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Use of PASP and ZnSO₄ mixture as depressant in the flotation separation of chalcopyrite from Cu-activated marmatite

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Abstract: In this study, the synergistic depressive effect of polyaspartic acid (PASP) and zinc sulfate (ZnSO₄) in the flotation separation of chalcopyrite from Cu-activated marmatite was investigated by micro-flotation experiments and ore sample flotation tests, and the possible depressive mechanism was proposed from contact angle measurements, fourier transform infrared (FT-IR) analysis, inductively coupled plasma (ICP) measurements and X-ray photoelectron spectroscopy (XPS) analysis. Micro-flotation tests indicated that the mixed depressant PASP/ZnSO₄ (PZ) exerted strong depressive effect on Cu-activated marmatite in the pH range of 9~12, but it had little effect on chalcopyrite flotation. The ore sample flotation experiments indicated the PZ system decreased the grade of Zn in Cu concentrate by 4.18%, and the depressant consumption was reduced by more than a half. The results from contact angle measurement demonstrated that the hydrophobicity of Cu activated-marmatite surface was higher than that of chalcopyrite surface in presence of PZ. FT-IR analysis demonstrated the more intensive chemisorption of PZ on Cu-activated marmatite surface. ICP measurements showed that PASP had an excellent complexing ability with Cu²⁺ and Zn²⁺, which not only reduced the activation of Cu species, but also generated Zn-PASP complex on marmatite surface. XPS analysis indicated a stronger interaction between PZ and Cu-activated marmatite surface, and the depressant PZ may mainly react with Cu-activated marmatite surface through the copper atoms.

Keywords: chalcopyrite, marmatite, polyaspartic acid, mixed depressant, adsorption

1. Introduction

The processing of polymetallic sulfide ore is an important and difficult issue in minerals processing. Theoretically, zinc sulfide minerals do not respond well to short chain thiol collectors, so the floatation of Zn-minerals requires the activation by heavy metal ions to promote adsorption of collectors (Chandra and Gerson, 2009; Ejtemaei et al., 2016; Liu et al., 2018; Qin et al., 2013). However, the flotation separation of chalcopyrite and zinc sulfide minerals (mainly sphalerite/marmatite) is difficult to realize because of unwanted activation in the complex and refractory Cu-Zn sulfide ore flotation system. Unintentional activating ions (copper (II), lead (II) and silver (I)), generated by secondary copper sulfide ore and other contaminants presented in recycled water are the main source of high impurity content in concentrate products in flotation separation (Chen et al., 2009; Ikumapayi and Rao, 2015; Rashchi and Finch, 2006). Sphalerite/marmatite are become floatable with chalcopyrite in copper differential flotation process, resulting in the decline of Cu concentrate grade and the loss of Zn recovery. Therefore, it is urgent to search selective collectors and depressants to solve the problem of the selectivity flotation of complex Cu-Zn ore.

Generally, inorganic depressants are often used to depress Cu-activated zinc sulfide minerals, including cyanide, zinc sulfate and sulfite/bisulfate (Reddy et al., 1991). However, despite the excellent depressive effect of cyanide, the use of cyanide caused serious environmental hazards (Qin et al., 2012).

Cao et al. reported the depression of Cu-activated sphalerite by $ZnSO_4$ in the pH range of 9~12, but the use of $ZnSO_4$ alone was not satisfactory because of high dosage and poor depressing performance (Cao and Liu, 2006). Qin et al. proposed the use of selective collector mercapto benzothiazole (MBT) for flotation separation of chalcopyrite and Cu-activated sphalerite (Qin et al., 2012). However, flotation separation of the two minerals was not satisfactory by only using MBT, and the mixture depressant ($ZnSO_4$ and $NaSO_3$) was also required. In addition, due to the low solubility and high reagent price of MBT, it will be difficult to promote application of MBT in actual industrial-scale flotation process. In recent years, organic depressants have become more and more widely used in flotation process (Khmeleva et al., 2006; Shen et al., 2001; Wang et al., 2017). Some organic reagents such as carboxymethyl cellulose (CMC), dextrin and starch were used to depress pyrite flotation (Boulton et al., 2001; Huang et al., 2013) (Mu et al., 2016). Non-ionic polyacrylamides (PAM) was reported to depress coal flotation (Sis et al., 2003). Qin et al. reported that the efficient inhibitory effect of N,N-dimethyl-di-thiocarbamate (DMDC) on Cu-activated sphalerite when pH above 9 (Qin et al., 2013). However, when DMDC concentration was greater than 1.0×10^{-5} mol/L, the chalcopyrite was also depressed, indicating that DMDC concentration was difficult to control to achieve the selective separation. Dextrin is a macromolecular depressant, and its application in the flotation separation of galena and Cu-activated sphalerite was studied, which indicated that dextrin effectively depressed galena from the artificial mixed ore at a pH of 12 but not Cu-activated sphalerite. However, in the actual industrial-scale flotation process, because of the high-alkaline pH conditions, the reagent consumption cost will be higher, and the water recycling will be difficult. Given those disadvantages of the conventional depressants, it is necessary to develop more environmentally friendly and efficient chemicals (Fang et al., 2019; Rashchi and Finch, 2006). Besides, the use of the combined flotation reagent became more and more extensive in recent years (Fang et al., 2018; Wu et al., 2018; Xu et al., 2013). Especially, the combined use of depressants was found to have good depressive effect and achieved better separation performance than use of single depressant. (Li et al., 2017; Sarquís et al., 2014).

Polyaspartic acid (PASP) is a kind of polycarboxylic acids. Due to its non-toxic, natural biodegradable and highly water-soluble properties, it has a good performance in corrosion inhibition (Chen et al., 2015; Xu et al., 2012). The functional action of PASP is related to its chemical structure (as shown in Fig. 2). Because of the large number of carboxylic groups in PASP molecular structure, it can easily complex with metal ions. Zhu et al. reported that PASP reacted with calcium ions and adsorbed on calcite surface, significantly causing the decline in calcium site density on calcite surface, and hindering the further adsorption of sodium oleate on calcite surface (Liu et al., 2011; Zhu et al., 2018). PASP was also regarded as a "heavy metal ions remover" in the field of waste water treatment. Based on the above researches, it can be assumed that these free carboxyl groups in PASP molecular structure should also be able to complex with inevitable heavy metal ions such as copper ions in flotation slurry to prevent accidental activation. However, little research has been reported on the use of PASP in sulfide ore flotation system, and the related interaction mechanism also have not been elucidated.

In this work, the synergistic depressive effect of PASP and $ZnSO_4$ in the flotation separation of chalcopyrite and Cu-activated marmatite was studied using ethyl thiocarbamate (DDTC) as collector. Flotation behaviours of chalcopyrite and marmatite under different flotation conditions, and the flotation separation of the ore sample were respectively studied by micro-flotation experiments and closed-circuit bench scale flotation. Moreover, contact angle measurements were carried out to investigate the hydrophilic and hydrophobic changes of mineral surfaces before and after the interaction with different flotation reagents. ICP measurements were conducted to analyse the chelating ability of PASP with metal cations in solution. FT-IR analysis was used to analyse the adsorption type of depressants on mineral surfaces. And the changes of chemical environment and chemical components on mineral surfaces before and after the interaction with depressants were studied by XPS surface analysis. Finally, the possible reaction mechanism is proposed.

2. Materials and methods

2.1. Materials

The pure chalcopyrite and marmatite samples were respectively obtained from Guangxi and Hunan province, China. Firstly, the samples were hand-selected, and the large particles were hammered into

small pieces. Then the treated samples were putted in a ceramic ball mill for grinding, the ground product was then sieved through a 74 μm standard sieve. The +74 μm samples continued to be milled and the -74 μm samples were then sieved through a 38 μm standard sieve, and the samples of -74+38 μm can be obtained. The samples with size fraction of -74+38 μm were used for micro-flotation tests, contact angle tests and XPS analysis. And the samples with particle size below 37 μm were further ground to smaller than 2 μm by agate mortar, which were used for chemical analysis, X-ray diffraction (XRD) analysis and FT-IR analysis. The purity of samples was tested by XRD analysis and the results were presented in Fig. 1, which indicated that chalcopyrite and marmatite were of high purity. According to chemical analysis results, the chalcopyrite contained 34.98% Cu, 29.92% S, 30.78% Fe and 0.023% Pb; and marmatite contained 50.59% Zn, 29.57% S, 14.64% Fe and 0.025% Pb, demonstrating the minerals are of a very high purity.

The ore sample for close-circuited flotation was tin-copper-zinc polymetallic ore from Yunnan province. The chemical elements analysis of the ore sample was carried out by X-ray fluorescence (XRF) spectroscopy and ICP analysis. Results of chemical elements analysis for ore sample was presented in Table 1. As presented in Table 1, the ore sample mainly contains 0.42% Sn, 0.089% Cu, 0.53% Zn, 49.17% SiO_2 , 14.38% Al_2O_3 , in which tin is the most valuable metal. The copper and zinc are also valuable metals that can be recovered comprehensively. The mineralogical research indicated that tin, copper and zinc mainly existed in the form of cassiterite, chalcopyrite and marmatite, respectively. There are other components like pyrrhotite and pyrite, and the gangue minerals are mainly quartz, mica, feldspar, etc.

Table 1. Chemical elements analysis of the studied sample (%)

Element	Sn	Cu	Zn	Fe	SiO_2	Al_2O_3	CaO	Na_2O
Content	0.42	0.089	0.53	5.15	49.17	14.38	7.98	0.96
Element	MgO	K_2O	S	As	CaF_2	Au (g t^{-1})	Ag (g t^{-1})	
Content	3.96	3.50	1.60	0.30	6.12	<0.1	4.95	

Reagents used in this study are listed as follows: DDTc (purity >90%), methyl isobutyl carbinol (MIBC) and terpenic oil were used as collector and frother, respectively. They were of industry grade and purchased from Mingzhu Flotation Reagents Factory in Hunan province, China. PASP, purchased from Shangdong Taihe Water Treatment Technologies Co., Ltd, was employed as depressant. The chemical structure of PASP was presented in Fig. 2. For PASP, the structure contains polymerized aspartyl residues with two configurations (α and β), and each has a carboxylic and amino group (Kołodziejka, 2011; Zhu et al., 2018), and the molecular weight is 1000-5000 (Xu et al., 2012). Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) from Tianjin Yongda Chemical Reagent Co., Ltd were of analysis grade and used as activator and depressant, respectively, and the purity are all $\geq 99\%$. The dilute solutions of hydrochloric acid (HCl) (2 mol/L), sodium hydroxide (NaOH) (1 mol/L). And lime (CaO) were applied for adjusting pH value. Distilled water (resistivity over 16 $\text{M}\Omega \cdot \text{cm}$) was used for all experiments.

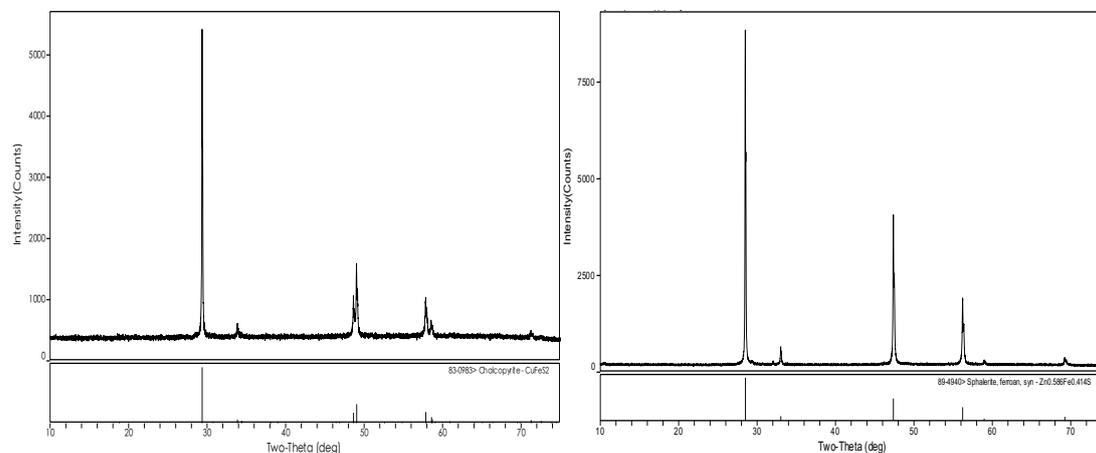


Fig. 1. XRD diagrams of chalcopyrite (left) and marmatite (right)

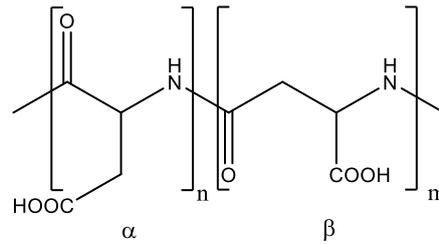


Fig. 2. Chemical structure of PASP

2.2. Micro-flotation tests

Micro-flotation tests on single minerals were carried out using XFG flotation machine (spindle speed 1602 r/min) (Jilin Exploration Machinery Plant, Changchun, China) with an effective volume of 40 mL. For each test, 2.0 g samples (-74+38 μm) were firstly cleaned by ultrasonic cleaner for 5 min, and then putted in the flotation cell with 35 mL distilled water. The testing procedure is presented as follows: (1) agitating the slurry for 1 min; (2) adjusting pH to a desired value by adding either HCl or NaOH and maintaining 2 min; (3) The desired amount of activator, depressant, collector and frother were sequentially added into flotation cell with 2 min interval; (4) collecting flotation concentrate for 2 min. The flowsheet of the micro-flotation is shown in Fig. 3. For single mineral tests, both the concentrates and tailings obtained were filtered, weighted for recovery calculation. And the flotation recovery was calculated by the following formula:

$$\varepsilon = \frac{m_1}{m_1 + m_2} \times 100\% \quad (1)$$

where ε represents flotation recovery; m_1 and m_2 represents weight (g) of concentrate and tailing, respectively.

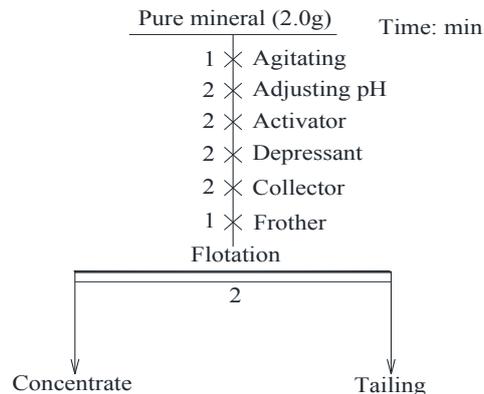


Fig. 3. Flowsheet of micro-flotation tests

2.3. Ore sample flotation experiments

Three kilograms of the sample was ground with a wet ball mill to achieve at 60% for particles passing through 74 μm . The slurry was then transferred into flotation cell, and flotation experiments were carried out using a self-aerated XFD-63 flotation machine (Jilin Exploring Machinery Plant, Jilin, China) of 8 L volume for Cu rougher-scavenger flotation and 0.5 L for Cu cleaner flotation, and the impeller speed was fixed at 1992 rpm. The desired amounts of pH adjustor, depressant, collector and frother were sequentially added into the rougher flotation cell with a 2 min interval, and the flotation time of each stage was determined by different conditions. The froth products were collected with an automatic froth scraper device. Both the concentrates and tailings obtained were filtered, dried, weighed, and analysed by chemical analysis, and the recovery was calculated.

In this study, the real ore tests mainly study the flotation separation of chalcopyrite and marmatite. Cassiterite is brittle and easy to be over-grounded, considering the subsequent recover of cassiterite, the grinding fineness of sulfide minerals should not be too fine. After performing multiple condition tests, the grinding fineness is set as 60% for particles passing through 74 μm . The coarser grinding fineness is

not conducive to the separation of sulfide ore, which increases the difficulty of Cu-Zn separation. Closed-circuit tests of Cu differential flotation were carried out according to the flowsheet depicted in Fig. 4.

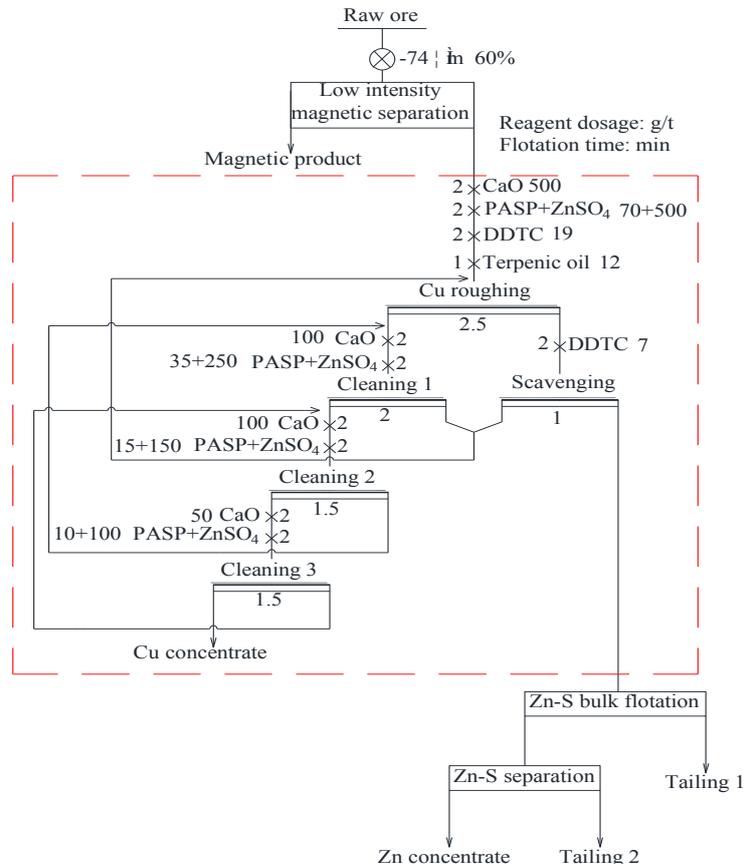


Fig. 4. Closed-circuit tests of flotation separation of sulfide ore

2.4. Contact angle measurements

Contact angle measurements were conducted to investigate the effect of flotation reagents on the hydrophobicity properties of mineral surfaces. JY-82C Automatic Video Contact Angle Meter was used in this test. The sessile drop method was utilized to determine the contact angle of water on the surface of a 12 mm diameter pressed tablet of powdered mineral samples. 2 g sample (-74+38 μm) was firstly mixed with 35 mL deionized water and agitated for 1 min to obtain suspension, and the addition sequence, reaction time (2 min) and the concentration of flotation reagents were consistent with that in micro-flotation tests. Then, the treated sample was filtered and dried in a vacuum desiccator at the temperature of 35°C. Subsequently, 0.3 g of mineral powder was pressed under the pressure of 18 Mpa (HY-12 Tablet Machine) for 15 min. A drop of distilled water was placed on the surface of the pressed tablet and a set of microscopic images between the drop and the tablet were taken immediately, then one photographs with the best stable view was chosen and analysed to determine the contact angle (Chau, 2009).

2.5. FT-IR analysis

The IR spectra of samples in the presence and absence of flotation reagents were recorded by a Fourier transform spectrometer (Nexus 670, Nicolet, USA), IR spectra were detected by transmission method with KBr as the background. The particle size of pure minerals was required to be less than 2 μm. After screening through a 38 μm standard sieve, samples with a particle size of less than 38 μm were further ground to below 2 μm in an agate mortar for FT-IR analysis. The mineral samples were completely conditioned with PASP and PZ at pH 9, then, the treated samples were filtrated, and rinsed three times with distill water, and finally dried in a vacuum desiccator at temperature of 35°C. The background

spectrum of single KBr was first measured, and the untreated and treated mineral samples and KBr were evenly mixed and tableted to measure the IR spectra of the minerals. And the IR spectrum of reagent was also measured in the same way.

2.6. ICP measurements

ICP measurements were carried out to explore the complexing ability of PASP. 0.2 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was mixed with 20 mL distilled water in a beaker to prepare simulated copper ion solution, and configured five parts of the same concentration of copper ion solution. Subsequently, adding different concentrations of PASP solutions to each of the above five beakers, respectively, with PASP concentration of 10 mg/mL, 20 mg/mL, 40 mg/mL, 60 mg/mL and 80 mg/mL. The solutions were evenly stirred and stood for nearly 20 min. Then the suspensions were filtered, and the filtrate was diluted 2500 times. And the final diluted solution was used to determine the Cu^{2+} concentration by SPECTROBLUE FMX28 (ICP-OES system of Germany). The test method and procedure for complexing Zn^{2+} are the same as those for complexing Cu^{2+} . The removal rates of metal ions were calculated by the following formula:

$$R = \frac{C_0 - C_1}{C_0} \times 100\% \quad (2)$$

where R represents removal rate of metal ions; C_0 and C_1 respectively represent concentration (mg/L) of metal ions concentration before and after interaction with PASP, respectively.

2.7. XPS analysis

XPS analysis was carried out to study the chemical composition of the mineral surfaces before and after interaction with flotation reagents. The preparation step of natural and treated chalcopyrite was basically consistent with that in micro-flotation tests, and the samples was filtered, washed three times by distilled water and dried in vacuum drying oven at temperature of 35°C. Specially, for marmatite, to investigate the activation effect of copper ion, the marmatite sample was conditioned in copper sulfate solution (pH=9) for 5 min, then the suspension was either filtered, washed and dried; or decanted and the solids was further treated with PZ solution at pH of 9 for 5 min (filtered, washed and dried).

The equipment of K-Alpha+ (Thermo Fisher Scientific, USA) was used for XPS analysis, with a monochromatic Al $K\alpha$ -ray source (1486.6 eV). It operated at 200 W, and the analysis chamber pressure was 2×10^{-7} mba. The narrow scanning spectra were performed by using a pass energy of 30 eV and an energy scan step size of 0.1 eV. Experimental data were processed using Thermo Avantage 5.954. The standard C 1s (value of 284.80 eV) was adopted as binding energy calibration.

3. Results and discussion

3.1. Micro-flotation tests

Fig. 5a shows the floatability of marmatite in the absence and presence of DDTC as a function of pH, and CuSO_4 is added to simulate the accidental activation. As shown in Fig. 5a, the flotation recoveries of untreated marmatite and DDTC-induced marmatite were low, and varied significantly with pH value. And the recovery of marmatite was improved under acidic condition. When pH was greater than 7.5, the recovery obviously declined. In flotation system, metal ions preferentially dissolve to from a metal-deficient sulfur-rich layer, and the surface of marmatite exhibits hydrophobic properties and is floatable under acidic conditions (Lotter and Bradshaw, 2010). As pH increasing, hydrophilic zinc and iron hydroxides formed on natural marmatite surface, the floatability of marmatite decreased (Mikhlin et al., 2016; Xiong et al., 2006). With regard to DDTC-induced floatability of marmatite, acidic pH condition facilitated the adsorption of DDTC onto marmatite surface and therefore, the flotation recovery of marmatite was slightly improved, but the recovery was still low in the pH range of 7.5~12 (Xiong et al., 2007). In the presence of both Cu^{2+} and DDTC, the recovery of marmatite dramatically increased. The recovery of Cu-activated marmatite was approximately 70% at pH below 9, probably because of $\text{Cu}(\text{OH})_{2(s)}$ precipitation on marmatite surface, followed by the exchange of copper and zinc, providing adsorption sites for DDTC (Liu et al., 2010). The recovery gradually decreased when pH was

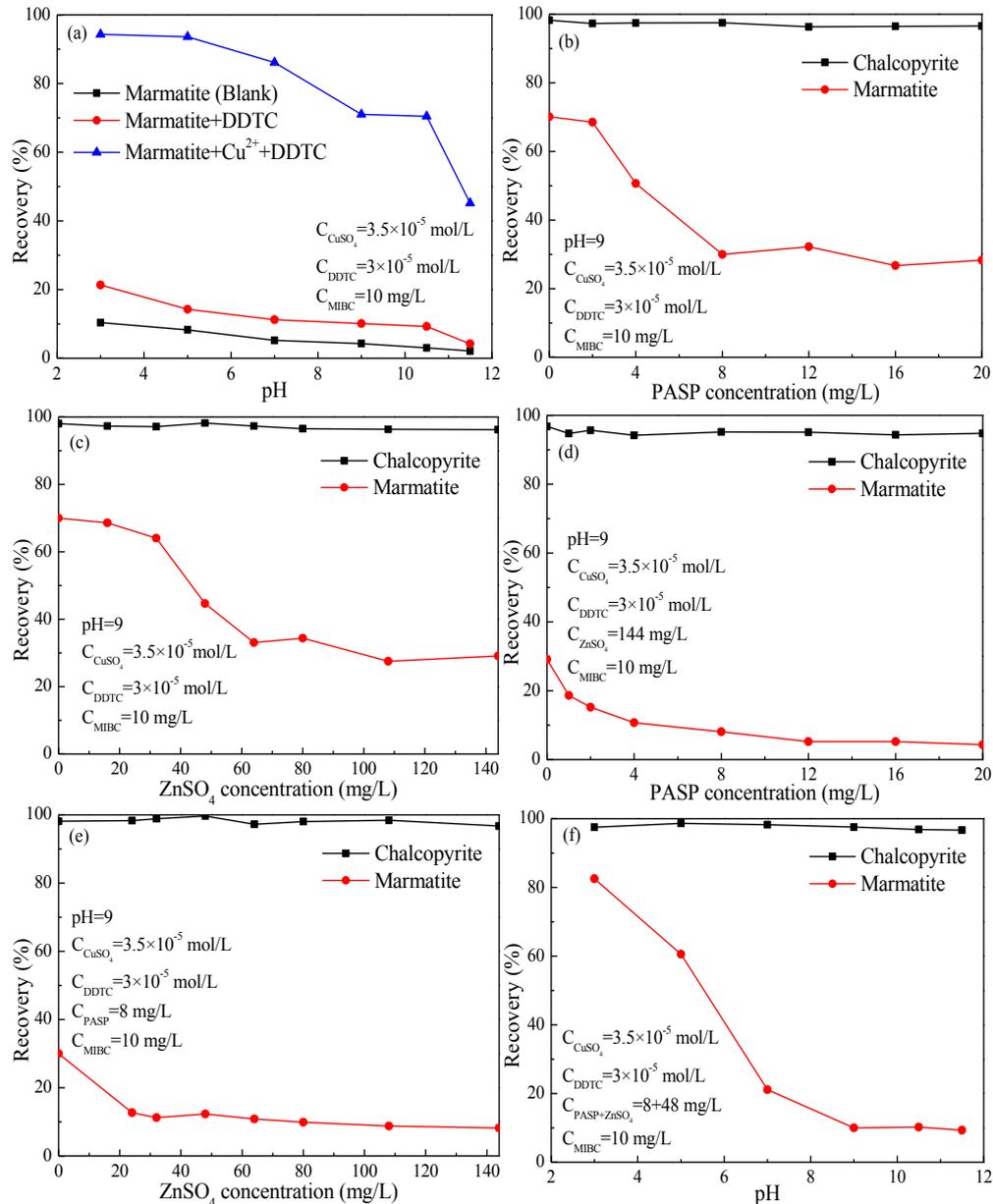


Fig. 5. Flotation recoveries of chalcopyrite and marmatite as a function of pH in the absence (a) and presence of PZ (f); as a function of single PASP concentration (b) and single $ZnSO_4$ concentration (c); as a function of PASP concentration in presence of $ZnSO_4$ (d); as a function of $ZnSO_4$ concentration in presence of PASP (e)

higher than 9, possibly due to the hydrolysis of metal ions, and the formation of zinc and iron hydroxides was encountered, exhibiting hydrophilicity of mineral surface (Quast and Hobart, 2006).

Fig. 5b and Fig. 5c respectively shows the effect of single PASP and $ZnSO_4$ concentration on the floatability of chalcopyrite and Cu-activated marmatite using DDTC as collector at pH 9.0. Results from Fig. 5b indicated that single PASP had a depressive effect on Cu-activated marmatite, and the recovery was declined from around 71% to approximately 25% as PASP concentration increased to 20 mg/L. However, the adverse influence of PASP on the floatability of chalcopyrite was minimal. As shown in Fig. 5c, single $ZnSO_4$ had a depressive effect on the floatability of Cu-activated marmatite, however, it had a negligible effect on the chalcopyrite flotation. When $ZnSO_4$ concentration reached 144 mg/L, the recovery of copper-activated marmatite dropped to around 25%.

Although a single depressant showed a depressing effect, there still existed disadvantages of low selectivity and large reagent dosage, especially when a separation problem of multi-element sulfide ore was present (Qin et al., 2012). Thus, the combined depressant was commonly used, and the depression

performance was significantly improved, which was mainly due to the synergistic effect. In this study, PASP and ZnSO_4 were added together to study the synergistic effect on the flotation separation of chalcopyrite and Cu-activated marmatite. When the ZnSO_4 dosage was 144 mg/L, Fig. 5d showed that the recovery of Cu-activated marmatite was dramatically decreased to below 10% while that of chalcopyrite maintained around 95% when the concentration of PASP was over 8 mg/L, suggesting that the mixed depressant exhibited stronger depression effect on Cu-activated marmatite. Fig. 5e showed the effect of ZnSO_4 dosage on floatability of minerals at a PASP dosage of 8 mg/L, it can be obviously seen that 24 mg/L ZnSO_4 was enough to achieve the excellent depressing action, and the minimum recovery of Cu-activated marmatite was 9.95%, while the chalcopyrite recovery maintained around 95%. Fig. 5f showed the flotation behaviours of minerals in presence of PASP/ ZnSO_4 (8+48 mg/L) as a function of pH. As shown in Fig. 5f, the floatability of chalcopyrite was not influenced in the pH range of 2~12, but the recovery of Cu-activated marmatite dramatically decreased with the increase of pH value. Under alkaline condition (especially $\text{pH}>9$), the Cu-activated marmatite was strongly depressed. Therefore, a pH of 9 was selected to investigate possible mechanism.

The floatability of marmatite under different addition order of flotation reagents were investigated and the results are shown in Fig. 6. When DDTC (D) was added prior to either PASP (P) or ZnSO_4 (Z), the depressive effect was dramatically reduced, suggesting that single PASP or ZnSO_4 cannot depress Cu-activated marmatite as easily once pre-reaction with DDTC had occurred. However, in the case of pre-addition of DDTC, the flotation recovery of Cu-activated marmatite increased from 10.59% to 21.85% in the presence of PZ. Fig. 6 also confirmed the strong synergistic depressive effect of PZ on Cu-activated marmatite. The results indicated that the mixed depressant PZ can also be used in cleaning stage.

Based on the results of micro-flotation tests, it can be inferred that the flotation separation of chalcopyrite and Cu-activated marmatite is possible with PZ as a new and efficient depressant mixture.

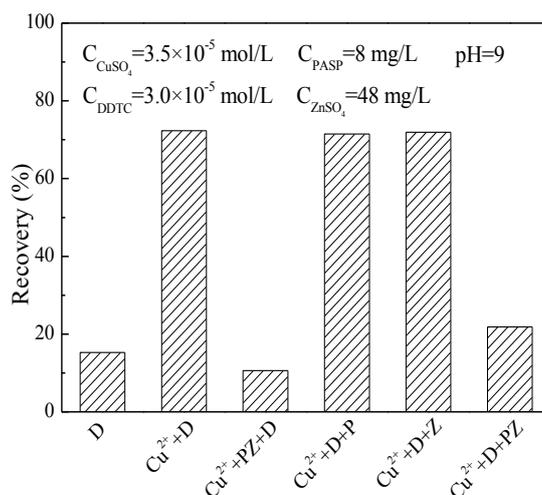


Fig. 6. Effect of sequence of reagents addition on marmatite flotation

3.2. Contact angle measurements

Fig. 7 shows the effect of different reagents on the hydrophilic and hydrophobic properties of mineral surfaces. The contact angle of natural chalcopyrite and marmatite was measured to be 65.07° and 40.04° , respectively. When marmatite was treated by Cu^{2+} , the contact angle increased from 40.04° to 60.33° . As shown in Fig. 7a, the contact angle of Cu-activated marmatite decreased from 60.33° to 41.93° with the increase of PASP concentration, while the contact angle of chalcopyrite remained almost constant. Fig. 7b shows the contact angle of chalcopyrite and Cu-activated marmatite decreased as ZnSO_4 concentration increased, declining to 52.21° and 41.54° , respectively. Corresponding tests were conducted to explore the effects of ZnSO_4 concentration on the contact angle of minerals in the presence of 8 mg/L PASP, and the results were shown in Fig. 7c. By increasing the concentration of mixed depressant PZ from 0+0 to 8+48 mg/L, the contact angle of chalcopyrite and Cu-activated marmatite significantly reduced to 51.08° and 30.36° , respectively. These results illustrated that PZ was more bene-

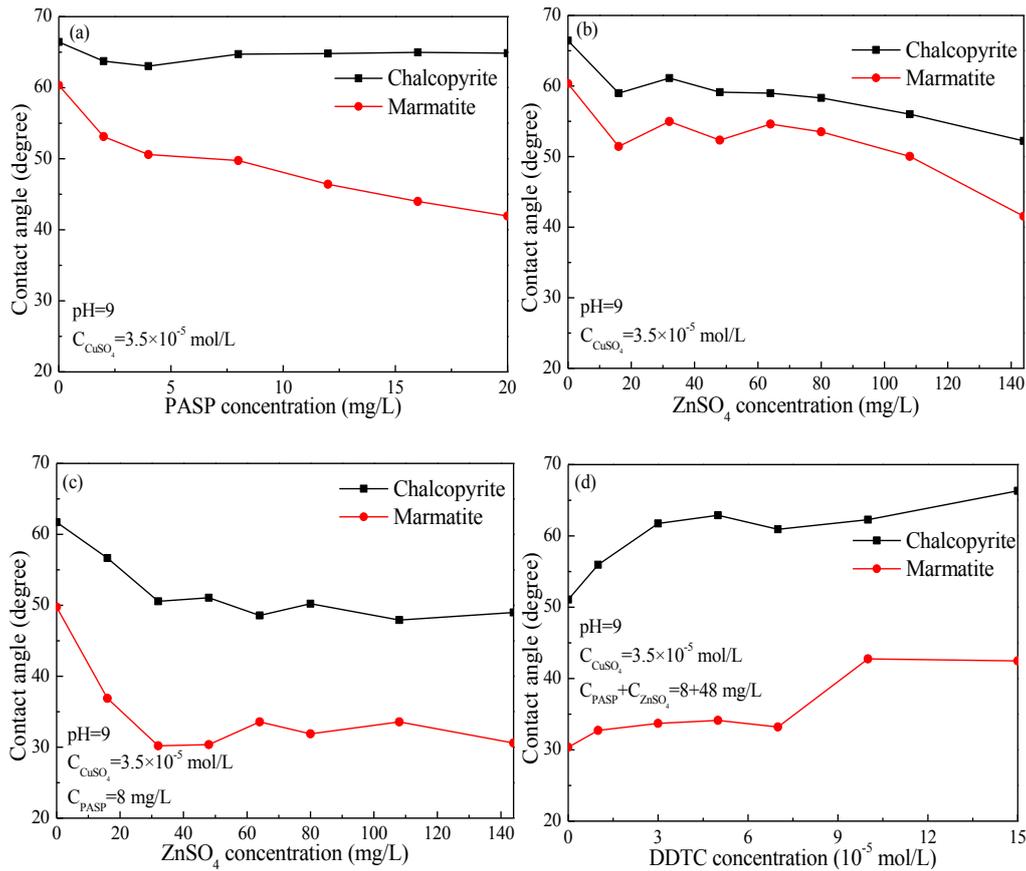


Fig. 7. Contact angle of chalcopyrite and Cu-activated marmatite as a function of PASP concentration (a) and $ZnSO_4$ concentration (b); as a function of $ZnSO_4$ concentration in presence of PASP (c); as a function of DDTC concentration in presence of PZ (d)

ficial to reduce the hydrophobicity of minerals surfaces compared with the single PASP or $ZnSO_4$. Fig. 7d shows the effect of DDTC on hydrophilic and hydrophobic properties of mineral surfaces pre-treated by PZ. It can be seen that the contact angle of chalcopyrite was rapidly restored from 51.08° to 61.74° while the contact angle of Cu-activated marmatite was basically keep constant in the range of $30^\circ\sim 40^\circ$ with the increase of DDTC dosage, indicating that the further adsorption of DDTC onto Cu-activated marmatite surface was prevented by PZ, which in turn resulted in selective depression. These results are consistent with the results of micro-flotation experiments.

Table 2. Results of the experimental system (PZ) and the comparative system (Z)/%

System Dosage (g/t ⁻¹)	Product	Yield rate	Grade			Recovery		
			Cu	Zn	As	Cu	Zn	As
PZ 130/1000	Magnetic product	3.42	0.32	0.42	0.10	12.03	2.61	1.14
	Cu Concentrate	0.25	22.37	5.15	0.29	61.46	2.34	0.24
	Zn Concentrate	0.90	1.49	50.86	1.01	14.74	83.23	3.03
	Tailing 2	1.44	0.51	1.56	19.01	8.07	4.08	91.25
	Tailing 1	93.99	0.0036	0.05	0.01	3.71	7.74	4.34
	Raw ore	100.00	0.091	0.55	0.30	100.00	100.00	100.00
Z 2500	Magnetic product	3.39	0.36	0.47	0.12	13.41	2.95	1.31
	Cu Concentrate	0.30	18.37	9.33	0.27	60.56	5.18	0.26
	Zn Concentrate	0.91	1.41	47.86	1.00	14.10	80.65	2.94
	Tailing 2	1.45	0.50	1.63	19.36	7.97	4.38	90.55
	Tailing 1	93.95	0.0038	0.04	0.02	3.96	6.84	4.94
	Raw ore	100.00	0.091	0.54	0.31	100.00	100.00	100.00

3.3. Ore sample flotation tests

The flowsheet and the reagent scheme of the real ore flotation tests were shown in Fig. 4, and the results were presented in Table 2. As shown in Table 2, compared with the use of single $ZnSO_4$, PZ system decreased the Zn content in Cu concentrate from 9.33% to 5.15%, moreover, the total dosage of depressant largely reduced.

The results suggest that PZ is an excellent depressant in the flotation separation of complex Cu-Zn sulfide ore, due to its low dosage, good depressing effect and environmentally-friendly characteristics.

3.4. FT-IR analysis

FT-IR spectrum of PASP is shown in Fig. 8. For PASP, significant characteristic adsorption peaks appeared at 1401 cm^{-1} , 1593 cm^{-1} and 3409 cm^{-1} . The adsorption peaks at 1401 cm^{-1} and 1593 cm^{-1} were respectively duo to the symmetric stretching vibration and antisymmetric stretching vibration generated by the two C=O vibration couplings of $-COO^-$. The sharp peak at 3409 cm^{-1} was attributed to vibration of N-H group (Alford et al., 1994; Kołodyńska, 2011).

In order to investigate the adsorption mechanism of the depressants on mineral surfaces, the FT-IR spectra of minerals before and after treatment with PASP and PZ at pH 9 are shown in Fig. 9. As shown in Fig. 9 (a), compared with the FT-IR spectrum of untreated chalcopyrite (spectrum 1), after treating chalcopyrite with PASP alone and PZ, no new adsorption peaks appeared. The adsorption band shifted from 1577 cm^{-1} (spectrum 1) to 1586 cm^{-1} (spectrum 2) and 1587 cm^{-1} (spectrum 3), which was contributed by asymmetric stretching vibration generated by the two C=O vibration couplings of $-COO^-$ in PASP molecule at 1593 cm^{-1} , indicating PASP was chemically adsorbed on the chalcopyrite surface. After interaction with PZ, the characteristic peak at 3183 cm^{-1} (spectrum 3) was obviously shifted from 3192 cm^{-1} (spectrum 1) and 3193 cm^{-1} (spectrum 2), which were assigned to the telescopic and bending vibration of O-H group of amphoteric hydroxide at 3239 cm^{-1} (Cao and Liu, 2006). These results indicated the co-existence of chemisorption of PASP and $ZnSO_4$ on chalcopyrite surface.

Fig. 9 (b) shows the FT-IR spectra of marmatite before and after the interaction with PASP and PZ. Compared with untreated marmatite (spectrum 1), after the interaction with PASP and PZ, as shown in spectrum 2 and spectrum 3, new peaks appeared at 1520 cm^{-1} (spectrum 2) and 1533 cm^{-1} (spectrum 3), which were attributed to antisymmetric stretching vibration generated by the two C=O vibration couplings of $-COO^-$ in PASP molecule, and the adsorption peaks were shifted from 1595 cm^{-1} . At the same time, the adsorption band shifted from 1455 cm^{-1} (spectrum 1) to 1432 cm^{-1} (spectrum 2) and 1436 cm^{-1} (spectrum 3), which was contributed to symmetric stretching vibration generated by the two C=O vibration couplings of $-COO^-$ in PASP molecule at 1401 cm^{-1} , implying the chemical adsorption of PASP on Cu-activated marmatite surface. From spectrum 3, several new peaks appeared at 1683 cm^{-1} and 1660 cm^{-1} , 1159 cm^{-1} and 1126 cm^{-1} , 773 cm^{-1} , which were attributed to the telescopic and bending vibration O-H, the vibration adsorption of (OH) of amphoteric zinc hydroxide, the vibration adsorption of (OH) of amphoteric zinc hydroxide (Dávila-Pulido and Uribe-Salas, 2014). Those results illustrated that PASP and $ZnSO_4$ chemically co-adsorbed on Cu-activated marmatite surface.

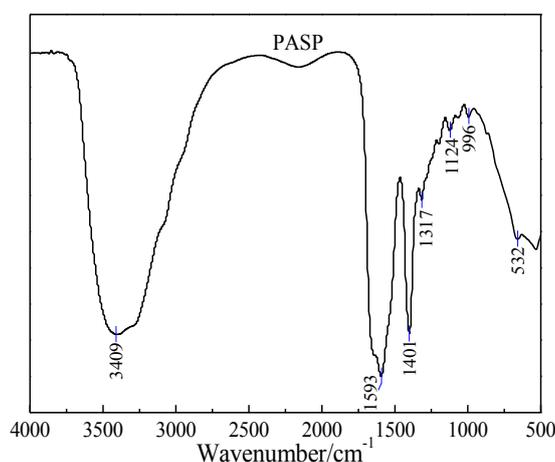


Fig. 8. FT-IR spectrum of PASP

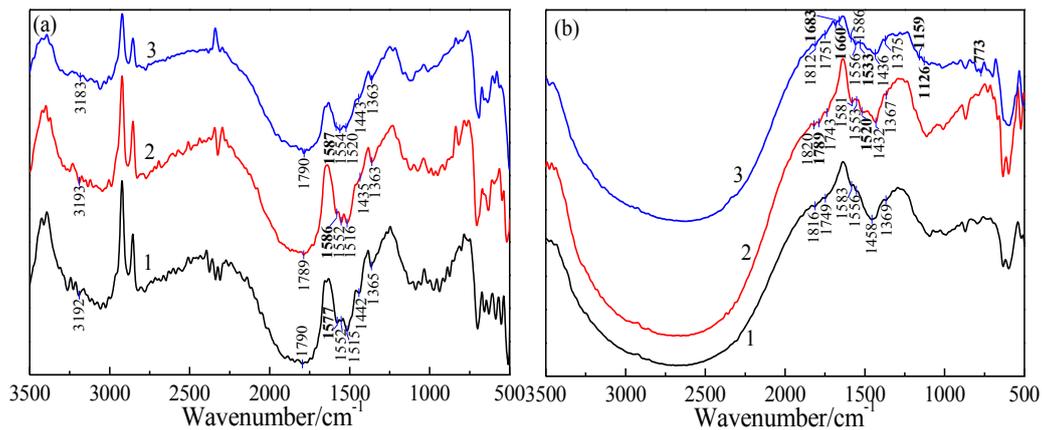


Fig. 9. FT-IR spectra of chalcopyrite (a): 1 Chalcopyrite; 2 Chalcopyrite+PASP; 3 Chalcopyrite+PZ; and Marmatite (b): 1 Marmatite; 2 Marmatite+Cu²⁺+PASP; 3 Marmatite+ Cu²⁺+PZ

Comparing the analysis results in Fig. 9 (a) with that in Fig. 9 (b), in the presence of PASP and PZ, no new characteristic absorption peaks appeared on the chalcopyrite surface. However, for Cu-activated marmatite, several new and pronounced characteristic absorption peaks appeared on its surface, besides, the shifts of adsorption peaks on Cu-activated marmatite surface is more obvious than that on chalcopyrite surface, therefore, implying the more intensive chemisorption of PZ on Cu-activated marmatite surface.

3.5. ICP measurements

As mentioned from relevant literatures (Demirbas et al., 2005; Kołodyńska et al., 2008; Susan et al., 2004), removal of heavy metal ions by PASP has been used for waste water treatment. In this study, ICP tests were employed to investigate the chelating ability of PASP with metal ions, and the removal rate of metal ions as a function of PASP concentration was shown in Fig. 10. As shown in Fig. 10, PASP had a stronger complexing ability with Cu²⁺ than Zn²⁺. And the Cu²⁺ removal rate significantly increased with the increase of PASP concentration until it reached a maximum value (71.53%), and then, it decreased dramatically. When the maximum Cu²⁺ removal rate was reached, the PASP concentration was 20 mg/mL. The complexing ability of PASP with Zn²⁺ was relatively weak, and the Zn²⁺ removal rate was not more than 25%. The results indicated that PASP can effectively weaken the activation of copper ions on marmatite surface and produce the selective depression.

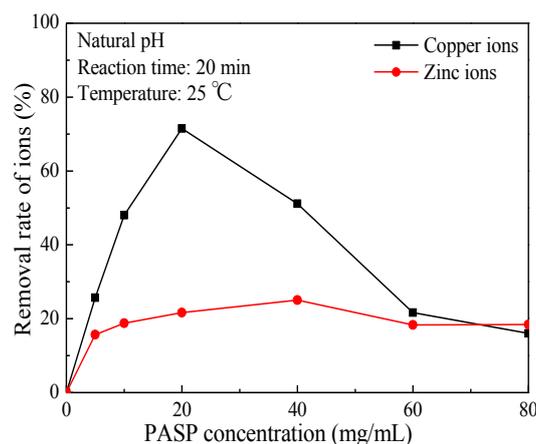


Fig. 10. Removal rate of metal ions as a function of PASP concentration

3.6. XPS analysis

XPS analysis is an efficient and useful method to determine the surface properties before and after the interaction with flotation reagents, which would be relevant in investigating the interaction mechanism between minerals and flotation reagents.

The survey spectra of chalcopyrite and marmatite as a function of different flotation reagents at pH 9 are shown in Fig. 11a and Fig. 11b, respectively. In order to more clearly compare the changes of Zn 2p and Cu 2p peak intensity before and after the reaction with flotation reagents, the spectra in Fig. 11b are separated and respectively listed in Fig. 11c and Fig. 11d. As can be seen from the spectra, C element was detectable on natural and Cu-activated mineral surface probably because of the adventitious carbon contamination.

Compared with the fresh marmatite surface (spectrum 1), after copper ions activation, spectrum 2 in Fig. 11b appeared a new and significant peak at around 932 eV, it was assigned with the copper layer formation on the marmatite surface (Fornasiero and Ralston, 2006; Prestidge et al., 1997). As described in Fig. 11c, after activation, the decrease of the Zn 2p peak intensity at 1021.63 eV was obvious. The atomic concentrations of detected elements identified on minerals surfaces after the interaction with CuSO_4 at a pH of 9 are depicted in Table 3 (4#), compared with that identified on the fresh marmatite surface (Table 3 (3#)), Cu-activated marmatite showed surface changes. Ejtemaei et al. described the Cu-activated marmatite surface as a copper-substitute marmatite lattice with the formation of a metal-deficient and sulfur-rich surface layer in the whole pH range (Ejtemaei et al., 2016). Besides, researchers also considered the S 2p spectra of the Cu-activated marmatite indicated two S 2p doublets, the first doublet (161.5 eV) can be assigned to S^{2-} species, and the other S 2p doublet at around 162.7 eV ascribed to S⁻ species or probably Cu-S type surface species (Ejtemaei and Nguyen, 2017; Kartio et al., 1998). Due to the formation of hydrophobic species on Cu-activated marmatite surface, the floatability of marmatite was significantly improved.

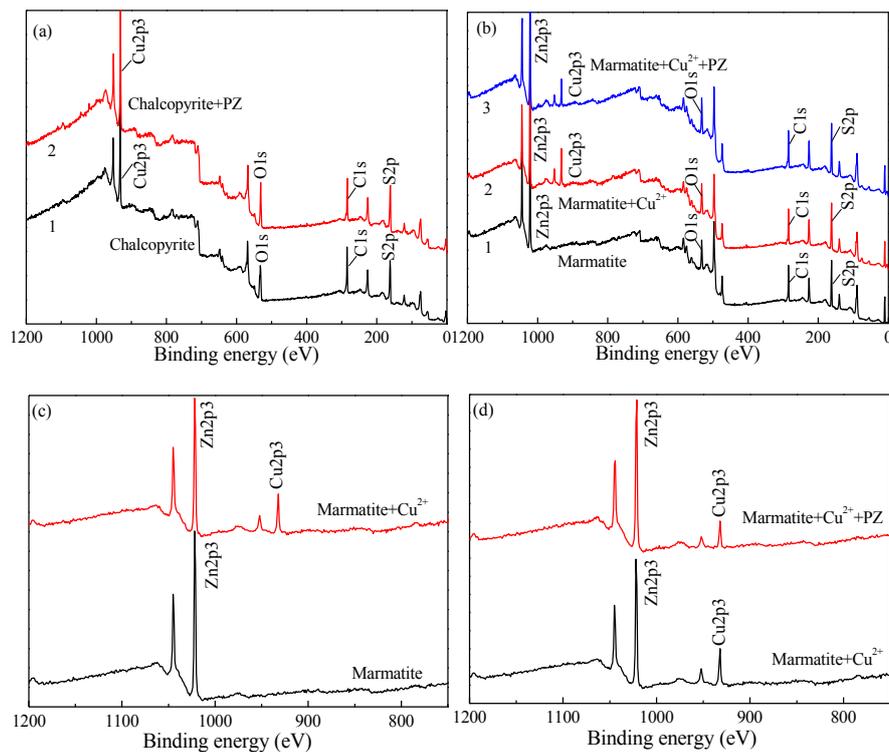


Fig. 11. XPS spectra of chalcopyrite (a) and marmatite (b) before and after the treatment with different reagents; The separated pictures (c) and (d) of (b)

As can be seen from Fig. 11a, after treatment with PZ, there was no new characteristic peak appeared on the chalcopyrite surface, the intensity of the peaks was almost not changed, but the relative atomic content and the binding energy of elements were changed, indicating PZ has a certain effect on the mineral surface. From Fig. 11d, after the interaction with PZ, there is also no new characteristic peak on the Cu-activated marmatite surface. However, the intensity of the peaks, the relative atomic content and the binding energy of elements were changed. Especially, the Cu 2p peak intensity (Fig. 11d) at around 932.0 eV was obviously decreased, indicating that the adsorption of copper became weak in the presence of PZ.

The relative atomic concentrations of detected elements identified on minerals surfaces before and after the interaction with PZ and the shift values of concentration are presented in Table 3. As shown in Table 3, the addition of PZ leads to the changes of the atomic concentration of the main elements, the relative atomic content of N 1s and Zn 2p on Cu-activated marmatite surface respectively suffers a more significant increase by 3.01% and 1.77% compared to that on chalcopyrite, chalcopyrite only undergoes an increase by 1.77% and 0.95%. The results indicate the co-adsorption of PZ and ZnSO₄ on minerals surfaces and a stronger adsorption between PZ and Cu-activated marmatite surface. For Cu-activated marmatite, after the treatment with PZ, the atomic concentration of Cu declined by 1.81%, which illustrated that the presence of PZ has a certain hindrance to the activation of sphalerite by copper ions in the flotation slurry, thus inducing depression action. The decrease of carbon and oxygen atomic content may be because of two reasons: the increase in the atomic content of N 1s, Zn 2p, Cu 2p, Fe 3p and S 2p caused the decline of C 1s and O 1s content. In addition, PZ adsorbed on the minerals surfaces covered part sites of the carbon and oxygen.

The deeper reaction mechanism of PZ was studied by chemical changes of elemental binding energies. Fig. 12 and Fig. 13 present the XPS spectra of Cu 2p and S 2p on two minerals surfaces, respectively, and the corresponding chemical changes of Cu 2p and S 2p binding energies values are shown in Table 4. As shown in Table 4, the Cu 2p and S 2p peaks of pure chalcopyrite are located at 931.93 eV and 161.39 eV, respectively, while those corresponding peaks of untreated Cu-activated marmatite surface are located at 932.22 eV and 161.80 eV. After the reaction between chalcopyrite and PZ, the binding energies of Cu 2p and S 2p peaks shifted by -0.15 eV and 0.09 eV, respectively. When Cu-activated marmatite was treated with PZ, more obvious binding energies changes are observed by -0.35 eV for Cu 2p and -0.11 eV for S 2p, where the binding energy shift of Cu 2p was larger than the instrument error (0.2 eV). A more pronounced shift indicates a stronger interaction between PZ and Cu-activated marmatite surface, and the depressant PZ may mainly react with Cu-activated marmatite surface through the copper atoms. And those results consistent with the stronger inhibition of PZ on Cu-activated marmatite in the micro-flotation process.

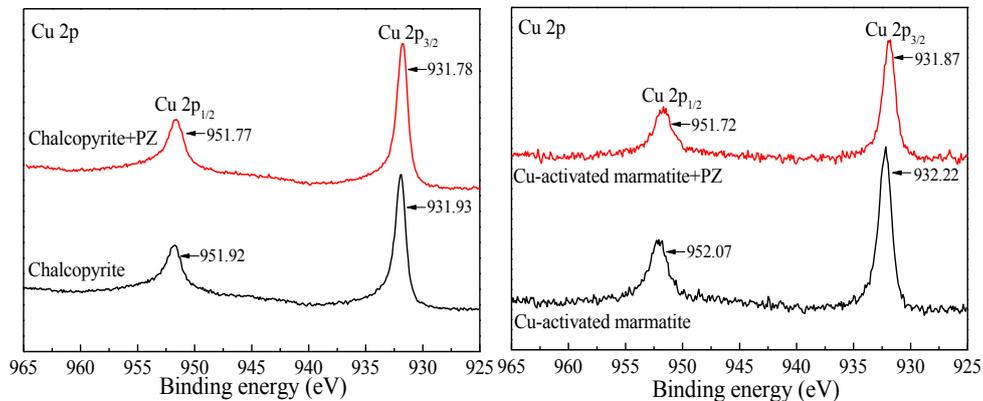


Fig. 12. XPS spectra of Cu on chalcopyrite and Cu-activated marmatite surface before and after treatment with PZ

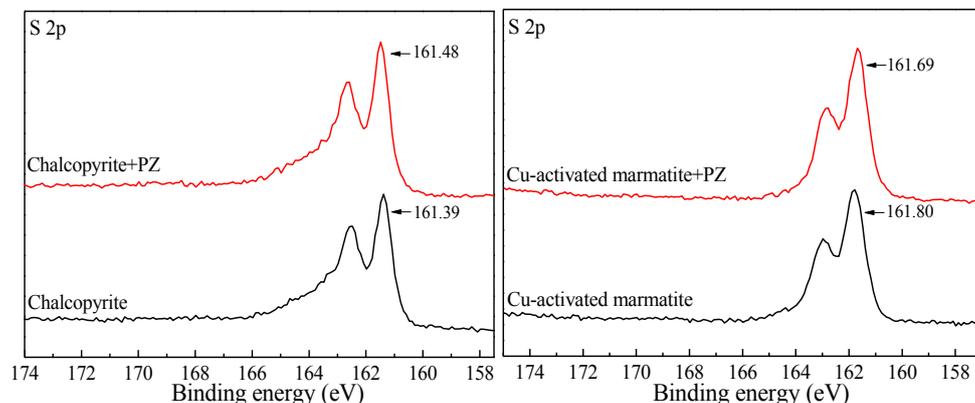


Fig. 13. XPS spectra of S on chalcopyrite and Cu-activated marmatite surface before and after treatment with PZ

Table 3. Atomic concentrations of elements identified on the surfaces of chalcopyrite and marmatite in the absence and presence of different flotation reagents

No.	Sample	Atomic concentration (%)						
		C1s	O1s	Cu2p	S2p	Fe3p	N1s	Zn2p
1 [#]	Chalcopyrite	39.50	19.54	12.01	21.80	7.15	/	/
2 [#]	Chalcopyrite+PZ	37.25	16.90	12.86	22.84	7.42	1.77	0.95
	D-value	-2.25	-2.64	+0.85	+1.04	+0.27	+1.77	+0.95
3 [#]	Marmatite	37.03	15.28	/	22.96	4.08	/	20.66
4 [#]	Marmatite+Cu ²⁺	35.13	14.89	5.16	24.07	4.08	/	16.67
5 [#]	Marmatite+Cu ²⁺ +PZ	34.30	14.77	3.35	22.62	3.97	3.01	17.98
	D-value (4[#] and 5[#])	-0.83	-0.12	-1.81	-1.45	-0.11	+3.01	+1.31

Table 4. Chemical changes of Cu 2p and S 2p binding energies of chalcopyrite and Cu-activated marmatite before and after the interaction with PZ

No.	Sample	Binding energy (eV)		No.	Sample	Binding energy (eV)	
		Cu 2p	S 2p			Cu 2p	S 2p
1 [#]	Chalcopyrite	931.93	161.39	3 [#]	Marmatite+Cu ²⁺	932.22	161.80
2 [#]	Chalcopyrite+PZ	931.78	161.48	4 [#]	Marmatite+Cu ²⁺ +PZ	931.87	161.69
	Chemical shift	-0.15	0.09		Chemical shift	-0.35	-0.11

4. Discussion

Marmatite has no natural floatability, unwanted activation by copper ions results in the formation of Cu-S type species on the marmatite surfaces, which allows the collector DDTC to form an insoluble Cu(I)-collector complex on its surface, therefore the Cu-activated marmatite had a good floatability (Ejtemaei, 2017; Fornasiero and Ralston, 2006; Kartio et al., 1998; Prestidge et al., 1997). This made the flotation separation of chalcopyrite and Cu-activated marmatite difficult.

ZnSO₄ is a common selective depressant for Cu-activated zinc sulfide minerals. The data from flotation tests show that the recovery of Cu-activated marmatite decreased in the presence of ZnSO₄ alone as pH above 9, which can be attributed to the precipitation of hydrophilic zinc hydroxide on marmatite surface in alkaline pH range (ELSHALL et al., 2000).

As demonstrated from PASP structure (Fig. 2), it contains a lot of carboxyl groups that can complex with metal cations to form M(II)-PASP complexes (Kołodziejńska et al., 2008). According to Dorota and Zhu, PASP is a type of polymer, and the dissociation and complexation of PASP in aqueous is complicated, thus, the molecular structure of PASP was simplified into a molecular model containing four acid structure units of [COCHCH₂COOHNH] (abbreviated as H₄L) (Kołodziejńska, 2011; Zhu et al., 2018). When pH above 7, PASP completely dissociated as a form of L⁴⁻ in solution, and the adsorption of anionic species of L⁴⁻ on minerals surfaces is the main adsorption model. Therefore, the depression mechanism of PASP alone is as follows: PASP complexed with copper ions in flotation slurry, weakening the activation effects of copper ions onto marmatite, thus resulting in the depressing action. In addition, PASP selectively chemisorbed on Cu-activated marmatite surface, and the remaining carboxyl groups are exposed on marmatite surface, resulting the hydrophilic property of its surface.

The combination of PASP/ZnSO₄ exerted a stronger inhibitory effect under low concentration over the pH range of 9~12. In that pH range, the dissolved species of ZnSO₄ in solution are mainly as Zn(OH)₂, and a very small amount of Zn(OH)⁺, Zn²⁺, and Zn(OH)³⁻. Duo to the complexation reaction between PASP and Zn ions, the chemical reaction between PASP and dissolved Zn species could be proposed and is shown in Fig. 14. From Fig. 14, one of the assistant depressing effect of dissolved Zn components was its ability to promote the formation of some polymeric species. And the polymeric species exerted more stronger chemisorption on Cu-activated marmatite surface, as illustrated from FT-IR analysis and XPS analysis. Therefore, low concentration of depressant mixture makes Cu-activated marmatite surface more hydrophilic, which agreed with the results of contact angle tests. In addition, the pre-adsorption of PZ strongly prevented the further adsorption of collector DDTC on Cu-activated marmatite surface. However, the present of PZ had little effect on the further adsorption on chalcopyrite

surface, which in turn resulted in selective flotation separation of chalcopyrite from Cu-activated marmatite.

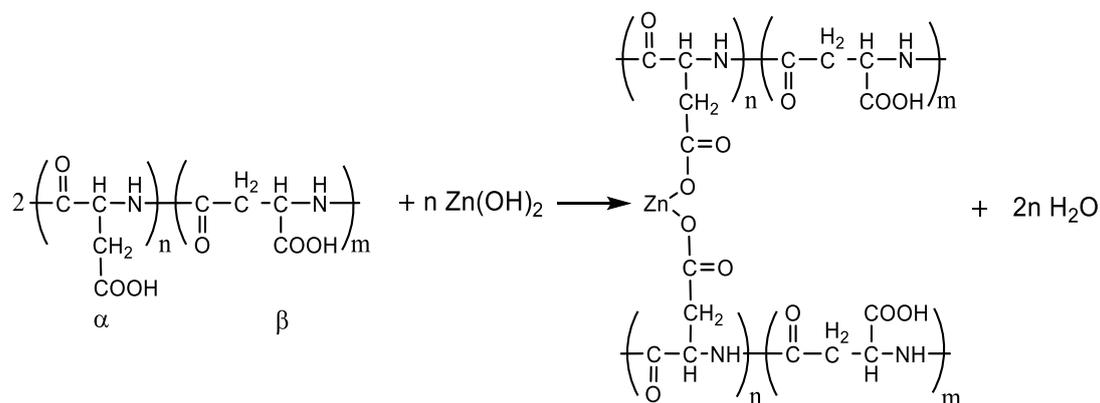


Fig. 14. The possible reaction between PASP and dissolved Zn species in alkaline pH condition

5. Conclusions

From the above results, the following conclusion can be obtained:

(1) Micro-flotation tests show that the depressant mixture of PASP and ZnSO_4 exerted an obvious selective depression effect on the floatability of Cu-activated marmatite but not chalcopyrite as pH above 9. From the results of real ore tests, compared to the use of single ZnSO_4 , the PZ system decreased the Zn content of Cu concentrate from 9.33% to 5.15% and reduced the depressant dosage by more than a half.

(2) From the results of ICP measurements, PASP can effectively weaken the activation of copper ions on marmatite surface and produce the selective depression.

(3) XPS analysis demonstrate a stronger interaction between PZ and Cu-activated marmatite surface, and the depressant PZ may mainly react with Cu-activated marmatite surface through the copper atoms.

(4) FI-IR analysis indicate the more intensive chemisorption of PASP and PZ on Cu-activated marmatite surface, resulting in a more hydrophilic surface. The pre-adsorption of PZ strongly prevented the further DDTC adsorption on Cu-activated surface, but exert little effect on DDTC adsorption on chalcopyrite surface, as demonstrated by the results of the contact angle measurements.

Therefore, it can be concluded that the effective flotation separation of chalcopyrite and Cu-activated marmatite can be achieved by PASP and ZnSO_4 as the combined depressant.

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