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## EFFECT OF H<sub>2</sub>O<sub>2</sub> AND NaSH ADDITION TO CHANGE THE ELECTROCHEMICAL POTENTIAL IN FLOTATION OF CHALCOPYRITE AND PYRITE MINERALS

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*The floatability of sulfide minerals can be affected by the redox conditions on particle surface and in the pulp and can be used as one of the parameters for the separation of sulfide minerals. In the present study, the presence of reducing and oxidizing agents in the pulp is investigated for pure samples of chalcopyrite and pyrite. A good correlation between pulp potential and recovery of chalcopyrite and pyrite was found when the potential was varied by addition of H<sub>2</sub>O<sub>2</sub> and NaSH as oxidizing and reducing agents, respectively. In general, flotation is possible in the mildly to moderately oxidizing region and in slight or absent in reducing solutions for sulfide minerals.*

**Keywords:** chalcopyrite, electrochemical potential, flotation, H<sub>2</sub>O<sub>2</sub>, NaSH, pyrite electrode

### INTRODUCTION

The pulp potential has been shown to be closely related to floatabilities of sulfide minerals by Gardner and Woods (1973), Chandurya, Vigdergauz, and Teplyakova (1988), Li and Iwasaki (1992), Woods (2003) and Chander (2003). It was found that chalcopyrite could be made to float and sink alternately by cycling the pulp between oxidizing and reducing conditions, and the value of the electrode potential of chalcopyrite determines whether or not the mineral will float. Therefore they were able to correlate flotation efficiency with the potential of the pulp in the various chemical environments investigated. However, the quoted potential range for good flotation varies significantly in the literature. For example, Gardner and Woods (1973) found flotation in the Eh range between –100 and 300 mV (SHE), and Li and Iwasaki (1992) found the range for flotation to be 140–240 mV (SHE).

Most electrochemical studies have been done by controlling the potential externally. However, in a flotation system it is not possible to control the potential of each of a large number of particles by the direct flow of electrons to or from an external apparatus. The addition of oxidizing or reducing agents is another attempt to control the potential. Hayes and Ralston (1988) have reported that chemical

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control of Eh is more directly related to plant practice and produces a more uniform electrochemical environment around the sulfide particles in the flotation pulp, whereas potentiostatic control is reported to be very dependent on the efficiency of electrode/particle contact.

On the other hand, Jones (1991) stated that chemical control of the redox potential by reagents such as hydrogen peroxide and sodium dithionite can produce side effects. Reducing agents, such as sodium sulfide or sodium hydrosulfide, depress copper sulfides under alkaline conditions. When the influence of the strongly reducing nature of sodium hydrosulfide on depressant action has been monitored by means of solution redox-potential measurements, it appears that the depressant activity is to some extent electrochemical, the HS<sup>-</sup> ions, by virtue of their large negative Eh, destabilizing the coating of thiol collector (Wills 1988).

Gebhart and Kotlyar (1991) have reported that hydrosulfide ion is responsible for depression and if the addition of hydrosulfide was sufficient to shift the potential cathodically, depression of the sulfide mineral occurs. Depression of sulfides floated with xanthate by the addition of sodium sulfide produced a drop in the redox potential, causing desorption of xanthate from the mineral and a subsequent loss of flotation. The second mechanism involved interaction of hydrosulfide with the collector-adsorbed copper sulfide surface with no shift in potential. Then, change in mineral floatability indicates that hydrosulfide has a greater affinity for surface sites than the adsorbed collector species (Gebhart and Kotlyar 1991).

Hoyack and Raghavan (1987) reported that sulfide and sulfite prevent the flotation of pyrite because their oxidation potentials are more positive than xanthate. Janetski, Woodburn, and Wood (1977) investigated pyrite flotation in the presence of sulfide, xanthate, and oxygen, and it was reported that the mixed potential would be cathodic to the xanthate/dixanthogen potential and hence dixanthogen would not be formed and the mineral will not be rendered floatable.

The role of oxygen in collector adsorption on pyrite was investigated by Fuerstenau, Natalie, and Rowe (1990a, 1990b). It was reported that the presence of oxygen at any concentration enhances xanthate adsorption for pyrite. It was stated that the high oxidation rate of the minerals and exhaustion of the dissolved oxygen in the pulps inhibited the oxidation of xanthate to dixanthogen on the mineral surface.

If there is a difference in the potential at which different minerals float with a particular collector then control of the potential should allow flotation separation (Woods 2003). Therefore knowledge of Eh changes in the flotation circuit would enable to select points of reagent additions so as to improve recovery and grade of the desired minerals (Chander 2003).

The target of the work reported in this paper was to determine the influences of oxidizing-reducing environments on chalcopyrite and pyrite flotation.

## EXPERIMENTAL

### Sample

Chalcopyrite and pyrite samples were obtained from Gregory, Buttley & Lloyd, London, but the origin of the sample is not known. For the quantitative

determination of the major elements present in the sample for microflotation, XRF analyses were performed. XRF results showed that chalcopyrite contains 23.20% Cu, 0.68% Pb, 1.67% Zn, and 23.22% Fe. The major contaminating elements were zinc and lead. Pyrite content was 0.05% Cu, 0.07% Zn, and 40.52% Fe. Minor contaminating impurities were not analyzed.

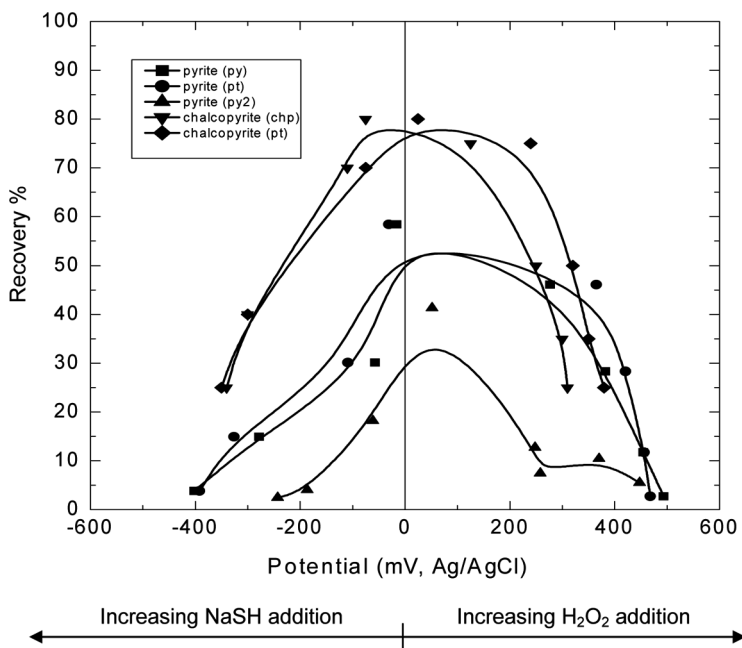
### Flotation Conditions

After the  $d_{80}$  of approximately 63  $\mu\text{m}$  size was obtained by milling in the micro-nizing mill, 10 g of sample was transferred to the designed microflotation cell, which is described in another study (Göktepe 2002), and suspended in 330 ml of double distilled water. Pulp potentials were measured by manufactured mineral electrodes and with platinum electrode to compare the electrodes, and pH was also measured. Double distilled water was used in all experiments. Air was used as flotation gas and was supplied at a measured rate from a cylinder. When nitrogen was used as a flotation gas in another study (Göktepe 2008), recoveries and potentials were similar with air, unless the pulp was conditioned with these gases. Collectors and frothers were allowed 1 min conditioning time. For  $\text{H}_2\text{O}_2$  and NaSH 2 min conditioning was used. Flotation gas was introduced and flotation was carried out for 4 min. Froth was removed by scraping manually with addition of double distilled water to maintain the pulp level. Floated and unfloated products were then filtered, dried, and weighed.

## RESULTS AND DISCUSSION

In the present study pulp potential was changed by using NaSH as a reducing agent and  $\text{H}_2\text{O}_2$  as an oxidizing agent for the pyrite and chalcopyrite minerals in the presence of xanthates. The frother (Aerofroth 65) was added pure in 25  $\mu\text{l}$  amounts. The conditions for chalcopyrite and pyrite were pH 9.5 and 0.7 mg/l KAX. Also pyrite flotations were performed at pH 6 and 2 mg/l SIBX. These pH levels and xanthate concentration were chosen where optimum flotation conditions were obtained in previous experimental studies. Figure 1 shows the pulp potential–recovery relationship for both minerals for both platinum electrode and mineral electrodes. Clearly, the recoveries of chalcopyrite and pyrite decrease at very positive and very negative potentials. It is the rate of decrease that is noteworthy. Separation of pyrite and chalcopyrite was possible when conditions were the same, pH 9.5 and 0.7 mg/l KAX, 75% chalcopyrite, and 5% pyrite recoveries were obtained. But when pH was 6, pyrite recovery was 50%, and separation was not possible. Different potential across pyrite electrode can be explained by different pH.

As Figure 1 shows, chalcopyrite displays a wider range of potentials where maximum recovery (80%) is possible between  $-100$  and  $+200$  mV (Ag/AgCl) with chalcopyrite and 25 and 250 mV with platinum electrode. The difference between chalcopyrite and platinum electrodes decreases in reducing environment as NaSH amount was increased and difference increases in oxidizing conditions. When maximum recovery was obtained, the difference between electrodes was 125 mV. As potential increases above 250 mV and decreases below  $-100$  mV, recovery decreases dramatically where high dosages of NaSH and  $\text{H}_2\text{O}_2$  were added. Ross et al. (1985) observed chalcopyrite flotation between  $-15$  and 185 mV (Ag/AgCl)



**Figure 1** Potential versus recovery of chalcopyrite and pyrite in flotation, (chp) chalcopyrite electrode, (pt) platinum electrode, and (py) pyrite electrode, (py): flotations were performed at pH 6 and 2 mg/l SIBX., (py2): flotations were performed at same conditions with chalcopyrite flotation, pH 9.5 and 0.7 mg/l KAX.

and have reported that copper ethyl xanthate (CuEtX) and dixanthogen formation have occurred at this potential range. It was noted that suppression above 185 mV (Ag/AgCl) was due to decomposition of the Cu-EtX species.

In this study, maximum recovery was obtained with minimum amount of NaSH and H<sub>2</sub>O<sub>2</sub> addition at moderate potential and increasing the amount of both reagents caused dramatic decrease of chalcopyrite flotation. Therefore, both reagent dosages are critical to the flotation recovery.

Pyrite recovery decreased with NaSH and H<sub>2</sub>O<sub>2</sub> addition, especially at very high and low potentials depression occurred. Maximum recovery, 60%, was obtained at pH 6 with 2 mg/l SIBX conditions at potential -50 mV. Recovery was 60–45% at potential between -75 and 400 mV (Figure 1). When pH was adjusted to 9.5 and 0.7 mg/l KAX was added to obtain the same conditions as in chalcopyrite flotation, maximum recovery was 40% at 50 mV with pyrite electrode, with 500 gr/t NaSH addition. Addition of H<sub>2</sub>O<sub>2</sub> dramatically dropped the pyrite flotation, above 250 mV pyrite was depressed. This shows that separation with chalcopyrite and pyrite could be obtained with minimum amount of H<sub>2</sub>O<sub>2</sub> addition because chalcopyrite could readily float at this amount but pyrite can not float with H<sub>2</sub>O<sub>2</sub> addition when conditions were the same at 250 mV. When NaSH amount was increased, potential decreased to -250 mV and depression occurred. Therefore, pH and reagents are very important factors as well as the NaSH and H<sub>2</sub>O<sub>2</sub> dosages. Gebhart and Dewsnap (1985) observed pyrite flotation to start at potentials of approximately -85 mV and floated best at 85 mV (Ag/AgCl). On the other hand, Chandurya and Vigdergauz

(1988) observed that pyrite floated best at  $-700$  mV (Ag/AgCl) without collector at pH 9.2. Kocabağ and Güler (2007) showed that both pyrite and chalcopyrite are floatable at their natural pulp conditions ( $-100$  to  $100$  mV SHE) and floatability increased in the presence of  $\text{Na}_2\text{S}$ . As reported above, different investigators have observed differences in the potential–recovery response. This could be due to the differences in the mineralogy and electrochemical reactivity of the sulfide minerals (Ekmekçi et al. 2005).

## CONCLUSIONS

For chalcopyrite and pyrite, the best flotation results were obtained at potential  $-100$  to  $200$  mV (Ag/AgCl) when NaSH and  $\text{H}_2\text{O}_2$  were used to control the potential of the pulp. Clearly, the recoveries of chalcopyrite and pyrite decrease at high positive and high negative potentials but it is the rate of decrease that is noteworthy. The mineral electrodes and platinum electrode displayed the similar potentials value with NaSH addition where reducing conditions occurred in both chalcopyrite and pyrite flotation but when  $\text{H}_2\text{O}_2$  was added and oxidizing conditions were created, they showed around  $100$  mV differences. Especially difference was more pronounced with chalcopyrite and platinum electrodes in chalcopyrite flotation. In general, flotation is possible in the mildly to moderately oxidizing region and in slight or absent of reducing solutions for sulfide minerals.

This study also shows that separation of chalcopyrite and pyrite could be obtained at around  $250$  mV (Ag/AgCl) with minimum amount of  $\text{H}_2\text{O}_2$  addition at pH 9.5 with  $0.7$  mg/l KAX where chalcopyrite could readily float ( $\sim 75\%$ ) at this potential range but pyrite cannot float ( $\sim 5\%$ ) at this potential range.

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