										
	Al_2O_3	Bi	CaO	Co	Cu	Fe	Pb	S	SiO_2	Ti	Zn
Chalcocopyrite	0.32	0.11	1.66	0.03	29.3	27.2	0.66	30.8	4.47	0.03	2.67
Pyrite	0.03	0.02	–	–	0.1	45.4	0.13	50.5	0.35	0.04	0.05

Table 2
Physiochemical properties of lignosulfonate-based biopolymers examined in this study.

Biopolymers	Counterion	Molecular weight		Main functional groups	
		M_w	M_n	Sulfonic/ mass%	Carboxylic/ mass%
DP-1775	Na^+	39,000	2400	6.1	8.7
DP-1777	Na^+	13,700	2000	8.5	9.5
DP-1778	Ca^{2+}	6000	800	4.8	14.5

All solutions used in this study were prepared with concentrated analytical grade reagents, diluted with deionized water and prepared just prior to the experiment.

2.2. Methods

2.2.1. Mineral grinding and flotation

Pyrite or chalcocopyrite single mineral (100 g) or their mixture (50 g each) was combined with 100 mL water and ground with 3.6 kg of stainless steel rods in a laboratory stainless steel rod mill for 6.5 min for pyrite, 5.2 min for chalcocopyrite and 4.1 min for the mixture to obtain a D_{80} of 106 μm . The particle size distributions of chalcocopyrite, pyrite and their mixture were measured by a Malvern sizer 2000 (Malvern, UK) and the results are shown in Fig. 1. The results show that the particle size distributions for the three samples were similar.

Flotation was performed at 1000 rpm in a 1.5 LJK flotation cell with an air flow rate of 6 dm^3/min . After transferring the grinding discharge to the flotation cell, NaOH solution was added to adjust the pH to 9.0, with a further addition of NaOH solution to maintain the pH at 9.0 during conditioning and flotation. Collector (120 g/t) and frother (120 g/t) were added and conditioned for 2 min each. Flotation froth was scraped every 10 s and four flotation concentrates were collected at time intervals of 1.0, 2.0, 3.0 and 4.0 min. When a biopolymer was used, it was added after pH adjustment but prior to collector addition. In the flotation of copper-activated pyrite, copper sulfate was added between pH adjustment and biopolymer addition. A 2 min conditioning period was allocated for both biopolymer and copper sulfate additions to allow sufficient time for the adsorption and copper activation to occur.

Flotation concentrate and tailing samples were dried, weighed and then assayed to determine elemental compositions. Cu and Fe concentrations were converted into mineral compositions using the following mathematical relations based on the stoichiometric compositions of chalcocopyrite (Cp) and pyrite (Py) (Owusu et al., 2014):

$$\%Cp = \%Cu \times (183.3/63.5) \quad (\text{Chalcocopyrite}) \quad (1)$$

$$\%Fe_{\text{pyrite}} = \%Fe_{\text{Total}} - \%Cu \times (55.8/63.5) \quad (\text{Iron present as pyrite}) \quad (2)$$

$$\%Py = \%Fe_{\text{pyrite}} \times (119.8/55.8) \quad (\text{Pyrite in sample}) \quad (3)$$

2.2.2. Adsorption isotherms

Pyrite or chalcocopyrite (1 g) was mechanically pulverized to $-38 \mu\text{m}$ just prior to the test. The pulverized sample was first conditioned in 50 mL deionized water with pre-adjusted pH 9.0 in a beaker agitated by a magnetic stirrer for 5 min. Then, biopolymer solution of known

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