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ROLE OF STARCH AND METABISUPHITE ON PURE PYRITE AND PYRITIC COPPER ORE FLOTATION

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Abstract. Depression of pyrite is very important in sulphide ore flotation. This paper investigates the role of non-toxic depressants on the flotation of pyrite. Starch and meta bisulphite were used as a depressant for pure pyrite sample and a pyritic copper ore at two different pHs values. pH was 6.5 and 10 in pure pyrite study while it was 6.9 and 12 in pyritic ore study. This study showed that metabisulphite is more effective at pH 6.5 or 6.9 than pH 10 or 12, while starch is more effective at pH 12. Also, higher dosages of meta bisulphite are required for depression of pyrite. Pure pyrite and pyritic copper ore study gave similar results.

keywords: flotation, pyrite, depressant, starch, metabisulphite

1. Introduction

Chalcopyrite is often associated with pyrite and economical extraction of copper demands selective depression of pyrite from chalcopyrite. Conventionally sodium cyanide is used as a depressant in alkaline conditions for the selective depression of pyrite from chalcopyrite during the froth flotation process, leading to potentially disastrous environmental consequences (Ball and Rickards, 1976). Therefore, development of alternate reagents, concerning environment, have been interested in for researchers. Polysaccharide based reagents have been utilized in the mineral industry, principally as a depressant for a variety of minerals. These organic polymers are not only nontoxic but are also biodegradable and relatively inexpensive (Rath et al., 1991).

Pioneering contributions have been made by Laskowski et al. (1991, 2007), Laskowski and Liu (1999a, 1999b), Liu et al. (2000) and by Lopez et al. (2004) with respect to interaction of dextrin with several sulfides and oxides. These studies

revealed that unmodified natural polysaccharides, such as dextrin, starch or guar gum, adsorbed on mineral surfaces through interactions with metal-hydroxylated species on the mineral surface. The direct consequence of the interaction of natural polysaccharides with metal-hydroxylated species and thus the adsorption is strongly dependent on pH.

Sulphur-oxy depressants are added to the flotation pulp in the form of sulphite (SO_3^{2-}), bisulphite (HSO_3^-), meta bisulphite ($\text{S}_2\text{O}_5^{2-}$) or sulphur dioxide (SO_2) for depression of pyrite, sphalerite and galena (Grano et al., 1997a, 1997b; Khemeleva et al., 2003, 2005, 2006; Shen et al., 2001; Chander and Khan, 2000). In general, mechanisms governing sulphide mineral flotation behavior by sulphur-oxy species can be grouped according to those that involve interaction of sulphite with collector (xanthate), either in solution or its adsorbed state (Grano et al., 1997).

Shen et al. (2001) studied the effect of sodium sulphite on the flotation of sphalerite and pyrite in the presence of copper ions and they reported that sulphite promoted the formation of copper hydroxide on the surface of pyrite leading depression. Yamamoto (1980) proposed that sulphite ions depressed pyrite by desorbing xanthate species from the surface.

Although the use of metabisulphite for the depression of sulphide minerals is rather limited, Gül (2007) and Gül et al. (2008) used non-toxic reagents such as sodium metabisulphate, coustic starch, zinc sulphate and activated carbon instead of highly toxic reagents potassium bichromate and sodium cyanide that successfully depressed pyrite and separation of chalcopyrite, galena and sphalerite have been achieved.

In this comparative study, starch and metabisulphite are used as an alternative and non-toxic depressant for the depression of pure pyrite. Then pyritic copper ore was used to compare the results with pure pyrite sample.

2. Experimental

2.1. Material

In this study pure a pyrite sample for fundamental studies and pyritic copper ore to prove fundamental studies in real situation were used. Pure pyrite sample was obtained from Murgul-Artvin in the northeast of Turkey. The sample was upgraded by hand picking and purified using some mineral processing methods such as jigging. Chemical analyses of pure pyrite and ore samples are given in Table 1. Analyses proved that the pyrite sample contained 97% pyrite, 1-2% chalcopyrite and 1-2% quartz. Chemical analyses and XRD results indicated that the pyrite sample is highly pure. Pyritic copper ore sample was taken from Siirt-Madenköy Copper Mine in South-East of Turkey. According to the mineralogical analyses, the ore sample contains chalcopyrite (CuFeS_2), sphalerite (ZnS), pyrite (FeS_2), galena (PbS), hematite (Fe_2O_3), limonite ($\text{FeO}(\text{OH})\cdot n\text{H}_2\text{O}$), calcite (CaCO_3) and quartz (SiO_2) (Ceylan, 2009 and Ceylan and Bulut, 2010). Figure 1 shows the above minerals growth in the ore.

Mineralogical study also showed that about 50% of ore is formed by pyrite, as a major mineral in the ore.

Table 1. Chemical analyses of the samples

| Compound | Pure Pyrite Sample % | Pyritic Copper Ore Sample % |
|------------------|----------------------|-----------------------------|
| Fe | 42.43 | 27.65 |
| S | 49.40 | 27.22 |
| Pb | 0.025 | 0.13 |
| Zn | 0.005 | 0.43 |
| Cu | 0.056 | 1.60 |
| SiO ₂ | 0.595 | 20.35 |

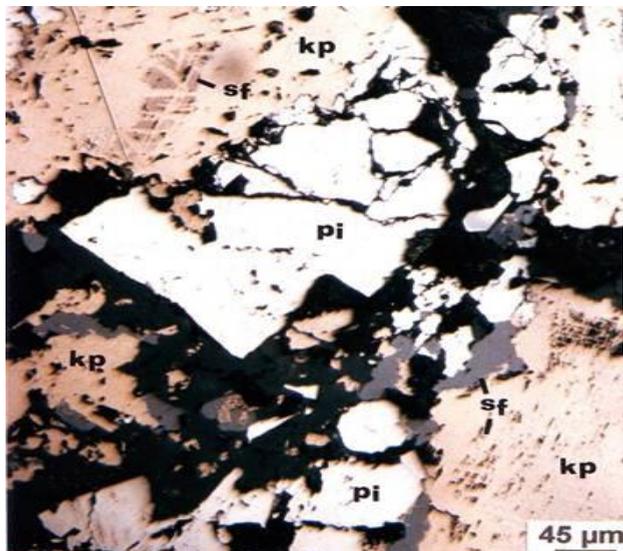


Fig. 1. Growth of minerals in the pyritic copper ore: chalcopyrite (kp) and sphalerite (sf) phases locked with cataclastic pyrite (pi) structure

2.2. Method

Experimental studies have been carried out with Denver flotation machines using 40 g of -100 μm pure pyrite in one dm^3 cell for pure pyrite study and 1 kg of approximately 53 μm ore sample in 2.5 liter cell for pyritic copper ore study. An agate mortar and pestle was used for grinding the pure pyrite sample while ore sample was ground with a ball mill prior to each test. In these experiments the effects of depressant type and dosages at two different pHs for flotation behavior of pyrite were investigated. The flotation flow-sheet with copper ore is given in Figure 2. Three stages cleaning were applied after obtaining a rougher-copper concentrate. Pyrite was removed with gangue minerals as tailings (Ceylan, 2009). In the rougher stage, reagents were added in three stages and 5 minutes flotation time was given for all the

stages. Therefore flotation time was totally 15 minutes in the rougher stage. In the cleaning stages, 8 minutes, 6 minutes and 4 minutes flotation times were given for the first, the second and the third stages respectively.

Aerophine 3418 A, which is a P-based sulphide collector and belongs to dialkyl dithiophosphinate group, was used as a collector in the flotation of pyrite. Sodium meta bisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) and caustified starch were used as depressants. Methyl isobutyl carbinol (MIBC) was used as a frother, and lime and H_2SO_4 were used as pH regulators.

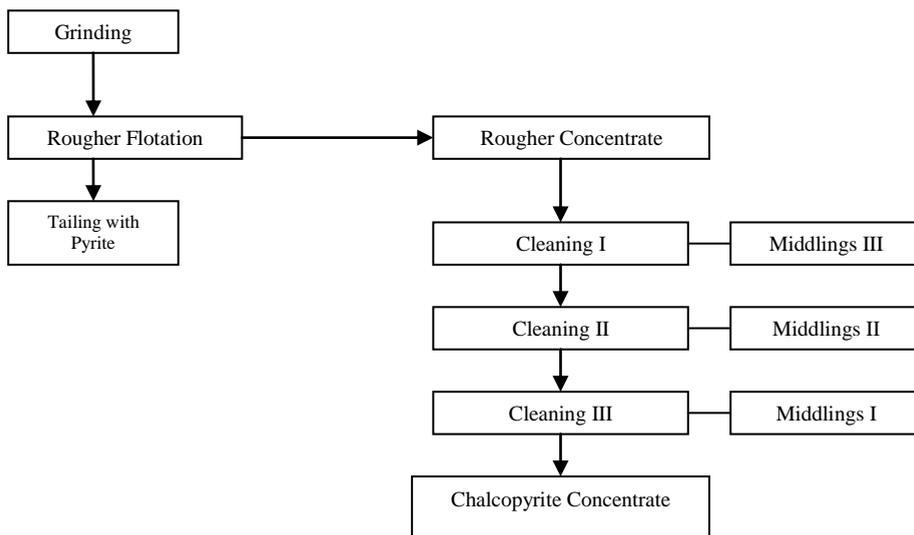


Fig. 2. The flow-sheet of ore flotation tests

3. Results and discussion

3.1. Pure pyrite study

3.1.1. Effect of starch

Starch was employed as a depressant on pyrite flotation at dosages between 1.7 and 17 mg/dm^3 at two different pHs; 6.5 (natural pH of sample) and 10. Aerophine 3418 A was used at 40 mg/dm^3 dosages and MIBC was used at 10 mg/dm^3 dosages. Collector dosages, frother dosages and conditioning time (3 min.) and flotation time (5 min.) were kept constant. The experimental results are given in Figure 3. This figure shows that flotation recovery decreased from 43.5 to 10.4% at pH 10 and it decreased from 74.9 to 59.2 % at pH 6.5. This shows that starch was more effective at pH 10 than pH 6.5. Although maximum depression was obtained with 1.7 mg/dm^3 starch at pH 6.5, increasing the starch dosages did not effect the pyrite flotation. In case of pH 10, again maximum depression occurred at 1.7 mg/dm^3 starch then increasing starch amount slightly depressed the pyrite. This shows that at low pH about 10% depression

occurred with 1.7 mg/dm^3 , while 21% depression occurred with the same dosages of starch at pH 6.5 where pyrite flotation is expected to be weak at pH 10. This can be explained as because starch adsorbed on mineral surface through the interaction with metal-hydroxylated species on the pyrite. So that increasing the pH caused the metal hydroxylated species on the pyrite and the adsorption of the starch occurred and more depression is occurred (Laskowski et al., 1991). Also organic reagents such as starch do not ionize in solution but form colloidal particles in the pulp which can be deposited on the mineral surfaces, preventing flotation in a similar manner to a slime coating (Wills, 1988). Similar results were obtained by Rath et al. (2000) who investigated the interaction of dextrin and guar gum with pyrite for adsorption, flotation and electrokinetic tests. They reported that higher adsorption densities of polysaccharides onto pyrite reveal in the pH range 7.5-11, that is maximum around pH 10 for dextrin and guar gum.

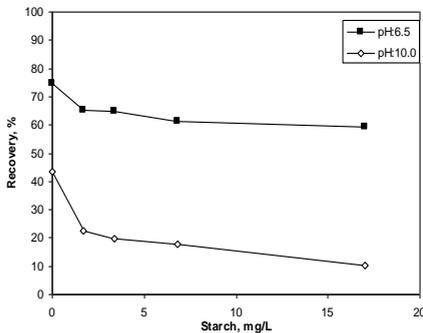


Fig. 3. The effect of starch on pure pyrite flotation

3.1.2. Effect of $\text{Na}_2\text{S}_2\text{O}_5$

The effect of $\text{Na}_2\text{S}_2\text{O}_5$ was investigated at pH 6.5 and 10. The amount of $\text{Na}_2\text{S}_2\text{O}_5$ was between 34 mg/dm^3 and 134 mg/dm^3 , and the amounts of Aerophine 3418 A and MIBC were the same as in starch experiments. The results are given in Fig. 4. Flotation recovery decreased from 43% to 4% at pH 10, and from 75% to 23.3% at pH 6.5 with 134 mg/dm^3 metabisulphide addition. Decrease in recovery with metabisulphate was about 40% at pH 10 where pyrite flotation is already low due to high pH and about 50% decrease in recovery was obtained at pH 6.5. Test results reveal that metabisulphite is more effective at pH 6.5 than at pH 10 but trend was similar. Actually almost complete depression has already occurred at 100 mg/dm^3 dosage at pH 10. But at pH 6.5, maximum depression, about 25%, was obtained by increasing dosages from 100 mg/dm^3 to 134 mg/dm^3 . That means that higher dosages are required to depress pyrite at lower pHs. In the literature it has been reported that when sulphur-oxy depressants are used these involve interaction of sulphite with collector either in solution or its adsorbed state and sulphite ions depressed pyrite by desorbing xanthate species from the surface (Grano et al., 1997 and Yamamoto, 1980).

The surface of pyrite can adsorb sulphite ions which prevent collector adsorption (Wills, 1988). Therefore the change in mineral floatability indicates that sulphide or

sulphite should have a greater affinity for surface sites than the adsorbed collector species. On the other hand, according to Woods (1972) activation and depression during flotation is worth considering in terms of mixed potential mechanism. In the literature, it is proposed that sulphide and sulphite prevent the flotation of pyrite because their oxidation potentials in alkaline solutions are more positive than that of xanthate (Hoyack and Raghavan, 1987). Janetski et al. (1977) investigated pyrite flotation and depression and reported that the solution containing sulphide, xanthate and oxygen, a mixed potential will be cathodic to the xanthate / dixanthogen potential and hence dixanthogen will not be formed and mineral will not be rendered floatable. Therefore presence of sulphide in solution introduces an anodic process which will occur in preference to xanthate oxidation. The mechanism for depression of sulphides floated with xanthate with addition of sodium sulphide producing a drop in the redox potential causing desorption of xanthate from the mineral (chemical displacement process) and a subsequent loss of flotation (Gebhardth and Kotlayar, 1991). Figure 5 shows the relation of pulp potential and depressant amount and pyrite recovery (Goktepe, 1992). This shows that increasing the addition of NaSH depresses pyrite and 1500 g/Mg dosage addition, complete depression occurred. Pulp potential was also recorded and the change in potential shows that pulp potential decreased as NaSH amount increased. When pulp potential-recovery and NaSH amount are considered together, it can be seen that recovery decreased as pulp potential decreased. In the literature there are some studies showing that solution redox potential may be reduced by the introduction of sulphite.

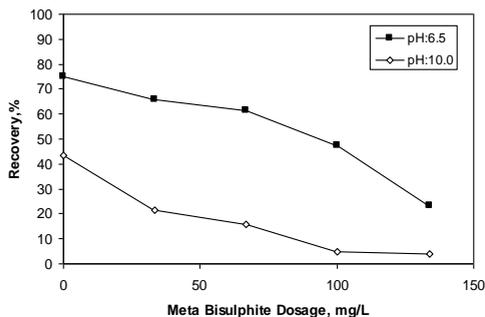


Fig. 4. The effect of sodium meta bisulphite on pyrite flotation

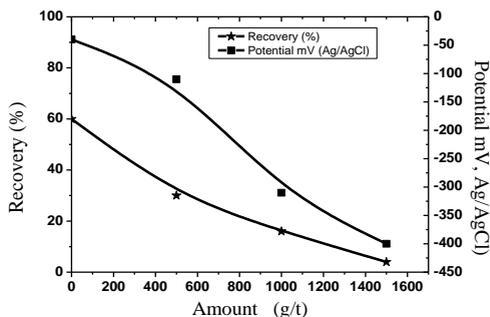


Fig. 5. Effect of NaSH amount for pyrite flotation and for pulp potential. (conditions: 2 mg/dm³ xanthate, pH 6, NaSH as a reducing reagent and potential was measured by platinum electrode) (Goktepe, 1992)

Miller (1970) considered that sulphite should act as a depressant for pyrite, due both to its reducing properties as well as its specific adsorption onto pyrite. As xanthate adsorption onto pyrite and a variety of other sulphide minerals is believed to take place via xanthate dimerisation to dixanthogen, the introduction of a more reducing couple may minimise adsorption via this mechanism but this mechanism is not specific with respect to the mineral Miller (1970). Zeta potential of pyrite in the

presence and absence of sodium sulphite was also measured by Miller (1970), which gave evidence of specific adsorption of sulphite ion onto pyrite.

When Figures 3 and 4 are compared to show the effect of depressant types, it can be said that to obtain the similar amount of depression, higher dosages of meta bisulphite is required than starch but metabisulphite is more effective as a depressant.

3.2. Pyritic copper ore

3.2.1. Effect of starch

First, flotation was carried out with ore sample without any depressant at natural pH of sample (pH: 6.9) where 50 g/ton Aerophine 3418 A and 50 g/ton MIBC (Methyl iso-butyl carbinol) were used as reagents in rougher stage. Three cleaning stages were applied and only 25 g/ton MIBC was used in these stages. Then the effect of starch was investigated at pHs 6.9 and 12.1 where 50 g/ton starch, 50 g/ton Aerophine 3418 A and 50 g/ton MIBC were kept constant in all rougher tests. In the three cleaning stages only 25 g/ton starch and 20 g/ton MIBC were used. The results are shown in Table 2.

Table 2. The effect of starch on the pyritic copper ore flotation

| pH | Products | Weight (%) | Cu (%) | |
|------------------------------|-------------|------------|--------|----------|
| | | | Grade | Recovery |
| 6.9 without depressant | Concentrate | 9.30 | 10.22 | 63.00 |
| | Middling 1 | 1.90 | 4.01 | 5.10 |
| | Middling 2 | 1.70 | 3.59 | 4.00 |
| | Middling 3 | 6.20 | 1.28 | 5.30 |
| | Tailing | 80.90 | 0.42 | 22.60 |
| | Total | 100.00 | 1.504 | 100.00 |
| 6.9 | Concentrate | 3.20 | 11.91 | 23.80 |
| | Middling 1 | 4.20 | 6.82 | 18.30 |
| | Middling 2 | 5.10 | 3.92 | 12.60 |
| | Middling 3 | 13.30 | 2.81 | 23.70 |
| | Tailing | 74.20 | 0.46 | 21.60 |
| | Total | 100.00 | 1.58 | 100.00 |
| 12.1 | Concentrate | 4.20 | 19.92 | 52.20 |
| | Middling 1 | 1.60 | 11.23 | 11.70 |
| | Middling 2 | 1.60 | 6.57 | 6.70 |
| | Middling 3 | 5.80 | 3.02 | 10.90 |
| | Tailing | 86.80 | 0.34 | 18.50 |
| | Total | 100.00 | 1.59 | 100.00 |

As Table 2 shows, using starch as a depressant at pH 6.9 did not improve the results, besides lower recovery obtained at concentrate. This means that starch also depresses the copper as well. It can be seen that starch depresses pyrite at higher pH level more selectively but still lower recovery obtained comparing to the flotation without starch. It is generally believed that the depressive behavior of polysaccharides in differential flotation is not specific, or not as specific as inorganic depressants.

Because starch does not ionize in solution but form colloidal particles in the pulp which can be deposited on the mineral surface, preventing flotation in a similar manner to slime coating. Large quantities of these reagents will depress all minerals and they are not as selective as the electrolytic depressants (Wills, 1988). Although the adsorption mechanism of the polysaccharides has not yet been fully understood (Yamamoto, 1980; Bogusz et al., 1997) pointed out that, in interaction polysaccharides with mineral surface metal-hydroxylated species, selective adsorption of polysaccharides would not likely be achieved. This is because the flotation pulp contains various metal ions derived from dissolution of minerals, which inevitably mask the surfaces of minerals and make them all similar. In this study, especially at natural pH, starch also depressed copper when it is used in cleaning stages.

3.2.2. Effect of $\text{Na}_2\text{S}_2\text{O}_5$

The effect of $\text{Na}_2\text{S}_2\text{O}_5$ was investigated at pHs 6.9 and 12.1 and 5000 g/ton $\text{Na}_2\text{S}_2\text{O}_5$, 50 g/Mg Aerophine 3418 A and 50 g/Mg MIBC were used in all rougher stage. In the three cleaning stages only 20 g/Mg MIBC was used and results are given in Table 3. It can be seen from Table 3 that at pH 6.9 copper grade and recovery are better than at pH 12.1.

Table 3. The effect of $\text{Na}_2\text{S}_2\text{O}_5$ on the pyritic copper ore flotation

| pH | Products | Weight (%) | Cu (%) | |
|------|-------------|------------|--------|----------|
| | | | Grade | Recovery |
| 6.9 | Concentrate | 3.10 | 22.62 | 44.90 |
| | Middling 1 | 0.40 | 11.35 | 2.70 |
| | Middling 2 | 0.60 | 7.40 | 2.70 |
| | Middling 3 | 4.90 | 3.46 | 10.50 |
| | Tailing | 91.00 | 0.69 | 39.20 |
| | Total | 100.00 | 1.60 | 100.00 |
| 12.1 | Concentrate | 2.40 | 21.20 | 31.30 |
| | Middling 1 | 2.60 | 15.43 | 25.10 |
| | Middling 2 | 3.20 | 7.93 | 15.90 |
| | Middling 3 | 5.90 | 2.64 | 9.80 |
| | Tailing | 85.90 | 0.33 | 17.90 |
| | Total | 100.00 | 1.59 | 100.00 |

A copper concentrate with 22.62% Cu grade and 44.9% metal recovery was obtained at pH 6.9. Although grade of copper concentrate was 21.2% with 31.3% recovery at pH 12.1. These results prove that pyrite is depressed more effectively at lower pH level with $\text{Na}_2\text{S}_2\text{O}_5$. But incase of middlings higher grades and recoveries were obtained at pH 12.1. If two tailings were compared, lower grade and lower recovery obtained at pH 12.1, which shows that copper loss in tailing is lower at pH 12.1.

When two depressants were compared by considering only concentrate, $\text{Na}_2\text{S}_2\text{O}_5$ looks more effective depressant than starch. If middlings were added to the concentrate or if tailings were considered for the loss of copper at pH 12.1, it can be seen that similar results were obtained. These results confirm to the results obtained from pure mineral study. When two depressants are compared, $\text{Na}_2\text{S}_2\text{O}_5$ ensures more selectivity than starch.

4. Conclusions

It was found that starch is an effective depressant for pyrite even with a very small amount of addition. Furthermore, the effect of starch is more pronounced at alkaline pH than natural pH. The sodium metabisulphite ensures more selectivity compared to starch at natural pH for pure pyrite and pyritic copper ore flotation. Fundamental findings of this study (pure mineral) can be applied to an ore sample. The findings confirms each other. Overall both metabisulphite and starch can be an alternative depressant for pyrite instead of toxic depressants such as cyanide in the industrial applications.

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