



Electrochemistry aspects of pyrite in the presence of potassium amyl xanthate and a lignosulfonate-based biopolymer depressant



Yufan Mu^a, Yongjun Peng^{a,*}, Rolf Andreas 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

The variation in surface properties of pyrite in the presence of potassium amyl xanthate (PAX) and a lignosulfonate-based biopolymer depressant (DP-1775) was investigated by electrochemical techniques to explain the depression behavior of DP-1775 on pyrite flotation. Electrical impedance spectroscopy and cyclic voltammetry of pyrite electrode were conducted in the absence and presence of PAX and DP-1775, individually or in combination. It was found that in the absence of PAX, DP-1775 was discontinuously distributed on pyrite surface and progressively passivating the pyrite surface. In the presence of PAX, the pre-adsorbed DP-1775 reduced the extent of electrochemical oxidation of PAX. The indication of a lower degree of PAX oxidation can explain why DP-1775 acts as a depressant in pyrite flotation.

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1. Introduction

Pyrite (FeS_2), a common constituent of base metal ore deposits, is widely associated with other base metal sulfide minerals (e.g., chalcopyrite) and precious minerals (e.g., gold) [1–5]. It is usually perceived as a gangue mineral and removed from valuable minerals by flotation which exploits the difference in surface properties [6,7]. Depending on the details of a flotation operation pyrite may be floated or depressed [1,3]. Therefore, the flotation and depression of this mineral is of great significance. Alkyl xanthates, known to selectively interact with sulfides and render their surfaces hydrophobic, are the most extensively used collectors in the flotation of base metal sulfide minerals [3,4]. Pyrite responds strongly with xanthates (X^-) in acidic to neutral pH conditions and it is generally acknowledged that dixanthogen (X_2 , oxidation product of xanthate ions) is the main product responsible for pyrite flotation [3,8]. The formation of dixanthogen is an electrochemical process involving charge transfer between pyrite and xanthate accompanied by the reduction of ferric hydroxides species on pyrite surface formed by surface oxidation [8–10]. Due to the semi-conductive nature of pyrite, electrochemical techniques have been widely applied in studying pyrite oxidation [7] and the fundamental interaction of xanthate with pyrite [9]. The previous studies have showed that dixanthogen is

only formed on pyrite when the mineral surface reaches a potential higher than the X^-/X_2 equilibrium value [11]. The FTIR-ATR study conducted by Leppinen [12] showed that the adsorption of xanthate on pyrite had a maximum at pH 5.0.

Inorganic reagents, such as cyanide, pH modifiers and sulfide, are commonly used depressants in flotation to reject pyrite. The depression action of these reagents has also been investigated by electrochemical techniques. It has been found that cyanide interacts with pyrite forming insoluble iron cyanide surface species and then inhibiting the oxidation of xanthate to dixanthogen [4,10]. Increasing pH can facilitate extensive pyrite oxidation which may replace xanthate oxidation as the dominant anodic process at high pH [4]. The application of sulfide in solutions brings in an anodic process (oxidation of sulfide ions), the oxidation potential of which is much lower than that for oxidation of xanthate to dixanthogen, thus the oxidation of xanthate is prevented [4]. However, the applications of these reagents all have some drawbacks. For example, cyanide is highly toxic and can be poisonous to humans and animals in excessive quantities. When it is deposited in tailings, it may also have the potential to contaminate the surrounding water sources [13]. High pH adjusted by lime addition can cause the erosion of equipment and difficulties in cleaning the machine. The use of sulfide is restricted by the relative high price of the reagent itself and the cost in its storage and operation. Because of the limitation of these methods, much attention has been drawn to develop an alternative, environmentally friendly reagent to depress pyrite.

* Corresponding author. Tel.: +61 7 336 57156.

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

In the previous study, it has been proved that a type of biopolymers, modified from lignosulfonates, are promising pyrite depressants [14]. These biopolymers are non-toxic and produced from renewable cellulosic biomass. They are highly cross-linked, containing both hydrophilic groups, such as sulfonic and carboxylic acid groups in addition to various hydroxyl groups, all grafted to a hydrophobic carbon skeleton [15]. In the previous study, the depressing effect of three lignosulfonate-based biopolymers (DP-1775, DP-1777 and DP-1778) was investigated and it was found that they depressed both the un-activated pyrite (at pH 5.0) and copper-activated pyrite (at pH 9.0) in flotation [14]. The pyrite recovery decreased with the dosage of the three biopolymers for both cases. For example, in the un-activated pyrite flotation at pH 5.0, the pyrite recovery decreased from 81.4% in the absence of DP-1775 to 39.8% and 21.0% in the presence of 300 g t⁻¹ and 500 g t⁻¹ DP-1775, respectively [14]. Flotation exploits the difference in surface wettability. The depression of pyrite flotation by the biopolymers indicates that the biopolymers make the pyrite surface more hydrophilic with a smaller contact angle. In another study, it was found that lignosulfonate calcium (LSC) depressed pyrite flotation in a certain pH range and had little effect on chalcopyrite flotation [16]. The depression mechanism was attributed to the competitive adsorption of LSC and xanthate on pyrite surface. It was assumed that LSC was adsorbed on pyrite surface through the interaction between hydroxylated metallic sites of pyrite and functional groups of the lignosulfonate calcium. This adsorption may inhibit the adsorption of collector, turn the pyrite surface hydrophilic and then depress pyrite in a flotation process [14,16]. However, this assumption has not been confirmed. Further, oxidation plays an important role in xanthate adsorption on pyrite. The depressing role of lignosulfonate-based biopolymers on pyrite may be through the interference of this oxidation. This aspect has not been studied but is a subject of this study.

In this study, electrical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were conducted to investigate the influence of lignosulfonate-based biopolymers on the electrochemical activity of xanthate oxidation on pyrite surface. The EIS is a very sensitive analytical method with high accuracy which allows in-situ detection of the formation of surface layers on the electrode which is well correlated with the electrode capacitance [10,17]. The measured impedance data can also reflect the kinetics of surface electrochemical reactions in-situ with a minimum of surface modification [10]. This study was conducted in an acidic pH condition where dixanthogen is the dominant product of xanthate oxidation responsible for pyrite flotation. The study on the depression of copper-activated pyrite by lignosulfonate-based biopolymers in alkaline conditions will be reported separately.

2. Material and experimental

2.1. Material

Large specimens of pyrite were obtained through GEO discoveries, Australia. The elemental composition of the pyrite sample analyzed by ICP-MS was shown in Table 1. The pyrite sample was mainly composed of Fe and S with trace amounts of other elements and the purity was 96%. The specimen was cut to rectangular dimensions of approximately 5 × 5 × 10 mm. A copper

Table 1
Elemental composition of the pyrite sample.

Mineral	Species present (wt.%)								
	Fe	S	Cu	Bi	Pb	Al ₂ O ₃	SiO ₂	Ti	Zn
Pyrite	45.40	50.50	0.10	0.02	0.13	0.03	0.35	0.04	0.05

wire was connected to one of the 5 × 5 mm faces. Then the electrode was mounted in a glass tube with an electrochemically inert epoxy resin (West System 105 Epoxy Resin / 207Hardener) leaving only one face of the pyrite exposed.

The collector, potassium amyl xanthate (PAX), was yellowish pellets and provided by the Orica Australia Pty Ltd. The lignosulfonate-based biopolymers were brown powder and supplied from Pionera, Norway. DP-1775 was chosen to perform the analysis in this study. The molecular weight of DP-1775 was 39,000 and it had 6.1 wt% sulfonic group and 8.7 wt% carboxylic group.

0.1 M potassium dihydrogen orthophosphate (KH₂PO₄) buffer solution was prepared with deionized water to maintain pH at 5.0.

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

2.2. Experimental

Electrochemical studies were performed with a Voltalab-VM4 equipped from Radiometer Analytical SAS, France, and a conventional three electrode electrochemical cell. A double-wall glass reactor was used as the electrochemical cell with an effective volume of 200 mL. An Ag/AgCl electrode with KCl as electrolyte, a platinum plate electrode and a pyrite electrode were used as reference, counter and working electrodes, respectively. Potentials were measured against an Ag/AgCl reference electrode filled with 3 M KCl which has a potential of +220 mV against a standard hydrogen electrode (SHE) [18].

The experiments were conducted in air. Before each test, the surface of pyrite electrode was renewed by wet polishing using 1200 grit silicon carbide paper and rinsed with deionized water for several times before it being inserted into solution for EIS and CV studies. One open circuit potential (OCP) sweep was conducted before each type of electrochemical experiments. Measurements were conducted when the OCP was stabilized (after approximately 5 min). The impedance spectra were obtained at the OCP by applying a sinusoidal excitation signal of 10 mV in the frequency range from 10 mHz to 10 kHz. The EIS diagram was displayed as Bode and Nyquist plots and analyzed using the ZView software. In CV studies, cycles were performed from the OCP to 600 mV (positive-going potential scan), then to -800 mV (negative-going potential scan) and back to the OCP at a scan velocity of 20 mV s⁻¹. Three cycles were scanned for each test and the third cycle was adopted as the cyclic voltammogram. The effect of different scan rates on electrochemical behavior of pyrite at pH 5.0 was also examined. It was found that the current density for each oxidation/reduction reaction peak increased with the scan rate, but the variation in scan rate did not introduce a new peak nor shift the peaks to a more anodic/cathodic direction.

Experiments were performed in the absence and presence of PAX and DP-1775, individually and in combination. When PAX and DP-1775 were both present, DP-1775 was added prior to PAX following the flotation procedure [14]. The pyrite electrode was conditioned for 15 min in electrolyte solutions after the addition of each reagent to reach the adsorption equilibrium before the electrochemical tests.

3. Results

3.1. Characterization of pyrite oxidation and xanthate adsorption

The electrochemical properties of pyrite electrode in the absence and presence of PAX without DP-1775 addition were first investigated. The measured impedance of pyrite electrode in the absence and presence of 1 × 10⁻³ M PAX at pH 5.0 is shown in Fig. 1

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