



Effect of Grinding Media on Grinding-Flotation Behavior of Chalcopyrite and Pyrite

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Grinding media have significant influence on the flotation of chalcopyrite and pyrite. This effect is mainly related to the change in the surface properties of chalcopyrite and pyrite. This paper investigates the influence of steel ball and nano-ceramic ball grinding on the floatability of chalcopyrite and pyrite. Flotation results, as well-scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), ultraviolet spectrophotometer, and zeta potential measurement results indicate that nano-ceramic ball grinding is beneficial to the flotation of chalcopyrite. Flotation results also indicate that chalcopyrite has better floatability after nano-ceramic ball grinding compared with steel ball grinding. Results of adsorption experiments show that nano-ceramic ball grinding contributes to the adsorption of isobutyl xanthate to chalcopyrite. XPS and SEM techniques demonstrated that steel ball grinding easily produces oxidation species at the surface of chalcopyrite, thereby reducing its floatability. Results from this study also confirmed that steel ball grinding is beneficial to the flotation of pyrite. Therefore, nano-ceramic media grinding produces better selective flotation in chalcopyrite than steel media grinding.

Keywords: chalcopyrite, pyrite, nano-ceramic ball, steel ball, grinding, flotation

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INTRODUCTION

Grinding operation is an essential process in a mineral processing plant. The primary purpose of grinding is to achieve monomer dissociation between useful minerals, gangue minerals, and other minerals. Grinding also provides the right-sized raw materials for the downstream sorting process. The grinding process is affected by different factors, such as ore characteristics, grinding media, and grinding concentration. Moreover, grinding media have important effect on subsequent flotation operations by changing the grinding pulp environment (Martin et al., 1991; Palm et al., 2010, 2011; Li and Gao, 2017, 2018; Corin et al., 2018; Feng et al., 2019), particularly the pulp chemistry and surface properties of minerals in the flotation. The effect of the grinding media on flotation is mostly determined using three parameters, namely dissolved oxygen concentration, slurry potential, and galvanic interaction between the medium and the mineral (Erdemoglu and Sarikaya, 2002; Gonçalves et al., 2003; Peng and Grano, 2010a,b). The electrochemical standard potentials interaction between sulfide minerals and grinding media during the grinding processing. The grinding media act as the anode, whereas the mineral acts as the cathode (Gonçalves et al., 2003). Steel media generate hydrophilic products on mineral surfaces, reduce the natural floatability of minerals, and also affect the adsorption of collectors at the surface of mineral (Heyes and Trahar, 1979; Greet et al., 2004; Huang and Grano, 2006; Bruckard et al., 2011; Feng et al., 2020).

Studies have shown that the grinding media can affect the flotation of chalcopyrite and pyrite. Galvanic interaction between the steel media and chalcopyrite forms iron hydroxide species at the surface of the chalcopyrite, which affects the adsorption of collectors and reduces the floatability of the chalcopyrite (Forssberg et al., 1988; Rao and Natarajan, 1988). However, it has been reported that mild steel grinding is beneficial to the flotation of pyrite (Learmont and Iwasaki, 1984). A possible explanation is that the collector produced dixanthogen at the surface of the pyrite (Woods, 1976). Another reason is that galvanic interaction between the iron medium and the mineral surface generated elemental sulfur at the surface of the pyrite (Rao et al., 1976). Yuan et al. (1996) and Van Deventer et al. (1991) found that chalcopyrite separation from pyrite has no advantage in strong oxidizing stainless media grinding environment but was restored in a mild steel medium reducing environment. Peng et al. (2003a) and Peng et al. (2003b) found that chalcopyrite separation from pyrite in a chromium medium grinding environment is better than in a mild steel medium. Stainless media or inert media (ceramic media, SAG pebble) are more beneficial to chalcopyrite flotation. Inert medium grinding can improve the pulp environment and flotation recovery of chalcopyrite (Forssberg et al., 1988; Ahn and Gebhardt, 1991; Martin et al., 1991; Guo et al., 2019). As compared with steel balls used as grinding media, SAG pebble is beneficial to improve the recovery rate of copper ore (Shi and Zhou, 2019; Wu et al., 2019). The flotation performance of calcite after ceramic ball grinding is better than that of steel ball grinding (Yao

et al., 2019). Zhang et al. have also compared the flotation kinetics of pyrite with nano-ceramic balls and cast iron balls (Zhang et al., 2019). Nano-ceramic balls, which were invented and patented by Jingdezhen Betterwear New Material Co, Ltd, Jiangxi Province, China (Zhang et al., 2013). Nano-ceramic balls were made of nano-scale alumina powder and other minerals. In our past research, nano-ceramic balls as a fine grinding media can improve the grade and recovery of copper concentrate of copper sulfur ore and have achieved good industrial applications in Yinshan Mining Concentrator of Jiangxi Copper Corporation, China. Nano-ceramic balls as new grinding media have light density, good wear resistance, no iron pollution of pulp and other characteristics (Liao et al., 2019).

However, the surface of ground chalcopyrite, pyrite and the flotation products, as well as the effect of the medium on adsorption of collectors to minerals have not been clearly clarified in nano-ceramic grinding media. This study investigated the effects of nano-ceramic ball and steel ball grinding on chalcopyrite and pyrite flotation behavior, as well as the effects on the surface morphology of the ground products and flotation concentrate. Adsorption between the collector and the mineral was analyzed using adsorption tests in two grinding media.

MATERIALS AND METHODS

Materials and Reagents

The purities of chalcopyrite and pyrite are above 90% (Table 1). The X-ray diffraction (XRD) analysis of chalcopyrite and pyrite is shown in Figure 1. The grinding medium of this experiment used 15 mm nano ceramic balls (95%Al₂O₃) and 12 mm steel balls(3%C) of equal quality. The nano-ceramic balls were sourced from Jingdezhen Betterwear New Material Co. Ltd., China, whereas the steel balls were from Goldpro New Material Co. Ltd., China. Grinding media with chemical compositions, densities were selected for the tests as shown in Table 2.

The collector used in this study was isobutyl xanthate obtained from Shanxi Baoji Chemical Reagent Factory. Pine oil was used as a frother in flotation. Analytical grade sodium hydroxide and

TABLE 1 | Chemical analysis results of chalcopyrite and pyrite.

Element	Composition (%)	
	Chalcopyrite	Pyrite
Cu	31.86	0.00
Fe	27.35	44.01
S	32.31	54.62

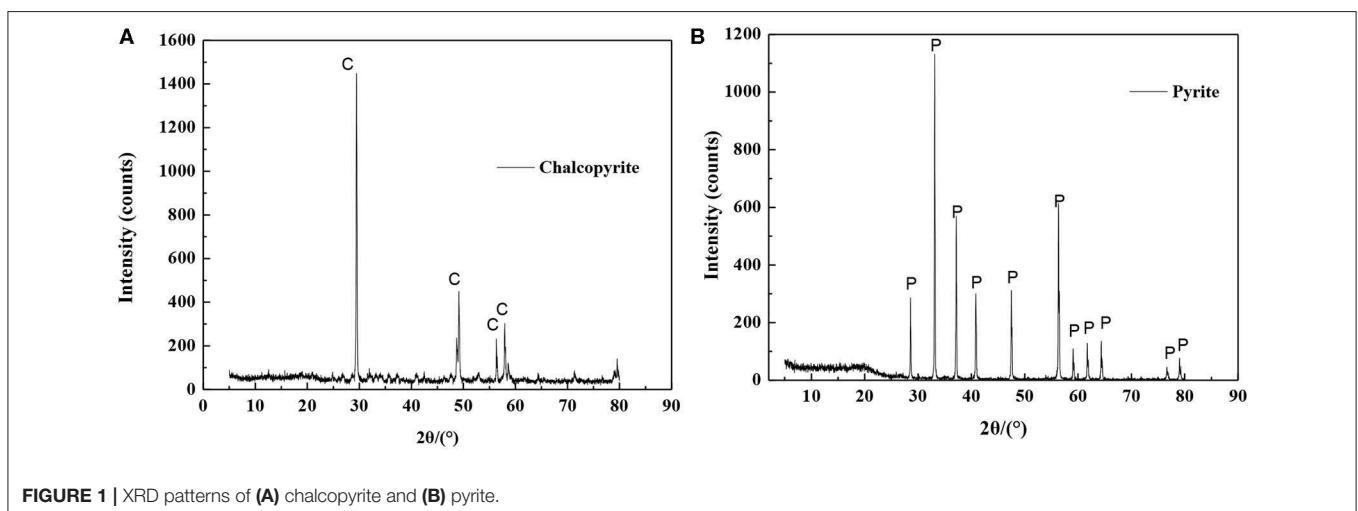


TABLE 2 | Grinding media, chemical compositions, densities.

Media type	Chemistry (wt.%)		Density (g/cm ³)
	Al ₂ O ₃	C	
Steel ball	0.00	3.00	7.80
Nano- ceramic ball	95.00	0.00	3.70

hydrochloric acid were used as pH adjusters, which were supplied by Xilong Scientific Co. Ltd., China.

Experimental Methods

Grinding Tests

The chalcopyrite and pyrite are crushed with a small hammer to 1–2 mm, then, the samples were ground in a grinding bowl using the 15 mm nano-ceramic balls and 12 mm steel balls (of the same weight) as grinding media. Firstly, the grinding medium and appropriate amount of sample were added in the grinding bowl. Secondly, the samples were ground with a grinding rod for 3 min. Then, the grinding medium were removed from the grinding bowl and the samples were sieved using 200 mesh and 400 mesh sieves. Finally, upper 200 mesh samples were return to regrind until all samples were reached passing 200 meshes. Samples with particles size of 0.038~0.075 mm were used for the flotation test, whereas samples with particle size of the passing 0.038 mm were used for the adsorption test. The surface morphology of the passing 0.038 mm ground samples were analyzed using an MIA650F scanning electron microscope (American FEI Company).

Micro-Flotation Tests

The flotation test was conducted in a 40 ml XFG flotation machine. The flotation machine rotational speed of the impeller was 1,992 r/min, and each flotation used 2 g of the samples. We added 2 g of the samples and distilled water into a 50 ml beaker. The suspended minerals were placed in an ultrasonic bath for 5 min. Then, the mineral added to the flotation cell was conditioned for 3 min and adjusted to the desired pH value with HCl or NaOH solutions. Isobutyl xanthate and pine oil were sequentially added into the flotation cell at a conditioning time of 3 and 1 min, respectively. The flotation concentrate was filtered and dried, and the flotation recovery rate was calculated using the mass ratios of floated and un-floated fractions. The surface morphology of the flotation concentrate product was analyzed using an MIA650F scanning electron microscope (SEM).

Adsorption Tests

The amount of adsorption at the surface of mineral was determined using the residual concentration method. The specific surface areas of pyrite and chalcopyrite were obtained using the BET test. The adsorption tests were conducted using an ultraviolet spectrophotometer. We placed 2.0 g of the passing 0.038 mm samples into a 40 mL conical flask, and adjusted the suspension to the desired pH value of 8 with dilute NaOH or HCl solutions. A given concentration of isobutyl xanthate mixed with distilled water was added into a 40 ml solution. After dispersion

in a high-speed centrifuge for 15 min at a rotation speed of 1,500 r/min, the supernatant was filtered for measurement using an ultraviolet spectrophotometer. The amount of isobutyl xanthate adsorbed at the surface of chalcopyrite and pyrite was calculated as given in Equation 1 (Qu et al., 2016):

$$Q_t = \frac{V \cdot C_s}{MS} \quad (1)$$

where Q_t is the amount of adsorption of isobutyl xanthate to the surfaces of chalcopyrite or pyrite surfaces at time t ($\text{mol} \cdot \text{m}^{-2}$), C_s is the adsorption concentration of isobutyl xanthate ($\text{mol} \cdot \text{L}^{-1}$), V is the volume (L), S is the specific surface area of chalcopyrite or pyrite ($\text{m}^2 \cdot \text{g}^{-1}$), and M is the mass of chalcopyrite or pyrite (g).

X-ray Photoelectron Spectroscopy (XPS)

The concentration of surface species on the flotation concentrates was determined using a Thermo Scientific ESCALAB 250Xi XPS instrument (USA). This instrument used the focused beam of monochromatic Al K α X-rays (1486.68 eV) operating at 140 W. Firstly, the survey mode was used to obtain the elements on the surfaces of flotation concentrates. Then, the high-resolution mode was used to observe the chemical bonds and oxidation states of Fe and S. The spectral data were processed using Avantage XPS and Origin software. Details of this procedure have been reported previously by Beke et al. (2009) and Rabieh et al. (2017).

Zeta Potential Measurement

The zeta potential was measured using an A80030E Zeta Probe. The mineral samples were added to distilled water to form a 0.5% mineral solution. After stirring for 5 min, the zeta potential of the solution was tested at a given pH in the presence and absence of isobutyl xanthate at a concentration of $1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

Results and Discussion

Effect of Different Grinding Media on Grinding Performance

Figure 2 shows the SEM images of chalcopyrite and pyrite after dry grinding in mortar. As seen from **Figure 2A**, it appears that the surface of chalcopyrite after dry grinding using steel balls is rough and has a structure consisting of cracks. **Figure 2B** shows the smooth surface of chalcopyrite after dry grinding using nano-ceramic balls which has little cracks on. **Figures 2C,D** indicated that the surface morphology of pyrite is rough after ground with nano-ceramic balls or steel balls. The surface of the pyrite after ground with steel ball (**Figure 2C**) has more fine particles attached to the large particles than the surface after ground with nano-ceramic ball (**Figure 2D**). There are less crack on the surface of the pyrite after grinding with nano-ceramic balls as shown in (**Figure 2D**) in comparison with steel balls (**Figure 2C**). Hence, in the case of dry grinding, the effect of the grinding media on the surface morphology of the mineral is related to the type of the mineral. Moreover, the surrounding of larger particles by smaller particles and crack on the surface of mineral may be owing to the mechanical force of grinding media,

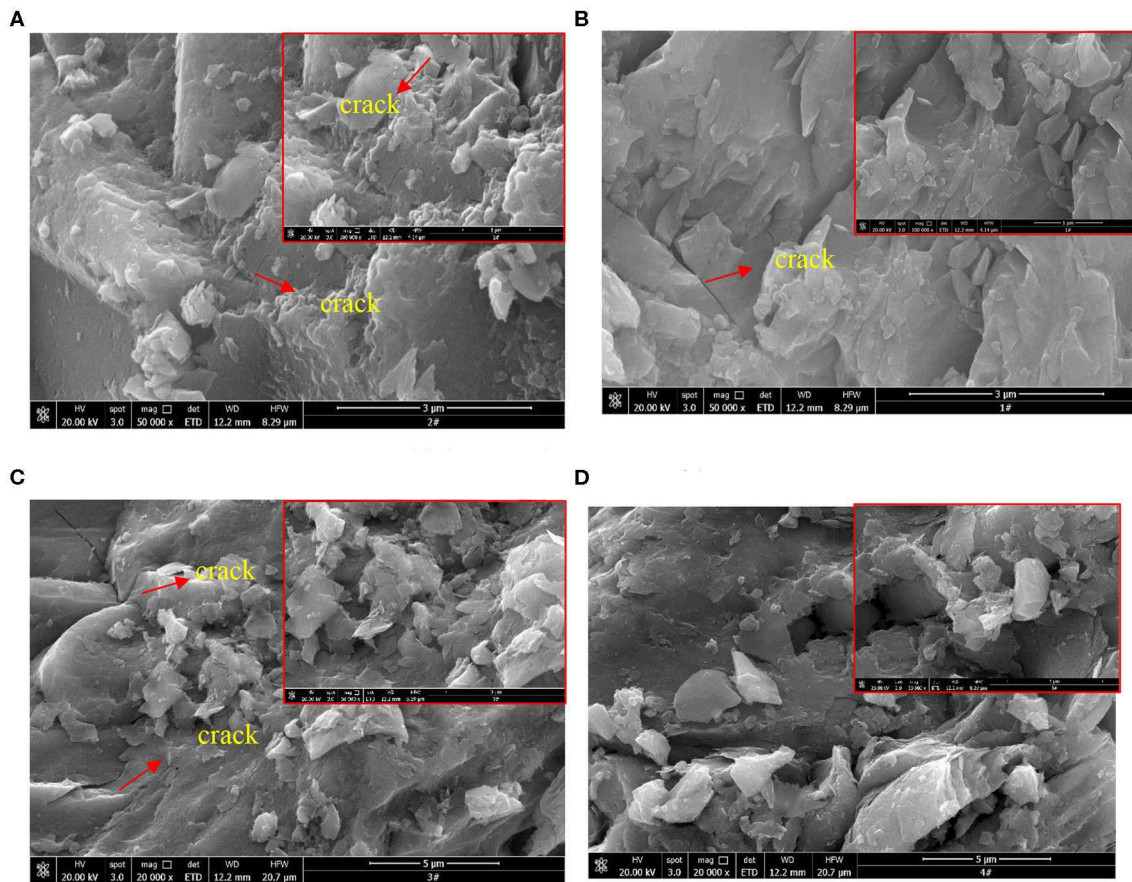


FIGURE 2 | SEM images of chalcopyrite and pyrite after dry grinding: **(A)** Chalcopyrite (steel ball); **(B)** Chalcopyrite (nano-ceramic ball); **(C)** Pyrite (steel ball); **(D)** Pyrite (nano-ceramic ball).

because the mechanical actions between the nano-ceramic balls and chalcopyrite or pyrite are small.

Effect of Different Grinding Media on Flotation

Figure 3 shows the effects of pH on the flotation recovery of chalcopyrite and pyrite after ground using nano-ceramic balls and steel balls. The recovery of chalcopyrite increased as the pH increased after ground using nano-ceramic balls and steel balls. Chalcopyrite exhibited good floatability after ground using nano-ceramic balls compared with ground using steel balls. Pyrite exhibited the opposite trend as the recovery of pyrite decreased with the increase in pH. Pyrite exhibited good floatability using steel ball grinding. This result is consistent with the result obtained in the study by Peng et al. (2003a,b).

Figure 4 shows the effects of isobutyl xanthate concentration on the flotation recovery of chalcopyrite and pyrite at pH 8.0 after ground using nano-ceramic balls and steel balls. The flotation recoveries of chalcopyrite and pyrite increased with the increase in the isobutyl xanthate concentration. The recovery of pyrite increased sharply before the initial concentration reached $1 \cdot 10^{-4}$ mol·L⁻¹ and then remained stable, whereas that of chalcopyrite increased slowly before the initial concentration reached $1 \cdot 10^{-4}$ mol·L⁻¹ and then remained stable. This indicates that the

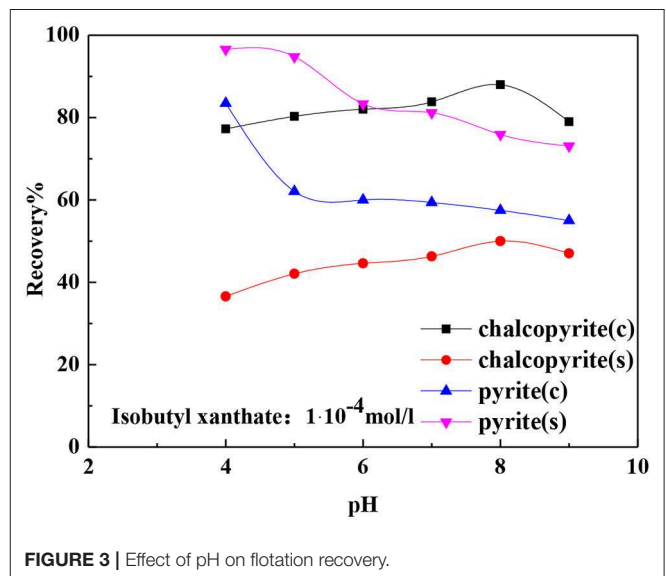
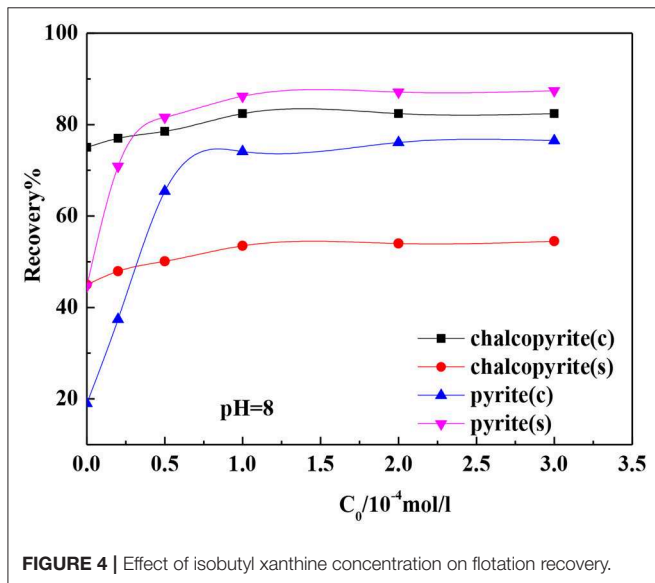


FIGURE 3 | Effect of pH on flotation recovery.

floatability of chalcopyrite in ceramic media and the floatability of pyrite in iron media are good.

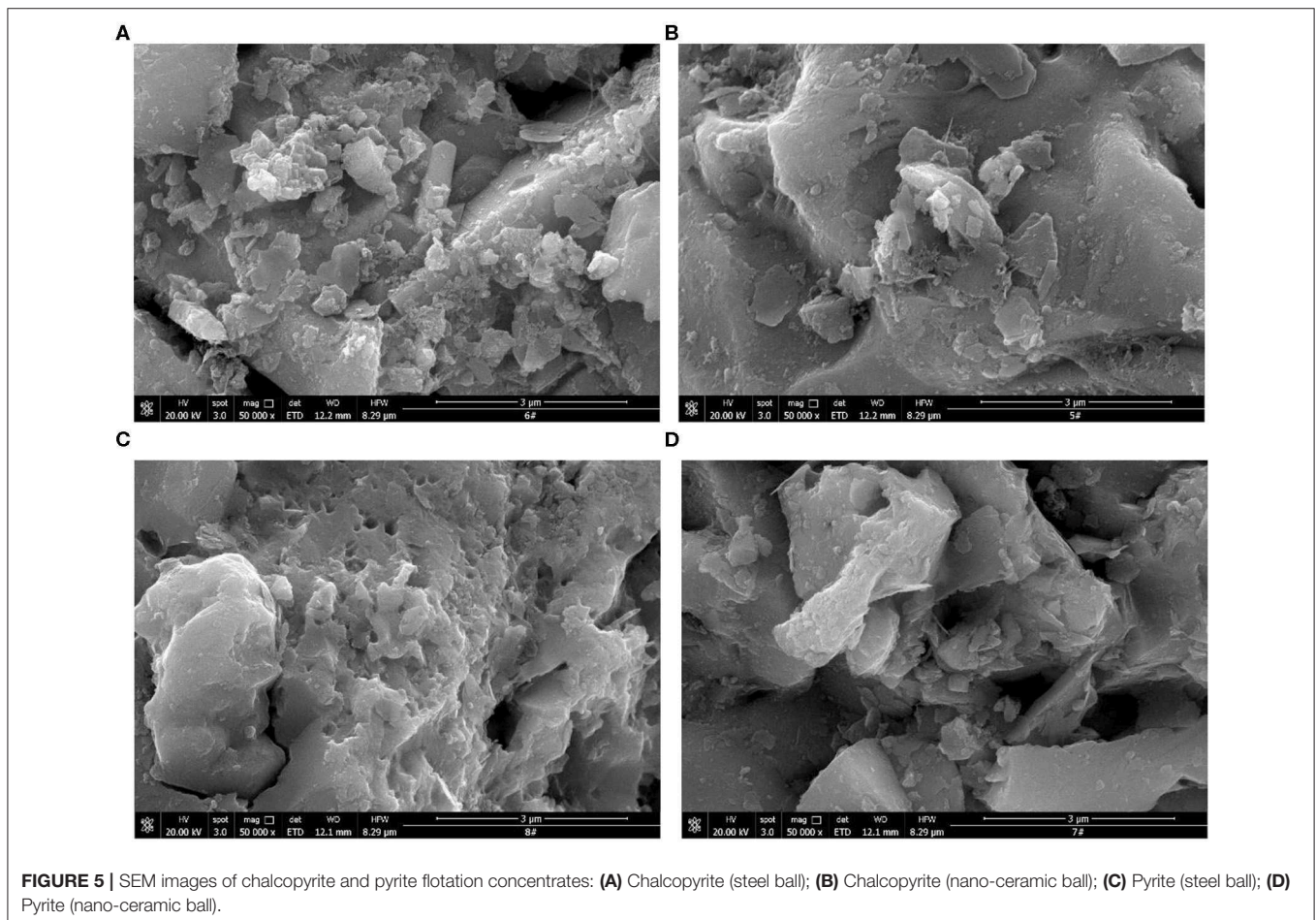
To investigate this trend, we performed scanning electron microscopy analysis of chalcopyrite and pyrite flotation concentrates at a pH of 8 and the addition of $1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$



of isobutyl xanthate concentration. **Figure 5** shows SEM images of chalcopyrite and pyrite flotation concentrates. The surface of the chalcopyrite flotation concentrate ground with nano-ceramic balls is smooth, whereas there are many flocs on the surface ground with steel balls. The flotation of chalcopyrite was affected by the hydrophilic products generated at the surfaces by the steel media grinding (Heyes and Trahar, 1979; Greet et al., 2004; Yekeler et al., 2004). The surface of the pyrite flotation concentrate has more flocs on the surface ground with steel balls than ground with nano-ceramic balls. The flotation of pyrite improved after ground with steel balls owing to the galvanic interaction between the steel media and the mineral surface, which generated elemental sulfur at the surface of the pyrite (Rao et al., 1976).

Effect of Different Grinding Media on Adsorption

The adsorption of chalcopyrite, pyrite, and the collector is affected by many factors such as the pH, the type of collector, and the grinding medium (Heyes and Trahar, 1979; Greet et al., 2004; Huang and Grano, 2006; Bagci et al., 2007; Qu et al., 2016; Huang X. et al., 2019). The adsorption of the collector to chalcopyrite is affected by the grinding medium mainly because the galvanic action of the iron medium results in adsorption of



the hydroxide of the iron at the mineral surface, which affects the adsorption of the agent at the surface of mineral (Heyes and Trahar, 1979; Greet et al., 2004; Huang and Grano, 2006). Qu et al. (2016) found that HATTs(3-hexyl-4-amino-1,2,4-triazole-5-thione)exhibited strong adsorption capacity for chalcopyrite at pH 4~8. Bagci et al. (2007) found that selective and non-selective collectors can improve the amount of adsorption of the collector at the surface of chalcopyrite.

Figure 6 shows the relationship between the amount of adsorption of isobutyl xanthate at the surfaces of chalcopyrite or pyrite and the isobutyl xanthate concentration. The figure shows that with the increase in the concentration of isobutyl xanthate, the amount of adsorption at the chalcopyrite surface increases, and the amount of adsorption of isobutyl xanthate with ceramic ball grinding is larger than that of steel ball grinding. This result is consistent with the result obtained by Qu et al. (2016). The authors reported that the adsorption of the collector at the surface of mineral increases as the concentration of collector increases. Nano-ceramic balls can improve the pulp environment and contribute to the adsorption of collectors molecules at the surface of chalcopyrite, which in turn enhances the flotation of minerals (Ahn and Gebhardt, 1991; Martin et al., 1991). Pyrite exhibits the opposite trend. In iron media grinding environment, the collector produces dixanthogen at the surface of the pyrite and forms Fe-collector complexes (Woods, 1976; Nagaraj and Brinen, 2001). Therefore, the amount of adsorption of isobutyl xanthate at the surface of pyrite in iron media is higher than that of ceramic media.

Figure 7 shows the relationship between the adsorption rate and isobutyl xanthate concentration. The figure shows that with the increase in the concentration of isobutyl xanthate, the adsorption rate at the surface of chalcopyrite first increased and then stabilized, and the adsorption rate of isobutyl xanthate to chalcopyrite ground with ceramic ball grinding is higher than that of ground with steel ball grinding; pyrite exhibited the opposite trend.

XPS Analysis

The chalcopyrite and pyrite flotation concentration at pH of 8 and addition of $1 \cdot 10^{-4}$ mol·L⁻¹ of isobutyl xanthate concentration were also analyzed using XPS. The survey spectra of chalcopyrite and pyrite were used to determine the surface element content of the samples under different grinding media. The high-resolution spectra of Fe and S provided information about the oxidation state and chemical bonding of Fe and S.

Figures 8A,B show the survey spectra of chalcopyrite and pyrite, respectively. The percentage of elements at the surface of the samples are presented in **Table 3**. Compared with chalcopyrite ground with steel balls, grinding with nano-ceramic balls decreased the iron concentration at the chalcopyrite surface from 11.02 to 10.63% and the oxygen concentration from 48.8 to 39.71%, whereas the sulfur concentration increased from 8.19 to 16.38%. The increase in sulfur concentration at the surface of chalcopyrite after the addition of isobutyl xanthate is due to the adsorption of isobutyl xanthate, whereas the decrease in oxygen concentration suggests the removal of surface oxidation species from the surface of chalcopyrite (Cao et al., 2018). This also

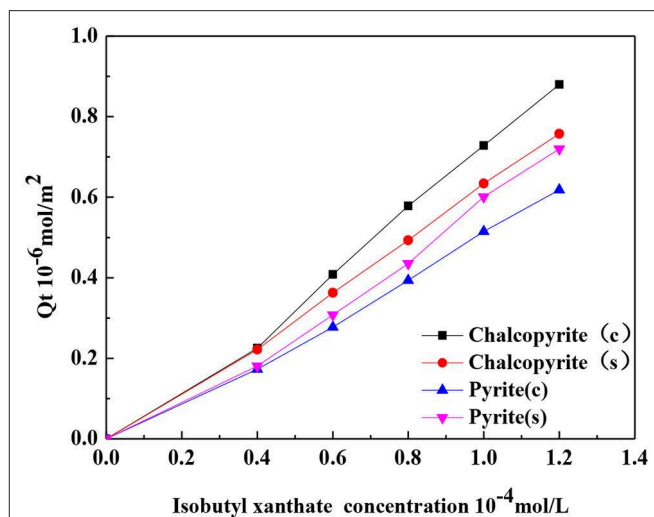


FIGURE 6 | Adsorption concentration at the surfaces of samples as a function of isobutyl xanthate concentration.

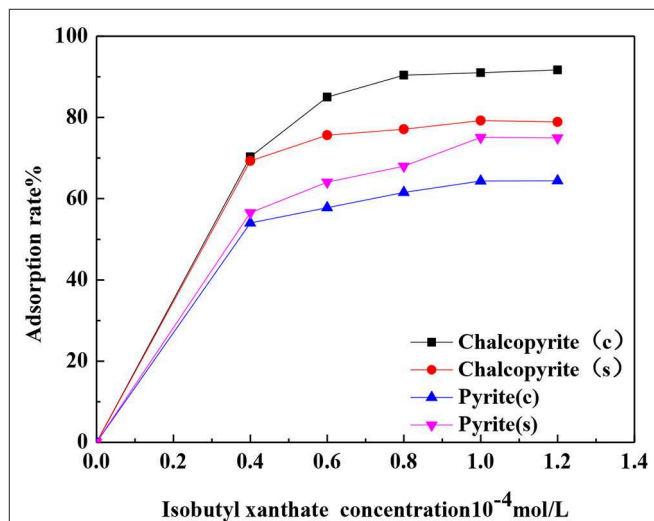
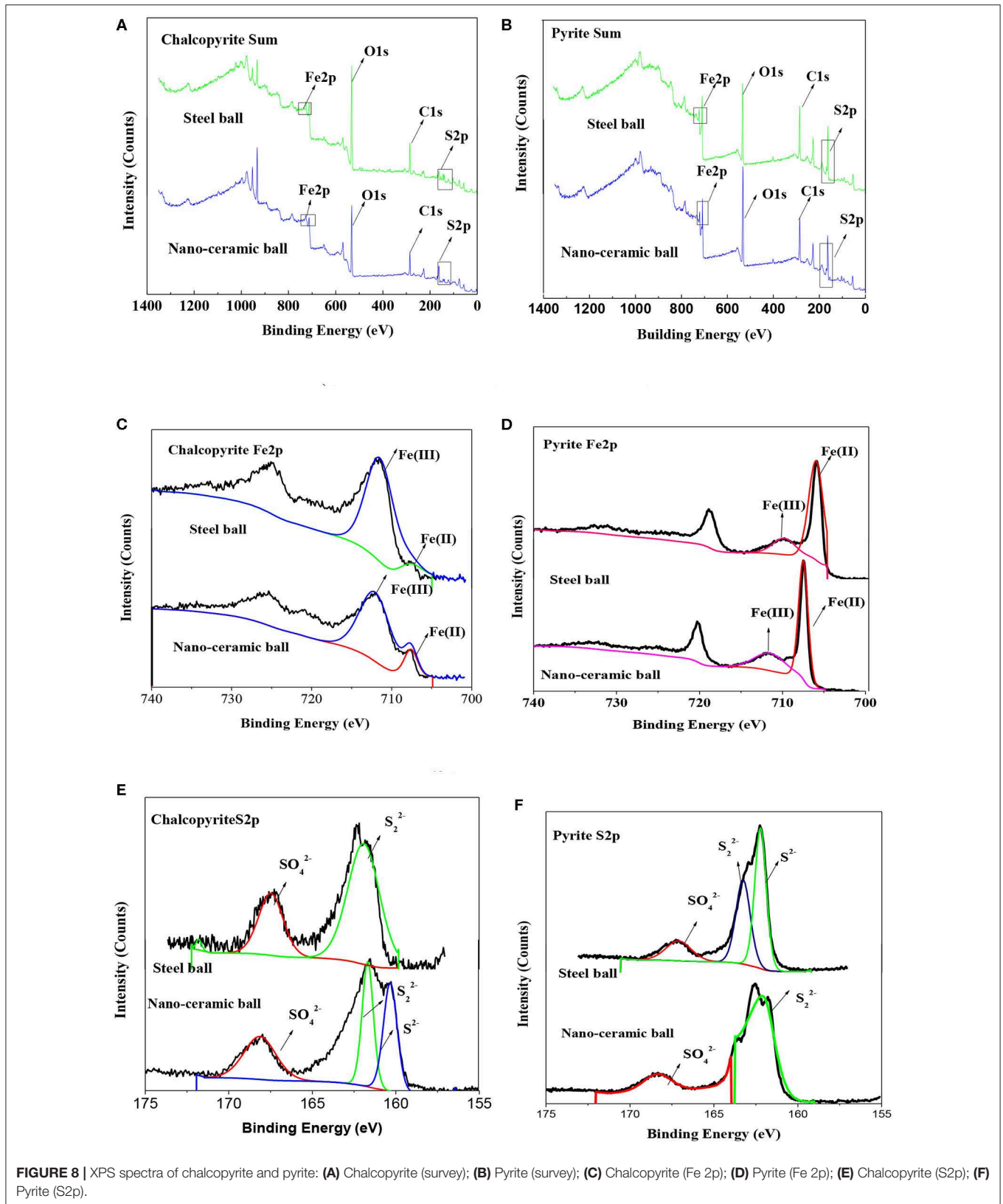


FIGURE 7 | Adsorption rates at the surfaces of samples as a function of isobutyl xanthate concentration.

indicates that ceramic media grinding is beneficial to the flotation of chalcopyrite, which is consistent with the flotation results of the dosage isobutyl xanthate. Compared with pyrite ground with steel balls, grinding with nano-ceramic balls decreased the iron concentration at the surface of pyrite from 7.98 to 7.71% and the sulfur concentration from 21.5 to 20.58%, whereas the oxygen concentration increased from 27.35 to 34.65%. This also indicates that steel media grinding is beneficial to the flotation of pyrite, which is consistent with the flotation results of the dosage isobutyl xanthate.

Figures 8C,D show the high-resolution spectra of Fe of chalcopyrite and pyrite, respectively, whereas **Table 4** presents the qualification of iron species based on Fe 2p XPS spectra.



In the Fe 2p_{3/2} spectra, the peaks near 711 eV for Fe(III)-O and at 708 eV for Fe(II)-S, the Fe(III)-O concentration at the surface of chalcopyrite ground using ceramic balls decreased

significantly from 90.96 to 86.01% (Taheri et al., 2014; Mikhlin et al., 2016; Peng et al., 2017; Rabieh et al., 2017; Cao et al., 2018). This indicates that ceramic ball grinding can reduce the

adsorption of iron oxide on the surface of chalcopyrite and is conducive to the flotation of chalcopyrite. Cao et al. (2018) found that pyrite has a higher energy site at approximately 707.2 eV; thus, Fe(II)-S has the highest concentration in the pyrite Fe 2p spectra. The Fe(II)-S concentration at the surface of pyrite

ground using ceramic balls significantly increased from 68.36 to 79.83%. Rabieh et al. (2017) also found the same regular pattern in pyrite.

Figures 8E,F show the high-resolution spectra of S of chalcopyrite and pyrite, respectively, whereas Table 5 presents the qualification of sulfur species based on the S 2p XPS spectra. Disulfide S_2^{2-} is produced at a binding energy range of 162.4–162.7 eV and S^{2-} is produced at a lower binding energy range of 161.3–162.1 eV, whereas SO_4^{2-} is produced at higher binding energies of approximately 168 eV (Peng et al., 2003a; Moslemi and Gharabaghi, 2017; Cao et al., 2018). Peng et al. (2003a) found that a 30 wt.% chromium medium produced more sulfate at the surface of chalcopyrite than a mild steel medium. Figure 8E shows that ceramic balls produced more S_2^{2-} at the surface of chalcopyrite than steel balls. Rabieh et al. (2017) found that there are more SO_4^{2-} at the surface of pyrite using ceramic media grinding compared with using steel media. In this paper, we also

TABLE 3 | Atomic concentration of elements in XPS at the surfaces of samples.

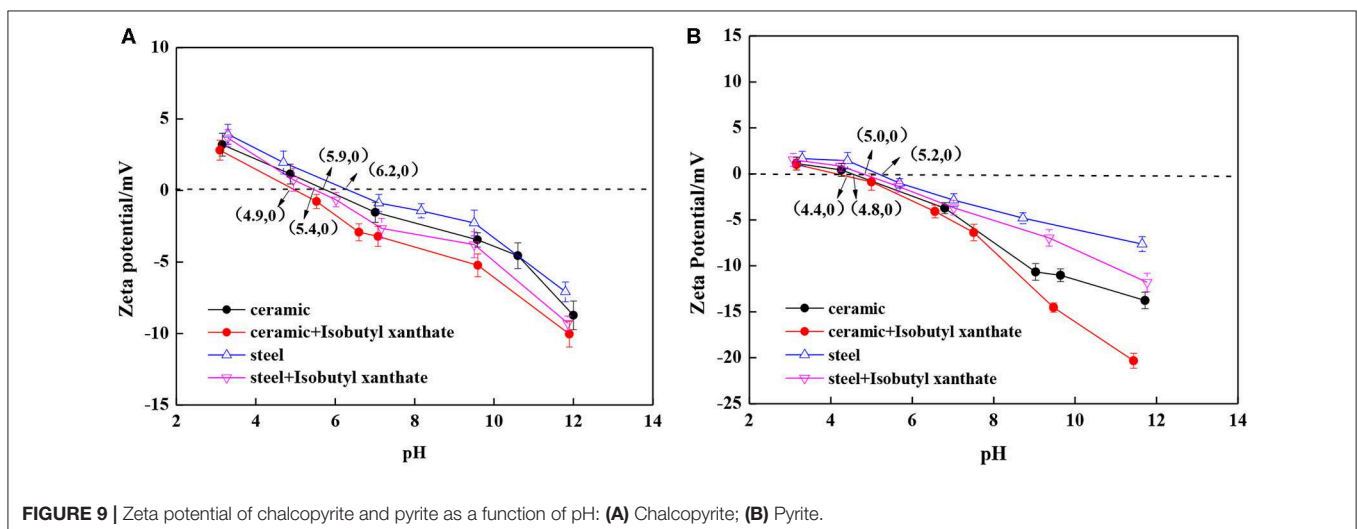
Mineral	Grinding media	Atomic concentration of element (%)			
		Fe	C	O	S
Chalcopyrite	Ceramic	10.63	33.28	39.71	16.38
Chalcopyrite	Steel	11.02	31.99	48.8	8.19
Pyrite	Ceramic	7.71	37.06	34.65	20.58
Pyrite	Steel	7.98	43.17	27.35	21.5

TABLE 4 | Quantification of iron species at the surface of samples based on Fe 2p XPS spectra.

Mineral	Chalcopyrite		Chalcopyrite		Pyrite		Pyrite	
	Ceramic		Steel		Ceramic		Steel	
	Grinding Media		Grinding Media		Grinding Media		Grinding Media	
Species	B.E.	at. %	B.E.	at. %	B.E.	at. %	B.E.	at. %
Fe(II)	707.58	13.99	707.52	9.04	707.48	68.36	706.28	79.83
Fe(III)	712.08	86.01	711.48	90.96	711.48	31.64	710.08	20.17

TABLE 5 | Quantification of sulfur species at the surface of samples based on S 2p XPS spectra.

Mineral	Chalcopyrite		Chalcopyrite		Pyrite		Pyrite	
	Ceramic		Steel		Ceramic		Steel	
	Grinding Media		Grinding Media		Grinding Media		Grinding Media	
Species	B.E.	at. %	B.E.	at. %	B.E.	at. %	B.E.	at. %
S^{2-}	161.68	2.49	161.13	71.55	161.95	78.48	161.53	48.62
S_2^{2-}	162.14	80.22	-	-	-	-	162.78	36.21
SO_4^{2-}	168.78	17.29	168.08	28.45	168.36	21.52	167.83	15.18



found the same regular pattern in pyrite, as presented in **Table 5** and **Figure 8F**.

Zeta Potential Measurement

The surface potential of minerals will be affected by the adsorption of collectors, the degree of oxidation of minerals, the flotation atmosphere, and the influence of the grinding media (Peng and Grano, 2010a,b; Yin et al., 2018; Huang Z. et al., 2019; Jia et al., 2019). **Figure 9** shows the zeta potential of chalcopyrite and pyrite as a function of pH in the absence and presence of $1 \times 10^{-4} \text{ mol L}^{-1}$ isobutyl xanthate using two different grinding media. Peng et al. (2003a) found that steel media tend to produce lower Eh values than a 30 wt.% chromium medium when Cu^{2+} was added. Moreover, Peng and Grano (2010a,b) found that the zeta potential of pyrite is affected by the flotation atmosphere and the oxidation of sulfide minerals increased its isoelectric points. As shown in **Figure 9A**, the isoelectric point of chalcopyrite after nano-ceramic ball grinding is 5.9, whereas that of steel ball grinding is 6.2. The isoelectric point of chalcopyrite after nano-ceramic ball grinding is consistent with that in the study by Huang X. et al. (2019). The increase in the isoelectric point of chalcopyrite after steel ball grinding is related to the hydroxide formed by the wear of the iron medium (Peng and Grano, 2010a,b). After the addition of isobutyl xanthate, the isoelectric point of chalcopyrite shifted to the left because the negatively charged collector reduces the isoelectric point of chalcopyrite (Huang X. et al., 2019). As shown in **Figure 9B**, the isoelectric point of pyrite after nano-ceramic ball grinding is 4.8, whereas that of the steel ball grinding is 5.2. This value is also similar to the values reported in previous studies (Yin et al., 2018; Huang X. et al., 2019). After the addition of isobutyl xanthate, the isoelectric point of pyrite shifted to the left. Iron media grinding can cause iron media pollution. Under alkaline conditions, a stable complex of xanthogen ions and iron hydroxides is adsorbed at the surface of pyrite (Yang et al., 2018; Yin et al., 2018). This is also consistent with the results shown in **Figures 3, 6, 7**.

CONCLUSIONS

Grinding media has significant influence on the flotation of chalcopyrite and pyrite. This effect is mainly related to the change in the surface properties of chalcopyrite and pyrite, which in turn affects their floatability. Grinding using steel medium easily produces oxidation species at the surface of chalcopyrite, thereby reducing its floatability. Scanning electron microscopy results show that the surface of the ground product

and the flotation concentrate of chalcopyrite using nano-ceramic balls grinding is smooth, whereas the surface of the product ground using steel balls is rough and the surface of chalcopyrite flotation concentrates have many flocs. The flotation recovery of chalcopyrite after nano-ceramic ball grinding is higher than that of steel ball grinding. XPS demonstrated that steel ball grinding produced more iron hydroxide species than nano-ceramic ball grinding, which is not conducive to the flotation of chalcopyrite. Adsorption experiments also show that nano-ceramic media grinding contributes to the adsorption of isobutyl xanthate to chalcopyrite. The zeta potential of chalcopyrite indicates that ceramic media grinding is beneficial to the reduction of the isoelectric point of mineral flotation. However, steel media grinding is conducive to the flotation of pyrite. XPS was used to verify the flotation recovery of pyrite and the adsorption of isobutyl xanthate at the surface of pyrite. Further research should be conducted on the effect of nano-ceramic media on the selective separation of chalcopyrite from pyrite. Therefore, the nano-ceramic ball is a good grinding medium for chalcopyrite grinding, it is beneficial to improve the recovery rate of chalcopyrite. Steel balls is better for grinding pyrite than nano-ceramic balls. For copper-sulfur ore which is chalcopyrite associated pyrite, nano-ceramic balls can be used to replace steel balls as grinding media in some ways.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

CW initiated the research topic. NL wrote the manuscript text. BF reviewed and edited the manuscript. JX, JW, YG, and NL performed experiments. All authors reviewed the manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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