

Research Article

Dual Role of Fe²⁺ in the Galena Flotation and Influence on Selective Separation

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Fe ions, as one of the unavoidable metal ions, are present in flotation pulp as ferric and ferrous species, and the effect of ferric species on the flotation behavior of sulfide minerals has been widely discussed in the above literatures. However, the effect of ferrous species has rarely been noticed. In this paper, the effect of ferrous species on the flotation behavior and surface characteristics of galena was investigated by using microflotation, zeta potential measurements, X-ray photoelectron spectrometer (XPS) analysis, and density functional theory (DFT) calculations. Microflotation tests indicated that the flotation recovery of galena with potassium butyl xanthate (KBX) as collector was significantly decreased with the addition of Fe²⁺ in the pulp, and the recovery was further decreased with increasing dosage of Fe²⁺. In addition, the finer the galena particles, the greater the decrease in flotation recovery. Zeta potential analysis illustrated that the isoelectric point (IEP) was shifted from 4.4 to 5.8 due to the adsorption of ferrous hydroxyl complexes on the galena surface and the zeta potential. XPS surface analysis suggested that the surface oxidation of galena was alleviated by the consumption of O₂ in the pulp, which reduced the adsorption of the collector KBX on and the oxidation of xanthates to dixanthogens. Density functional theory (DFT) calculations confirmed that the ferrous hydroxyl complex FeOH⁺ could be adsorbed on the galena surface by interactions between Fe and S atoms.

1. Introduction

Galena (PbS), an essential raw material for producing lead metal, is commonly intergrown with chalcopyrite, sphalerite, and pyrite, making its direct utilization challenging [1]. The prebeneficiation of galena is commonly essential before the metallurgical process, and the flotation was considered as the most economical and efficient method for the prebeneficiation of galena [2, 3]. In froth flotation, galena is selectively floated from other minerals based on differences in surface hydrophilicity or hydrophobicity [4, 5]. Therefore, the surface characteristics are crucial for the flotation of galena. As we all know, the surface characteristics of mineral can be selectively controlled by changing the flotation condition [6, 7]. For galena, the surface characteristics are regulated by

factors such as the depressant type, the collector concentration, and the pH and Eh of the pulp [8]. In industrial flotation, galena was floated prior to sphalerite and pyrite under a suitable pH and collector concentration. Collectors such as ethyl xanthate and butyl xanthate are commercially used for galena flotation. The Pb-xanthate species formed on galena surface is responsible for the improvement in hydrophobicity. In addition, sodium diethyl dithiocarbamate (SN-9[#]) has been used industrially for galena flotation under strongly alkaline conditions. Wang et al. found that nitrogen functional groups in the structure of collector could improve the selectivity of collector owing to the chelating reaction of N atoms with surface Pb atoms [9].

The electrochemical environment of the pulp (pH, Eh, and DO) is another crucial factor affecting the flotation

behavior of galena. Galena exhibits an excellent collectorless and collector-induced floatability under acidic pH conditions, and its floatability gradually decreases with increasing pH [10]. Hu et al. have suggested that the surface oxidation and collector adsorption of sulfide minerals are involved in a redox reaction, which are closely correlated with the electrochemical environment of a flotation pulp [11]. In the flotation of galena, the moderate surface oxidation is necessary for improving the floatability and adsorption of the collector. The oxidation products such as elemental sulfur, polysulfide, or Pb-xanthate species are formed on the galena surface, which depend on the electrochemical environment of the pulp. Therefore, the galena separation efficiency can be significantly improved by controlling the pH and Eh of the flotation pulp [12].

In addition to the collector and electrochemical environment of the pulp, some metal ions can influence the flotation behavior and surface characteristics of minerals [13]. It is well known that many metal ions like as Cu^{2+} , Pb^{2+} , Mg^{2+} , Fe^{3+} , Ca^{2+} , and Al^{3+} occurred in the flotation pulp, which are mainly derived from the use of flotation reagents and recycled water and the oxidation dissolution and corrosion of mineral surface and grinding media [14, 15]. Some metal ions such as Cu^{2+} and Pb^{2+} can activate the flotation of sphalerite and pyrite, enhancing their flotation performance [7, 16]. However, other metal ions such as Zn^{2+} , Mg^{2+} , and Ca^{2+} in flotation pulp can inhibit the flotation of sulfide mineral because of the adsorption of metal hydroxyl species on the surface [17]. On the other hand, the flotation performance of gangue minerals, such as quartz or calcite, can be significantly improved due to the adsorption of Ca^{2+} or Mg^{2+} on the surface, which leads to the decrease in selectivity. For galena, the influence of metal ions on the flotation behavior depends on the kind of metal ions and the electrochemical environment of the pulp [18, 19].

Fe ions, as the most abundant metal ions in pulp, are mainly derived from the oxidation dissolution of Fe-containing minerals and grinding media. Previous studies have indicated that the oxidation dissolution of grinding media has the most significant contribution to the Fe ions existed in the pulp, and this process can be significantly accelerated by galvanic interactions between the sulfide mineral and grinding media (as shown in Figure 1) [20–22].

Different from other metal ions, Fe ions and hydroxyl species have two valence states: Fe^{3+} and Fe^{2+} . It will be known that Fe ions or Fe species in the pulp play an essential role in the flotation of sulfide minerals, and the floatability of sulfide mineral is distinctly depressed due to the competitive adsorption of Fe ions or Fe species with collectors on the surface. In addition, Fe hydroxyl complexes, a type of colloidal species that exist in alkaline pH conditions, can enhance the hydrophilicity of minerals through the adsorption of $\text{Fe}(\text{OH})_3$ and reduce the floatability of minerals [23, 24]. Under alkaline pH conditions, ferrous or ferric species can coexist in a flotation system by forming ferric and ferrous complexes. However, the effects of ferric ions or complexes on the flotation performance and surface characteristics of sulfide minerals have received more attention than those of ferrous ions or complexes. Therefore, the influence of

ferrous ions or complexes on the flotation behavior and surface properties still needs to be addressed. In this study, the effects of ferrous ions or ferrous complexes on the flotation behavior and surface characteristics of galena were investigated, and the related mechanisms are discussed.

2. Experimental

2.1. Materials. The highly mineralized galena samples from Yunnan Province of China were treated with the method described as the previous work [2]. The galena samples with the three particle size of the coarse (+0.074 mm), the intermediate (-0.074 mm to +0.038 mm), and the fine (-0.038 mm) were prepared. The chemical composition and X-ray diffraction (XRD) of the galena samples were shown in Table 1 and Figure 2, respectively. These results suggested that the galena samples used in this work are of high purity.

Potassium butyl xanthate (KBX) of the industrial grade from the Kunming Tiefeng Reagent Factory was used as the flotation collector. Methyl isobutyl carbinol (MIBC) of the analytical purity from Shanghai Aladdin Biochemical Technology Co., Ltd. was employed as the frother. Analytical-purity $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ from the Xilong Chemical Reagent Factory was used as the source of Fe^{2+} . In addition, NaOH and HCl from the Chengdu Kelong Chemical Co., Ltd. with a concentration of 0.001 mol/L were used as the pH regulators, and the deionized water was used for all tests.

2.2. Methods

2.2.1. Microflotation. A 40 mL flotation cell (Wuhan Exploring Machinery Plant, Hubei, China) was used for the microflotation tests. The mineral suspension was prepared by adding 2.0 g of the intermediate galena to 40 mL deionized water; the pH of the suspension was adjusted by using 0.001 mol/L HCl and NaOH. Subsequently, the regulator $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, the collector KBX, and the frother MIBC with the given dosage were added to the suspension and conditioned for 1, 2, and 1 min, respectively. After that, the mineral suspension was floated for 3 min. The concentrates and tailings were filtered and dried. Flotation recovery was calculated based on the weight of the concentrates and tailings. Microflotation tests were conducted in duplicate. The flotation recovery of galena was calculated by

$$\text{Galena recovery} = \frac{\text{weight of the concentrates}}{\text{weight of the concentrates and tailings}} \times 100\%. \quad (1)$$

2.2.2. Zeta Potential. The effect of Fe^{2+} on zeta potential of galena was investigated by using zeta potential analyzer (Malvern Zetasizer Nano ZS90, Malvern Panalytical Ltd., Britain). The fine galena sample was firstly ground to a particle size of less than 0.010 mm. The mineral suspension was prepared by adding 0.1 g of galena (-0.010 mm) to 20 mL of deionized water. The pH of the mineral suspension was adjusted by using HCl and NaOH solution, and the regulator FeCl_2 and collector KBX with the desired concentration were added to the suspension and conditioned for a given

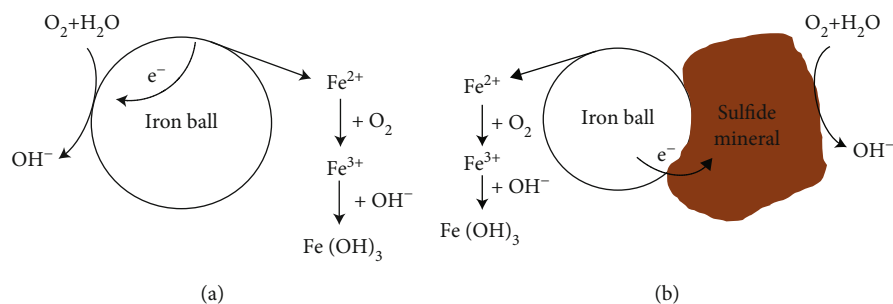


FIGURE 1: Production of ferrous or ferric species in flotation: (a) oxidative dissolution; (b) galvanic interaction.

TABLE 1: Elemental composition of galena sample.

Mineral	Composition wt.%			
	Pb	S	Zn	SiO ₂
Galena	85.16	13.65	0.23	0.16

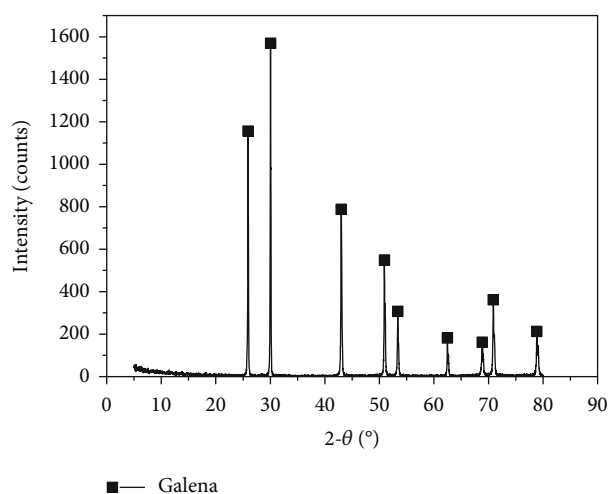


FIGURE 2: X-ray diffraction spectrum of galena sample.

time. After conditioning, 5.0 mL of the suspension was transferred to sample cell using a syringe for zeta potential measurements. All tests were repeated three times, and the value reported in zeta potential was the average [5].

2.2.3. XPS Surface Analysis. The XPS measurement of galena was carried out using a PHI 5000 Versa Probe II (PHI-5000, ULVAC-PHI, Japan) equipped with a monochromatic Al K α X-ray source at 1486.6 eV. The sample used for XPS study was prepared by adding 1.0 g of fine galena to a 100 mL beaker with 40 mL deionized water; the pH of the mineral suspension was adjusted by NaOH and HCl solution. The desired dose of Fe²⁺ was added to the suspension and conditioned for 3 min. After that, the solid particles were filtered and washed with deionized water. After drying at a vacuum, the solid particles were subjected to the XPS analysis. Firstly, a qualitative spectral scan was conducted in to identify the chemical components on galena surface. According to the scan results, a high-resolution scan of some specific elements was carried out. The element distribution

and chemical state were obtained and calculated using MultiPak Spectrum software.

2.2.4. DFT Study. In mineral processing, the density functional theory (DFT) calculation has become a useful tool for studying the adsorption of flotation reagents on mineral surfaces. In this work, the adsorption of Fe²⁺ or ferrous complexes on galena surface was studied by CASTEP module in Materials Studio 8.0. The exchange correlation function GGA-PW91 was selected for all calculations, and only the valence electrons were considered by using the ultrasoft pseudopotentials. A plane wave cut-off energy of 400.0 eV and a k-point sampling density of $4 \times 4 \times 1$ were used [25]. According to the geometry optimization tests, the galena (100) surface was chosen as the calculation model, and the vacuum thickness was set to 15 Å (shown in Figure 3). The convergence tolerances for geometry optimization and property calculations were set to a maximum displacement of 0.001 Å, a maximum force of 0.03 eV Å⁻¹, a maximum energy change of 1.0×10^{-5} eV atom⁻¹, and a maximum stress of 0.05 GPa. The self-consistent field convergence tolerance of 2.0×10^{-6} eV atom⁻¹ was used for all calculations [26].

3. Results and Discussion

3.1. Effect of Fe²⁺ on the Flotation Behavior of Galena. In flotation system, the abundant Fe²⁺ and Fe³⁺ species can be detected in the pulp, which are derived from the surface oxidation of grinding medium. Typically, Fe³⁺ or ferric complexes can reduce the flotation performance of sulfide minerals and lead to the decrease in recovery [27, 28]. However, the effect of Fe²⁺ on the flotation behavior of sulfide minerals is commonly ignored because of the relatively low concentration of Fe²⁺ or ferrous complexes in the pulp. The effect of Fe²⁺ on the flotation behavior of the intermediate galena as a function of the pH is shown in Figure 4.

It is obvious in Figure 4 that without the addition of Fe²⁺ to the pulp, the galena exhibits an excellent floatability with approximately 90% recovery at pH < 10, and a sharp decrease in recovery can be observed at strongly alkaline pH ranges (pH > 10.5) when using KBX as the collector. This result is in agreement with Cheng and Iwasaki's report that a low pH is beneficial to the flotation of galena, and galena is easily depressed under alkaline conditions [29]. Compared with the absence of Fe²⁺ in the pulp, however,

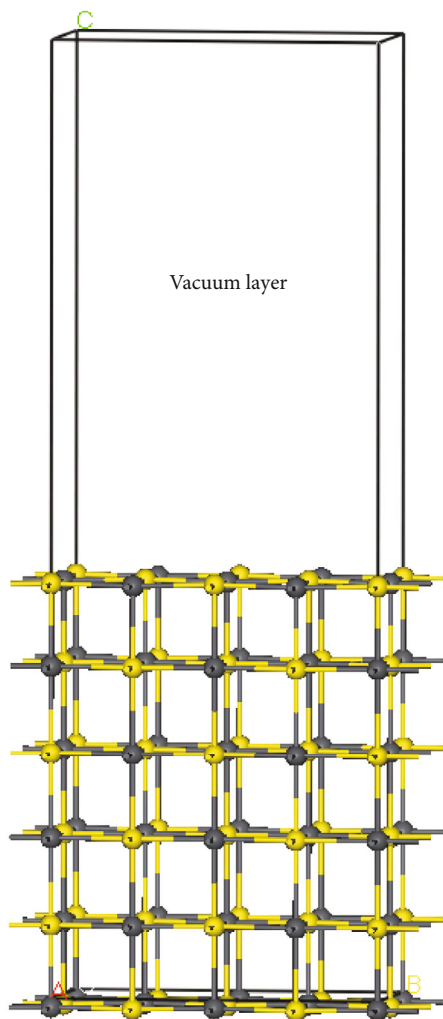


FIGURE 3: Calculation model of the galena (100) surface.

the recovery of galena at the same pH was distinctly decreased with the addition of Fe^{2+} to the pulp, and the recovery further decreased with increasing dosage of Fe^{2+} under alkaline pH conditions. Meanwhile, the decrease in recovery of galena at the alkaline pH was greater than that at the acidic and neutral pH. The results indicate that the presence of Fe^{2+} in the pulp significantly reduces the floatability of galena.

In addition, many studies have suggested that the flotation performance of galena is closely correlated with its particle size [30, 31]. To investigate the influence of Fe^{2+} on flotation behavior of the different particle sizes of galena, the coarse (+0.074 mm), the intermediate (-0.074 mm to +0.038 mm), and the fine (-0.038 mm) galena samples were used in the microflotation tests, respectively. As shown in Figure 5, the effect of Fe^{2+} on the flotation behavior of galena was closely related to the particle size of galena. Under the same pH and concentration of Fe^{2+} , the decrease in galena recovery for the fine particles was greater than that for the coarse particles and intermediates. It appears that the finer the galena particles, the lower the flotation recovery of galena. Galena with fine particle sizes was easily oxidized

and tended to be depressed by Fe hydroxyl complexes in the pulp, which decreased recovery.

3.2. Effect of Fe^{2+} on the Zeta Potential of Galena. Microflotation tests demonstrated that the floatability of galena decreased distinctly with the presence of Fe^{2+} in the pulp. Generally, the adsorption of metal ions on mineral surface can cause the change in surface electrical properties of mineral, which can be revealed by zeta potential. The zeta potentials of galena with the absence and presence of Fe^{2+} in pulp are shown in Figure 6.

As shown in Figure 6, the zeta potential of galena was gradually decreased with the increasing pH and the isoelectric point (IEP) is approximately 4.4, and this result is consistent with the research achieved by Song et al. [31]. However, the zeta potential of galena was distinctly increased at all studied pH ranges with the presence of Fe^{2+} in the pulp, and the IEP was also increased from 4.4 to 5.8. The result indicates that Fe^{2+} in the pulp has an important effect on the zeta potential of galena. According to the species distribution diagram of Fe^{2+} in solution (Figure 7), Fe^{2+} is the predominant component and its adsorption on the galena surface can cause the change in the zeta potential at $\text{pH} < 8.0$. At $\text{pH} > 8.0$, the adsorption of ferrous hydroxyl species on surface was responsible for the increase in zeta potential [32].

Besides, the zeta potential of galena became more negative, and the IEP was shifted from 4.4 to 2.8 with the addition of 20 mg/L KBX in the pulp. As we all know, the adsorption of collector xanthate on the galena surface is achieved by the chemical interaction between collector molecule and mineral surface, which cause a decrease in zeta potential [33, 34]. Therefore, it can be concluded that the zeta potential of galena was increased by the adsorption of Fe^{2+} or ferrous hydroxyl species and decreased by the adsorption of collector KBX. However, with the addition of 100 mg/L Fe^{2+} and 20 mg/L KBX in the pulp, the decrease in the zeta potential of galena was significantly lower than that with the addition of 20 mg/L KBX alone. This result indicates that the adsorption of collector KBX on galena surface was affected by the presence of Fe^{2+} in the pulp, which reduced the adsorption of KBX on surface.

3.3. XPS Studies. After adsorption of flotation reagents on mineral surface, the variation in chemical composition and elemental state of surface can be detected by XPS. In the work, the XPS analysis of galena in the absence and presence of Fe^{2+} was performed, and the results are given in Figures 8 and 9.

Figure 8 illustrates the Pb 4f spectra on galena surface; the Pb 4f spectra are usually fitted using the Pb $4f_{7/2}$ and Pb $4f_{5/2}$ doublets with a fixed peak area ratio of 10:8 and an energy separation of 4.86 eV [35]. In the absence of Fe^{2+} in the pulp (Figure 8(a)), the Pb $4f_{7/2}$ peak at the binding energy of 137.45 eV represented Pb^{2+} from the surface or bulk, and the Pb $4f_{7/2}$ peak at 138.39 eV can be identified as the $\text{Pb}(\text{OH})_2$ adsorbed on surface. The weak peak of Pb $4f_{7/2}$ at 139.02 eV was attributed to the oxidation product PbSO_4 formed on surface [36, 37]. However, compared to Figure 8(a),

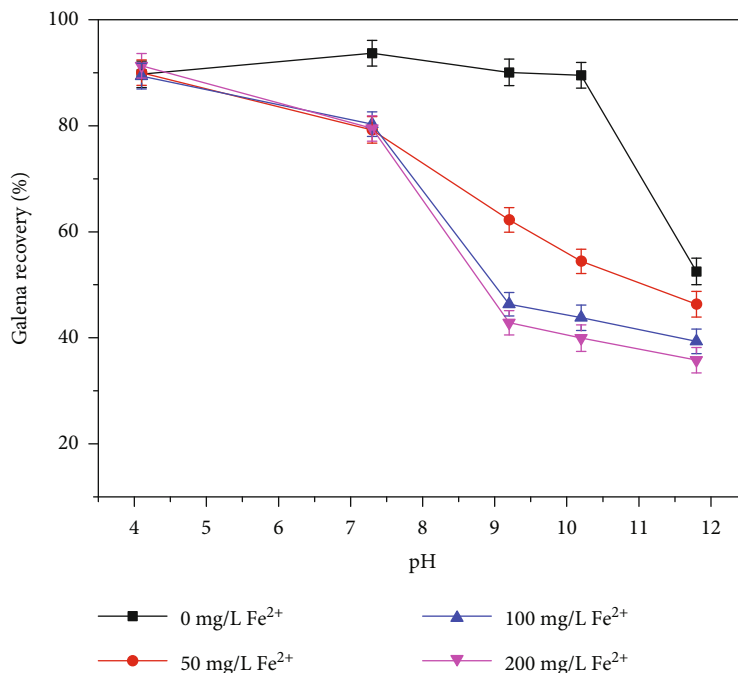


FIGURE 4: Effects of Fe²⁺ on flotation behavior of galena as a function of pH (collector KBX 20 mg/L).

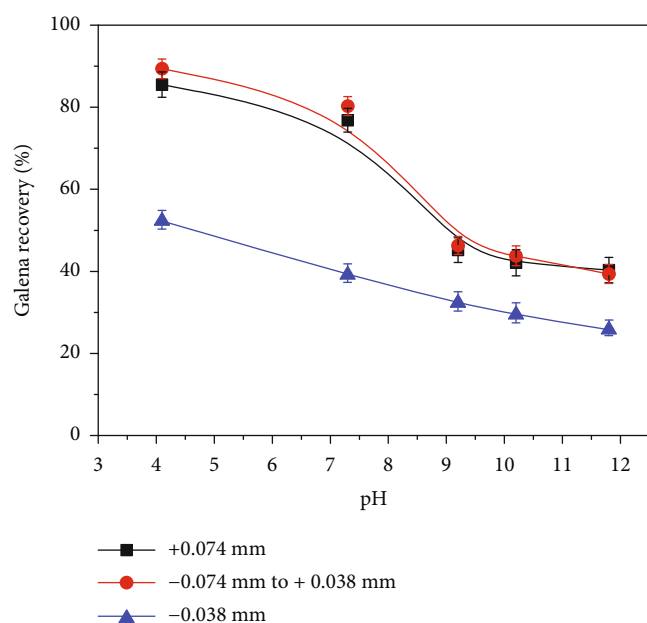


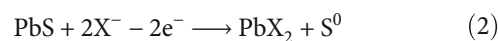
FIGURE 5: Effects of Fe²⁺ on the recovery of galena with different particle sizes (collector KBX 20 mg/L, Fe²⁺ 100 mg/L).

the weak peak of Pb 4f_{7/2} at 139.02 eV was completely disappeared in Figure 8(b) with the presence of Fe²⁺ in the pulp. These results indicate that the surface oxidation of galena was distinctly weakened because of the addition of Fe²⁺, and a similar result was also detected in the S 2p spectra of galena surface. In Figure 9(a), the S 2p_{3/2} peak at the binding energy of 160.66 eV and 162.14 eV can be attributed to S₂²⁻ and S²⁻ from the surface or bulk, respectively. The S 2p_{3/2} peak

at 163.46 eV was identified as the oxidation product of S_n²⁻ formed on galena surface, which is a hydrophobic species. The S 2p_{3/2} peak at 168.32 eV was ascribed to SO₄²⁻, a hydrophilic oxidation product formed on galena surface [38]. Similarly, compared with Figure 9(a), the S 2p peak of the oxidation product SO₄²⁻ in Figure 9(b) was distinctly disappeared with the presence of Fe²⁺ in the pulp.

These results from XPS studies suggested that the surface oxidation of galena was weakened due to the addition of Fe²⁺ to the pulp. From an electrochemical perspective, Fe²⁺ or ferrous complexes are easily oxidized to Fe³⁺ and ferric complexes, which accompanied by the reduction of O₂ in the pulp. As a result, the concentrations of the dissolved oxygen and the Eh of the pulp were lowered to some extent. The decreasing in the concentration of O₂ has two important effects on the flotation behavior of galena. The first is to reduce the surface oxidation of galena and the formation of hydrophilic oxidation products (thereby enhancing the floatability of galena). The other is to reduce the adsorption of collector KBX on surface. According to the above studies, the adsorption of xanthate collector on sulfide mineral surfaces is an electrochemical reaction, and the moderate oxidation of the mineral surface prior to the adsorption of collector is essential [39, 40]. During the flotation of galena, the galena surface is firstly oxidized to produce lead polysulfide or metal-deficient sulfur, which provides active sites for the adsorption of collector on surface. Meanwhile, the oxygen in the pulp was reduced to OH⁻ on surface. The related reaction can be expressed as follows [41, 42]:

The anodic reaction:



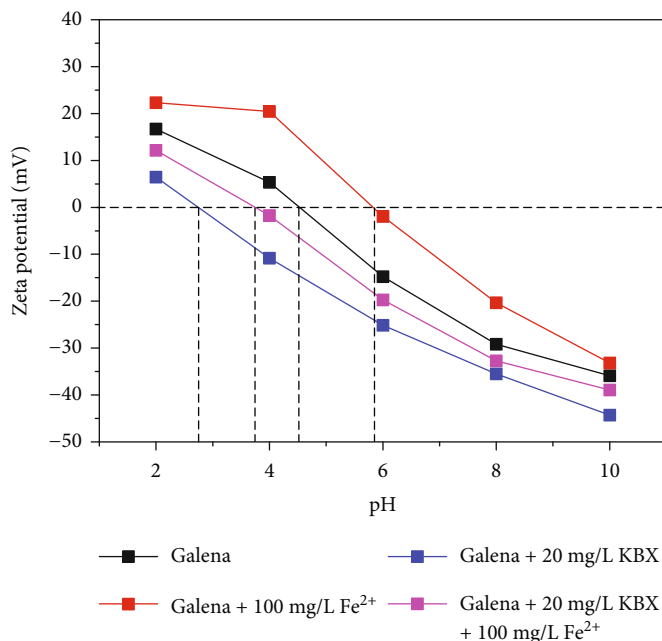


FIGURE 6: Zeta potential of galena in the absence and presence of Fe²⁺.

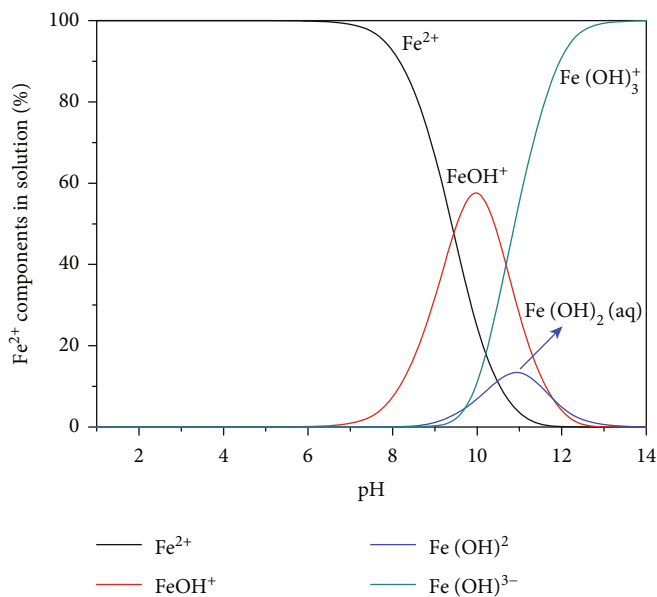
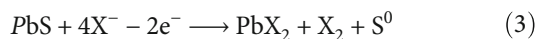
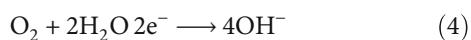


FIGURE 7: Species distribution diagram of Fe²⁺ in solution as a function of pH.



The cathodic reaction:



Therefore, the decreasing in concentration of dissolved oxygen is detrimental to the adsorption of collector KBX on surface, which reduces the surface hydrophobicity of galena. In addition, some xanthate ions (X⁻) in the pulp can be oxidized to dixanthogens (X₂) by O₂, and these dixanthogens are readily adsorbed on surface and is responsible

for the improving floatability (as shown in equation (3)). However, the surface oxidation and adsorption of collector xanthate are weakened because of the consumption of O₂ with the presence of Fe²⁺ in the pulp, which leads to a decrease in the floatability of galena.

3.4. DFT Calculation. DFT calculations were employed to further study the adsorption of Fe²⁺ or ferrous complexes on galena surface. Based on the Fe²⁺ species distribution (Figure 7), FeOH⁺ was considered the predominant component of Fe²⁺ under alkaline conditions of 8.0 to 12.0. The stable adsorption configuration of FeOH⁺ on galena (100)

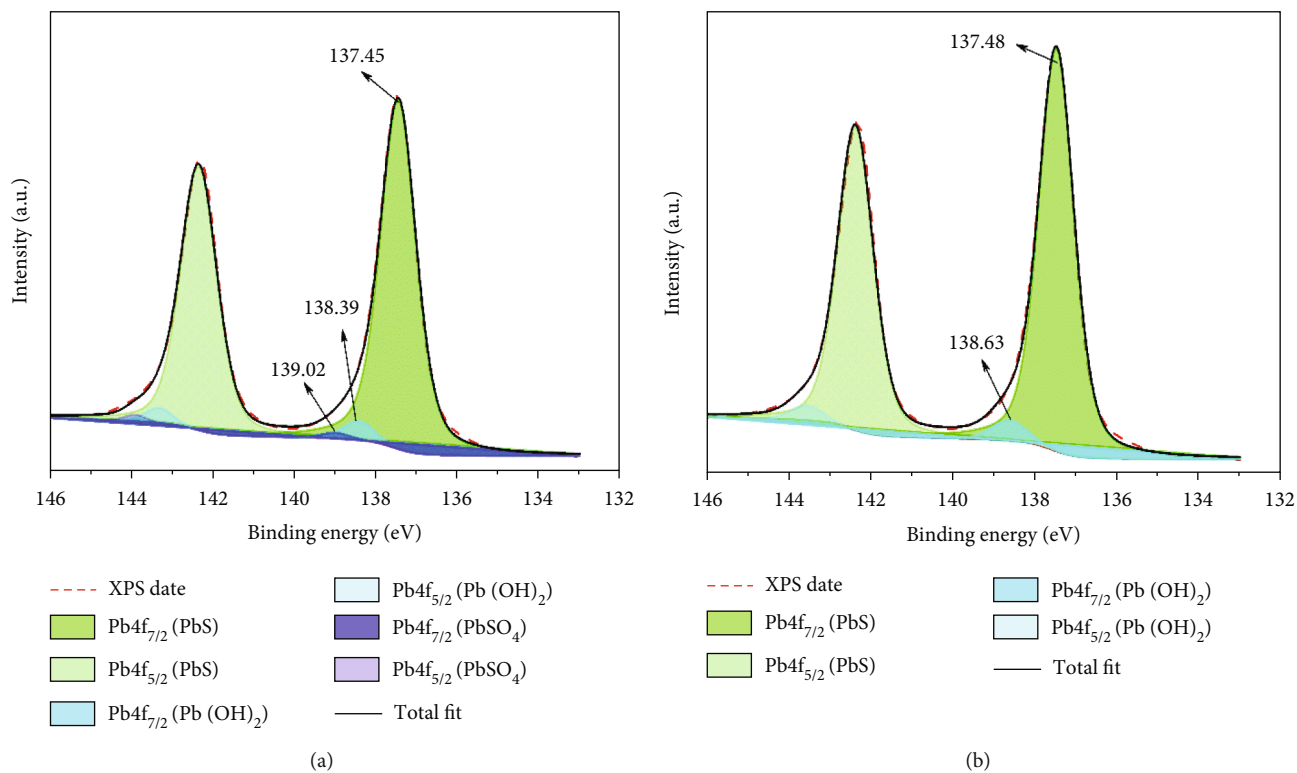


FIGURE 8: Pb 4f spectra on the galena surface at pH = 10.0: (a) untreated; (b) addition of 100 mg/L Fe²⁺.

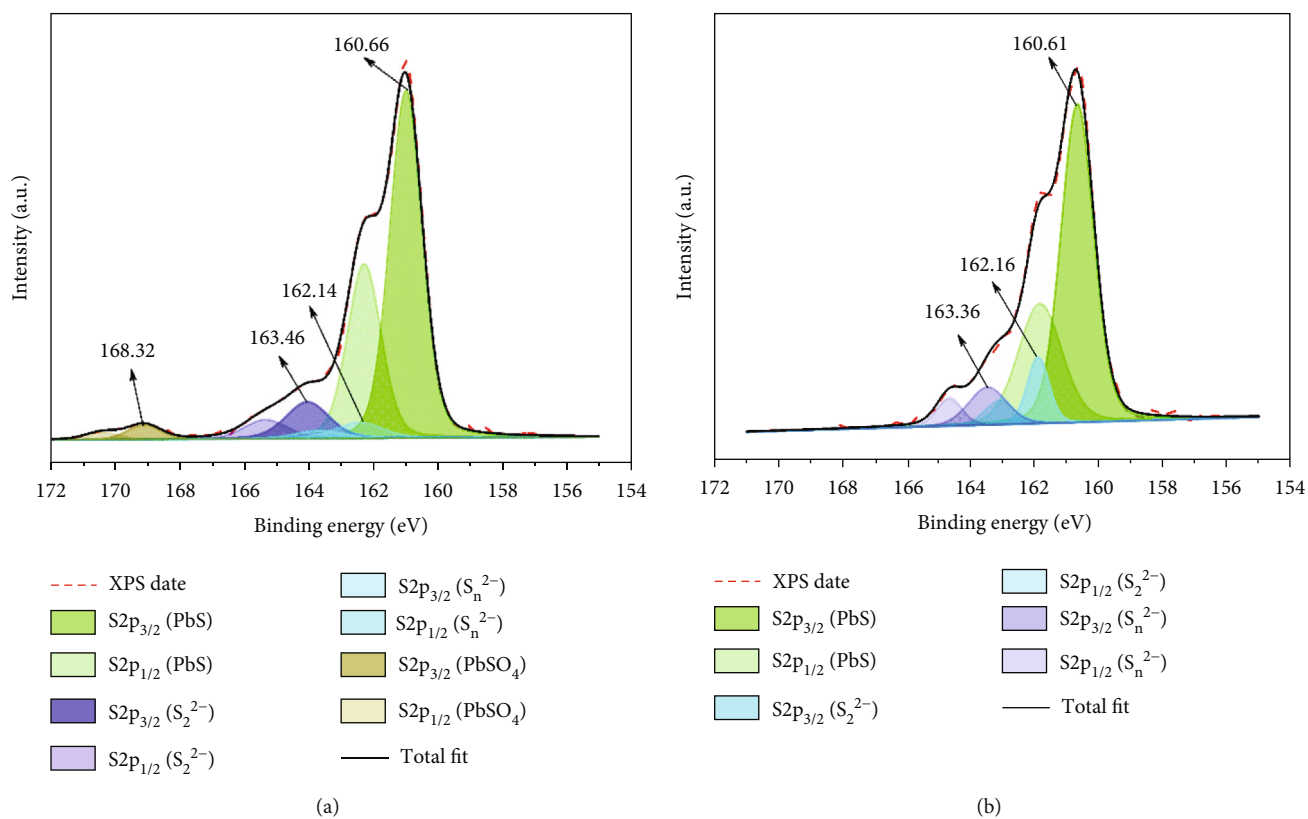


FIGURE 9: S 2p spectra on the galena surface at pH = 10.0: (a) untreated; (b) with an addition of 100 mg/L Fe²⁺.

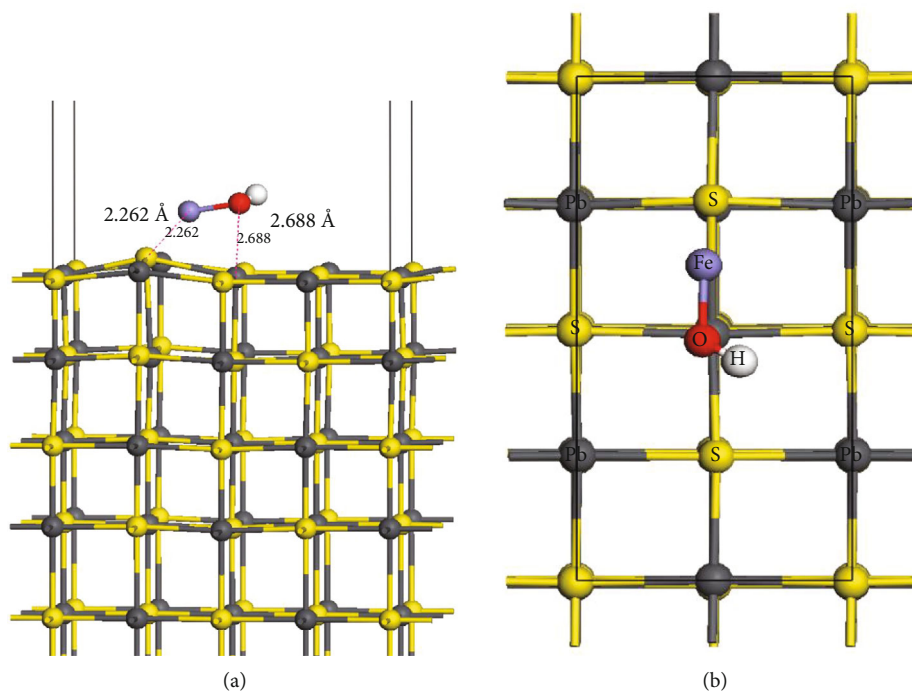


FIGURE 10: The stable adsorption configuration of FeOH^+ on galena (100) surface: (a) side view; (b) top view.

TABLE 2: The Mulliken atomic charge and population before and after FeOH^+ .

Atom	Adsorption status	s	p	d	Total	Charge (e)
Fe	Before adsorption	0.78	0.14	6.75	7.67	0.33
	After adsorption	0.66	0.32	6.59	7.56	0.44
O	Before adsorption	1.84	5.02	0.0	6.86	-0.86
	After adsorption	1.85	5.06	0.0	6.91	-0.91
Pb	Before adsorption	1.98	1.45	10.0	13.43	0.57
	After adsorption	1.90	1.51	10.0	13.41	0.59
S	Before adsorption	1.93	4.71	0.0	6.64	-0.64
	After adsorption	1.92	4.75	0.0	6.67	-0.67

surface was tested, and Figure 10 illustrates the stable adsorption sites FeOH^+ on galena (100) surface. The values labeled in Figure 10 represent the atomic distance in unit of angstroms.

After FeOH^+ adsorption, the atomic distances of Fe-S and Pb-O on galena surface are 2.262 Å and 2.688 Å, respectively, which is closed to the sum of two atomic radii. The result indicates that there is an interaction between galena (100) surface and FeOH^+ [43]. In addition, the adsorption of flotation reagents on surfaces can result the variation in atomic charge transfer, and this variation can be revealed by analyzing the density of states (DOS) and the Mulliken population. The DOS and Mulliken populations of galena (100) surface and FeOH^+ before and after adsorption are shown in Table 2 and Figure 11, respectively.

For FeOH^+ , the Fe 4s and 3d states lost electrons after adsorption and the positive charge of Fe atom was increased. Meanwhile, the O 2s and 2p states obtained electrons after adsorption, and the negative charge of O atom was

increased. For galena, the surface Pb atom loses electrons and S atom obtains electrons after adsorption, which increases the positive charge of Pb atom and the negative charge of S atom. By combination with the atomic distance, it can be concluded that the O atom of FeOH^+ obtained electrons from the Pb atom and the S atom of galena surface obtained electrons from the Fe atom of FeOH^+ , which leads to the adsorption of FeOH^+ on galena surface. DOS analysis before and after adsorption of FeOH^+ is shown in Figure 11.

Before adsorption, the Fermi level (E_f) of Fe atom was occupied by the Fe 3d state. The 2p state of O atom was located in the upper part of the valence band, and only a weak O 2p peak occurred at the E_f level. After adsorption, the DOS peak of Fe 3d state was decreased and split into four peaks near E_f . In addition, the nonlocality of the 2p electrons for the O atom was enhanced after adsorption. However, for the Pb and S atoms, the DOS peaks of the S 3p state near E_f and the Pb 6p state in the bottom parts of the conduction band were distinctly reduced. Generally, electrons near the

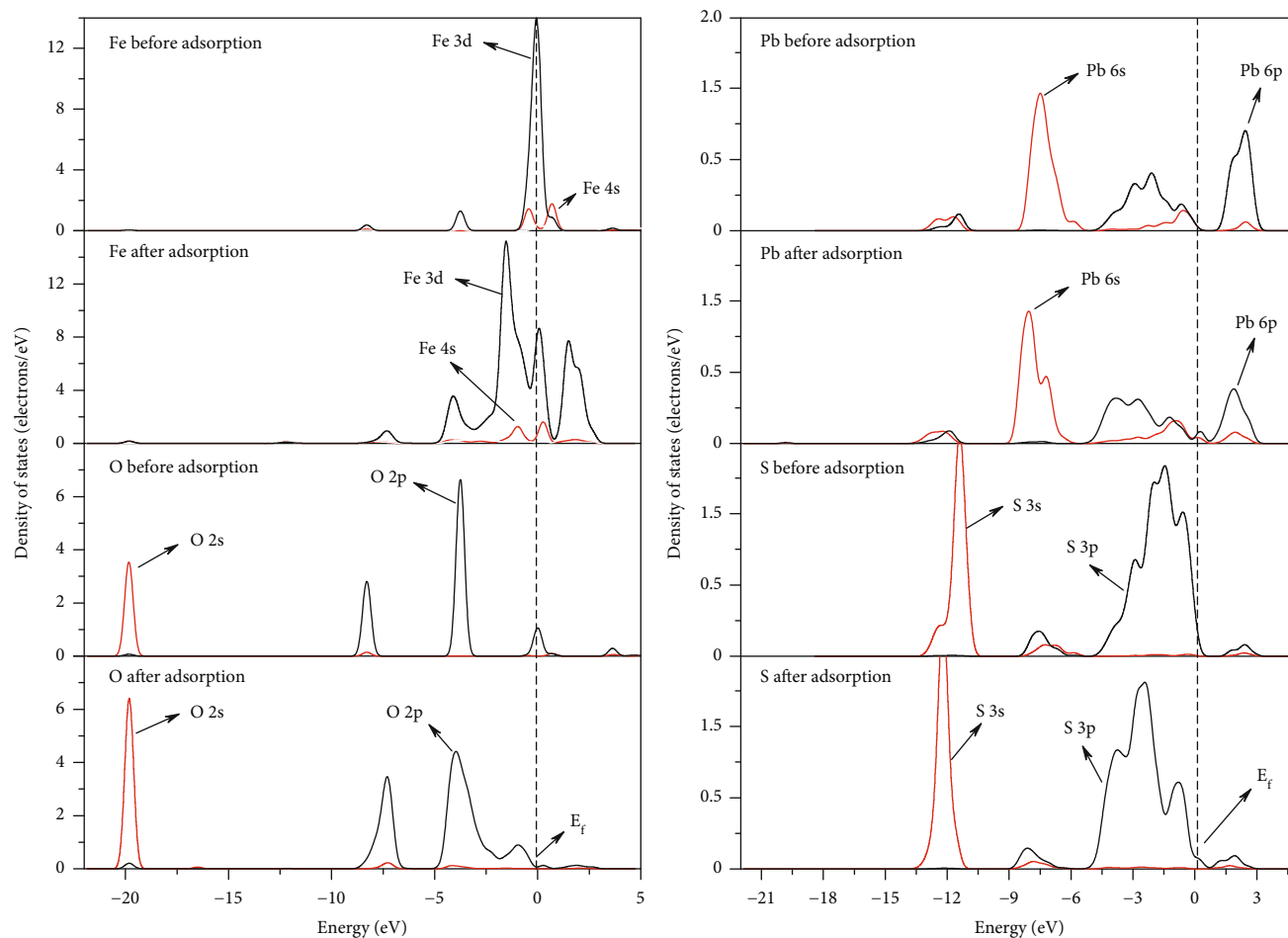


FIGURE 11: DOS of FeOH^+ and galena before and after adsorption.

E_f are more active and easily transferred between atoms. DOS analysis confirmed that a new chemical bond was formed between the Fe atom of FeOH^+ and the S atom of galena surface by the transfer of the electron, which results in the adsorption of FeOH^+ on galena surface.

4. Conclusions

Fe^{2+} , one of the unavoidable metal ion in the flotation pulp, has a dual influence on the flotation behavior of galena. First, Fe^{2+} or ferrous hydroxyl complexes in the pulp can adsorb on the galena surface through the interaction between the Fe atom and the S atom, which leads to an increase in the zeta potential and a decrease in the floatability of the galena. Second, the surface oxidation of galena is alleviated due to the consumption of dissolved oxygen for the oxidation of ferrous species to ferric species. Meanwhile, the adsorption of collector KBX on galena surface and the oxidation of xanthate to dixanthogen were lowered because of the consumption of dissolved oxygen. Therefore, the floatability of galena was decreased with the presence of Fe^{2+} in the pulp, which leads to difficulties in the selective separation of galena from other sulfide minerals.

Data Availability

The data presented in this study will be made available on reasonable request.

Conflicts of Interest

All authors declare that they have no conflicts of interest.

Authors' Contributions

Bo Yang and Xiao Wang conceived and designed the experiments. Zixuan Yang and Bo Yang prepared the samples and performed the experiments. Xian Xie analyzed the data. Bo Yang and Xiao Wang contributed to the writing and revising of the paper.

Acknowledgments

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