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COLLECTORLESS FLOTATION OF COPPER SULPHIDE ORES

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ABSTRACT

In this work, the flotation of copper sulfide ores is achieved without using collectors. The results of the collectorless flotation tests are comparable to those obtained by using thiol collectors. The grade of the Cu concentrate obtained in the laboratory close-circuit tests is 26.15% Cu with a recovery of 95.3%, where a disseminated copper ore containing 1.88% Cu is used. The effects of some factors, such as redox potential, pH and the addition of sodium sulfide, lime and frother, on the collectorless flotation of chalcopyrite are discussed.

Key words: Flotation; Collectorless flotation; Copper ores; Chalcopyrite; Sulfide minerals; redox potential

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Thiol-type collectors are widely used in the conventional flotation for sulphides. However, recently some experiments have revealed that chalcopyrite and sphalerite can be floated successfully without using collectors. This has rekindled an old argument with regard to whether sulfide minerals are naturally hydrophobic or not. Therefore, much attention has been paid to the investigation of collectorless flotation.

Lepetic (1974)[1] studied the collectorless flotation of chalcopyrite at pH6.1～6.6 with seven different frothers. The results showed that chalcopyrite can be floated successfully by using all these frothers after dry autogenous grinding. He attributed the results to the adsorption of oxygen on the fresh surface of dry-ground chalcopyite. The adsorption promoted the dehydration of the surface, and so made the surface hydrophobic and the mineral floatable.

Heyes and Trahar (1977)[2] tested four different kinds of mixtures of chalcopyrite and quartz. They found that chalcopyrites display natural floatability under oxidizing environment. The copper recovery ranged from 63.6 to 99.2%. But chalcopyrite will be non-floatable under reducing environment formed by adding some reducing reagents (sodium dithionite and ferrous sulfate). It may be concluded that the collectorless flotation behavior of the mineral mainly depends on the redox condition of the pulp rather than the presence or absence of oxygen.

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Gardner and Woods (1979)[3] had an electrochemical investigation of the natural floatability of chalcopyrite particles with a modified Hallimond tube and voltammeter, in which the potential at the mineral-solution interface was controlled potentiostatically. The experimental results demonstrated that chalcopyrite was naturally floatable if the potential of the mineral-solution interface was above a critical value but not if it was below this value, and thus confirmed Heyes and Trahar's observations (1977) that the natural floatability was associated with anodic oxidation of the surface of chalcopyrite. Linear potential sweep voltammeter has identified the products of the anodic reaction as CuS, $Fe(OH)_3$ and S. The presence of sulphur on the mineral surface is considered to be the critical factor in rendering chalcopyrite floatable.

On the other hand, however, M. C. Fuerstenau and J. Sabacky (1981)[5] confirmed that fresh chalcopyrite, chalcocite, galena, pyrite and sphalerite were naturally floatable in the absence of oxygen. The phenomena have been further supported by the collectorless flotation of chalcopyrite and sphalerite when the wet-ground ore samples are treated with sodium sulfide in the steel-ball grinding mill (Yoon, 1981[4]). The results are comparable to those obtained by using thiol collectors (see table 1). Elemental sulfur has not been detected by ESCA on the surfaces of concentrates produced by the collectorless flotation technique. Sodium sulfide is considered as a cleaning agen t which can remove hydrophilic oxides on the surfaces.

Table 1 Results of collectorless flotation, compared with those of collector flotation (from Yoon, 1981)

Feed and products	Collectorless flotation				Collector flotation			
	Assays (%)		Distribution(%)		Assays(%)		Distribution(%)	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
Feed	2.53	6.53	100.00	100.00	2.60	6.46	100.00	100.00
Cu conc.	23.24	6.53	81.8	8.91	25.48	4.68	83.70	6.19
Zn conc.	1.34	37.33	7.29	78.77	2.82	52.96	10.55	79.78

It is clear that Yoon, Fuerstenau and Sabacky's interpretation is different from that by Heyes, Trahar (1977), Gardner and Woods (1979) on the mechanisms of collectorless flotation of chalcopyrite, with special reference to roles of sodium sulfide and oxygen. Trahar (1983)[6] reported, later on, that chalcopyrite was not floatable in reducing conditions with or without sodium sulfide but became floatable when oxygen was made available. No evidence was found to suggest that chalcopyrite ground in the nearly absence of oxygen was highly floatable, or that chalcopyrite was not floatable in the presence of oxygen, either.

In 1984, Luffrell and Yoon[7] made a further study on collectorless flotation of chalcopyrite by using six different sources. The experimental results showed that some chalcopyrite can be floated by only using a frother but others can not unless they were treated with sodium suifide, depending on the surface oxidation of chalcopyrite. Chalcopyrite exhibits natural floatability at oxidizing potentials but not at reducing potentials. Anodic oxidation of the mineral surface, which forms elemental sulphur, is responsible for the change of the surface from a hydrophilic to a hydrophobic condition. It has also been found that there exists the dependence of the collectorless flotation on pH, the lower the pH, the better the flotation, These observations further confirmed the previous reports (Heyes and Trahar, 1979; Gardner and Woods, 1979; Trahar, 1983) that collectorless flotation only occured under oxidizing conditions, and threw doubt upon Yoon's early explanation (1981) that collectorless flotation of chalcopyrite can be achieved in reducing conditions.

During the course of our research, beginning at the end of 1983, we have found that the flotation of copper sulfide ores from four different mines can be achieved successfully without using collectors (see table 2). The results of collectorless flotation are almost the same as those obtained with collectors, in spite of the ore types (from porphyry, skarn or dissemination) or the ore grade. The grade of Cu concentration obtained in the laboratory close-circuit tests is 26.15% Cu with a recovery of 95.3%, where the disseminated copper ore containing 1.88% Cu is used.

Table 2 Results of collectorless flotation

Types of ore	Feed and product	Collectorless flotation		Collector flotation	
		Grade (%Cu)	Recovery (%)	Grade (%Cu)	Recovery (%)
Porphyry	Feed	0.53	100.00	0.53	100.00
	Rough conc.	7.23	90.75	6.66	90.76
Skarn	Feed	1.55	100.00	1.63	100.00
	Rough conc.	15.05	93.21	17.25	91.68
Dissemination	Feed	5.33	100.00	5.22	100.00
	Rough conc.	19.41	97.23	17.64	97.82
	Feed	3.45	100.00	3.45	100.00
	Rough conc.	22.95	95.30	22.14	95.20
	Feed	3.11	100.00		
	Conc.	27.91[1)]	96.20[1)]		
	Feed	1.88	100.00		
	Conc.	26.15[1)]	95.30[1)]		

Note: 1)——Results of close-circuit flotation test through one rougher stage followed by one cleaning stage

1 EXPERIMENTAL

1.1 Ore Samples

The ore samples used in the work are disseminated copper ores, which contain chalcopyrite, pyrite, quartz, talc and chlorite, etc.. The samples are crushed to – 3mm and stored without taking any precautions against the surface oxidation of the sulphide minerals. The samples consist of two different ores: high grade ore containing 3.28% Cu and 5.77% S, and low grade ore containing 1.79% Cu and

4.17% S.

1.2 Procedures

A 500g ore sample was ground in a laboratory steel ball mill with tap water until 76.1% by weight (high grade ore) or 68.8% by weight (low grade ore) through a 200 mesh stainless-steel screen, and the ground pulp was transferred into the flotation cell (0.5 or 1.5 L in volume), mounted on a XF-D Laboratory Model Flotation Machine made in China. For rougher flotation, the flotation time is about 15 min. For closed-flotation operation the final concentrates were produced through one rougher flotation followed by one cleaning flotation.

The redox potential of pulp was measured by using a high-impedance S-29A Model pH Meter made in China with platinum-calomel electrode pair inserted into the stirred slurry. The performance of the electrode pair was checked before each measurement by calibration in freshly prepared ZoBell's solution (Garrels and Christ, 1965)

1.3 Criteria

The concentration efficiency (E) is calculated as follows:

$$E = (R - W)/(1 - Ce/Cm)$$

where R—recovery; W—weight percent; Ce—feed grade; Cm—theoretic content of Cu in $CuFeS_2$ (34.5% Cu).

The flotation rate constants of chalcopyrite is calculated in terms of the model (Wu YiRui, 1985)[10].

$$R_0 - R = \sum_{i=1}^{3} R_{0i} \exp(-K_{Ri} t)$$

where R_0—theoretic recovery (%), R—recovery at t(%), R_{0i}—the theoretic recovery of i constituent (%), K_{Ri}—the flotation rate constant of i constituent, t—flotation time, i—constituent (including the fast, middle, and slow).

2 RESULTS AND DISCUSSION

2.1 The Redox Potential of Pulp

In order to study the effect of the redox potential of pulp on the collectorless flotation of copper sulphide ores, oxidizing agent ($(NH_4)_2S_2O_8$) and reducing agent ($Na_2S_2O_4$) are added respectively during the flotation which is carried out by the aeration of air or nitrogen. When oxidizing agent is added or air is blown, high redox potentials ($+250 \sim +350$mV) are obtained, and when reducing agent is added or nitrogen is blown, low redox potentials ($-100 \sim +140$mV) are achieved (Fig. 1). The results of the collectorless flotation show that chalcopyrite can be floated better at high redox potential than at low redox potential (See table 3). It may be concluded that the increase of the redox potential of pulp is beneficial to the collectorless flotation of chalcopyrite, this is consistent with early reports (Heyes and Trahar, 1977; Gardner and Woods, 1979),

It has also been found in our work that the potential of wet-ground pulp in a steel ball mill is about +125mV and lowered when sodium sulfide is added. But the pulp potential can be upraised to +325～+365 mV when the flotation is carried out under the condition of the aeration. This shows that the aeration of air can upraise pulp potential, thus copper sulphide ore can be floated well by the aeration of air without using collector even if the ore is ground with tap water in a reducing condition. This is fundamentally different from Yoon(1981) and Lepetic's (1974) reports.

2.2 Effect of pH

The collectorless flotation of sulphide ores as a function of pH is presented in Fig. 2, pH is regulated by NaOH or HCl. It is found that chalcopyrite can be floated better in acidic and basic pulp than in neutral conditions and that the optimum pH value for the flotation is about 10.

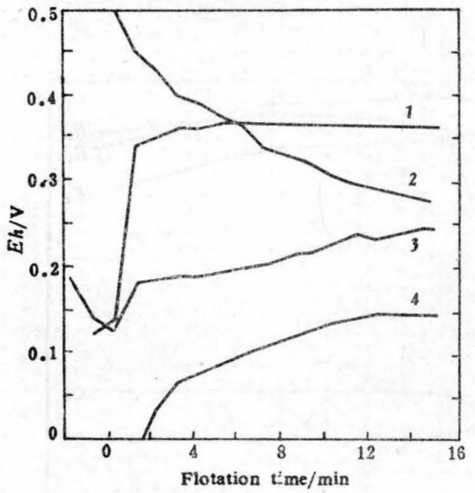

Fig.1 Pulp potential as a function of flotation time

1—Aeration of air
2—Addition of oxidizing agent and aeration of nitrogen
3—Aeration of nitrogen
4—addition of reducing agent and aeration of nitrogen

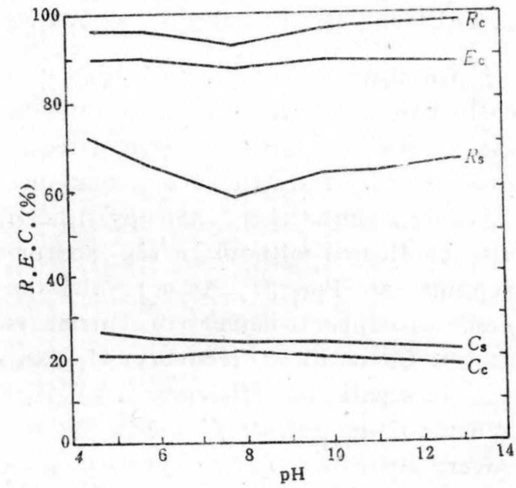

Fig.2 Effect of pH on collectorless flotation

R—Recovery; R_C—Cu recovery;
R_S—S recovery; *C*—Grade;
C_C—Cu grade; C_S—S grade;
E—Separation efficiency;
E_C—Separation efficiency of copper

Table 3 Effect of redox potential of pulp on the collectorless flotation of copper sulphide ores

Flotation conditions	Concentrate grade(%Cu)	Recovery of copper (%)
1	20.23	89.00
2	19.09	91.80
3	18.43	79.40
4	9.69	22.70

1, 2, 3, 4 represent respectively the same conditions as those in Fig.1.

Gardner and Woods (1979) have showed that the anodic oxidation of chalcopyrite's surface occures as follows:

at basic pH

$$CuFeS_2 + 3H_2O = CuS + Fe(OH)_3 + S + 3H^+ + 3e \quad (1)$$

at acidic pH

$$CuFeS_2 = CuS + Fe^{2+} + S + 2e \quad (2)$$

As shown above, S and CuS can be formed on the surface of chalcopyrite in acidic pulp, and basic pulp. The presence of element sulphur on the surface is responsible for the collectorless flotation of chalcopyrite. Reaction 1 and 2 are more likely to occur at higher potential, and the pH range in which reaction 1 takes place is wider at higher potential than that at lower potential. Our observations are not completely in agreement with Yoon's report that the collectorless flotation of chalcopyrite is achieved more readily at lower pH.

2.3 Effect of the Addition of Sodium Sulphide

Yoon has ever suggested that the collectorless flotation of chalcopyrite can be achieved by using strong reducing agent (Na_2S). However, our observations show that chalcopyrite can also be floated without using sodium suphide (see Fig. 3). As a result, the grade of copper rougher concentrate is 21.1% Cu with the recovery of 95% and the separation efficiency of 89.5%. When sodium sulfide is added, the recovery increases slightly, but the grade and the separation efficiency decrease, meanwhile the distribution of pyrite in copper concentrate increases. The addition of sodium sulphide results in reducing environment, but when air is blown into the flotation cell, the redox potential upraises rapidly to +345mV at which the collectorless flotation of the ore can be still achieved. However, if the dosage of sodium sulfide is above 1800 g/t, the pulp potential will maintain lower in spite of the aeration, which is not suitable for the collectorless flotation of chalcopyrite.

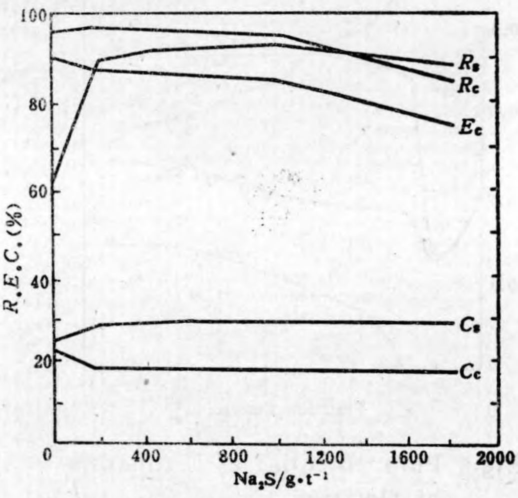

Fig.3 The effect of the addition of sodium sulphide on the collectorless flotation

2.4 Role of Lime

The relationship between pulp pH and floatability (Fig. 2) suggests that it is possible for the sulphide minerals to be floated in basic pulp by using NaOH as a pH regulator. However, if lime may be used instead of NaOH, the collectorless flotation in basic pulp will be more readily established in plant operation.

Therefore, the effects of lime on the collectorless flotation were investigated. As given in Fig. 4 and Fig. 5, the experimental results show that disseminated copper sulphide ore can be floated well with varying addition of lime, and that the potential of the pulp is slightly reduced by the addition of lime, but still ranged within that of collectorless flotation. In addition, the flotation of pyrite can be strongly suppressed by the addition of lime, which improves the grade of copper concentrate.

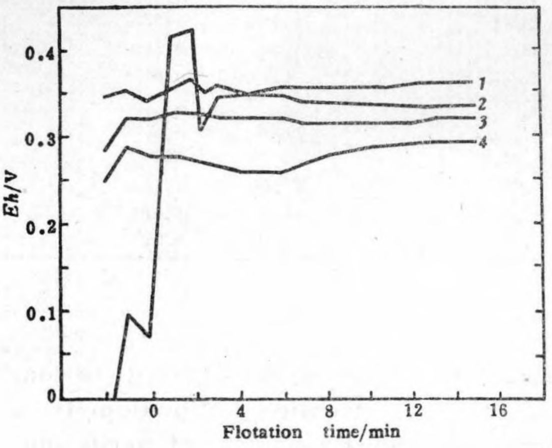

Fig.4 Effect of the addition of lime on the redox potential of the pulp
Addition of lime (g·t⁻¹) 1—0 2—500 3—1000 4—2000

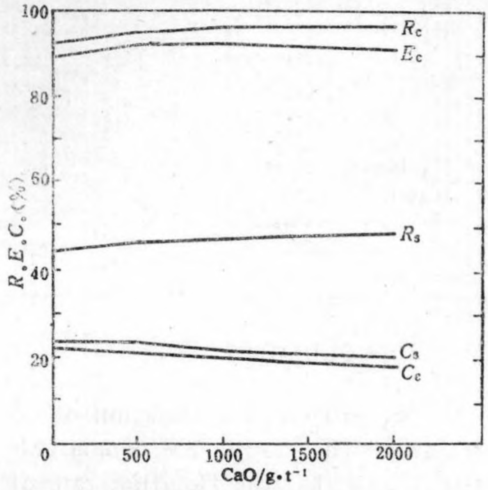

Fig.5 Effect of the addition of lime on the collectorless flotation

2.5 Role of Frother

The performance of a frother in the collectorless flotation system is greatly different from that in the conventional flotation system. In the collector flotation, a frother and collector may be coadsorbed at the surface of the air bubbles and the interfaces of mineral-solution. When the particles adhere to the bubble, frothers and collectors adsorbed on the interfaces of solution-air and mineral-solution may result in cross-coupling. However, in collectorless flotation system, a frother can be adsorbed alone. Because of the semiconductivity of sulphide minerals, such as that of chalcopyrite, a frother may also be adsorbed physically on the surface of sulphide minerals (Ronald. D. Crozier, 1980)[8]. The adsorption of the frother increases with the raising of the redox potential of the pulp (V. A. Chanturya, (1984)[9].

2.6 Comparison Between the Collectorless Flotation and the Conventional Flotation

The results of the flotation of high grade disseminated copper ores show that the collectorless flotation of chalcopyrite is almost as efficient as the flotation with collectors. However, the distribution of pyrite in copper concentrate is higher by the conventional flotation than by the collectorless flotation. In addition, the rate constants of the collectorless flotation of sulphide minerals are greater than those of the conventional flotation (see Table 4). Thus, it is found that the collectorless flotation can separate chalcopyrite from pyrite more efficiently.

Table 4 The flotation rate constants of sulphide minerals

Constitution	Collectorless flotation		Collector flotation	
	Distribution (%)	Rate constant	Distribution (%)	Rate constant
Chalcopyrite				
The highest theoretical recovery	98.99		99.67	
High rate constitution	58.33	2.34	44.43	1.976
Middle rate constitution	40.21	0.529	51.05	0.399
Low rate constitution	0.45	0.051	4.19	0.051
Pyrite				
The highest theoretical recovery	66.17		100.00	
High rate constitution	36.28	2.28	31.85	1.753
Middle rate constitution	27.62	0.371	36.10	0.181
Low rate constitution	2.27	0.051	32.05	0.051

3 CONCLUSIONS

The collectorless flotation of copper sulphide ore has been achieved in our research. The results are comparable to those of the conventional flotation. It is also found that the flotation rate of chalcopyrite is higher than that of pyrite during the collectorless flotation, and that the collectorless flotation of chalcopyrite is easily achieved at a higher redox potential.

Chalcopyrite can be floated better in the acidic or basic medium than in the neutral conditions. Lime may be used as pH regulator which can depress the flotation of pyrite and establish stable and suitable redox potential for the collectorless flotation.

The addition of sodium suphide can lower the redox potential of the pulp, but when air is blown, the potential rises rapidly, thus, the collectorless flotation can always be achieved in the presence or absence of sodium sulphide.

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硫化铜矿石的无捕收剂浮选

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摘　要

在本研究中硫化铜矿石无捕收剂浮选取得了与加捕收剂浮选相同的选别指标，含铜1.88％的浸染铜矿无捕收剂浮选小型闭路试验，获得品位26.15％，回收率95.3％的铜精矿．研究结果表明，无捕收剂浮选中，黄铜矿的浮选速率比黄铁矿高，对铜-硫矿石的优先浮选有利；氧化还原电位较高的矿浆中容易实现硫化铜矿石的无捕收剂浮选；黄铜矿在酸性或碱性矿浆中的可浮性都比在自然 pH 状态下好；用石灰调浆能获得硫化铜矿浮选所需的 pH 值和稳定、适宜的氧化还原电位，对黄铁矿又有较好的抑制作用；加入硫化钠时，矿浆的氧化还原电位相应降低，但当充空气浮选时，随即上升为较高的氧化还原电位，适合于无捕收剂浮选，本研究不用硫化钠处理，也能实现硫化铜矿石无捕收剂浮选．

关键词：浮游选矿；无捕收剂浮选；铜矿石；黄铜矿；硫化矿物；氧化还原电位

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