

Synergistic Effect of Diethylenetriamine and Sodium Metabisulphite on Xanthate-Induced Flotation of Cu-activated Pyrite*

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Abstract

The present study investigates the effect of diethylenetriamine (DETA) and sodium metabisulfite (SMBS) on Cu-activated pyrite flotation induced by xanthate using X-ray spectroscopy (XPS) under aerated and non-aerated conditions. The study showed that DETA is more effective for pyrite depression than SMBS on an individual basis; however, high dosages of DETA (500 g/t) are required. Oxidation (aeration of the flotation pulp) of Cu-activated pyrite induced by xanthate before 500 g/t DETA addition has a greater effect on the surface chemistry of the pyrite particles and subsequently increased pyrite depression. The above condition decreased pyrite recovery drastically from 92% to 12%. The XPS analysis showed that the significant pyrite depression observed in the presence of DETA than SMBS, was due to significant removal of adsorbed surface Cu and the formation of Cu(I)-DETA complex on pyrite surface.

Keywords: Pyrite, DETA, SMBS, Flotation, Surface Analysis

1 Introduction

There is a major challenge in selective flotation of copper sulphides (e.g. chalcopyrite, etc.) from pyrite due to "inadvertent" activation of pyrite by dissolved copper ions and its inherent mineralogical association with pyrite as fine complex intergrowth. This promotes pyrite interaction with the collector and therefore improved flotation. The inadvertent Cu activation and flotation of pyrite adversely affect concentrate grades.

Therefore, in order to improve Cu flotation, most processing plants resort to using depression strategies (e.g. aeration, pH, Eh, cyanide, sulphur-oxy depressants) to minimise pyrite flotation. The mechanisms of depressing sulphide minerals using these depressants involve the formation of ferric oxy-hydroxide species, decomposition of xanthate and oxygen consumption from the pulp (Mistra *et al.*, 1985; Yamamoto, 1980; Miller, 1970; Mermillod-Blondin *et al.*, 2005). As an alternative to these depressants, diethylenetriamine (DETA) has been used extensively in the selective depression of pyrrhotite from pentlandite in Ni-Cu ore flotation. The role of DETA is to remove activated Cu from pyrrhotite surface and hence decrease its interaction with xanthate (Kelebek *et al.*, 1995). Despite the numerous studies on DETA application in Ni-Cu ore flotation, little work has been done on its use in selective flotation of copper sulphides from pyrite (Sui *et al.*, 1998; Zanin and Farrokhpay, 2011; Agorhom *et al.*, 2014).

In this study, the effect of DETA in combination with aeration and sodium metabisulphite (SMBS) on Cu-activated pyrite flotation was investigated. Surface (X-ray spectroscopic, XPS) was used to understand the mechanisms of DETA and SMBS on Cu-activated pyrite depression.

2 Resources and Methods Used

2.1 Ore and Reagents

A high-grade pyrite sample (>98% Py) was obtained from a copper mine in Peru. The chemical composition of the pyrite sample was analysed by inductively coupled plasma mass spectroscopy (ICP-MS). The pyrite sample contained 44.9% Fe, 53.5% S, 0.13% Cu, 0.44% Ca, 0.69% Si and traces of Pb, Mg, Mn and Zn.

Potassium amyl xanthate (PAX) and methyl isobutyl carbinol (MIBC) were used as collector and frother as supplied by Orica Mining and Cytec Chemicals, respectively. Copper sulphate was used as an activator for pyrite during conditioning time. Air, DETA and SMBS were used as depressants. DETA and SMBS were supplied by Sigma-Aldrich and Orica Chemicals, respectively. Each solution was prepared as 1% solution strength before used in the flotation process.

2.2 Methods

2.2.1 Flotation

The experiment was carried out in a 0.5 dm³ Gliwice mechanically agitated flotation cell.

Ceramic agate mortar and pestle were used to grind the pyrite sample to produce particles of $P_{80} = 38 \mu\text{m}$. The particle size distribution of the feed pyrite was determined using the Malvern MasterSizer (Malvern Instrument Ltd, UK). The ground products were divided into 50 g each using micro-riffle splitter, kept under a desiccator to remove all moisture content before storing in a freezer below -4°C to minimise surface oxidation. After grinding, 50 g of the sample was pulped in the flotation cell and agitated for 5 min before reagent conditioning. In these tests, the effect of depressants, DETA and SMBS, at different dosages under aerated and non-aerated conditions, was examined at pH 10 (Fig.1). The experimental procedure is shown schematically in Fig.1.

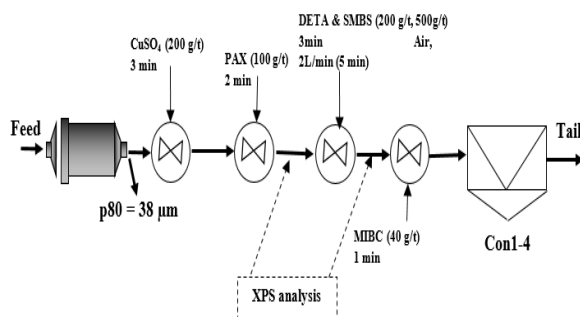


Fig.1. Schematic Representation of the Experimental Procedure for Studying the Effect of DETA and Smbs in Single Pyrite Flotation under Aerated and Non-Aerated Conditions

2.2.2 Surface Analysis (X-ray Spectroscopy – XPS)

Surface analysis using X-ray spectroscopy (XPS) was performed to understand the mechanism of DETA and SMBS on Cu-activated pyrite depression (as indicated in Fig.1). The XPS measurements were performed using a Kratos Axis-Ultra X-ray photoelectron spectrometer equipped with a delay-line detector. A monochromatic Al $K\alpha$ X-ray source was used, operating at $\sim 300\text{W}$ and the spectrometer analysis area was $\sim 0.3 \times 0.7 \text{ mm}$. The broad scan survey and high-resolution spectral data were processed using CasaXPS version 2.3.5. High-resolution scans were also collected of the C 1s, O 1s, Fe 2p, Cu 2p and S 2p photoemission lines.

3 Results and Discussion

3.1 Flotation Recovery - Effect of DETA and SMBS

The depression effect of DETA and SMBS on xanthate-induced flotation of Cu-activated pyrite was studied under aerated and non-aerated

conditions; aerated shown in Agorhom *et al.*, 2014. The results are presented in Fig.2.

In the absence of air, DETA and SMBS, higher pyrite recovery was achieved (i.e., 92 wt.%). However, addition of 200 g/t and 500 g/t of DETA and SMBS decreased pyrite recovery from 92 wt.% to 44 wt.% and 33 wt.% for DETA and 61 wt.% and 39 wt.% for SMBS, respectively (Fig. 2). The DETA depressed pyrite to a large extent than SMBS at all concentrations. The significant pyrite depression at 500 g/t DETA suggests that DETA can depress the flotation of Cu-activated pyrite, however, a high dosage of DETA is required (Fig. 2).

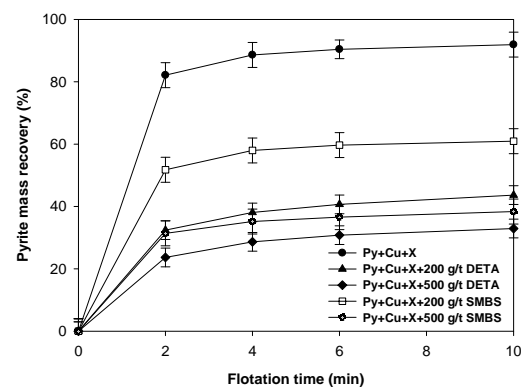


Fig. 2. Effect of DETA and SMBS under non-Aerated Condition on the Flotation of Cu-Activated Pyrite induced by Xanthate (PAX) at pH 10. [CuSO₄] = 200 g/t, [PAX] = 100 g/t, [DETA] and [SMBS] = 200 g/t & 500 g/t and Aeration Rate was 2 L/min for 5 min

The depression of Cu-activated pyrite in the presence of DETA and SMBS using xanthate was described using the Klimpel flotation model (Eqn.1). This is a modified form of a first order rate process.

$$R = R_{max}(1 - e^{-kt}) \quad (1)$$

Differentiating with respect to t , the slope of the curve (i.e. R vs t) is given by:

$$\frac{dR}{dt} = R_{max}k(e^{-kt}) \quad (2)$$

At $t = 0$,

$$\frac{dR}{dt} = R_{max}k \quad (3)$$

Thus, the RHS of eq.3 gives the rate of change of R and is represented as k_0 .

The reduction or rejection of pyrite in the presence of DETA and SMBS correlated well with the rate

of change of R , k_0 under experimental conditions (Table 1). The rate of change of R (k_0) for 200 g/t and 500 g/t of SMBS decreased from 1.06 min^{-1} to 0.58 min^{-1} and 0.33 min^{-1} , compared with k_0 for DETA which decreased from 1.06 min^{-1} to 0.29 min^{-1} and 0.20 min^{-1} , respectively.

Table 1 The Initial Rate Constants of Cu-Activated Pyrite after Conditioning and Flotation with DETA at Different Dosages and Conditions

Rate constant	Xanthate	SMBS (g/t)		DETA (g/t)	
		200	500	200	500
k_0	1.06	0.58	0.33	0.29	0.20
k	1.16	0.97	0.89	0.69	0.64

Generally, addition of sulphur-oxy species in the form of sulphite ions depressed sulphide minerals through the formation of metal sulphite hydrophilic species, decomposition of xanthate and the consumption of oxygen in solution (reduction in Eh) (Yamamoto, 1980; Miller, 1970; Misra *et al.*, 1985). The reduction of oxygen in solution hampered the formation of dixanthogen and collector adsorption (Illyuvieva *et al.*, 1984). SMBS has similar properties to sulphur dioxide and also shows mild acidic character. In alkaline medium (Ca^{2+}), SMBS causes precipitation reaction to occur. This can lead to the precipitation of $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} ions on the surface of pyrite as hydrophilic species. This may be responsible for the low recovery of pyrite in the presence of SMBS (Kelebek and Tukul, 1999).

Comparing DETA and SMBS on individual basis showed that DETA is more effective in depressing significant pyrite than SMBS. This may be due to the combined effect of DETA as a deactivation agent and its ability to adsorb onto the active sites of pyrite to compete with xanthate.

3.2 Flotation Recovery – Synergistic Effect of DETA and SMBS

Synergistic effect on pyrite depression was carried out with 500 g/t DETA and 500 g/t SMBS under aerated and non-aerated conditions. The results in Fig. 3 showed that without aeration of the pulp, synergistic effect of DETA and SMBS on pyrite was not significant (only 50 wt.% pyrite depression) and was even lower than when 500 g/t DETA alone was used. However, aeration of the pulp before DETA and SMBS additions resulted in total rejection of pyrite as shown in Fig. 3 (i.e. from 91 wt.% to 7 wt.%). The rate of change of k_0 of pyrite under this condition was completely negligible (0.01 min^{-1}) and this could be responsible for the lower pyrite recovery.

Also, aeration of the pulp before DETA addition further decreased pyrite recovery to 12.2% and 28.1% for 500 g/t and 200 g/t DETA, respectively (Fi. 3) (Agorhom *et al.*, 2014). The result indicates that DETA is more effective for depressing oxidised pyrite than non-oxidised pyrite. When Cu^{2+} comes into contact with pyrite, it adsorbs and reduces to Cu(I) to form sulphide of Cu, Cu(I)-S species (Voigt *et al.*, 1994; von Oertzen *et al.*, 2007). This promotes collector (xanthate) adsorption onto pyrite surface. Aeration of the pulp oxidises the pyrite surface to transform the activation product to oxide/hydroxide species, which are more soluble in DETA. This facilitates the Cu removal from pyrite surface and its subsequent depression in the presence of DETA.

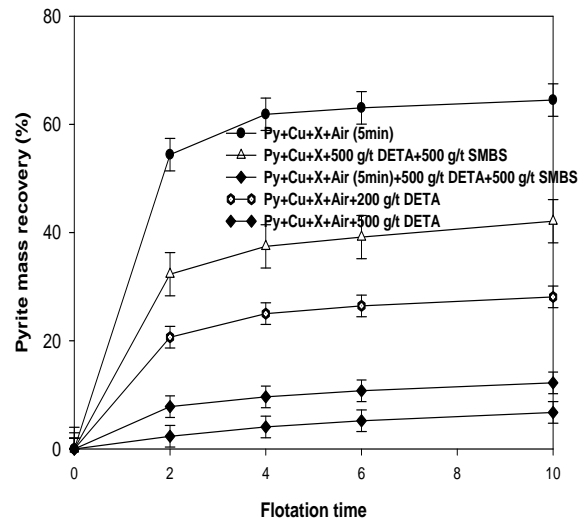


Fig. 3. Combined effect of DETA and SMBS (Aerated and Non-Aerated Condition) on Depression of Cu-Activated Pyrite induced by Xanthate (PAX) at pH 10. [CuSO₄]=200 g/t, [PAX] =100 g/t, [DETA] and [SMBS] =200 g/t & 500 g/t and Aeration Rate was 2 L/min for 5 min

3.3 Surface Chemical Effect on Cu-Activated Pyrite Flotation

The results in Fig. 4 show the XPS analysis of Cu-activated pyrite induced by xanthate before and after conditioning with DETA and SBMS for 5 min. The atomic percent of the elements were calculated from the intensity of the following signals: S (2p), Fe (2p), Cu (2p), O (1s) and C (1s). After contacting DETA, SBMS and DETA+SBMS with Cu-activated pyrite, it was observed that the amount of Cu on pyrite surface decreased considerably.

About 75% of the Cu was removed from pyrite surface in the presence of DETA than SMBS and DETA+SMBS mixture. This suggests that DETA is an effective Cu deactivator than SMBS. The surface exposure of N on pyrite subsequently increases after contacting with DETA. This shows that DETA removes surface Cu and at the same time binds with Cu sites on pyrite in a Cu(I)-DETA form.

Kelebek and Tukul (1999) observed that in a SMBS-TETA system, there is the possibility of adsorption of Ca^{2+} or $\text{Ca}(\text{OH})^+$ ions onto the negatively charged pyrrhotite surface through electrostatic mechanism. Also, the use of lime in the presence of unreacted SO_3^{2-} could result in precipitation of CaSO_3 . The use of SMBS in combination with DETA is expected to have a similar depression effect on pyrite as SMBS-TETA system (on pyrrhotite depression).

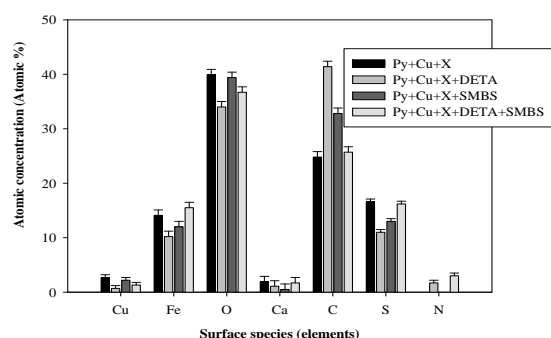


Fig. 4 The Surface Species present on Cu-Activated Pyrite induced by Xanthate in the presence of DETA, SMBS and a Mixture of DETA plus SMBS

4 Conclusions

The flotation (Fig. 2-3) and spectroscopic (Fig. 4) results clearly show that DETA is a more effective depressant for pyrite than SMBS under the studied experimental conditions. It is well known that DETA is an excellent complexing agent capable of forming complexes with Cu^{2+} , Ni^{2+} , Co^{2+} and Fe^{2+} ions but not Fe^{3+} (Yoon *et al.*, 1995). It was found that two mechanisms play a major role in pyrite depression using DETA than SMBS:

- (i) Removal of Cu in either solution or adsorbed state from pyrite surface - this slows down collector interaction with pyrite, hence its depression.
- (ii) Formation of Cu(I)-DETA complex which competes with xanthate for adsorption onto the active sites of pyrite and hence reduces pyrite surface hydrophobicity.

These findings are consistent with other studies in the literature (Sui *et al.*, 1998), which showed that DETA can deactivate Pb contaminated pyrite and later adsorb onto its surface. However, this is opposite to the depression mechanism of pyrrhotite observed in the presence of DETA (Yoon *et al.*, 1995). The spectroscopic results confirmed the flotation results and clearly show why DETA was more effective for depressing pyrite than SMBS.

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