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Electrochemical mechanism of thioglycolic acid depressing sulphide minerals^①

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[Abstract] The effects of thioglycolic acid (TGA) on the rest potential and zeta potential of sulphide minerals were studied and the electrochemical mechanism of TGA depressing sulphide minerals was put forward. Results of flotation test show that galena, pyrite and chalcopyrite can be well depressed by TGA, but sphalerite and arsenopyrite can not be depressed. Tests also show that TGA has a little influence on zeta potential of sulfide minerals covered by xanthate coatings and TGA can lower the rest potential of sulphide minerals. The electrochemical mechanism of TGA depressing sulphide minerals is that the dioxanthogen adsorbing on the mineral surface will be unstable and reduced when rest potential value of sulphide mineral (φ_{MS}) is less than the reversible potential of reduction of dioxanthogen to xanthate $\varphi_{X^-|X_2}$ in the presence of TGA, flotability of sulphide mineral becomes weak; inversely, the coatings of dioxanthogen on mineral surface will keep stable when $\varphi_{MS} > \varphi_{X^-|X_2}$, sulphide mineral keeps flotability. In the system of mixed minerals, the electrochemical condition of separation of two sulphide minerals by TGA is $\varphi_{MS1} < \varphi_{X^-|X_2}(\varphi_{X^-|PbX_2}) < \varphi_{MS2}$.

[Key words] TGA; sulphide minerals; electrode potential; separation; pulp concentrate

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1 INTRODUCTION

Recently there are a number of reports about the organic depressants in sulfide flotation, such as thioglycolic acid^[1, 2], dextrin^[3, 4], CTP^[5-9] and other organic depressants^[10]. There are many advantages of using organic compounds as depressants of sulfide minerals in separation, such as low pulp alkaline, no heavy metal ions pollution and low dosages. The studies of mechanism on organic depressants interacting with sulfide minerals focus on chemical factors and few involve electrochemical factors. In fact electrochemical factors play an important part in the process of sulfide flotation. It is well known that flotation of sulfide is an electrochemical mechanisms^[11], the products of xanthate on the sulfide minerals can be adjusted by controlling pulp potential. In addition, the mechanism of many inorganic depressants in sulfide separation, such as reducing agent and oxidant, can be explained by electrochemical principles. It is obvious that stability of collector coating on the sulfide mineral surface (such as dioxanthogen or metal xanthate) controlled by electrochemical factors plays an important part in the separation of sulfide minerals in the presence of organic depressant. So it is necessary to consider the electrochemical factors into the mechanisms of organic depressant interacting with sulphide minerals.

In this paper the effects of TGA on zeta potential and rest potential of sulfide mineral are tested to investigate the correlation between electrochemical activity of TGA and depressing ability of TGA on sulfide minerals.

2 EXPERIMENTAL

2.1 Minerals sample

Chalcopyrite with particle size of 0.13 ~ 0.09 mm and purity of 95.2% was from Zhongtiaoshan Mine in Anhui Province. Pyrite with particle size of 0.09 mm ~ 0.06 mm and purity of 93.4% was from Dongbo Mine in Hunan Province. Sphalerite with particle size of 0.09 mm ~ 0.06 mm and purity of 94.3% was from Dachang Mine in Guangxi Province. Galena with particle size 0.13 mm ~ 0.09 mm and purity of 94.5% was from Shui Koushan Mine in Hunan Province. Arsenopyrite with particle size of 0.13 mm ~ 0.11 mm and purity of 96.8% was from Yao Gangxuan Mine in Hunan Province.

2.2 Flotation tests

2.2.1 Flotation tests of pure mineral

For better understanding the depressing ability of depressants, the bulk flotation system was adopted in this test. Butylxanthate of 2.5×10^{-5} mol/L was added after 2 g mineral sample was cleaned by super-

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sonic waver, then depressant was added after 2 min, flotation was carried out after 3 min, flotation time was 5 min. All tests were done in the buffer solution of pH 6.86.

2.2.2 Separation tests of artificial mixed bulk concentrate

Two different pure minerals were mixed with mass ratio of 1:1, then foam products were floated as bulk concentrate by butylxanthate and tailing was discarded, at last the foam product was separated by TGA.

2.3 Zeta potential and rest potential measurement

Zeta Potential Analyzer made by Brookhaven Instruments Corporation was used to measure zeta potential on the mineral surface. Rest potential, in fact, was the electrode potential of mineral in the case of open circuit (when current of electrode is zero) in the solution, which could be measured by means of Potentiometer. All data were measured for many times and arithmetic means were taken as the results of measurement.

2.4 Test of surface products

Dual-wavelength/Double-beam Recording Spectrophotometer UV-3000 was used to detect the xanthate concentration in solution at $\lambda_{\max}$ of 301~303 nm. For dixanthogen, cyclohexane was used to extract dixanthogen from mineral surface and then the Dual-wavelength/Double-beam Recording Spectrophotometer UV-3000 was used to detect dixanthogen concentration at $\lambda_{\max}$ of 238~242 nm and $\lambda_{\max}$ of 278~281 nm.

3 ELECTROCHEMICAL MECHANISMS OF THIOGLYCOLLIC ACID

3.1 Depressing ability

Thioglycolic acid (TGA) is often used to depress chalcopryite in the separation of Cu and Mo. Here, five pure sulfide minerals were used to test the depressing ability of thioglycolic acid. It can be seen from Fig. 1 that TGA can depress chalcopryite, pyrite and galena but can not depress sphalerite and arsenopyrite. Tests of products of xanthate show that the xanthate products on the pyrite surface, arsenopyrite surface, chalcopryite surface and sphalerite surface (activated by Cu^{2+}) are dixanthogen. Dixanthogen can electrochemically adsorb on the sulphide mineral surface without involving metal atoms of mineral, so if TGA can depress the sulphide mineral whose surface is covered by dixanthogen coatings, then TGA should depress all minerals whose surface are also covered by dixanthogen, but here TGA can not depress arsenopyrite and sphalerite whose surface are covered by dixanthogen. This result indicates that the depressing interaction of TGA on sulfide minerals

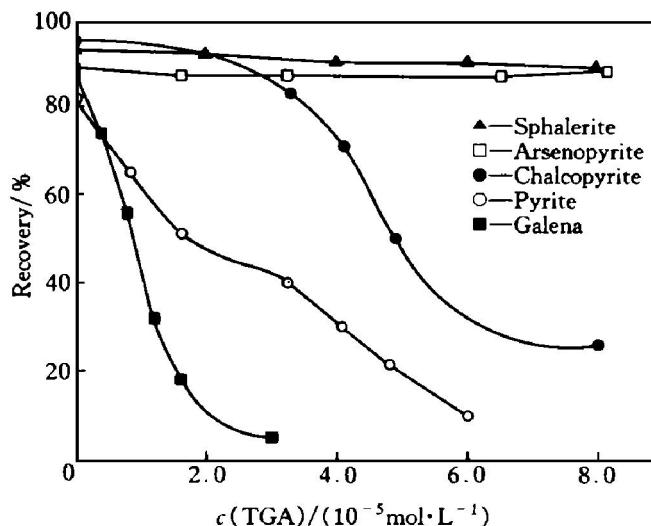


Fig. 1 Effect of thioglycolic acid on flotation behavior of sulfide minerals at pH 6.8
(Concentration of buthyl xanthate is $2.5 \times 10^{-5} \text{ mol/L}$.)

is not only related to chemical interaction factor but also related to other factors.

TGA is a strong reducing agent, its standard redox potential value is -0.33 V , which is obviously low to the standard redox potential value of buthyl xanthate (-0.128 V). The pulp potential value is about -0.07 V when TGA concentration is $5 \times 10^{-5} \text{ mol/L}$, which is low to the thermodynamic potential (0.148 V) of buthyl xanthate of $2.5 \times 10^{-5} \text{ mol/L}$ oxidized to buthyl dixanthogen, so dixanthogen would be reduced into xanthate and all minerals covered by dixanthogen coatings should be depressed at this negative pulp potential caused by TGA due to reduction of dixanthogen, but there were only pyrite and chalcopryite to be depressed, arsenopyrite and sphalerite kept good flotability. This result indicates that pulp potential is not enough to explain the mechanism of TGA depressing sulfide minerals. In order to further explore the depressing mechanisms of TGA on sulphide minerals, the effects of TGA on zeta potential and rest potential of sulphide minerals have been researched.

3.2 Effects of thioglycolic acid on zeta potential and electrode potential of minerals

At first, we measured the zeta potential of sulfide mineral covered xanthate in the presence of thioglycolic acid at pH 6.8. It can be seen from Table 1 that thioglycolic acid has little influence on zeta potential of sulfide minerals, which may indicate that chemical interaction is not main mechanisms in the process of thioglycolic acid depressing sulfide minerals.

The concentrations of butyl xanthate (BX) after interaction with five minerals were tested by Dual-wavelength/Double-beam Recording Spectrophotometer UV-3000. It can be seen from Table 2 that there are different concentrations of xanthate in dif-

Table 1 Effect of thioglycolic acid on zeta potential of sulfide minerals

Minerals	Zeta Potential/ V	
	No TGA	TGA
Sphalerite	- 0.025 5	- 0.029 8
Galena	- 0.023 7	- 0.026 9
Pyrite	- 0.023 5	- 0.026 3
Arsenopyrite	- 0.031 8	- 0.032 5
Chalcopryite	- 0.029 2	- 0.033 7

All data are measured many times and arithmetic mean is taken as the result of measurement; Butyl xanthate concentration is 2.5×10^{-5} mol/L, TGA concentration is 1.0×10^{-4} mol/L

Table 2 Concentration of BX after interaction with different sulfide minerals (10^{-5} mol/L)

Sphalerite	Chalcopryite	Pyrite	Arsenopyrite	Galena
0.35	0.43	1.45	1.30	0.40

ferent mineral system, which means that there are different values of $\varphi_{X^-|X_2}$ or $\varphi_{X^-|PbX_2}$ in different mineral pulp.

According to data of Table 2, we can obtain the following thermodynamic reversible potential of reducing dioxanthogen to xanthate on the surface of pyrite, sphalerite, pyrite and arsenopyrite, and reversible potential of reduction lead buthyl xanthate on galena surface.

For galena^[12]:



$$\varphi^\ominus = 0.178 \text{ V}$$

When $c(BX^-) = 0.40 \times 10^{-5}$ mol/L, $\varphi_{X^-|PbX_2} = 0.139 \text{ V}$.

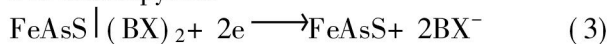
For pyrite^[12]:



$$\varphi^\ominus = 0.128 \text{ V}$$

When $c(BX^-) = 1.45 \times 10^{-5}$ mol/L, $\varphi_{X^-|X_2} = 0.157 \text{ V}$.

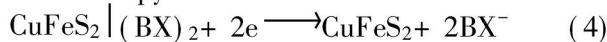
For arsenopyrite:



$$\varphi^\ominus = 0.128 \text{ V}$$

When $c(BX^-) = 1.30 \times 10^{-5}$ mol/L, $\varphi_{X^-|X_2} = 0.160 \text{ V}$.

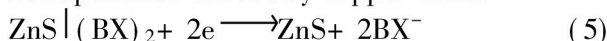
For chalcopryite:



$$\varphi^\ominus = 0.128 \text{ V}$$

When $c(BX^-) = 0.43 \times 10^{-5}$ mol/L, $\varphi_{X^-|X_2} = 0.189 \text{ V}$.

For sphalerite acted by copper anion:



$$\varphi^\ominus = 0.128 \text{ V}$$

When $c(BX^-) = 0.35 \times 10^{-5}$ mol/L, $\varphi_{X^-|X_2} = 0.197 \text{ V}$.

The rest potential of sulphide minerals in the ab-

sence and the presence of TGA are listed in Table 3. It can be seen from Table 3 that TGA can lower the rest potential of sulfide mineral electrode, the rest potential values of chalcopryite, pyrite and galena are low to the reduction potential values of its collector coatings respectively, while the rest potential values of arsenopyrite and sphalerite are over to the reduction potential values of its collectors coatings respectively. It can be known from the mixed pulp potential model of electrochemical flotation^[11] that when rest potential of sulfide mineral (φ_{MS}) is below to the $\varphi_{X^-|X_2}$, dioxanthogen on the sulfide mineral surface will be unstable and reduced into xanthate (this conclusion can be expanded to the system of metal xanthate). It can be expected that the adsorbing density of xanthate on the mineral surface is decreased and dioxanthogen is reduced into xanthate when $\varphi_{MS} < \varphi_{X^-|X_2}(\varphi_{X^-|PbX_2})$, the adsorbing density of xanthate on mineral surface keeps unchanged when $\varphi_{MS} > \varphi_{X^-|X_2}(\varphi_{X^-|PbX_2})$. On the basis of above electrochemical model, it can be predicted from Table 3 that the dioxanthogen on the surface of chalcopryite, pyrite and lead xanthate on the galena surface will be unstable but dioxanthogen on arsenopyrite surface and sphalerite surface will keep stable in the presence of TGA. Tests of adsorbing density of xanthate and surface products^[13~15] have verified these results.

Table 3 Effect of TGA on rest potential of sulphide minerals

Minerals	Rest potential of mineral/ V		$\varphi_{X^- X_2}$ or $\varphi_{X^- PbX_2}/ \text{V}$
	No TGA	TGA	
Chalcopryite	0.213	0.114	0.189
Pyrite	0.262	0.090	0.157
Arsenopyrite	0.223	0.170	0.160
Sphalerite	0.24	0.237	0.197
Galena	0.145	0.082	0.139

$c(\text{TGA}) = 1.0 \times 10^{-4}$ mol/L

3.3 Separation of artificial mixed bulk concentrates

According to results of pure minerals tests, TGA can be possibly used to carry out the separation of galena-arsenopyrite, pyrite-arsenopyrite, arsenopyrite-chalcopryite and sphalerite-chalcopryite. Results of artificial mixed bulk concentrate test show that the bulk concentrates of pyrite-arsenopyrite, galena-arsenopyrite and sphalerite-chalcopryite are separated in the presence of TGA (results listed in Tables 4~6), however the bulk concentrate of arsenopyrite and chalcopryite can not be separated by TGA.

There are at least two reasons to cause flotation behavior difference between single mineral system and mixed minerals system, one is due to the contact potential between minerals, the other is due to the change of $\varphi_{X^-|X_2}(\varphi_{X^-|PbX_2})$ which is related to xan-

thate concentration. The value of $\varphi_{X^-|X_2}$ ($\varphi_{X^-|PbX_2}$) will be different in different mineral system due to different adsorbing capacity of mineral to xanthate, for example, $\varphi_{X^-|X_2}$ is 0.157 V in the pulp of pyrite and 0.189 V in the pulp of chalcopyrite. But when two sulfide minerals are put into one pulp, the value $\varphi_{X^-|X_2}$ must be only one for two minerals due to one xanthate concentration, for example, $\varphi_{X^-|X_2}$ is 0.184 V in chalcopyrite and pyrite pulp.

Table 7 lists the data of φ_{MS} of sulfide mineral and $\varphi_{X^-|X_2}$ ($\varphi_{X^-|PbX_2}$) of xanthate in different mixed mineral system in the presence of TGA. It can be seen from Table 7 that $\varphi_{FeS_2} < \varphi_{X^-|X_2} < \varphi_{FeAsS}$ in the FeAsS+ FeS₂ mixed system, $\varphi_{CuFeS_2} < \varphi_{X^-|X_2} < \varphi_{ZnS}$ in the ZnS+ CuFeS₂ mixed system, $\varphi_{FeAsS} > \varphi_{X^-|X_2}$ and $\varphi_{PbS} < \varphi_{X^-|PbX_2}$ in the PbS+ FeAsS mixed system. According to the electrochemical principle of collector desorption, collector coatings on mineral surface whose rest potential is below to $\varphi_{X^-|X_2}$ ($\varphi_{X^-|PbX_2}$) will be unstable and reduced, the flotabil-

ity of mineral will become bad; while the collector coatings on mineral surface which rest potential is over to $\varphi_{X^-|X_2}$ ($\varphi_{X^-|PbX_2}$) will keep stable, the flotability of mineral will keep good. So the separation of above three mixed bulk concentrate can be carried out in the presence of TGA. As for arsenopyrite and chalcopyrite mixed system, dioxanthogen on both minerals will keep unstable due to rest potential of CuFeS₂ and FeAsS are both less than $\varphi_{X^-|X_2}$, therefore TGA has no selectivity to separate CuFeS₂ and FeAsS.

4 CONCLUSIONS

1) The electrochemical mechanism of TGA depressing sulfide mineral is to lower the rest potential of sulfide mineral. When $\varphi_{MS} < \varphi_{X^-|X_2}$ ($\varphi_{X^-|PbX_2}$), collector coatings of sulfide mineral will be unstable and reduced, sulfide mineral can be depressed by TGA; when $\varphi_{MS} > \varphi_{X^-|X_2}$ ($\varphi_{X^-|PbX_2}$), collector coatings of sulfide mineral will keep stable, sulfide mineral can not be depressed by TGA.

2) The electrochemical condition of two sulfide

Table 4 Separation results of bulk concentrate of pyrite-arsenopyrite

Product	Mass/ g		Recovery/ %		Condition
	FeS ₂	FeAsS	FeS ₂	FeAsS	
Concentrate	0.32	0.83	33.33	84.69	TGA: 4.0×10^{-5} mol/L
Tailing	0.64	0.15	66.67	15.31	pH 6.86
Total	0.96	0.98	100.00	100.00	

Table 5 Separation results of bulk concentrate of galena-arsenopyrite

Product	Yield/ %	Assay/ %		Recovery/ %		Condition
		Pb	As	Pb	As	
Concentrate	46.98	8.74	32.86	9.05	86.24	TGA: 2.0×10^{-5} mol/L
Tailings	53.02	77.83	4.66	90.95	13.76	pH 6.86
Total	100.00	45.37	17.90	100.00	100.00	

Table 6 Separation results of bulk concentrate of sphalerite-chalcopyrite

Product	Yield/ %	Assay/ %		Recovery/ %		Condition
		Pb	As	Pb	As	
Concentrate	41.18	63.80	1.64	80.00	3.84	TGA: 7.5×10^{-5} mol/L
Tailings	58.82	11.17	28.75	20.00	96.16	pH 6.86
Total	100.00	32.84	17.59	100	100	

Table 7 Effect of TGA on rest potential of sulfide mineral

Mixed minerals system	Rest potential of mineral/ V		$\varphi_{X^- X_2}$ or $\varphi_{X^- PbX_2}$ / V
	φ_{MS2}	φ_{MS1}	
CuFeS ₂ + FeAsS	φ_{CuFeS_2} : 0.170	φ_{FeAsS} : 0.114	$\varphi_{X^- X_2}$: 0.176
FeAsS+ FeS ₂	φ_{FeAsS} : 0.170	φ_{FeS_2} : 0.092	$\varphi_{X^- X_2}$: 0.159
ZnS+ CuFeS ₂	φ_{ZnS} : 0.234	φ_{CuFeS_2} : 0.114	$\varphi_{X^- X_2}$: 0.192
FeAsS+ PbS	φ_{FeAsS} : 0.170	φ_{PbS} : 0.082	$\varphi_{X^- X_2}$: 0.167; $\varphi_{X^- PbX_2}$: 0.156

minerals separation in the mixed mineral system in the presence of TGA is $\Phi_{MS1} < \Phi_{X^-|X_2}(\Phi_{X^-|PbX_2}) < \Phi_{MS2}$. Results of surface product test and artificial mixed ore separation verified above conclusion.

[REFERENCES]

- [1] Nagaraj D R. Structure activity relationships for copper depressants [J]. Trans IMM, 1986, 2: 17– 20.
- [2] Reghavan S R and Unger K. Interaction of thioglycolic acid with chalcocite [J]. Trans Instn Min: Metall, Sect C: Mineral Process Extr Metall, 1983, 92: 95– 97.
- [3] Paugh R J. Macromolecular organic depressants in sulphide flotation [J]. International Journal of Mineral Processing, 1989, 25: 101– 146.
- [4] Bolin N J and Laskowski J S. Polysaccharides in flotation of sulfides, part II copper/lead separation with dextrin and sodium hydroxide [J]. International Journal of Mineral processing, 1991, 33: 235– 241.
- [5] CHEN Jiarhua, FENG Qiming, OU Leming, et al. Separation of pyrite from chalcopyrite with organic depressant CTP [J]. Trans Nonferrous Met Soc China, 1998, 8(1): 132.
- [6] CHEN Jiarhua, FENG Qiming, LU Yiping, et al. Mechanism of organic depressant CTP on separation of pyrite and chalcopyrite [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 1998, 8(1): 122.
- [7] CHEN Jiarhua, FENG Qiming, OU Leming, et al. A new organic depressant in flotation of chalcopyrite and pyrite in alkaline medium [J]. Nonferrous Metals (quarterly), (in chinese), 1997, 49(4): 45.
- [8] CHEN Jiarhua and FENG Qiming. Mechanism and depression behavior of CTP on pyrite and chalcopyrite in different alkaline media [J]. Nonferrous Metals (quarterly), (in Chinese), 1998, 50(1): 67.
- [9] CHEN Jiarhua, FENG Qiming, OU Leming, et al. Industrial test of Cu-S separation in low alkaline medium [J]. Mining and Metallurgical Engineering, (in Chinese), 1997, 17(4): 24.
- [10] CHEN Jiarhua, FENG Qiming and LU Yiping. Research of structure and depressing on sulfide mineral organic depressants [J]. Nonferrous Metal (quarterly), (in Chinese), 1998, 50(3): 60– 64.
- [11] FENG Qiming and CHEN Jin. Electrochemistry of Flotation of Sulfide Minerals [M], (in Chinese). Changsha: Central South University of Technology Press, 1992.
- [12] FENG Qiming and CHEN Jiarhua. The electrochemical kinetic studies on bulk concentrate separation of pyrite and galena [J]. Trans Nonferrous Met Soc China, 1999, 9(2): 368.
- [13] CHEN Jiarhua, FENG Qiming and LU Yiping. Energy band model of electrochemical flotation and its application(I) —theory and model of energy band at semiconductor solution interface [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 2000, 10(2): 240.
- [14] CHEN Jiarhua, FENG Qiming and LU Yiping. Energy band model of electrochemical flotation and its application(II) —model of xanthate interacting with sulphide minerals [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 2000, 10(3): 42.
- [15] CHEN Jiarhua, FENG Qiming and LU Yiping. Energy band model of electrochemical flotation and its application(III) —the effects of organic depressants on structure of sulphide minerals [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 2000, 10(4): 529.

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