

Decoupling the Effects of Pulp Potential and pH on the Flotation of Pyrite

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Forson, P., Ayedzi, L. D. and Abaka-Wood, G.B. (2020), "Decoupling the Effect of Pulp Potential and pH on the Flotation of Pyrite", *Proceedings of 6th UMaT Biennial International Mining and Mineral Conference*, Tarkwa, Ghana, pp. 366-371.

Abstract

Pulp pH and potential play important roles in the flotation of pyrite. Control of pH determines surface species formed on the mineral whereas solution potential favours the oxidation of xanthate to dixanthogen for its flotation. Interestingly, changes in pulp pH produces a corresponding change in potential, that is, increase in pH reduces pulp potential and vice versa. This study employs sodium hydrosulphite and sodium dithionite as potential control reagents to unravel the roles of Eh and pH on pyrite flotation. It was observed that, an increase in the potential of the pulp at high pH conditions resulted in pyrite depression whereas at low pulp pH, pyrite recovery was enhanced although the pulp potential was lowered below the reversible potential for the dixanthogen couple. At high pulp pH, the increased surface oxidation product coverage on pyrite would exceed the hydrophobicity of adsorbed collector species, thus depressing the mineral in the process. Adsorption of collector as xanthate ion and sulphur from sodium hydrosulphite addition were responsible for the successful recovery of pyrite at low potential conditions.

Keywords: Reversible potential, Flotation, Pyrite, Thiol collectors

1 Introduction

Pyrite is by far the most abundant sulphide mineral in the earth crust (Rimstidt and Vaughan, 2003). It is commonly associated with valuable metals such as copper, lead, gold as well as coal (Wang and Forssberg, 1991; Keith *et al.*, 2018). In the separation of value-containing pyrite from other gangue minerals in process streams, froth flotation is often employed. Most sulphide minerals do not exhibit natural floatability (Hu *et al.*, 2010). They have, however, collectorless floatability in specific pulp potential ranges, under the condition of which the sulphide mineral surface has been rendered hydrophobic by surface self-oxidation. (Cheng and Iwasaki, 1992; Zhang *et al.*, 2004). Typically, sulphhydryl collectors are added to render the mineral hydrophobic to promote its recovery.

Thiol collectors are the most widely used collectors in pyrite flotation (Hu *et al.*, 2010). Xanthates which form part of this group have extensively been studied in the flotation of sulphides. Several

mechanisms for the adsorption of the collector have been put forward with the oxidation of xanthate to dixanthogen (X^-/X_2) as the most important and prominent adsorption step (López Valdivieso *et al.*, 2005). The anodic oxidation of xanthate ion is accompanied with cathodic reduction of oxygen. For dixanthogen to form on the mineral surface, the measured reversible potential in the pulp should exceed the reversible potential of the X^-/X_2 couple (Bulut *et al.*, 2002; Cheng and Iwasaki, 1992; López Valdivieso *et al.*, 2005). Thus, depression of the mineral should be observed when the pulp potential is lower than the calculated reversible potential. Contrary to what is expected, Newmont's patented N₂Tec was able to achieve high recovery of pyrite in a nitrogen-purged system where potentials between -0.1 and 0.5 V were reported (Miller *et al.*, 2006). The reversible potential for PAX concentrations used on the plant was 1×10^{-3} M with calculated 0.019 V. The authors ascribed the flotation of pyrite to creation of 'clean', low polarity surface which

enhanced the adsorption of the collector (Miller *et al.*, 2006).

Pulp pH plays an important role in the flotation of pyrite (Hu *et al.*, 2010). Bonnissel-Gissing *et al.* (1998) determined the species formed on pyrite mineral surface and subsequently ascertained the extent of oxidation. At low pH conditions, lower surface oxidation species are observed. As pH increases there is a corresponding increase in hydrophilic ferric hydroxide species depressing the mineral as a result (Bonnissel-Gissing *et al.*, 1998). Interestingly, there is a decrease in Eh of pulp with increase in pH. For each pH unit, the oxygen reduction process decreases by 59 mV, as a result potential of pulps approaches negative at highly alkaline pH (Winter and Woods, 1973).

The depression of pyrite in alkaline environment is high (Bulut *et al.*, 2002; Mermillod-Blondin *et al.*, 2005; Shen *et al.*, 1998; Zhang *et al.*, 1997). Unfavorable thermodynamic conditions for oxidation of dixanthogen has been proposed by some authors (López Valdivieso *et al.*, 2005) while others have suggested surface oxidation product as the reason for this observation (Mermillod-Blondin *et al.*, 2005). In the acidic condition, high flotation recovery is linked primarily with increased formation of dixanthogen.

To decouple the effects of pulp pH and Eh on flotation, redox reagents were employed in pyrite flotation. This was done to help address the themes of this study, which include:

- a) Would pyrite float in acidic conditions if pulp potential does not support dixanthogen formation and
- b) would pyrite float in alkaline conditions if the pulp potential is thermodynamically favorable to form dixanthogen.

2 Materials and Methods Used

2.1 Materials

A model pyrite mineral obtained from Peru was used in the study. The sample was prepared to -75+38 μm

Table 1 Elemental composition of pyrite

| Al ₂ O ₃ | As | CaO | Cu | K ₂ O | MgO | Mn | Na ₂ O | P ₂ O ₅ | Pb | SiO ₂ | TiO ₂ | Zn | Fe | S |
|--------------------------------|-----|-------|------|------------------|-------|-----|-------------------|-------------------------------|------|------------------|------------------|-----|-------|-------|
| % | ppm | % | ppm | % | % | ppm | % | % | ppm | % | % | ppm | % | % |
| <0.02 | 268 | <0.02 | 2597 | <0.02 | <0.01 | 64 | <0.02 | <0.01 | 1049 | <0.03 | <0.02 | 134 | 44.23 | 48.57 |

for flotation study. The elemental composition of the mineral determined using ICP-MS is shown in Table 1. Quantification of the mineral phases (Figure 1) for the sample was carried out on an Empyrean XRD and determined to be 99.4 wt.% pyrite and 0.6 wt.% quartz. In all experimental work, demineralized water was used to condition the mineral.

The potassium amyl xanthate (PAX) collector used in all experiments was purified three times by dissolution in acetone and recrystallization with ethyl ether and fresh solution prepared each day for the experiment. All additional chemicals used were of analytical reagent grade quality. Sulphuric acid and Sodium Hydroxide were used to control pH from 4.5 to 11. For pulp potential modification, Sodium hypochlorite and Sodium dithionite were employed for redox-potential control.

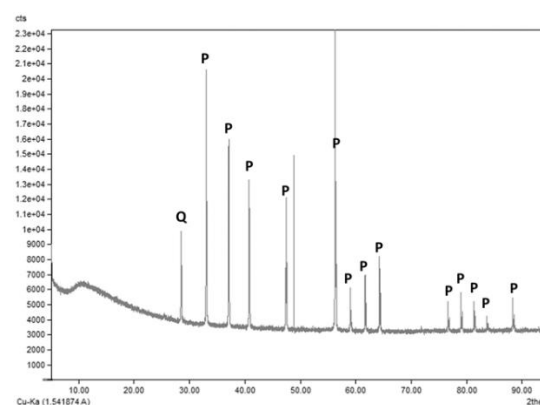


Figure 1 XRD of pyrite used in the study

2.2 Effect of pH and Collector Concentration on Flotation

To determine the effects of pulp pH on the flotation recovery of the pyrite mineral, representative subsamples were conditioned and floated at pH 4, 6.4, 8, 9.2 and 11. Conditioning of the pulp was carried out at the set pH and allowed 5 mins to equilibrate. Collector is added for 5 mins followed by frother for 2 mins and flotation of the mineral for 10 mins. Notice is made of the Eh before the start of flotation. Concentrate is collected from the froth layer every 15 seconds. The recovery for each time is calculated from the dry mass obtained and a cumulative reported. The flowsheet for the flotation

run is shown in Figure 2. Collector concentration was varied at 1×10^{-6} and 1×10^{-5} M.

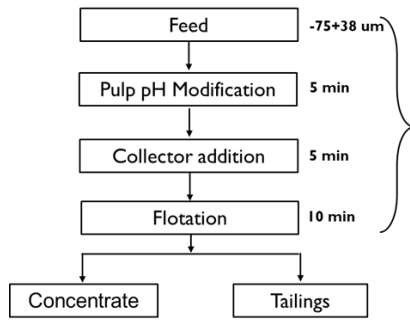


Figure 2 Flow sheet for flotation experiment.

2.3 Redox Potential–Controlled Flotation

For flotation run under redox control, a 1% solution was prepared from concentrated sodium hypochlorite whereas 3% sodium hydrosulphite was used. To control the Eh of the pulp, continuous measurements were undertaken. Simultaneously, dropwise addition of the redox reagent into the flotation pulp was carried out to maintain the pulp potential in the range required. In some instances, collectorless flotation of the mineral was carried out in the absence and presence of sodium hydrosulphite to determine the contribution of the reagent to flotation.

3. Results and Discussions

3.1 Effect of Pulp pH and Collector concentration

The flotation recovery as a function of pH and collector concentration is presented in Figure 3. Under acidic to circum-neutral pH conditions, pyrite maintained high flotation recovery for both 1×10^{-5} and 1×10^{-6} M PAX concentration. At high pH however, pyrite was depressed. This observation was made although the recorded pulp potential exceeded the calculated reversible potentials (Equations 1 and 2) for dixanthogen formation under the collector concentration investigated (Table 2). This was ascribed to the formation of ferric hydroxide on pyrite surface preventing collector attachment. Maximum surface density of ferric hydroxide on pyrite surface is found between pH 5-9 (Wang and Forseberg, 1990).

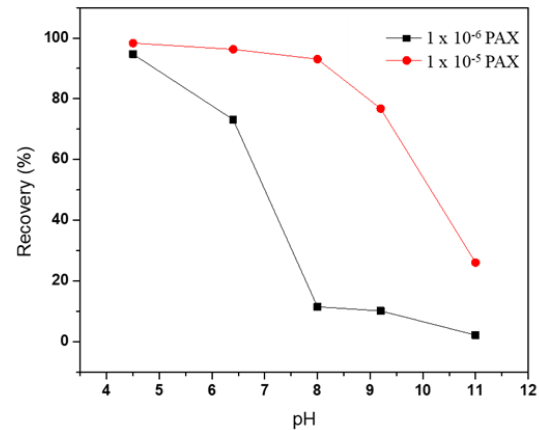


Figure 3 Recovery of pyrite with variation in pulp pH

At high PAX concentration however, recovery is generally high under the pH conditions tested except for pH 11 where pyrite was depressed. The authors conjecture that, this observation could be as a result of an increase in hydrophobic dixanthogen coating on the mineral surface which exceeded the hydrophilicity of surface oxidised species. Simultaneous cleaning of ferric hydroxide from the mineral surface on adsorption of dixanthogen reported elsewhere is also a possibility. A decrease in pulp potential is observed with an increase in solution pH as shown in Figure 4. From the thermodynamic standpoint, the low potentials recorded at pH 11 would not favour the oxidation of xanthate to dixanthogen and thus depress the mineral.



$$E_{rev.} = -0.158 - 0.059 \log[X^-] \quad (2)$$

Table 2 Calculated Reversible Potentials for Collector Concentrations Used

| PAX Conc. M | $E_{rev.}$, Mv (SHE) |
|--------------------|-----------------------|
| 1×10^{-5} | 196 |
| 1×10^{-6} | 137 |

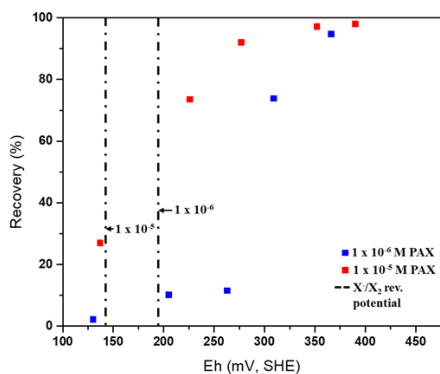


Figure 4 Plot of Eh against flotation recovery. Dotted lines demarcate regions of calculated reversible potentials

3.2 Redox Potential-Controlled Flotation of Pyrite

To ascertain the impact of redox potential on the flotation and depression of pyrite, a reduction and an increase in potential at pH 4.5 and 11, respectively was carried out using chemical reagents; sodium hydrosulphite and sodium hypochlorite shown in Figures 5 and 6. An average of 396 mV (SHE) was attained at pH 11 using sodium hypochlorite.

At low collector concentration and pH 11, pyrite was still depressed although the recorded potential was higher than the calculated reversible potential. Sodium hypochlorite is a powerful oxidant. The authors proposed that, its addition could increase the ferric hydroxide coverage on the mineral surface. More so, the oxidation and adsorption of xanthate on the mineral surface would be impeded. On the contrary, there was only a slight decrease in the flotation recovery at high collector concentration in comparison with recoveries recorded in the absence of sodium hypochlorite (Figure 4). Flotation carried out using sodium hypochlorite conditioning only yielded no mass recovery.

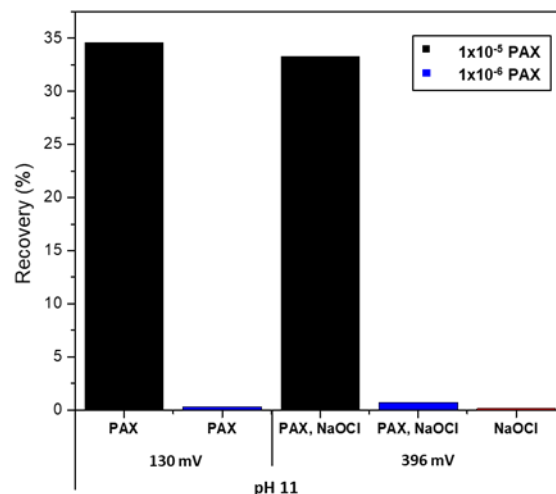


Figure 5 Pyrite recovery at high pH and Eh

Under acidic pH condition (pH 4), an average potential of 124 mV (SHE) was achieved using sodium hydrosulphite. This value is lower than the reversible potential for the collector concentrations investigated. Notwithstanding, flotation recovery of 81% was achieved at high collector concentration; a 2% drop in recovery in comparison with values recorded in the absence Eh modification. At low PAX concentration, there was a decrease in recovery from 70.2% in the absence sodium dithionite to 52.6% in the presence of dithionite. Flotation carried out in the presence of dithionite only gave a recovery of 36%. The authors explained the drop in flotation recovery to be as a result of both a coating of the pyrite surface with elemental species from dithionite addition as well as the absence of dixanthogen on the mineral surface. The adsorption of xanthate ion onto the mineral surface is also likely. It is worth noting that, pyrite was completely depressed in the absence of Eh modification and collector addition confirming the contribution of sodium dithionite to the flotation of pyrite.

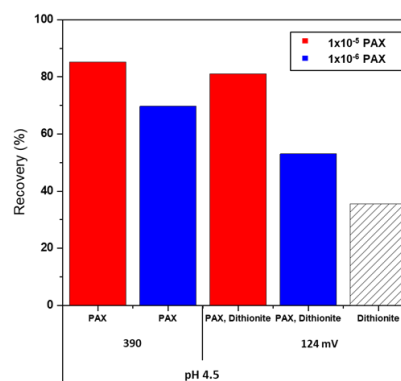


Figure 6 Pyrite recovery at low pH and Eh

4 Conclusion

The use of redox reagents; sodium hypochlorite and sodium dithionite were able to control the potential of pulp during pyrite flotation conditioning. At low PAX concentration of 1×10^{-6} M, pyrite was depressed at alkaline pH. An increase in collector concentration however, increased the flotation recovery due to an increase in collector species on the mineral surface.

At 1×10^{-6} M PAX concentration, high pH and Eh, pyrite was depressed although the recorded Eh value exceeded the calculated reversible potentials. The authors ascribed this to a high ratio of hydrophilic oxidation species to hydrophobic collector species on the mineral surface. Under the same condition, there was only a slight decrease in recovery.

Pyrite maintained good floatability at low collector concentration, pH and Eh. The poor oxidation of the pyrite mineral surface was the reason for the good flotation response. The use of sodium hydrosulphite only induced flotation of pyrite.

Acknowledgements

The authors would like to thank the University of South Australia and the Australian government for providing funding for this work.

References

- Bonnissel-Gissinger, P., Alnot, M., Ehrhardt, J.-J. and Behra, P. (1998), "Surface Oxidation of Pyrite as a Function of pH", *Environmental Science & Technology*, Vol. 32, No. 19, pp. 2839-2845.
- Bulut, G. and Atak, S. J. M. (2002), "Role of dixanthogen on pyrite flotation: solubility, adsorption studies and Eh, FTIR measurements", *Metallurgy and Exploration*, Vol. 19, No. 2, pp. 81-86.
- Cheng, X. and Iwasaki, I. (1992), "Pulp Potential and Its Implications to Sulfide Flotation", *Mineral Processing and Extractive Metallurgy Review*, Vol. 11, No. 4, pp. 187-210.
- Hu, Y., Sun, W. and Wang, D. (2010) *Electrochemistry of flotation of sulphide minerals*, Springer Science & Business Media.
- Keith, M., Smith, D. J., Jenkin, G. R. T., Holwell, D. A. and Dye, M. D. (2018), "A review of Te and Se systematics in hydrothermal pyrite from precious metal deposits: Insights into ore-forming processes", *Ore Geology Reviews*, Vol. 96, pp. 269-282.
- López Valdivieso, A., Sánchez López, A. A. and Song, S. (2005), "On the cathodic reaction coupled with the oxidation of xanthates at the pyrite/aqueous solution interface", *International Journal of Mineral Processing*, Vol. 77, No. 3, pp. 154-164.
- Mermillod-Blondin, R., Kongolo, M., De Donato, P., Benzaazoua, M., Barres, O., Bussière, B. and Aubertin, M. (2005), "Pyrite flotation with xanthate under alkaline conditions-application to environmental desulfurization, translated by Citeseer", *Century of Flotation Symposium*, Brisbane, QLD, Australia, pp. 683-692.
- Miller, J. D., Kappes, R., Simmons, G. L. and LeVier, K. M. (2006), "Pyrite activation in amyl xanthate flotation with nitrogen", *Minerals Engineering*, Vol. 19, No. 6, pp. 659-665.
- Rimstidt, J. D. and Vaughan, D. J. (2003), "Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism", *Geochim Cosmochim Acta*, Vol. 67, No. 5, pp. 873-880.
- Shen, W. Z., Fornasiero, D. and Ralston, J. (1998), "Effect of collectors, conditioning pH and gases in the separation of sphalerite from pyrite", *Minerals Engineering*, Vol. 11, No. 2, pp. 145-158.
- Winter, G. and Woods, R. (1973), "The Relation of Collector Redox Potential to Flotation Efficiency: Monothiocarbonates", *Separation Science*, Vol. 8, No. 2, pp. 261-267.
- Wang, X. and Forssberg, E. (1990), "EDTA-induced flotation of sulfide minerals", *Journal of Colloid and Interface Science*, Vol. 140, No. 1, pp. 217-226.
- Zhang, Q., Xu, Z., Bozkurt, V. and Finch, J. A. (1997), "Pyrite flotation in the presence of metal ions and sphalerite", *International Journal of Mineral Processing*, Vol. 52, No. 2, pp. 187-201.

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