

Collectorless flotation of chalcocite by controlling redox potential

S. Razmjouee¹, M. Abdollahy^{2*}, S.M.J. Koleini³

1-MSc Student, Tarbiat Modares University (TMU), Tehran, Iran

2- Prof. Tarbiat Modares university (TMU), Tehran, Iran

3- Assoc. Prof. Tarbiat modares university (TMU), Tehran, Iran

Received 10 March 2012; received in revised form 13 November 2012; accepted 06 December 2012

*Corresponding author: minmabd@modares.ac.ir (M. Abdollahy).

Abstract

Using microflotation method, this study explored the collectorless flotation of Chalcocite and its dependence on the redox potential of pulp. Electrochemical studies were performed by cyclic voltammetry in specific potential ranges and at different pH values. The results show that significant floatability of Chalcocite occurs in the specific reducing conditions. By increasing potentials, on the other hand, the floatability of Chalcocite is reduced. The effect of pH was also examined: At pH=4, the maximum recovery of 73%, was obtained at $E = -222$ mV ($E_h = -17$); and at pH=9, the maximum recovery of 71% was obtained at $E = -501$ mV ($E_h = -296$). On the basis of the results obtained, the possible mechanisms of collectorless flotation of Chalcocite in different conditions were discussed.

Keywords: collectorless flotation, redox potential, Chalcocite, cyclic voltammetry.

1. Introduction

It is well known that sulphide minerals are semiconductors and can accept or donate electron. This shows the importance of electrochemistry on the floatability of sulphide minerals [1]. E_h plays a key role in dictating the properties of the sulphide – solution interface. The collectorless flotation of some sulphide minerals has been studied since the beginning of this century. Zheng and Manton showed that chalcopyrite in the Telfer ore had collectorless floatability characteristics while pyrite did not float without a collector [2]. A different point of view has been expressed recently suggesting that collectorless flotation of chalcopyrite occur in reducing environments [3]. It has further been stated that collectorless floatability of chalcopyrite occurs in a nearly Oxygen- free environment. It is clear that the interpretation of Yoon fundamentally differs from that of Trahar and Guo and Yen. They believe that the collectorless flotation of chalcopyrite is possible in an oxidizing environment [4, 5].

Luttrell and Yoon, Shuiyu, Lekki and Drzymala, and Chander used surface study techniques such as ESCA and Cyclic Voltammetry and showed that elemental sulfur was responsible for the collectorless flotation of chalcopyrite. The collectorless floatability of each sulphide is directly linked to its ease of oxidation as well as the stability of the hydrophobic surface state [6,7,8,9]. Chander, Fuerstenaund, and Walker et. al studied collectorless flotation of Chalcocite in reducing conditions [10,11]. Other sulphide minerals such as galena, pyrite, sphalerite and anargite has been studied by Robert et.al., Fornasiero et.al. Ceylan et.al. and Trahar et.al.[12,13,14,15,16].

This research aims at studying the collectorless flotation of Chalcocite in oxidation, which has no precedent, and reducing conditions. Cyclic voltammetry was used in order to recognize the surface species that are responsible for the collectorless flotation of Chalcocite.

2. Materials and methods

A high grade Chalcocite sample including 71% Cu_2S was prepared from the Meidoc copper ore, Iran. The other compounds in the sample were Pyrite, Chalcopyrite and quartz. The sample was crushed and sized using a ball mill to obtain a -75+38 microns fraction. Pulp potential was measured by means of an Ag/AgCl electrode. Microfloatation experiments were conducted in the Hallimond tube in the presence of nitrogen. In each test, a three-gram sample was used with 170 ml distilled water. Pulp potential was controlled by adding varying amount of ditionite sodium (0.05M) and potassium permanganate (0.05M) as reducing and oxidizing agents respectively. The conditioning time was 7 minutes and the gas flow rate was 1.5 l/min. MIBC was used as frother. The tests were conducted in buffer solutions in order to prevent the pH variation of solution because of the reactions that might take place between the mineral and the aqueous solution.

A conventional three-electrode system was used for electrochemical measurements in which an Ag/AgCl electrode as a reference, a platinum as counter electrode and mineral electrode as working electrode were used.

The working electrode was made by a mixture of high purity of Chalcocite, graphite and paraffin oil. These materials were packed completely in a mortar and pestle. After polishing the surface, electrode was quickly transferred to the cell. The electrochemical measurements were performed at 100 mv/s scan rate with Sama potentiostat.

Cyclic voltammetry tests were conducted in the flotation conditions. Before each test, nitrogen was purged in solution in order to remove the trace of oxygen from the electrode surface.

3. Results and Discussion

Figure 1 shows the recovery of collectorless flotation of Chalcocite against potential at pH=4. Chalcocite showed good floatability in reducing conditions and the maximum recovery, 73%, was obtained at $E = -222$ mV ($E_h = -17$). By increasing the potential, the floatability of Chalcocite was reduced to 18% at potential 602 mV ($E_h = 807$). E_h refer to potential at hydrogen electrode.

Figure 1. Collectorless flotation of Chalcocite as a function of pulp potential at pH=4

Cyclic voltammetry technique was used to elucidate reaction mechanism in Chalcocite flotation.

The voltammogram of Chalcocite which was obtained with various switching potentials at pH=4 is given in Figure 2.

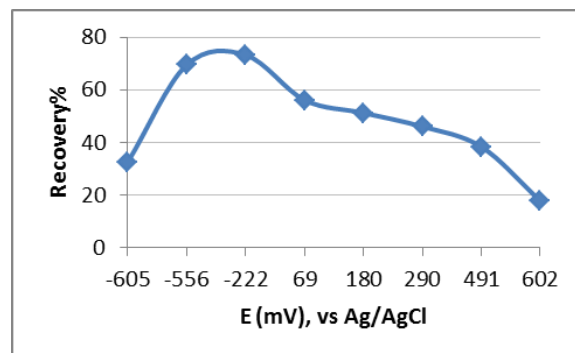


Figure 1. Collectorless flotation of Chalcocite as a function of pulp potential at pH=4.

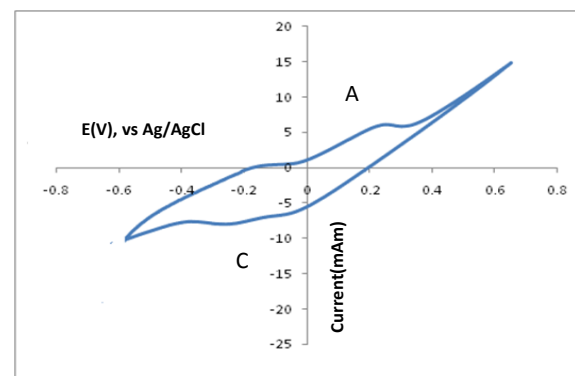
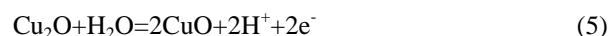
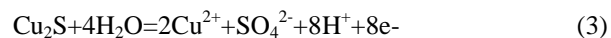
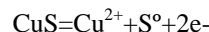


Figure 2. Cyclic voltammograms of Chalcocite scanned at 100 mV/s in collectorless flotation conditions (pH= 4).

At $E = 250$ mV ($E_h = 455$) an anodic peak, A, is observed. One of the following reactions may be related to this peak. According to Figure 3, Reactions 1, 4 and 5 are not stable in acidic region, so one of the Reactions 2 or 3 may be related to peak A.



Regarding to Figure 1, Chalcocite shows poor floatability at $E = 250$ mV ($E_h = 455$) so the components that are formed at point A (anodic peak) should be hydrophilic species (Equation 3). On the other hand, Eh-pH diagram of water-sulphur-copper (Figure 3) shows that the hydrophobic components are not formed in acidic conditions (pH=4). This confirms the results obtained in Figures 1 and 2. So hydrophilic species, that are formed in Reaction 3, may be related to peak A.

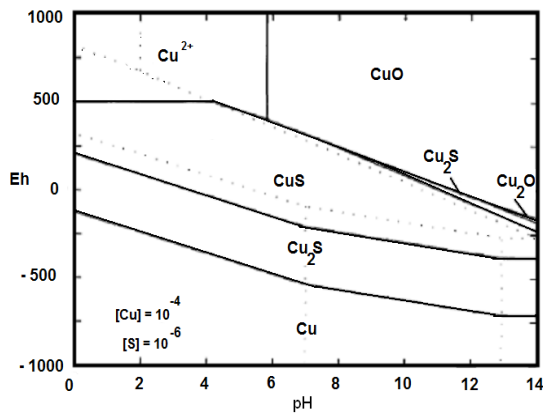


Figure 3. Eh-pH diagram of water-sulphur-copper [17]

The cathodic peak C (Figure 2) at $E = -250\text{mV}$ ($Eh = -45$) may be due to the reduction of oxidised products at more negative potential. Therefore the increase in floatability of Chalcocite in that potential may correspond to the Reaction (6) that produces hydrophobic species (S°).



As shown in Figure 4, the collectorless flotation of Chalcocite at $\text{pH}=9$ shows the same behavior as the one considered at $\text{pH}=4$ (Figure 1). Maximum recovery was obtained in moderately reducing conditions, 71%, at $E = -501\text{mV}$ ($Eh = -296$). By increasing the potential, the floatability of Chalcocite was reduced to 10% at 382 mV ($Eh=587$).

In voltammogram of Chalcocite, Figure 5, an anodic peak (A) appears at $E=100\text{ mV}$ ($Eh=305$). In this potential, Chalcocite showed poor floatability (Figure 4) since oxidized products were formed in the mineral surface (hydrophilic species). The study of Eh-pH diagram of Chalcocite in water also showed that in this potential CuO is stable. Therefore, peak A was attributed to the oxidation of Chalcocite to CuO in surface mineral (Reaction 5).

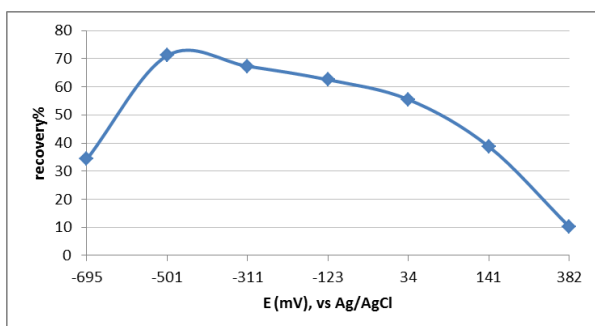


Figure 4. Recovery of collectorless flotation of chalcocite as a function of pulp potential at $\text{pH}=9$.

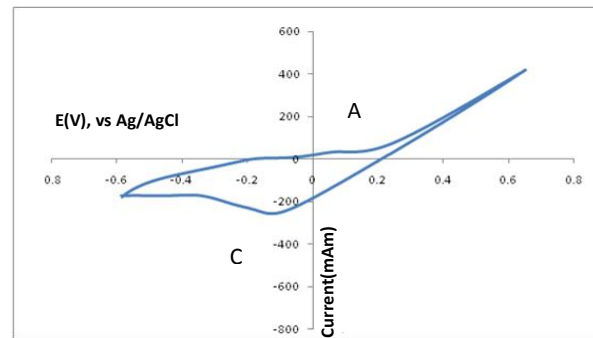


Figure 5. Cyclic voltammograms of Chalcocite scanned at 100 mV/s in collectorless flotation conditions ($\text{pH}=9$)

Voltammogram of Cu_2S showed that the inability of Cu_2S to float in oxidation region is attributed to the presence of hydrophilic species. The slight increase in flotation at moderate reducing potentials may arise from two separate processes: 1- Reduction of hydrophilic oxide or hydroxide groups to hydrophobic species. 2- The simultaneous reformation of Cu_2S or other Cu-S compounds on the surface.

4. Conclusions

The result of the collectorless flotation of Chalcocite at $\text{pH} 4$ and 9 showed that Chalcocite floated in moderately reducing region while depressed in oxidized conditions. Cyclic voltammetry studies showed two anodic peaks, one at $E=250\text{mV}$, $\text{pH}=4$ (Figure 2) and another at $E=100\text{mV}$, $\text{pH}=9$ (Figure 5). These peaks related to hydrophilic layer present in the chalcocite surface resulted in the depression of Chalcocite. In both voltammograms, two cathodic peaks were also observed at two points: 1) $E = -250\text{ mV}$, $\text{pH}=4$, 2) $E = -100\text{mV}$, $\text{pH}=9$, these peaks were attributed to the cathodic reactions followed by hydrophobic layer formation on the surface of Chalcocite which improved floatability.

Acknowledgement

The authors would like to thank Tarbiat Modares University for funding this study.

References

- [1]. Guler, T., Hicyilmaz, C., (2004). Hydrophobicity of chalcopyrite with dithiophosphate and dithiophosphinate in electrochemically controlled condition, *Colloids and Surfaces*, 235:11-15.
- [2]. Zheng, X., Manton, P., (2010). A potential application of collectorless flotation in a copper/gold operation, *Mineral engineering*, 23: 895-902.
- [3]. Yoon, R.H., (1981), Collectorless flotation of chalcopyrite and sphalerite ores by using sodium sulfide, *International Journal of Mineral Processing*, 8: 31-48.

- [4]. Trahar, W.J., (1983). A laboratory study of the influence of sodium sulfide and oxygen on the collectorless flotation of chalcopyrite, *International Journal of Mineral Processing*, 11: 57-74.
- [5]. Guo, H., Yen, W.-T, (2003). Pulp potential and floatability of chalcopyrite, *Minerals Engineering*, 16: 247-256.
- [6]. Luttrell, G.H., Yoon, R.H., (1984). Surface studies of the collectorless flotation of chalcopyrite, *Colloids and Surface*, 12: 239-254.
- [7]. Shuiyu, S., Dianzuo, W., and Bodan, L., (1994). Hydrophobicity-Hydrophilicity balance relationship collectorless flotation of sulfide minerals, *Journal of south university technology*, 1.
- [8]. Lekki, J., Drzymala, H., (1990). Flotometric analysis of the collectorless flotation of sulfide minerals, *Colloids and Surfaces*, 44: 179-190.
- [9]. Chander, S., (2003). Electrochemistry of sulfide flotation: Growth characteristics of surface coatings and their properties, with special reference to chalcopyrite and pyrite, *International Journal of Mineral Processing*, 33: 121-134.
- [10]. Chander, S., Fuerstenau, D.W., (1974). The effect of potassium diethyldithiophosphate on the electrochemical properties of platinum, copper and copper sulfide in aqueous solutions, *Electroanalyticalchemistry and Interfacial Electrochemistry*, 56: 217-247.
- [11]. Walker, G.W., Stout, J.V., and Richardson P.E.,(1984). Electrochemical flotation of sulfides: reactions of Chalcocite in aqueous solution, *International Journal of Mineral Processing*, 12: 57-72.
- [12]. Robert, A., Hayes, R.A., and Ralston, J., (1998). The collectorless flotation and separation of sulphide minerals by Eh control, *International Journal of Mineral Processing*, 23: 55-84.
- [13]. Fornasiero, D., Ralston, J., (2006). Effect of surface oxide/hydroxide products on the collectorless flotation of copper-activated sphalerite, *International Journal of Mineral Processing*, 78: 231-237.
- [14]. Khmeleva, T.N., Skinner, W., and Beattie, D.A., (2005). Depressing mechanisms of sodium bisulphite in the collectorless flotation of copper-activated sphalerite, *International Journal of Mineral Processing*, 76: 43-53.
- [15]. Ceylan, H., Hicyilmaz, C., Guler, T., (2002).Collectorless flotation of lead and zinc sulfide from Derekoyoredeposit, *Physicochemical Problems of Mineral Processing*, 36: 197-208.
- [16]. Trahar, W.J., Senior, G.D. and Shannon, L.K., (1994). Interactions between sulphideminerals - the collectorless flotation of pyrite, *International Journal of Mineral Processing*, 40: 287-321.
- [17].Chander, S., Fuerstenau, D.W., 1974, The effect of potassium diethyldithiophosphate on the electrochemical properties of platinum, copper and copper sulfide in aqueous solutions, *Electroanalyticalchemistry and Interfacial Electrochemistry*, v. 56, p. 217-247.