Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(6):2794-2800

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Combined Depressant for the Cu-S Separation in Low Alkaline Medium

AI Guang-hua[1,2], TAO Xiu-xiang[1] and YAN Hua-shan[2]

[1]School of Chemical Engineering and Technology ,China University of Mining and Technology, Xuzhou, Jiangsu 221116, China
[2]School of Resources and Environmental Engineering ,Jiangxi University of Science and Technology, Ganzhou, Jiangxi 341000, China

---

ABSTRACT

The Cu-S separation tests have been conducted at pH=7~8 with five combined depressants, namely, Starch + pyrogallic acid, sodium hypochlorite + pyrogallic acid, pyrogallic acid + Tannic, sodium hypochlorite + Tannic and calcium hypochlorite + DT-2$^{\#}$. The tests show that calcium hypochlorite + DT-2$^{\#}$ is the best depressor for pyrite, which leads to the Cu-S separation at a low alkalinity of pH=7~8 without lime. From the chemical analysis and Raman spectroscopy of the mineral surface, the inhibition mechanism of pyrite at a pH of 7~8 is as following: calcium hypochlorite + DT-2$^{\#}$ oxidizes the pyrite surface to produce a hydrophilous film of $Fe(OH)_3$ and $CaCO_3$, which enhances the hydrophilicity of the pyrite surface, and pyrite is fully depressed during the Cu-S separation, thus the separation of copper from sulfur has come true.

Keywords: low alkaline; combined depressant; Cu-S separation; pyrite; inhibition mechanism

---

INTRODUCTION

The key to the copper sulfide ore flotation is to separate copper from iron sulfide. The copper sulfide ores are usually covered by pyrite. High alkalinity technology has been used for a long period in order to achieve the Cu-S separation because of the interference of some fast-flotation pyrite. However they have four shortcomings: (1) some copper minerals are depressed and the recovery of copper is affected; (2) flotation froth becomes sticky and entrains more slime in the high alkalinity, which at last affects the copper concentrate is affected; (3) lime is easy to block the pipes because of its scale formation and concretion; (4) the recoveries of Au and Ag are affected. In a word, a study on the Cu-S separation technology in low alkalinity has important theoretical and practical significance for the Cu-S ore dressing. This paper studies the single mineral floating effects of pyrite and chalcopyrite with the five combined depressors in low alkaline (namely: Starch + pyrogallic acid(1:1), sodium hypochlorite + pyrogallic acid(1:2), pyrogallic acid + Tannic(1:2), sodium hypochlorite + Tannic(1:1) and calcium hypochlorite + DT-2$^{\#}$(1:1)), and the depressing mechanism of combined depressant of pyrite in low alkaline medium.

EXPERIMENTAL SECTION

A. Samples of single minerals

Pyrite (FeS_2) single minerals are taken from Anhui province, particle size range: -0.090+0.038 mm, purity: 95.64%; the major element analysis of pyrite is shown in Table 1. Chalcopyrite ($CuFeS_2$) single minerals are taken from Dexing Copper (off drugs after flotation), particle size range: -0.075+0.038 mm, purity :98.87%; the major element analysis of Chalcopyrite is shown in Table 2.

Table 1 Element analysis of Pyrite (%)

components	Cu	Fe	S
content	0.47	44.80	51.03

Table 2 Element analysis of Chalcopyrite (%)

components	Cu	Fe	S
content	34.45	30.35	34.80

B. Flotation of pure minerals

Each flotation with 5 grams sample is in a small-scale flotation of 50ml. The steps are as following: 1. add the mineral into the 100ml beaker, 2. add 15ml distilled water, 3. treat the mineral with ultrasonic cleaner for 5 minutes, 4. move to flotation cell, 5. add mineral flotation agents, 6. do pyrite and chalcopyrite flotation experiments in a variety of conditions.

RESULTS AND DISCUSSION

A. Effect of collector dosage

The effect of Xanthate dosage on the recovery of chalcopyrite and pyrite is shown in Figure 2.1. The results show that the recoveries of chalcopyrite and pyrite increase with the increasing amount of xanthate, but when the dosage reaches to 5.80×10^{-4} mol•L^{-1}, increasing the dosage of xanthate has no obvious effect on the recovery of pyrite and chalcopyrite. So the condition of single mineral tests are as following: butyl xanthate dosage, 5.80×10^{-4}mol•L^{-1} ; 2$^{\#}$ oil dosage , 60 mg•L^{-1}.

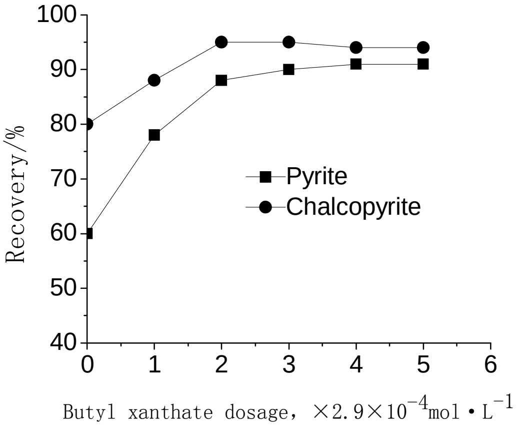

Fig2.1 The effect of collector dosage on the floatability of chalcopyrite and pyrite

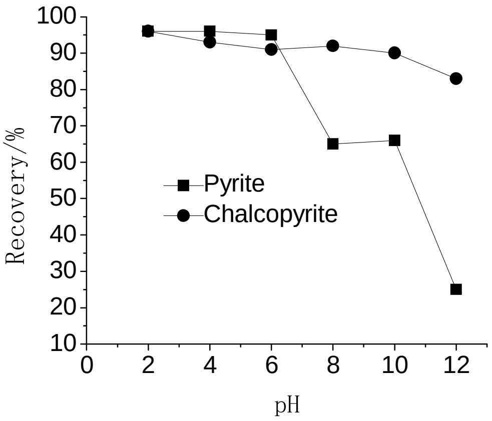

Fig2.2 The effect of varying the pH on the floatability of chalcopyrite and pyrite

B. The effect of varying the pH on the floatability of chalcopyrite and pyrite

Under the conditions of butyl xanthate dosage 5.80×10-4mol•L^{-1}, 2$^{\#}$ oil dosage of 60 mg•L^{-1} and no depressant, the experiment studies the effect of varying the pH on the floatability of chalcopyrite and pyrite. The result is shown in Figure 2.2.

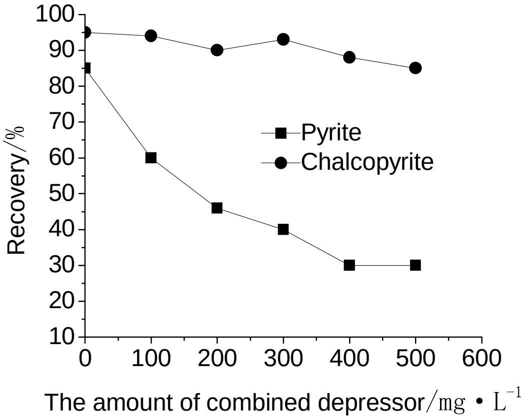

Fig2.3 The effect of Starch + pyrogallic acid dosage on the floatability of chalcopyrite and pyrite

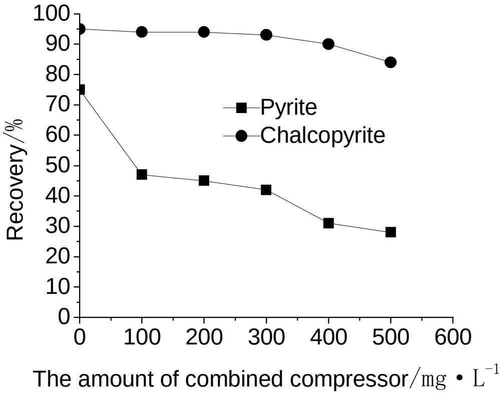

Fig2.4 The effect of sodium hypochlorite + pyrogallic acid dosage on the floatability of chalcopyrite and pyrite

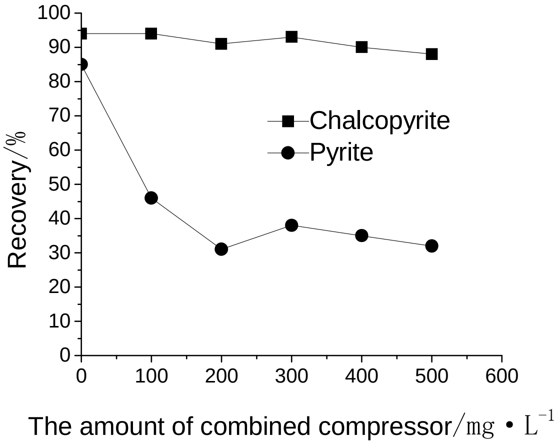

Fig2.5 The effect of pyrogallic acid + Tannic dosage on the floatability of chalcopyrite and pyrite

The floatability of chalcopyrite is better when the pH value is in the range from 2 to 12, and the recovery of chalcopyrite is not affected by pH value of slurry. The floatability of pyrite is better under acid conditions, but when the pH value of slurry increases to 7~8, its floatability begins to decline, and the recovery only reaches to 25.18% when the pH value is 12. At low pH value, it is possible that only adding the depressant can achieve the Cu-S separation.

C. The effect of combined depressant on the floatability in low alkalinity

When the slurry pH value is adjusted to 7 to 8, butyl xanthate dosage is 5.80×10^{-4}mol•L^{-1} and $2^{\#}$ oil dosage is 60 mg•L^{-1}, the effects of five combined depressants on the floatability of chalcopyrite and pyrite in low alkalinity have been reached. The results are shown in Figure 2.3 to 2.7.

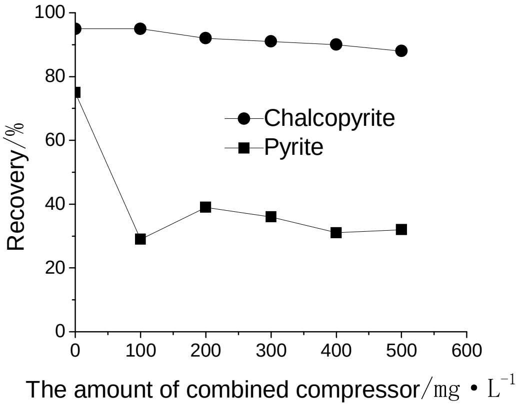

Fig2.6 The effect of sodium hypochlorite + Tannic dosage on the floatability of chalcopyrite and pyrite

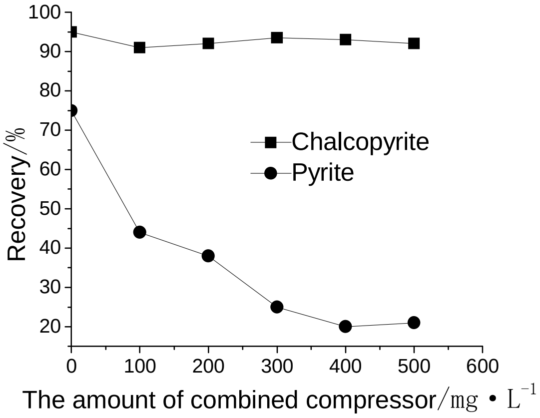

Fig2.7 The effect of calcium hypochlorite + DT-$2^{\#}$ dosage on the floatability of chalcopyrite and pyrite

The above results show that five combined depressants do not change the floatability of chalcopyrite, but they have a certain degree of inhibiting pyrite. $Ca(ClO)_2$ + DT-$2^{\#}$ has the best inhibitory effect of the pyrite. The floating rate of pyrite greatly reduces with the dosage increasing. When the dosage is 400 mg•L^{-1}, the recovery of pyrite is only 19.88%.

D. Flotation of artificial mixed ore

According to the previous single mineral tests, we can see that in the low alkalinity, $Ca(ClO)_2$ + DT-$2^{\#}$ has good inhibitory effect on the pyrite, but it does not basically change the floatability of chalcopyrite. To further study the $Ca(ClO)_2$ + DT-$2^{\#}$ on the inhibition of pyrite and the possibility of the Cu-S separation, this paper studies the flotation separation in different copper and sulfur proportion of artificial mixture ore in low alkalinity. The slurry pH value is adjusted to 7 to 8, butyl xanthate dosage is 5.80×10^{-4}mol•L^{-1} and $2^{\#}$ oil dosage is 60 mg•L^{-1}.The results are shown in Table 3.

Table 3 The results of flotation of chalcopyrite and pyrite by flotation %

chalcopyrite：pyrite	Products	Yield	Grade		Recovery	
			Cu	S	Cu	S
1：1	Concentrate	55.26	31.17	35.12	95.06	45.50
	Tailings	44.74	2.01	51.95	4.94	54.50
	Ore	100	18.12	42.65	100	100
1：5	Concentrate	25.48	21.75	43.65	88.67	23.52
	Tailings	74.52	0.95	48.52	11.33	76.48
	Ore	100	6.25	47.28	100	100
1：10	Concentrate	17.08	17.24	45.86	92.60	16.61
	Tailings	82.92	0.28	47.43	7.40	83.39
	Ore	100	3.18	47.16	100	100
1：20	Concentrate	13.68	16.24	44.27	89.58	12.58
	Tailings	86.32	0.3	48.77	10.42	87.42
	Ore	100	2.48	48.16	100	100

From table 3, we can see that $Ca(ClO)_2$ + DT-$2^{\#}$ has the good characteristic of suppression and adaptability, can successfully achieve the separation of chalcopyrite and pyrite, and can get better flotation indicators.

E. Depressing mechanism of combined depressant of pyrite in low alkaline medium

To further understand the role of the $Ca(ClO)_2$ + DT-$2^{\#}$ in the Cu-S separation, and to better direct practice, the depressing mechanism of $Ca(ClO)_2$ + DT-$2^{\#}$ of pyrite in low alkaline medium has been studied by chemical analysis and Raman spectroscopy of mineral surface.

- **The electrochemical analysis of pyrite surface**

In alkaline or neutral conditions, the (1) to (3) oxidation reactions may occur to the surface of pyrite. The zerovalent sulfur (S^0) of sulfide mineral surface is very unstable. It will be oxidized into $S_2O_3^{2-}$, SO_4^{2-} and HSO_4^- in the flotation pulp when adding $Ca(ClO)_2$ + DT-$2^{\#}$ oxidation, as shown in (4) to (6) equation.

$$FeS_2 + 2H_2O \rightarrow Fe(OH)_2 + S^0 + 2H^+ + 2e \tag{1}$$

$$FeS_2 + 5H_2O \rightarrow Fe(OH)_2 + S_2O_3^{2-} + 8H^+ + 6e \tag{2}$$

$$FeS_2 + 10H_2O \rightarrow Fe(OH)_2 + 2SO_4^{2-} + 18H^+ + 14e \tag{3}$$

$$2S^0 + 3H_2O \rightarrow S_2O_3^{2-} + 6H^+ + 4e \tag{4}$$

$$S^0 + 4H_2O \rightarrow SO_4^{2-} + Fe(OH)_2 \tag{5}$$

$$S^0 + 4H_2O \rightarrow HSO_4^- + 7H^+ + 6e \tag{6}$$

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e \tag{7}$$

A large quantity of $Fe(OH)_2$ formed on the surface reaction will be further oxidized to $Fe(OH)_3$, as shown in (7) equation. The $Fe(OH)_3$ is slightly soluble in water, its Ksp is smaller than the Fe $(OH)_2$, and it can be stable in alkaline medium. Therefore, we can determine $Fe(OH)_3$ formed on the pyrite surface is the important reason for the pyrite inhibition.

On the other hand, $Ca(ClO)_2$ can produce Ca^{2+} when it dissolves in water. Ca^{2+} and SO_4^{2-} formed on the pyrite surface can produce precipitation. Pulp in the flotation process will absorb part of CO_2 and produce a certain amount of CO_3^{2-}. Because of $Ksp_{\text{calcium carbonate}} < Ksp_{\text{calcium sulfate}} < Ksp_{\text{calcium hydroxide}} < Ksp_{\text{calcium chloride}}$, the (8)~(10) reactions will take place in the solution, which leads to the main component of mineral surface, calcium carbonate, and its chemical property of calcium carbonate is very stable in an alkaline environment, so it can securely wrap on pyrite surface. This is also another reason why the floatability of pyrite becomes worse.

$$CaSO_4 + CO_3^{2-} = CaCO_3 \downarrow + SO_4^{2-} \tag{8}$$

$$Ca(OH)_2 + CO_2 = CaCO_3 \downarrow + H_2O \tag{9}$$

$$CaCl_2 + CO_3^{2-} = CaCO_3 \downarrow + 2Cl^- \tag{10}$$

From the above analysis, it can be seen that the mechanism of the Cu-S separation is that $Fe(OH)_3$ and Calcium carbonate have synergistic effect, which leads to the formation of the hydrophile film on the surface of pyrite with the main components of Fe$(OH)_3$ and $CaCO_3$ and which greatly enhances the hydrophilicity of the pyrite surface, then pyrite is inhibited in the pulp, and the Cu-S separation can be achieved in lime-free condition.

- **Raman spectroscopy analysis of pyrite**

The inhibition mechanism of pyrite has been studied with Raman spectroscopy. After its being treated with xanthate, Raman spectroscopy analysis of the pyrite surface has been done respectively when $Ca(ClO)_2$+DT-$2^{\#}$ is added or not added. The results are shown in Figure 3(a) and Figure 3(b).

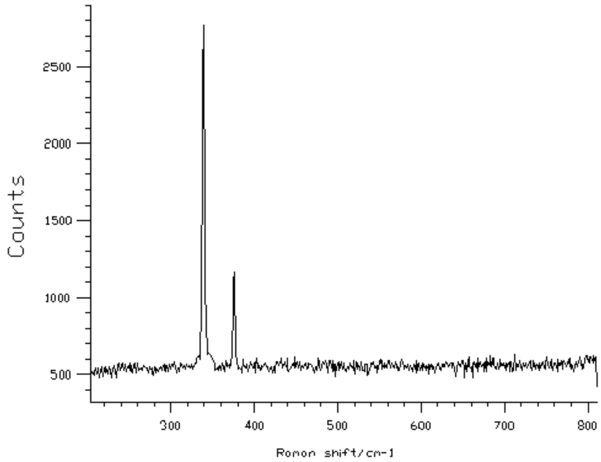

Fig3(a) Raman spectroscopy of Pyrite surface after adding butyl xanthate Butyl xanthate:5.80×10-4mol•L^{-1};PH value adjusted to 7~8 with NaOH

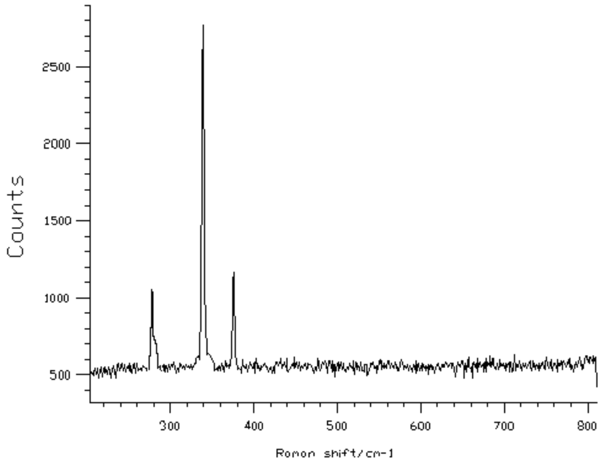

Fig3(b) Raman spectroscopy of Pyrite surface after adding calcium hypochlorite + DT-2#
Butyl xanthate:5.80×10-4 mol•L^{-1};calcium hypochlorite: 200 mg•L^{-1}; DT-2#:200 mg•L^{-1};PH value adjusted to 7~8 with NaOH

Some findings have been made about the action mechanism of flotation reagent by Raman spectroscopy analysis of mineral surface: the pyrite surface changes a lot after adding $Ca(ClO)_2$+ DT-2#, there is a peak near 280cm^{-1}, which belongs to the typical peak of calcium carbonate; a new hydrophilic film of calcium carbonate has formed and butyl xanthate is very difficult to trigger the chemical reaction on the pyrite surface, which then increases the difference in floatability of chalcopyrite and pyrite on their surface so that pyrite is fully inhibited during the Cu-S separation process and the Cu-S separation in lime-free condition has come true.

CONCLUSION

(1) Single mineral results show that five combined depressants do not change the basic floatability of chalcopyrite, and Ca $(ClO)_2$ + DT-$2^{\#}$ has a good depressing action on pyrite in low alkaline.

(2) Separation tests of artificial mixed ore show that $Ca(ClO)_2$ + DT-$2^{\#}$ has good selectivity and strong adaptability, which can achieve a successful separation of artificial mixed ore with different proportions of chalcopyrite and pyrite, and gets a good dressing performance.

(3) From the chemical analysis and Raman spectroscopy of the mineral surface, we can reach a conclusion that $Ca(ClO)_2$ + DT-$2^{\#}$ makes the pyrite surface form a hydrophilic film, which greatly enhances the hydrophilicity of the pyrite surface. Pyrite is inhibited in the flotation process, and the Cu-S separation in lime-free condition has come true.

Acknowledgements

The study has been supported by the Natural Science Foundation of Jiangxi Province (20122BAB216021) and also by Jiangxi Province branch of the office of science and technology support program (20121BBG70005), and also by Department of Education projects in Jiangxi Province (GJJ13400 and GJJ13400)，both of which are gratefully acknowledged.

REFERENCES

[1] Liu B, Zhou Y. *Journal of jiangxi university of science and technology*, **2008**, 29(3): 24-25. (In Chinese)
[2] Yu XY, Zhou Y, zhong H. *Metal Mine*, **2009**(9): 65-67. (In Chinese)
[3] Zhou Y, Liu L, Zeng J. *Metal Mine*, **2009**(6): 69-72. (In Chinese)
[4] Liu ZL, Xu F. *Mining and Metallurgical Engineering*, **2005**, 25(5): 33-34. (In Chinese)
[5] Ai GH, Zhou Y. Study on Benefic iation P rocess ofCopper Sulphide Ore in Low A lkali Conditions. *Metal Mine*, **2010**(7): 41-42. (In Chinese)
[6] Nagaraj Dr, Wang Ss, Frattaroli D R. Flotation of copper sulfide minerals and pyrite with new and existing sufur-containing collectors. *Proc.13th CMMI Congress Metall. Singapore CMMI and Ausr.Institute of Mining and Metallurgy*, **1986**: 49-57.
[7] Nagaraj D R, Lewwllyn M E, Wang S S, Frattaroli D R. New sulfide and precious metals collector: for acid,neutral and mildly alkaline circuits). *International mineral processing congress*. **1988**: 1221-1232.
[8] Liu GY, Zhong H, Dai T G. *Minerals and Metallurgical Processing*, **2008**, 25 (1): 19-24.
[9] Zhan XS, Zhong H, Liu GY. *Non-ferrous metals (mineral part)*, **2009**, (2): 36-37.