



# Electrochemical behaviour of chalcopyrite in the absence and presence of dithiophosphate

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## Abstract

Electrochemical behaviour of chalcopyrite was investigated in collectorless condition and in the presence of dithiophosphate (DTP), which is a selective collector for chalcopyrite, by cyclic voltammetry (CV) study. Diffuse Reflectance Infrared Fourier Transformation (DRIFT) spectroscopy was employed to identify surface species of DTP at chalcopyrite surface. CV tests established the certain degree of irreversibility in the absence of DTP possibly due to preferential dissolution of iron ions in slightly acid solution, and irreversible surface coverage by iron hydroxides in neutral and alkaline solutions.  $\text{Cu(DTP)}+(\text{DTP})_2$  formation as major DTP-compounds on chalcopyrite in slightly acid and neutral conditions was estimated from DRIFT spectroscopy study. However, heavy surface oxidation inhibited the identification of collector species in alkaline condition.

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## 1. Introduction

Chalcopyrite ( $\text{CuFeS}_2$ ) is the most abundant copper sulphide mineral and is the major commercial source of copper. Electrochemistry of collectorless

and xanthate induced flotation of chalcopyrite, and composition of the surface layer formed on chalcopyrite have been studied extensively (Bozkurt et al., 1998; Buckley et al., 1985; Cases et al., 1997; Chander, 1991; Ekmekçi, 1995; Leppinen et al., 1988; Persson and Malmensten, 1991; Woods et al., 1995; Zhang et al., 1993; etc.). However, in most of plant practice of chalcopyrite flotation, more selective collectors, like dithiophosphates (DTPs), are generally used in place of xanthates. DTP generally is thought of being less powerful and kinetically slower in the

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recovery of sulphide minerals than xanthates. On the other hand, DTP generally shows better iron sulphide rejection capability than do the xanthates (Ackerman et al., 1987; Fuerstenau et al., 1971). Therefore, selective collectors, like DTP, are generally used in conjunction with xanthate type of collectors in order to maintain high recovery (Adkins and Pearse, 1992; Bradshaw, 1997; Crozier, 1992; Wakamatsu and Numata, 1979).

The redox potentials and the electrochemical interactions of DTP with platinum, copper and chalcocite have been studied extensively (Buckley and Woods, 1992; Chander and Fuerstenau, 1974; Fuerstenau et al., 1971; Goold and Finkelstein, 1972; Kakovskii et al., 1959; Solozhenkin and Koptsia, 1968; Woods et al., 1993). In these reports, the interaction of DTP with the sulphide minerals is considered similar to that of xanthate. Cu(I)-DTP is reported as the collector species on the surface of copper-containing minerals covellite, chalcocite and chalcopyrite. However, the results of voltammetry experiments with DTP and chalcocite have shown a prewave formation at potentials prior to formation of Cu(I)-DTP (Buckley and Woods, 1992; Chander and Fuerstenau, 1974). This prewave has been considered to arise from the adsorption of DTP which renders the mineral hydrophobic and induces flotation. However, DTP adsorption on chalcopyrite surface is expected to be different due to heterogeneity of the chalcopyrite surface, consisting of unoxidised chalcopyrite, iron-deficient chalcopyrite and iron hydroxide (Grano et al., 1997). Therefore, pH and Eh of the solution are the critical parameters determining the surface species of chalcopyrite and the interaction with DTP. There are a few reports in the literature on the chalcopyrite–DTP interactions. While the results of Diffuse Reflectance Infrared Fourier Transformation (DRIFT) spectroscopy studies reported by Valli et al. (1994) indicated Cu-DTP formation at chalcopyrite surface, Grano et al. (1997) emphasised the influence of surface oxidation of chalcopyrite on the adsorption of DTP. Formation of iron oxyhydroxide at chalcopyrite surface has been found to inhibit adsorption of DTP and depress the flotation. No direct evidence of Cu(I)-DTP formation has been reported by Grano et al. (1997).

The aim of this paper is, therefore, to contribute to the understanding of the reaction mechanisms

between chalcopyrite and DTP at different pH values by cyclic voltammetry (CV) and DRIFT spectroscopy techniques. Cyclic voltammetry experiments have been carried out at chalcopyrite electrode in the absence and presence of DTP in solutions of different pH values (4.67, 6.97, 9.2 and 11). DRIFT spectroscopy was employed for identification of surface species of DTP at chalcopyrite surface.

## 2. Materials and methods

### 2.1. Materials and reagents

High-purity chalcopyrite samples (>96% CuFeS<sub>2</sub>) were obtained from Artvin–Murgul deposit, Turkey. Experiments were made in pH 4.67, pH 6.97, pH 9.2 and pH 11 buffer solutions (Table 1). All the chemicals used for buffer preparation were of analytical grade. Buffer solutions were used in order to prevent the changes that might occur in the pH of the solution as a result of the reactions that might take place between the mineral and the aqueous solution (Gardner and Woods, 1979; Garrels and Christ, 1965). Buffer solution was deoxygenated with intensive bubbling of high-purity nitrogen gas (99.998%) before each run for 15 min to eliminate the effects of dissolved oxygen on experimental results. During experimentation, the flow of nitrogen was stopped and experimental condition was completely sealed to prevent the diffusion of atmospheric oxygen into the cell. Potassium diethyl dithiophosphate (DTP) with 97% purity was obtained from Aldrich Chem.

### 2.2. Electrochemical measurements

A conventional three-electrode system was used for electrochemical measurements in which a saturated calomel electrode, a platinum foil electrode with 1 cm<sup>2</sup> area and a mineral electrode were used as

Table 1  
Composition of buffer solutions employed

pH	Composition
4.67	0.5 M CH <sub>3</sub> COOH+0.5 M CH <sub>3</sub> COONa
6.97	0.025 M KH <sub>2</sub> PO <sub>4</sub> +0.025 M Na <sub>2</sub> HPO <sub>4</sub>
9.2	0.05 M Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>
11	0.025 M NaHCO <sub>3</sub> +0.023 M NaOH

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