Physicochemical Problems of Mineral Processing

Comparison of anionic, cationic and amphoteric collectors used in pyrite flotation

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Abstract: In this study, flotation tests were conducted with purified pyrite and ore samples. The collectors employed were anionic and cationic type such as potassium ethlyl-amyl xanthate, Tomamine M73 and Resanol Bal. According to the flotation tests, it was found that pyrite floated at low pH and depressed at high pH values with xanthates. On the other hand, in the case of cationic collectors which are Tomamine M73 (alkyl ether amine, an amphoteric surfactant) and Resanol Bal (N-3-tridecyloxy propyl 1-3 diamine, branched acetate) pyrite floated at high pH values. It was shown that amine type collectors could be efficient to selectively float pyrite from chalcopyrite at alkali pH ranges in the case of ore samples.

1. Introduction

Pyrite in many cases is a kind of undesired mineral mine yet it is an important input for sulphuric acid production. Pyrite is often associated with other valuable metal sulphides such as chalcopyrite, galena, sphalerite, etc. Feasible extraction of those valuable minerals demands selective depression of pyrite during flotation. Thiol type collectors are almost unique used in the flotation of sulphide ores. When separating chalcopyrite from pyrite, chalcopyrite is always floated first and then pyrite is enriched in industrial applications. Short chain xanthates are often employed in chalcopyrite flotation and lime is used the pH regulator to depress iron sulphides, if required, cyanide may be used as the secondary depressant.

One of the very important characteristics of pyrite is that at an alkaline pH it is well depressed and at an acidic pH the floatability improves significantly. Depressants other than lime such as organic compounds, sulphates and cyanide may be quite effective. Successful pyrite depression is very much dependent on the ability of the pyrite to oxidize rapidly. As a result of oxidation, iron hydroxide $Fe(OH)_3$ is formed on the surface of the pyrite, which increases hydration and reduces adsorption of the collector (Fornasiero and Ralston, 1992; Bulatoviç, 2007; Altun et al., 2010).

Xanthates and dithiophosphates are thiol type collectors having been widely used in sulphide flotation. Xanthate is the most commonly employed collector in sulphide flotation and it reverses the positive surface charge of pyrite in acid pH pulps, and gets it more negative at neutral and alkaline pH range as the xanthate concentration increases (Fuerstenau et al., 1968; Jiang et al., 1998; Bulut et al., 2004; López Valdivieso et al., 2005; Blondin et al., 2005). It is generally accepted that xanthates render pyrite hydrophobic adsorbing as dixanthogen and, in the meantime, the loss of positive charge associates with surface ferric hydroxide formation on the surface resulting in an increase in the negativity of the zeta potential of pyrite. Some authors have also suggested that various ferric xanthate compounds might form during pyrite flotation. Xanthate has been proposed to adsorb on pyrite chemically in acidic condition as a compound of xanthate and dixanthogen.

Amines are cationic surfactants consisting of an organic compound, which constitutes the hydrophobic part of the collector, and a hydrophilic, polar group based on pentavalent nitrogen (Atak,

2017; Bulatoviç, 2007). The adsorption mechanism of amine type collectors is proposed to be through columbic forces (Smith and Akhtar, 1976) between the polar group of the collector and the charged electrical double layer on the mineral surface. In general, the amines are characterized by low selectivity and mainly used for oxide minerals (Smith and Akhtar, 1976; Filippova et al., 2014) and silicate mineral (Pearse, 2005; Weng et al., 2013), and not for sulphide minerals. Studies on the flotation of sulphide minerals with amines started more than 70 years ago [Kellogg et al., 1946). However, because of the success of thiol type collectors, amines have not been paid much attention. Few studies have been conducted in order to compare the flotation response of amine and xanthate when used as collectors for sulphides. A different pH dependency was noted by Sirkeci (2000; a, b) who conducted flotation experiments on pyrite using HTA (hexyl thioethylamine hydrochloride; i.e. a derivative of a primary amine). Up to pH 9.3, flotation of pyrite was observed to be poor, almost lacking, while the maximum flotation recovery was maintained between pH 10.5 and 11.5. Good relationship was found between flotation recoveries and adsorption measurements as a function of pH, whereas no correlation was found between surface charge (zeta potential) and flotation behaviour.

A comparative study of the adsorption mechanisms of an amine thioacetate (Armac C) and the well-known amyl xanthate on pyrite was studied (Kongolo et al., 2004). Armac C gave the best results for cyanide bearing tailings compared with KAX even after washing and sulphide activation.

Nanthakumar and Kelebek (2007) conducted flotation tests on pyrrhotite using EDTA (ethylene diamine terraacetic acid), TETA (tri ethylene tetra amine) and KAX at pH 9.2. The results showed that the flotation of pyrrhotite was improved on using EDTA, compared to KAX and TETA.

In the production of ground calcium carbonate for the paper industry, any colouring contaminants such as pyrrhotite and pyrite, were removed using flotation method at alkaline pH with the use of amine collectors (Bunkholt and Kleiv, 2015).

Conventional flotation of pyrite is achieved employing xanthate type collectors at slightly acidic pH medium. In the selective separation of chalcopyrite from pyrite, chalcopyrite is floated first at very high alkaline conditions and then pyrite is floated after pH is regulated to acidic pH values. In this study, amine type collectors were used to eliminate the low pH requirement stage, which causes a lot of acid consumption.

2. Materials and method

2.1. Materials

In this study a purified pyrite sample and a pyrite containing chalcopyrite ore were used in the tests. Pyrite samples were collected from open pit Murgul mine and handpicked to obtain the purified sample. The chalcopyrite bearing ore sample was taken from Siirt-Madenköy deposit, in Turkey. Chemical analyses of the test samples are given in Table 1 and Table 2.

Table 1. Chemical analysis of the purified pyrite sample

Element	%
Fe	45.07
S	51.75
Si	0.18
Cu	0.12
Al	0.11
Ca	0.04
Zn	0.02
Pb	0.03

Table 2. Chemical analysis of the Siirt-Madenköy ore

Element	Fe	Cu	Al	Zn	Pb	SiO_2
(%)	40.29	2.95	0.75	0.21	0.03	20.22

According to the mineralogical analyses, the ore sample contains chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) as the major sulphide minerals and to a lesser degree sphalerite (ZnS), galena (PbS), hematite (Fe_2O_3), limonite ($FeO(OH) \cdot nH_2O$), calcite ($CaCO_3$) and quartz (SiO_2). The chalcopyrite phase was seen to be locked with cataclastic pyrite structure and to fill in the fractures of pyrite as a matrix material as well as it showed a colloidal structure within pyrite. Furthermore, chalcopyrite particles between 5 and 70 μm were seen to scatter in gangue minerals (Ceylan et al., 2014).

In this study, the effect of different collectors have been examined, they are;

Potassium amyl xanthate (KAX), potassium ethyl xanthate (KEX) are thiol type conventional collectors for sulfide flotation.

Resonal Bal; N-3-tridecyloxy propyl-1,3 diamine branched acetate, is a simple diamine with the formula $(CH_2)_3(NH_2)_2$.

Tomamine M73, alkyl ether amine, is an amphoteric surfactant for use in alkaline and acidic cleaner circuits (Rodrigues et al., 2013).

Aerophine 3418A is an aqueous solution of sodium diisobutyldithiophosphinate $[(C_4H_9)2PH]$. Aerophine 3418A has been widely used in the flotation of copper and lead-sulfide minerals, particularly they associate in complex sulfide ores containing sphalerite mineralization, and ores with high levels of pyrite and/or pyrrhotite (Cytec, 2002; Pecina –Trevio et al., 2003).

2.2. Method

Fundamental flotation experiments were carried out in a microflotation cell using 1 g of -105 +44 μm purified pyrite sample, methyl isobutyl carbinol (MIBC) as a frother and nitrogen gas for bubble generation. An agate mortar and pestle was used for grinding fresh sample prior to each test. All tests were conducted using four different collectors at a constant collector concentration of 1×10^{-4} M. The pH value of the slurry was modified using HCl and NaOH. The floating and non-floating fractions were dewatered, dried and weighed for assessment. Double distilled water was used in micro flotation tests and zeta potential measurements, whereas bench flotation tests were conducted with tap water.

Zeta potential of pyrite particles freshly ground below 44 μm was measured using a Zeta- Meter 3.0+ equipment. The electrokinetic potential of pyrite particles was investigated with and without collector addition at different pH values.

In flotation tests crushed ore was wet ground by ball milling prior to each test. Table 3 presents the size distribution of the flotation sample.

Table 3. Size distribution of the flotation sample

Size (μm)	Weight (%)	Cumulative Passing (%)
+106	0.2	100.0
-106+75	1.8	99.8
-75+53	8.8	98.0
-53+38	17.4	89.2
-38	71.8	71.8
Total	100.0	

In the Siirt-Madenköy Copper Plant, Aerophine 3418 A, MIBC, sodium silicate and lime are used as flotation reagents. Pyrite together with silicates is discharged as tailings. In the bench flotation experiments test conditions were adopted in accordance with the conditions the plant, i.e., the type of reagents, pH etc. In the plant operation pyrite is not recovered as a by-product. In this study, the flotation of pyrite has also been studied comparing various collectors. In the investigation bench scale flotation tests were carried out to confirm microflotation tests.

The bench scale flotation experiments were performed using a 2.5 litre mechanically agitated flotation cell. Each experiment was conducted using 500 g of the chalcopyrite ore sample. The slurry was agitated for 5 mins in the cell while adjusting the pH to the desired level using lime.   Following this initial conditioning stage, the collector Aerophine 3418 A for chalcopyrite was added and additional

5 min conditioning was given. The collector and frother dosages were 50 and 20 g/ton of ore respectively in the copper flotation circuit where the pH was 12 impeller speed was 1500 rpm. Following Chalcopyrite pyrite flotation was continued at pH 11. In this stage, four different collectors were tested adding 150 g/ton of collector dosage. The flowsheet of batch flotation tests is given in Fig. 1.
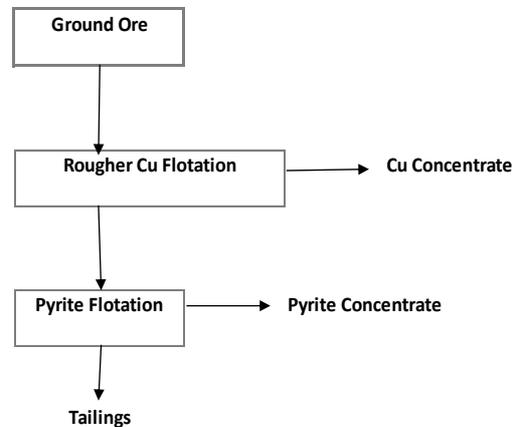
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        ┌─────────────────┐
        │   Ground Ore    │
        └─────────────────┘
                 │
                 ▼
        ┌─────────────────────┐
        │ Rougher Cu Flotation│ ────────▶  Cu Concentrate
        └─────────────────────┘
                 │
                 ▼
        ┌─────────────────┐
        │ Pyrite Flotation│ ────────▶  Pyrite Concentrate
        └─────────────────┘
                 │
                 ▼
            Tailings
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Fig. 1. The flowsheet of the batch flotation tests

3. Results and discussion

3.1. Microflotation tests

The flotation behavior of pyrite with different collectors was investigated as a function of pH and the results are given in Fig. 2. The purified pyrite sample was floated well between pH 3 and 6, with the highest recovery around pH 4 using xanthate. The decrease in flotation ability below pH 4 with xanthates may be attributed to the to the rapid decomposition of xanthates (Bulut, 1999; Bulut and Atak, 2002; Bulut et al., 2004). On the other hand, when pH increases above 6, a competition between OH^- and X^- ions starts to adsorb on the pyrite surface, therefore, when pH increases, OH^- ions accumulate on the surface of pyrite sample. Thus, pyrite is completely depressed above pH 6 when xanthates are employed.

In the microflotation experiments, it is seen that the pyrite recoveries have obtained the best values with the amine type collectors around pH 11, where the recoveries are very low when xanthates are used. Amines are found in undissociated form at alkaline pH values particularly above pH 10 (see Fig. 4), therefore, the interaction with the surface of pyrite in a flotation done at pH 11 is unlikely to be due to coulombic forces.
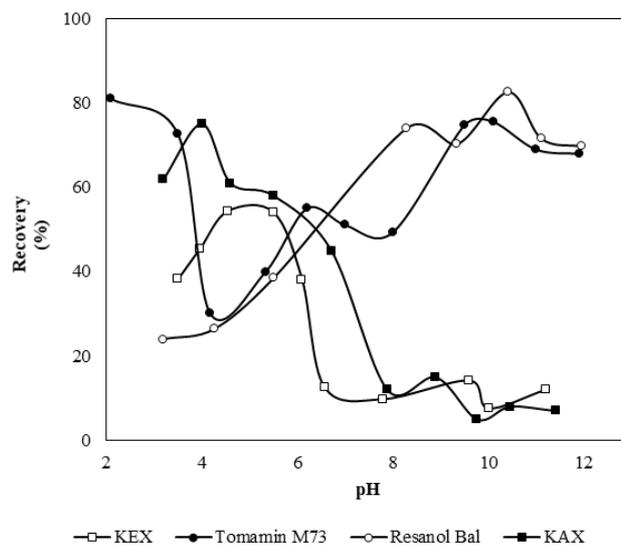

Fig. 2. Flotation experiments of pyrite using different collectors

The result of flotation using Tomamin M73 reflects its amphoteric nature giving two maxima in acidic and basic pH ranges.

3.2. Zeta potential measurements

Electrophoretic mobility measurements of pyrite were conducted at various pH values in the absence and presence of collectors. The results of measurements are given in Fig. 3.
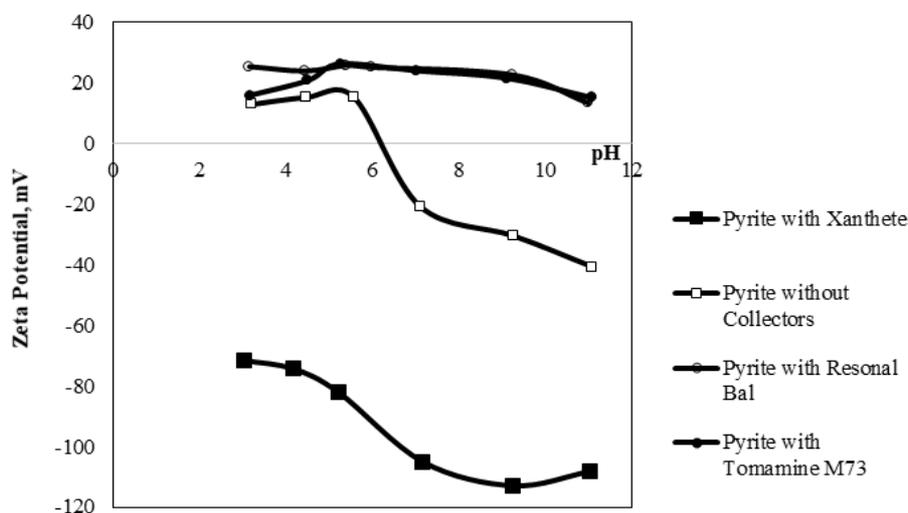

Fig. 3. Zeta potential of pyrite with and without collectors

As shown in Fig. 3, results indicated that the isoelectric point (i.e.p.) of pyrite was around pH 6 in the absence of any collectors whereas the surface charge seems to be altered by the presence of collectors. The surface charge of pyrite at all pH values is highly negative in the presence of xanthate, however, it becomes positive at all pH values examined with amine type of collectors. Results showed that the positively charged pyrite surface in acidic pH region became negatively charged due to the presence of xanthate. This situation was observed in the pH range 3 to 6, where pyrite was well floated. In some studies (Fornasiero and Ralston, 1992; Bulut et al., 2004; Fuerstenau and Mishra, 1980), it was reported that the addition of xanthate ions, especially in the acidic region, shifts the surface charge of pyrite to negative values. This was explained by the replacement of positively charged iron hydroxide species, which adsorbed onto negatively charged sulfide sites on the pyrite surface, by uncharged iron hydroxide-xanthate complexes.

When the zeta potential of pyrite in the existence of Resonal Bal and Tomamine is examined, it was observed that amines shift the zeta potential curve towards positive, particularly in alkaline pH ranges. Regarding the flotation of pyrite in alkali conditions the reversal of zeta potential towards positive values can contribute to the increase in the floability. These results showed that amine-type collectors may electrostatically adsorb on the surfaces of pyrite in alkali pH ranges. Amines are weak bases derived from ammonia, so they are present in the pulp as molecular, ionic or dimers species, depending on the pH (Gao et al., 2015). The amine ionization occurs by protonation and the cationic species RNH^{3+} predominates at the acid to low alkaline pH range. In the pH range where amine molecular species predominates (Fig. 4), a non-electrostatic mechanism for collector adsorption on the pyrite surface is implied. Therefore, the adsorption occurs by a chemical interaction mechanism. The amine molecule (RNH_2) has unshared electron pairs in the nitrogen atom that has a strong ability to complex metals by means of coordinated covalent bonds (Cartmell and Fowles, 1956). This adsorption mechanism was also suggested by Freeman et al. (2009), Gao et al. (2015), Oliveira and Baltar (2020).

3.3. Bench scale flotation experiments

Figs. 4, 5, 6 and 7 present the results from bench scale flotation tests of the chalcopyrite-pyrite bearing ore using different collectors.
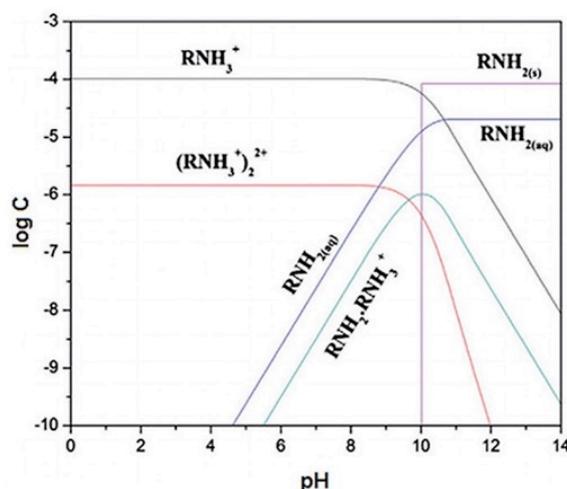
Fig. 4. Species distribution diagram for DDA (1×10^{-4} M) as a function of pH (Liu et al., 2015)

The results of bench scale floatation tests conducted with the ore showed that pyrite best floated with amine type Tomamine M73 and Resanol Bal collectors. Pyrite recoveries of 71.6 and 76.2% were obtained with Resanol Bal and Tomamine M73, respectively. On the other hand, comparatively low recoveries were achieved on using xanthates. The results of bench scale flotation tests were seen to be compatible with those of micro flotation experiments.

In industrial applications it is a common practice to float pyrite at a slightly acidic pH following flotation of copper at high pH with xanthates. This study shows that pyrite can be floated using amine type collectors maintaining the same pH value where copper is floated. Thus, acid consumption will be prevented and control of the flotation process will be simpler.

Table 4. Effect of KEX on pyrite flotation

Products	Weight	Pyrite (%)		Cu (%)	
	(%)	Content	Recovery	Content	Recovery
Cu Conc.	11.4	23.70	5.3	14.32	61.0
Pyrite Conc.	7.8	40.03	6.1	6.31	18.4
Tailing	80.8	56.31	88.7	0.68	20.5
Total	100	51.33	100.0	2.67	100.0

Table 5. Effect of KAX on pyrite flotation

Products	Weight	Pyrite (%)		Cu (%)	
	(%)	Content	Recovery	Content	Recovery
Cu Conc.	9.2	26.40	5.0	16.52	57.3
Pyrite Conc.	9.0	39.46	7.3	9.30	31.6
Tailing	81.8	52.27	87.7	0.36	11.1
Total	100	48.73	100.0	2.65	100.0

Table 6. The results of pyrite flotation with Resanol Bal

Products	Weight	Pyrite (%)		Cu (%)	
	(%)	Content	Recovery	Content	Recovery
Cu Conc.	11.7	28.52	6.6	14.19	59.7
Pyrite Conc.	65.0	56.01	71.6	1.46	34.1
Tailing	23.3	47.62	21.8	0.74	6.2
Total	100.0	50.84	100.0	2.78	100.0

Table 7. The results of pyrite flotation with Tomamine M73

Products	Weight (%)	Pyrite (%)		Cu (%)	
		Content	Recovery	Content	Recovery
Cu Conc.	11.5	28.89	6.7	14.8	61.5
Pyrite Conc.	68.2	55.64	76.2	1.34	33.0
Tailing	20.3	42.02	17.1	0.75	5.5
Total	100.0	49.80	100.0	2.77	100.0

4. Conclusions

In this study, the flotation behaviour of pyrite using xanthates as an anionic collector and amines as an cationic collector was investigated. As a result of these experimental studies, the following findings were obtained:

- Micro flotation tests with purified pyrite sample showed that amine type collectors, unlike xanthates, were effective to float pyrite at alkali pH region.
- Bench flotation studies on the real ore sample showed that amine type collectors floated pyrite at much higher recoveries compared to xanthates. The results of tests using amines as the collector showed excellent flotation performance for pyrite at high pH values. In industrial applications, the use of amine type collectors will provide an advantage over conventional methods, particularly in the circuits where chalcopyrite and pyrite are recovered as separate products without the need to reduce the pH for pyrite flotation following alkaline range copper flotation. Thus, acid consumption and the corrosion caused by the low pH will be reduced the in the flotation plants.

5. References

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