



Effects of galvanic interaction between galena and pyrite on their flotation in the presence of butyl xanthate

Wen-qing QIN, Xing-jie WANG, Li-yuan MA, Fen JIAO, Rui-zeng LIU, Ke GAO

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 5 September 2014; accepted 10 June 2015

Abstract: The effects of galvanic interaction between galena and pyrite on their flotation and electrochemical characters were studied by electrochemical, adsorption, flotation and FTIR techniques, respectively. Electrochemical tests indicate that galena is electrochemically more active than pyrite and serves as an anode in galvanic combination with pyrite. The galvanic current density from a mixture of galena and pyrite is 4 times as high as the self corrosion current density of galena, which indicates that the corrosion rate of galena is accelerated. Adsorption tests show that the adsorption of butyl xanthate on galena surface is enhanced, and affected by a combination of pyrite–galena mixtures and conditioning time. Compared with individual mineral particles, galvanic interaction reduces the floatability difference between galena and pyrite. The flotation recovery of galena decreases while that of pyrite increases when two minerals are mixed together due to the influence of galvanic interaction on the formation of hydrophilic/hydrophobic product. The FTIR results show that the formation of dixanthogen on pyrite surface is depressed due to the galvanic interaction.

Key words: galvanic interaction; galena; pyrite; butyl xanthate; flotation

1 Introduction

The interaction between collector and sulphide mineral is the dominant factor in the effective flotation separation and it remains partially understood because the process involves many variables such as pH, pulp potential, and species introduced by the addition of regulators or released from minerals [1]. Generally, the electrochemical reactions occurring in the sulfide mineral flotation system include oxidation and reduction processes [2].

Most of the fundamental investigations to understand the mechanism of minerals in aqueous solutions with surfactant were undertaken on isolated sulphide mineral [3]. However, exploitable ores are usually found as an association of different sulphide minerals [4]. It has been known that the flotation behavior of the single mineral is different from that of the mixed mineral, and this may be attributed to galvanic interaction between sulfide minerals. To better understand the flotation system, it is essential to study

collector–mineral interactions in a mixed mineral system. Most of sulfide minerals possess semiconducting properties. The contact between a cathodic material and an anodic one results in the formation of galvanic cell [5]. In a mixture of two sulphides, the mineral with higher rest potential will act as the cathode, while that with the lower rest potential will be the anode. A lot of researches on electrochemical interaction in sulfide mineral extraction were completed including the grinding [6,7], flotation [8,9] and leaching [10–12] systems. In the presence of collector, different kinds of galvanic cells have been present for the prediction of mineral reactivity, while the electrochemical interaction between galena and pyrite has not been studied thoroughly [8,9,13–15]. Meanwhile, most of the quantitative studies of the collector adsorption on mineral used FTIR-ATR spectroscopy with block electrode [1,16], which was different from the actual flotation system. In order to simulate the actual flotation system, a special apparatus was introduced in this work. The aim of this work was to determine the electrochemical interaction between galena and pyrite

under different conditions and its effect on the adsorption of butyl xanthate (BX) by using electro- chemical, flotation, adsorption and FTIR techniques.

2 Experimental

2.1 Materials

The mineral samples, pyrite (FeS_2) and galena (PbS), were purchased from Yunnan Province, China. Detailed description of the mineral samples can be found in Table 1. XRD analysis (Fig. 1) confirms that the main mineral phases are galena and pyrite. The mineral samples were prepared by dry hand-grinding pure crystals in an agate mortar and pestle and by screening out the $-74 - +38 \mu\text{m}$ fraction for micro flotation and adsorption study. The powder of $-38 \mu\text{m}$ was further ground to $-2 \mu\text{m}$ for FTIR experimental study. For electrochemical measurements, the mineral electrode was cut from highly mineralized rock specimens and polished using emery paper. The experimental data

Table 1 Chemical composition of mineral sample

Mineral	Mass fraction/%				
	Pb	Fe	Cu	Zn	S
Galena	83.92	0.26	0.05	0.01	13.55
Pyrite	0.05	44.25	0.11	0.05	53.42

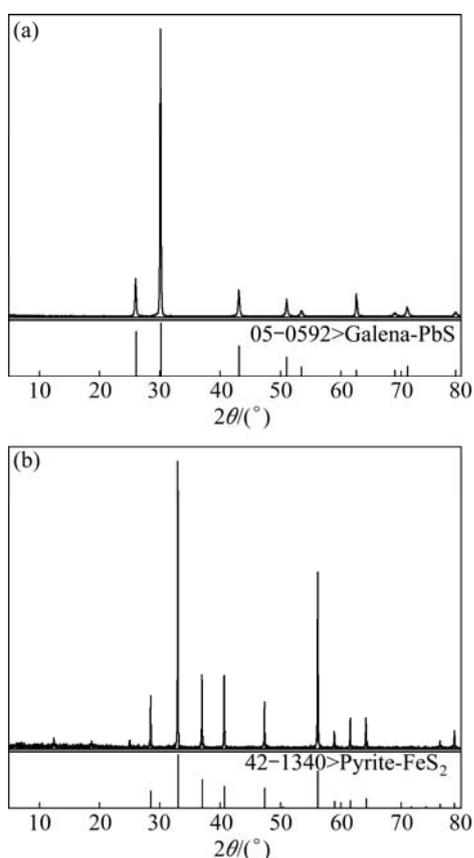


Fig. 1 XRD patterns of galena (a) and pyrite (b)

presented in this work were collected on the same mineral sample for each mineral in order to avoid sample variation. Sodium butyl xanthate ($\text{C}_4\text{H}_9\text{OCS}_2\text{Na}$) used in this study was with purity of above 90%. Buffer solution, prepared with commercial $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (pH 10) of analytical grade in twice distilled water was used throughout the experiments. All the other reagents used were of analytical grade.

2.2 Electrochemical equipment and procedures

The electrochemical studies were carried out using an EG & G PAR potentiostat/galvanostat model 283 with power suite software. The traditional three-electrode system consisted of working electrode, counter electrode (graphite rod) and reference electrode (Ag/AgCl electrode) was used. Mineral electrodes were cut from highly mineralized rock specimens as described previously. To simulate the mixed mineral system, the galena and pyrite electrodes were electrically connected to each other through the potentiostat, and the galvanic currents and potentials were measured by the galvanic corrosion/ZRA technique at any desirable time interval. Before the experiment, the solution was bubbled with air for 30 min.

2.3 Flotation test

A 40 mL flotation cell was used for micro flotation tests with a total of 2 g mineral. The samples were conditioned for 3 min in 40 mL specified solution under an open air condition to enhance electrochemical interaction. The pH values were measured with a pH meter (PHS-3C) and adjusted by NaOH and HCl . The recovery of each mineral was calculated after chemical analysis. In addition, pine oil was used as the frother in the flotation tests. The pulp potentials during the conditioning stages were monitored by a Pt electrode with reference to Ag/AgCl electrode (3.0 mol/L KCl) and the values were quoted with respect to a standard hydrogen electrode. The pulp potential values reported in this work corresponded to the potentials at the end of conditioning stage.

2.4 Adsorption tests

The adsorption speed and capacity of collector on the mineral surface are two methodologies to measure the floatability of minerals in froth flotation. A special apparatus as drawn in Fig. 2 was used.

A total of 4 g mineral sample was added into 120 mL solution with 1×10^{-4} mol/L butyl xanthate. The pulp was stirred in a temperature-controlled water bath at 293 K for different conditioning time. To enhance the solution exchange, a syringe was introduced and pushed-and-pulled at a frequency of 10 min^{-1} . At desirable time interval, 1 mL test specimen was collected

and diluted to 10 mL, and then the suspensions were separated with a centrifugal separator at a rate of 9000 r/min. Finally, the solutions were run through a UV spectroscope (UV-2000 Shimadzu, Japan) at 301 nm. The amount of xanthate ion adsorbed was calculated from the difference between the initial and final concentrations of the solutions. Different combinations of pyrite–galena mixtures and conditioning time were designed to investigate the influence of galvanic interaction on adsorption of butyl xanthate on galena and pyrite.

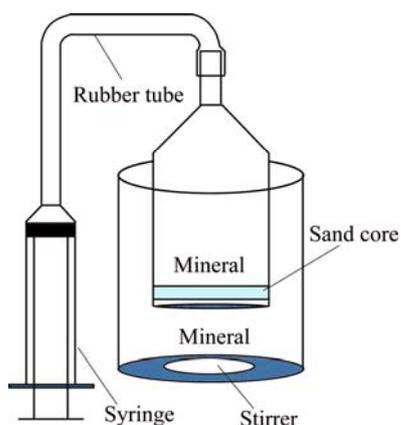


Fig. 2 Sketch of apparatus used to study adsorption of butyl xanthate (For uncontacted condition of mixed mineral (denoted as separate below) different minerals were isolated with help of sand core)

2.5 FTIR analysis

The FTIR absorption spectra were recorded on a Shimadzu FTIR spectrometer with a resolution of 4 cm^{-1} . 0.5 g mineral sample was dispersed in 20 mL acetone and homogenized by stirring, and then, a polished mineral electrode was added. When the electrode was covered with the target mineral by sedimentation, the electrode was transferred to a 20 mL solution of 1 mmol/L butyl xanthate. The solution was carefully stirred to keep the target mineral still covered on the electrode and conditioned for 30 min at specified pH. After conditioning, the mineral particles were washed by twice distilled water and dried under vacuum for FTIR measurements.

3 Result and discussion

3.1 Electrochemical measurement

3.1.1 Open circuit potential

In a galvanic couple, the open circuit potential (OCP) determines the role of galena and pyrite when they are exposed to the same solution. As one of the important electrochemical properties, the open circuit potentials of single and mixed electrodes were monitored at different concentrations of the collector. Figure 3 shows the open circuit potentials of different samples at pH 10. In all cases, the potential changes with prolonging

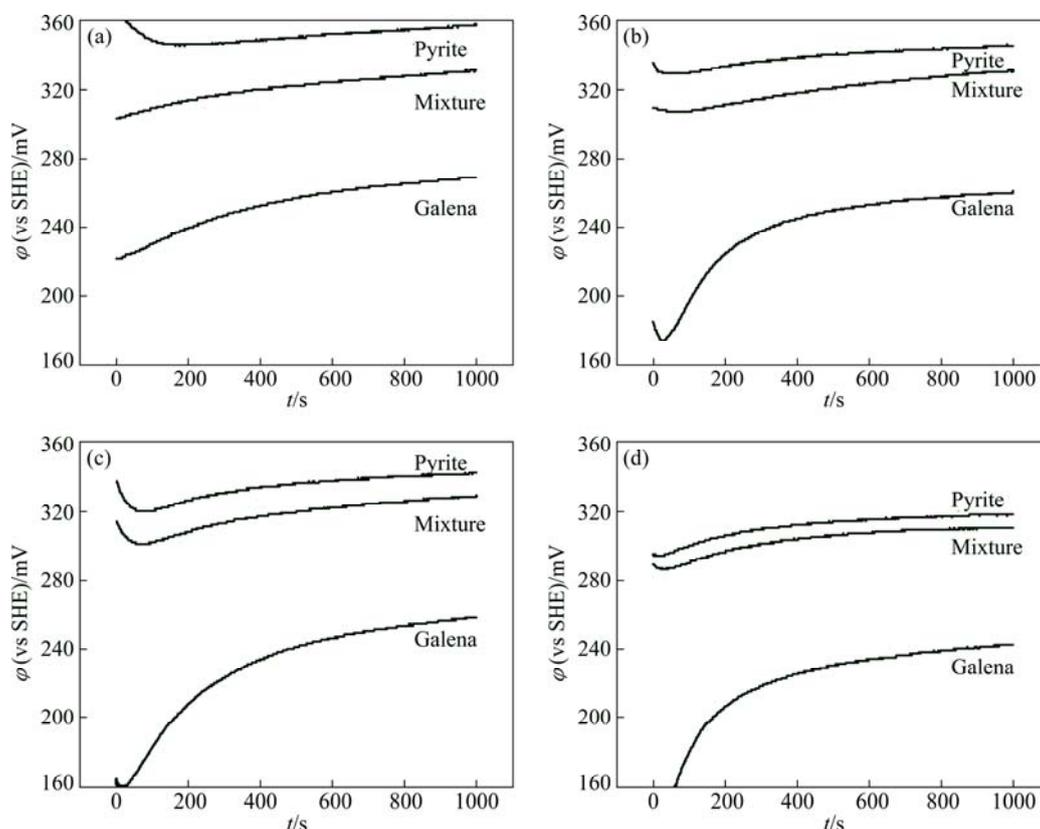


Fig. 3 OCP of galena, pyrite and their combination at pH 10 and different concentrations of butyl xanthate: (a) 1×10^{-5} mol/L; (b) 5×10^{-5} mol/L; (c) 1×10^{-4} mol/L; (d) 5×10^{-4} mol/L

time, reaching a constant (equilibrium) value after about 15 min.

The equilibrium OCPs of galena and pyrite decrease and the mixture potential approaches to the value for pyrite with the increase of butyl xanthate concentration. Compared with pyrite, the OCP of galena is found to be lower under all conditions. Galena is electrochemically more active than pyrite and hence serves as an anode in galvanic combination with pyrite. The following two kinds of interaction on PbS electrode might exacerbate:

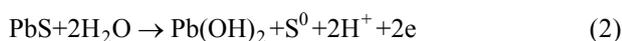
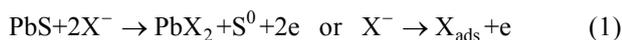


Figure 4 graphically illustrates the galvanic interaction between the two minerals in the presence of butyl xanthate.

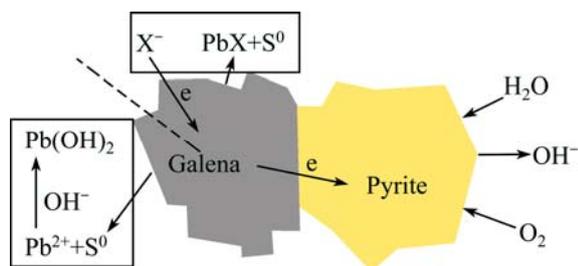


Fig. 4 Model of galvanic interaction between galena and pyrite

3.1.2 Effects of galvanic contact on speed of electrode reaction

The cathodic reaction will be accelerated in a galvanic couple. The self-corrosion current density of single mineral at specific collector concentration was calculated from polarization curves of each electrode, and the galvanic current density between galena and pyrite was measured by the galvanic corrosion/ZRA technique at pH 10. The results are illustrated in Fig. 5.

The electrochemical parameters obtained by data fitting and processing of Fig. 4 are listed in Table 2.

It can be seen from Table 2 that the corrosion current density of galena significantly increases from 0.18 to 0.78 $\mu\text{A}/\text{cm}^2$ when it is coupled with pyrite. The results indicate that the electrode reaction on galena surface is obviously accelerated.

3.2 Flotation test

Flotation tests were carried out under different conditions. The recoveries of galena and pyrite alone and the mixture with equal mass fraction of the two mineral as a function of pH are shown in Fig. 6. No agent was added to adjust pulp potential. The decrease of the pulp potential as a function of pH can be attributed to the rise in pH.

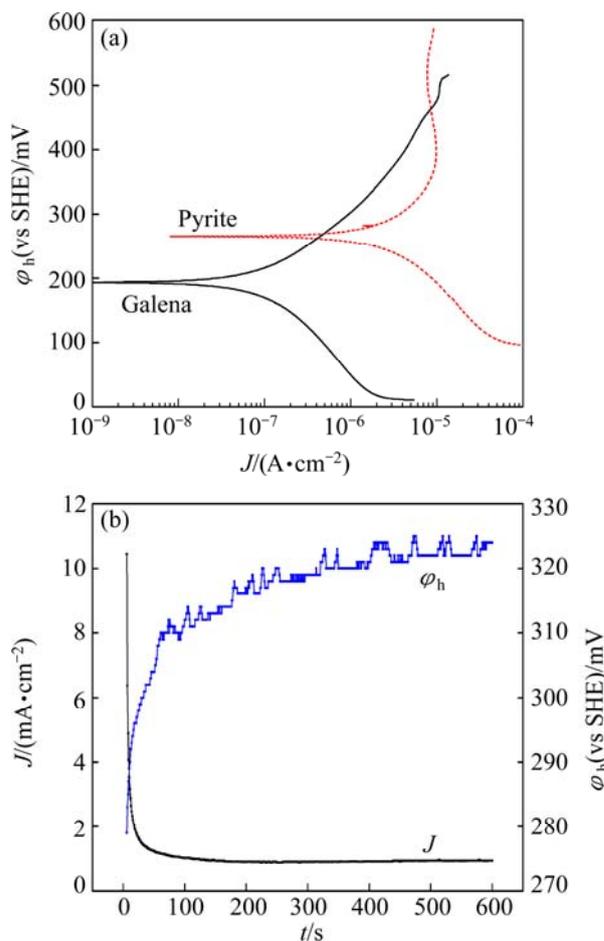


Fig. 5 Polarization curves of galena and pyrite (a), and galvanic potential and current density between galena and pyrite (b) at BX concentration of 1×10^{-4} mol/L and pH 10

Table 2 Fitting parameters of Tafel polarization and galvanic corrosion plots

Mineral	Galena	Pyrite	Galvanic corrosion
$J_{\text{corr}}/(\mu\text{A}\cdot\text{cm}^{-2})$	0.18	7.81	0.78

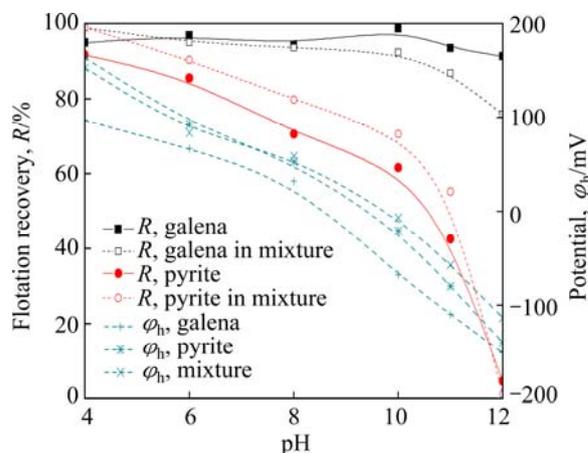


Fig. 6 Influence of galvanic interaction on flotation behavior of galena and pyrite at different pH values and BX of concentration 1×10^{-5} mol/L

Figure 6 shows that the flotation behaviors of galena and pyrite in a mixture are different from individual mineral. Compared with individual condition, the recovery of pyrite increases in the pH range of 4–10, while that of galena decreases at pH 8–10. The decrease in floatability of galena in the presence of pyrite can be attributed to the galvanic interaction, which results in an increasing dissolution of the active mineral or/and adsorption of the collector to form lead-xanthate, elemental sulphur and $\text{Pb}(\text{OH})_2$ in alkaline solutions. The metal ions hydrolyzed to form hydroxo-complexes or precipitated hydroxides, which adsorbed on the mineral surface, may have counteracted the adsorption of collector and rendered the mineral hydrophilic. This model was described in Ref. [17].

The increase of the recovery of pyrite mixed with galena could be explained by the model described by PECINA-TREVI et al [8], due to the fact that the pyrite surface supports the adsorption and cathodic reduction of dissolved oxygen. Hydroxyl ions produced on pyrite favor the formation of iron hydroxides, thus generating a positively charged surface. Hydroxo-complexes of lead are electrically repelled by the positively charged iron hydroxides formed on pyrite surface, and the final consequence is that the adsorption of lead species onto pyrite decreases.

3.3 Adsorption capacity and speed

The xanthate uptake was determined at different combinations of pyrite-galena mixtures and conditioning time. The equilibrium adsorption rates under different conditions are shown in Fig. 7.

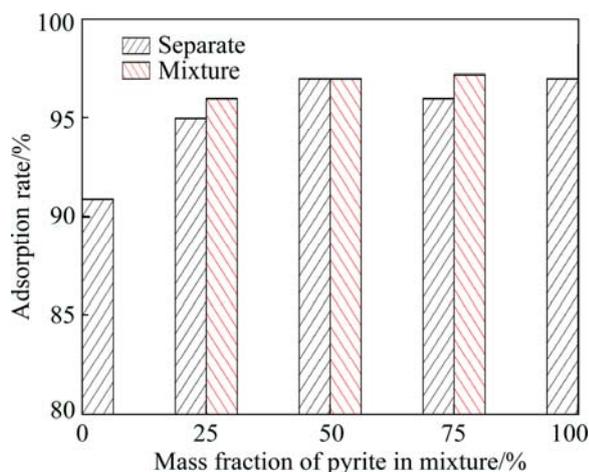


Fig. 7 Equilibrium adsorption rates of different combinations and condition mode of pyrite-galena mixtures (Separate: Galena and pyrite without in contact with each other; Mixture: Galena and pyrite in contact with each other, conditioning time 30 min, concentration of BX 1×10^{-4} mol/L and pH 10)

It is noted that the uptake of xanthate to galena is lower than that to pyrite. Adsorption results of different combinations and conditioning modes of pyrite-galena mixtures show that the adsorption capacity of butyl xanthate does not appear to be much different, which may be caused by the unsaturated adsorption at this reagent concentration. Considering that higher concentration of collector is meaningless in the actual situation, we can draw a conclusion that the influence of galvanic interaction on adsorption capacity of butyl xanthate on mineral is negligible.

Another method to measure floatability of minerals in froth flotation is the adsorption speed. The influence of galvanic interaction on adsorption speed of butyl xanthate was investigated at different combinations of pyrite-galena mixtures and conditioning time, as illustrated in Figs. 8 and 9, respectively.

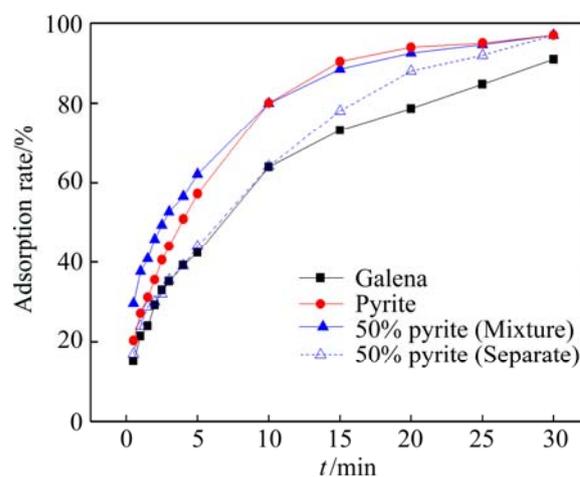


Fig. 8 Adsorption of butyl xanthate on galena, pyrite single minerals and pyrite-galena mixtures at different conditioning time, BX concentration of 1×10^{-4} mol/L and pH 10

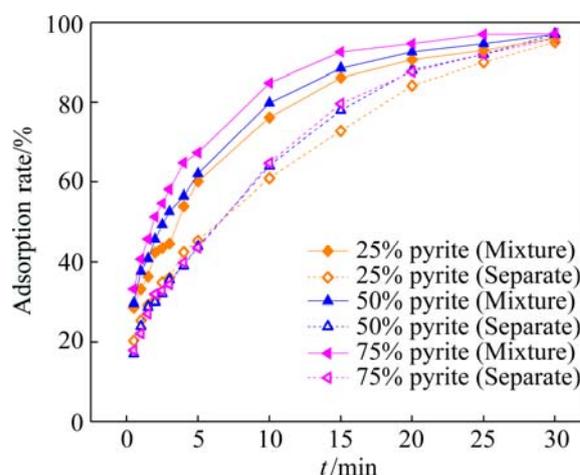


Fig. 9 Adsorption of butyl xanthate on different combinations of pyrite-galena mixtures in different contact modes at different conditioning time, BX concentration of 1×10^{-4} mol/L and pH 10

It is obvious in Fig. 8 that the adsorption speed of pyrite is faster than that of galena, while the adsorption speed of the mixture system is faster than that of pyrite. Compared with separate condition, the adsorption speed of the mixture shows an obvious increase. For example, the adsorption rate of butyl xanthate reaches 50% at 2.5 min for mixture mode and 7.5 min for separate mode.

The results of different combinations of pyrite and galena in both separate and mixed modes with each other show that with the increase of pyrite content, the adsorption speed of the separate mode only shows a slight increase, but that of the mixed mode is obvious.

In the separate mode, as the adsorption speed of the collector on pyrite is faster than that of galena, the adsorption speed of the mixture increases with the increase of pyrite content. It is easy to deduce that the adsorption speed of the mixture in separate mode cannot be higher than that of pyrite alone. In mixed mode, as collision between minerals is random, three kinds of adsorption of the collector exist: normal adsorption on pyrite, normal adsorption on galena, enhanced adsorption on galena and at the same time depressed adsorption on pyrite when galvanic contact exists. With the increase of pyrite content in the mixture, the collision probability between galena and pyrite increases. A faster adsorption on galena and stronger depression on pyrite happen. Considering the fact that the adsorption speed of the collector on the mixture is much higher than pyrite alone when galvanic interaction exists, we can draw a conclusion that the acceleration is caused by the enhanced adsorption on galena. The result of the adsorption test indicates that the flotation of galena should be increased, but it is contrary to flotation result. According to the flotation and adsorption results, the galvanic contact increases both the adsorption of collector and the dissolution of galena, while the generation of hydrophilic product caused by dissolution is dominant, rendering the mineral hydrophilicity.

3.4 FTIR analysis

In the galvanic couple of pyrite and galena, the potential of pyrite decreases and the potential of galena increases, which may alter the reaction products between mineral and collector. Infrared spectroscopy was used to identify the surface species resulting from interactions between the minerals with butyl xanthate. The FTIR spectra only show the region of 500–1500 cm^{-1} since this area includes most of characteristic xanthate bands.

Figure 10 shows the FTIR spectra obtained from pyrite and galena with and without the presence of another mineral. The characteristic bands at 1020 and

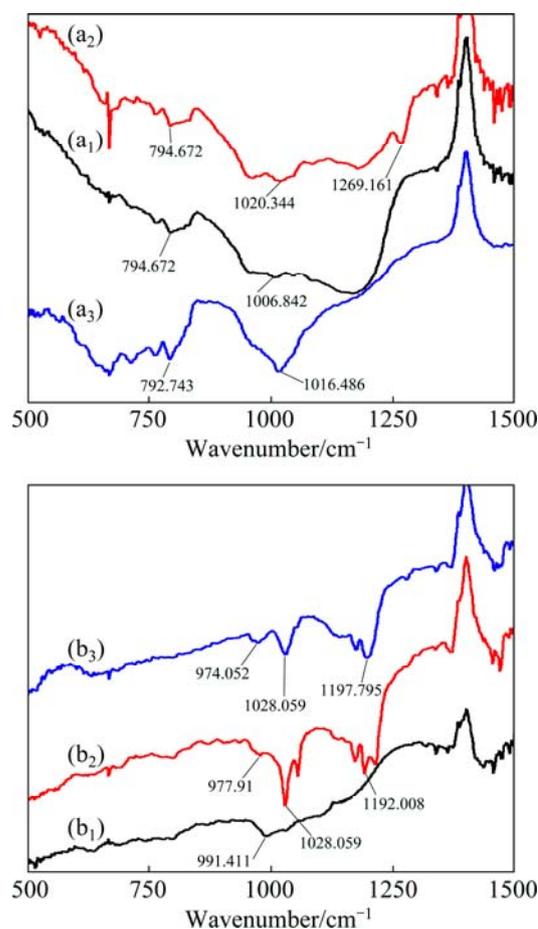


Fig. 10 Infrared spectra for pyrite (a₁), BX adsorbed on pyrite (a₂), BX adsorbed on pyrite in the presence of galena (a₃), galena (b₁), BX adsorbed on galena (b₂), BX adsorbed on galena in the presence of pyrite (b₃) at pH 10 and BX concentration of 1 mmol/L

1269 cm^{-1} are observed when pyrite (Fig. 10(a₂)) is conditioned in butyl xanthate solutions, suggesting that the adsorbed species of butyl xanthate on pyrite is dioxanthogen, as expected [18]. After contact with galena (Fig. 10(a₃)), the characteristic band of dioxanthogen at 1269 cm^{-1} disappears, which indicates that the formation of dioxanthogen on pyrite surface is depressed due to the galvanic interaction. UV spectra of the product on pyrite surface were measured, as shown in Fig. 11. The result indicates that the main adsorption product of BX on pyrite contacted with galena is the same as that of pyrite alone, but the amount decreases. When galena (Fig. 10(b₂)) is conditioned in butyl xanthate solutions, characteristic bands at 1028 and 1197 cm^{-1} are observed, suggesting that the adsorption product of butyl xanthate on galena is lead xanthate. After contact with pyrite (Fig. 10(b₃)), no additional characteristic bands appear.

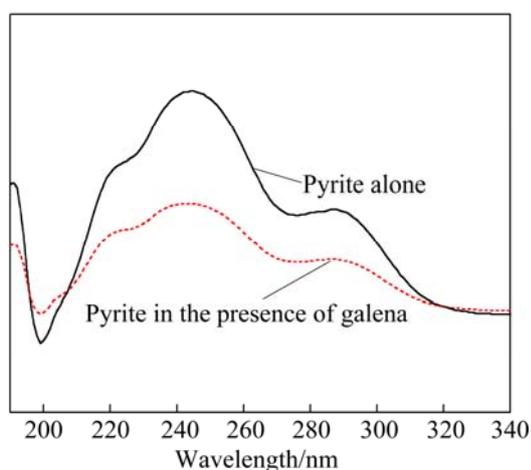


Fig. 11 UV spectra of product on pyrite surface extracted by cyclohexane

4 Conclusions

1) Galena is electrochemically more active than pyrite and hence serves as anodes in galvanic combination with pyrite. When coupled with pyrite, the corrosion current density of galena significantly increases from 0.18 to 0.78 $\mu\text{A}/\text{cm}^2$, which indicates that the electrode reaction is exacerbated.

2) Adsorption study shows that the acceleration of butyl xanthate adsorption is caused by the enhanced adsorption on galena surface, and this is affected by combination of pyrite–galena mixtures and conditioning time. The flotation recovery of galena decreases and that of pyrite increases compared with individual mineral particles and can be attributed to the galvanic interaction which increases the adsorption of collector and dissolution of galena, while the generation of hydrophilic product caused by dissolution is dominant, rendering the mineral hydrophilicity.

3) The formation of dixanthogen on pyrite decreases to some extent when galvanic interaction between galena and pyrite happens.

References

- [1] BOZKURT V, XU Z, FINCH J. Pentlandite/pyrrhotite interaction and xanthate adsorption [J]. *International Journal of Mineral Processing*, 1998, 52(4): 203–214.
- [2] GREET C. The influence of pyrite on galena oxidation and subsequent flotation [C]//*Proceedings of Centenary of Flotation Symposium*. Brisbane: The Australian Institute of Mining and Metallurgy, 2005: 959–966.
- [3] HE Ming-fei, QIN Wen-qing, LI Wen-zhong, ZENG Ke. Pyrite depression in marmatite flotation by sodium glycerine–xanthate [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(5): 1161–1165.
- [4] PIAO Zeng-jie, WEI De-zhou, LIU Zhi-lin, LIU Wen-gang, GAO Shu-ling, LI Ming-yang. Selective depression of galena and chalcocopyrite by O, O-bis (2, 3-dihydroxypropyl) dithiophosphate [J]. *Transactions of Nonferrous Metals Society of China*, 2013, 23(10): 3063–3067.
- [5] CHENG X, IWASAKI I. Pulp potential and its implications to sulfide flotation [J]. *Mineral Processing and Extractive Metallurgy Review*, 1992, 11(4): 187–210.
- [6] HUANG G, GRANO S. Galvanic interaction of grinding media with pyrite and its effect on floatation [J]. *Minerals Engineering*, 2005, 18(12): 1152–1163.
- [7] AZIZI A, SHAFAEI S Z, NOAPARAST M, KARAMOOZIAN M, IBRIC S. Galvanic interaction between chalcocopyrite and pyrite with low alloy and high carbon chromium steel ball [J]. *Journal of Chemistry*, 2013, 2013: 817218.
- [8] PECINA-TREVI O E T, URIBE-SALAS A, NAVA-ALONSO F. Effect of dissolved oxygen and galvanic contact on the floatability of galena and pyrite with aerophine 3418A [J]. *Minerals Engineering*, 2003, 16(4): 359–367.
- [9] ESLAMI ANDARGOLI M B, JANNESAR MALAKOOTI S, DOULATI ARDEJANI F, ABDOLLAHI H. Effect of galvanic contact on the floatability of galena in the presence and absence of a collector [J]. *International Journal of Mining Science and Technology*, 2012, 22(5): 629–632.
- [10] AZIZI A, PETRE C F, OLSEN C, LARACHI F. Untangling galvanic and passivation phenomena induced by sulfide minerals on precious metal leaching using a new packed-bed electrochemical cyanidation reactor [J]. *Hydrometallurgy*, 2011, 107(3–4): 101–111.
- [11] DAI X, JEFFREY M I. The effect of sulfide minerals on the leaching of gold in aerated cyanide solutions [J]. *Hydrometallurgy*, 2006, 82(3–4): 118–125.
- [12] DA SILVA G, LASTRA M R, BUDDEN J R. Electrochemical passivation of sphalerite during bacterial oxidation in the presence of galena [J]. *Minerals Engineering*, 2003, 16(3): 199–203.
- [13] EKMEK I Z, DEMIREL H. Effects of galvanic interaction on collectorless flotation behaviour of chalcocopyrite and pyrite [J]. *International Journal of Mineral Processing*, 1997, 52(1): 31–48.
- [14] YELLOJI RAO M, NATARAJAN K. Electrochemical effects of mineral-mineral interactions on the flotation of chalcocopyrite and sphalerite [J]. *International Journal of Mineral Processing*, 1989, 27(3): 279–293.
- [15] RAO S, FINCH J. Galvanic interaction studies on sulphide minerals [J]. *Canadian Metallurgical Quarterly*, 1988, 27(4): 253–259.
- [16] FREDRIKSSON A, HOLMGREN A. An in situ ATR-FTIR investigation of adsorption and orientation of heptyl xanthate at the lead sulphide/aqueous solution interface [J]. *Minerals Engineering*, 2008, 21(12–14): 1000–1004.
- [17] ZHANG Q, XU Z, BOZKURT V, FINCH J. Pyrite flotation in the presence of metal ions and sphalerite [J]. *International Journal of Mineral Processing*, 1997, 52(2): 187–201.
- [18] ZHANG Y, CAO Z, CAO Y, SUN C. FTIR studies of xanthate adsorption on chalcocopyrite, pentlandite and pyrite surfaces [J]. *Journal of Molecular Structure*, 2013, 1048: 434–440.

丁黄药体系中方铅矿与黄铁矿的伽伐尼作用对其浮选行为的影响

覃文庆, 王兴杰, 马丽媛, 焦芬, 刘瑞增, 高科

中南大学 资源加工与生物工程学院, 长沙 410083

摘要: 采用电化学、吸附、浮选和红外光谱测试技术, 研究方铅矿和黄铁矿之间的电化学相互作用对其矿物浮选行为的影响。电化学实验结果表明, 方铅矿的电化学活性比黄铁矿的高, 在与黄铁矿组成的电偶对中对为阳极, 偶合体系中方铅矿的腐蚀电流密度为自腐蚀电流密度的 4 倍, 腐蚀速率增加。吸附实验结果表明, 偶合体系中丁黄药在方铅矿表面的吸附量和吸附速率增加, 并且受方铅矿与黄铁矿组成比例和作用时间的影响。与单矿物浮选相比, 电化学相互作用减小了方铅矿与黄铁矿的可浮性差异, 电偶对中矿物间的电化学作用同时影响表面亲水性和疏水性产物的生成, 从而使方铅矿的浮选回收率降低, 而黄铁矿的增加。红外光谱测试结果表明, 方铅矿与黄铁矿间发生电化学作用时, 丁黄药在黄铁矿表面的吸附产物双黄药减少。

关键词: 伽伐尼作用; 方铅矿; 黄铁矿; 丁黄药; 浮选

(Edited by Wei-ping CHEN)