

Research Article

Effect of Copper and Iron Ions on the Sulphidizing Flotation of Copper Oxide in Copper Smelting Slag

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Received 13 October 2017; Revised 6 December 2017; Accepted 4 January 2018; Published 11 March 2018

Academic Editor: Jun Liu

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The treatment of smelting slag has attracted much attention nowadays. This study investigates the influence of Na_2S , CuSO_4 , and FeCl_3 on sulphidizing flotation of copper oxide. The results show that a proper Cu^{2+} concentration can increase the sulphidizing effect of copper oxide, while Fe^{3+} inhibits the sulphidizing effect. Further analysis shows that Cu^{2+} ions can reduce the surface potential, increase the S^{2-} adsorption, then generate more polysulfide, and therefore promote the sulphidizing flotation. However, Fe^{3+} ions would increase the surface potential, reduce the S^{2-} adsorption, generate more sulfur element, and therefore inhibit the sulphidizing flotation.

1. Introduction

Nowadays, more than 97% copper in the world is produced by pyrometallurgical smelting, and a large amount of smelting slag is produced at the same time. The copper smelting slag mainly consists of products crystallized from high-temperature molten material, and their compositions are very complicated. The separation of the slag is quite difficult, and the depleted residue can still contain a certain amount of heavy metal compounds [1–4]. If these wastes are not properly treated and directly discharged into the natural environment, they would cause not only the waste of resources but also serious pollution of the environment.

The Ruolanda slag is mainly composed of matte [5, 6], along with a small amount of copper oxide, copper, and traces of diffluent copper salts. The main constituents that need to be recycled are matte, copper oxide, and copper, and the most commonly used technique for the recycling is flotation [7, 8]. In the past, most researches about the recycle and utilization of the copper slag were conducted to optimize the flotation agents, processes, and procedures in the flotation process of copper recycling [9–11]. However, the composition of copper smelting slag differs from that of ordinary copper minerals,

and the flotation mechanism of copper oxide and copper in the process has been rarely reported in the published literatures.

The researches on flotation mechanism mainly focus on the interaction between ions and minerals in the pulp and the adsorption behavior between the metal ions and the minerals [12–14]. Wei et al. studied the influence of metal ions (such as Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , and Al^{3+}) in the pulp on the chalcopyrite and galena floatability [15]. Yuan et al. investigated the influences and mechanism of metal ions on the flotation of molybdenite by flotation experiments and measurements of zeta potential [16]. Multiple unavoidable metal ions also exist in the copper smelting slag pulp, mainly consisting of iron and copper ions. Different metal ions have different impacts on various flotation targets, activation, or inhibition. Deng et al. [17] investigated the adsorption behaviors of copper ions on the chalcopyrite surfaces and found a new viewpoint about self-activation of the copper ions. The same group also studied the types, structures, and compositions in natural pure chalcopyrite and measured the total concentrations of Cu (C_{CuT}) and Fe (C_{FeT}) released from the inclusions [18, 19]. Zhang et al. investigated the effect of Fe (III) ions on the flotation of spodumene, albite, and quartz

minerals using sodium oleate (NaOL) and found Fe (III) as an activator for the flotation [20].

In this study, the effects of Cu^{2+} and Fe^{3+} on the sulphidizing and flotation of copper oxide in copper smelting slag are systematically investigated based on the analysis of chemical composition and phase of copper smelting slag. The interaction mechanism of the Cu^{2+} and Fe^{3+} on the copper oxide surface is studied.

2. Experimental

2.1. Material Preparation. The raw material used in this experiment is Ruolanda copper smelting slow cooling slag. The main composition of the slag is shown in Table 1. The percentage of the copper compounds is shown in Table 2.

The raw slag was crushed and ground, and particles with a size of around 0.1 to 0.074 mm were filtered out. Copper oxide with a relatively high purity was selected using a microscope, and the samples were examined with X-ray diffraction (XRD). Figure 1 shows the XRD pattern of the selected particles. The main peaks of the XRD patterns of particles were identified as copper oxide according to the JCPDS cards. Although the material contains other impurities, their concentration was relatively low. The chemical test confirms the copper grade was 76.28%, and the percent of copper oxide should be more than 95%. The determination results by XRF (PANalytical Axios Advanced) are shown in Table 3. The obtained copper oxide was used in the following experiments.

2.2. Flotation Experiments. The flotation experiments were carried out using a RK/FGC-35 mL groove-type flotation machine. 2 g of CuO was added into 25 mL Na_2S (0.156 g/L) aqueous solution at different pH values. The flotation temperature was room temperature. The stirring speed was 1000 r/min, and the concentration of the collector butylxanthate and compound higher alcohols frother 2# pine camphor oil was 0.167 g/L and 0.027 g/L, respectively. The flowsheet of flotation process is shown in Figure 2. The pH value which produced the highest recovery was applied in the following experiments. The final concentrates and tailings were filtered, dried, and then weighed and tested to calculate the recovery rate.

2.3. Zeta Potential Measurement. The zeta potential of the mineral surface was measured using BDL-B zeta potential particle size analyzer, in an aqueous solution of 0.025 g/L CuSO_4 , 0.156 g/L Na_2S , and 0.0162 g/L FeCl_3 . CuO particles were milled to obtain a particle size less than $38 \mu\text{m}$. 0.05 g particles were added in a 100 mL beaker. Deionized water, CuSO_4 , Na_2S , and FeCl_3 were added as given in Table 4 and diluted with deionized water to 50 mL. HCl and NaOH solutions were used to adjust the pH value. After that, the solutions were magnetically stirred for about 5 minutes and then the zeta potential measurements were carried out.

2.4. ICP and XPS Measurements. The CuO particles were ground into small particles with size less than $74 \mu\text{m}$. 2.5 g of the particles was added to 100 mL solution to conduct the

TABLE 1: Composition of the Ruolanda copper smelting slag (wt.%).

Cu	Fe	S	Zn	Pb	SiO_2	Al_2O_3	CaO	MgO	Others
4.07	42.14	1.71	0.57	0.09	23.38	2.52	5.25	2.74	17.53

TABLE 2: Chemical composition of copper compounds in raw materials (wt.%).

Copper sulfide	Copper	Copper oxide	Diffluent copper salt	Other copper compounds	Total
3.003	0.827	0.204	0.002	0.0334	4.07

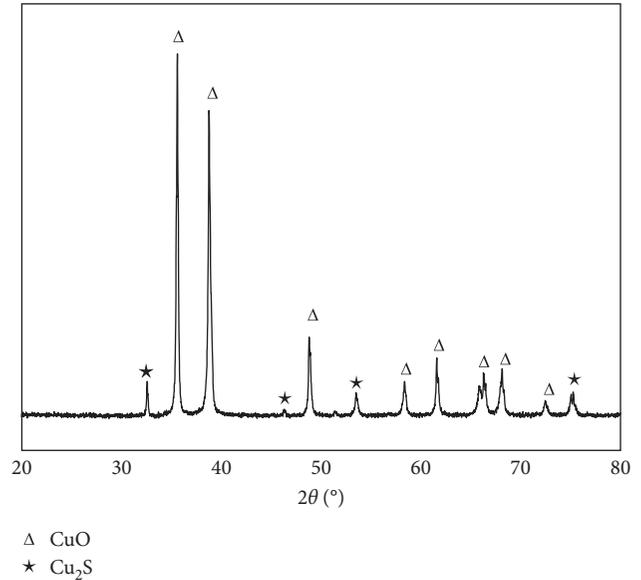


FIGURE 1: XRD pattern of the selected CuO particles.

leaching experiments. The stirring speed was 100 r/min. After the leaching process was completed, the mixed solution was separated by centrifugation. The supernatant liquor was collected for the measurement of ion concentration using an inductively coupled plasma emission spectrometer (ICP, Optima 4300DV), and the solid portion was dried and stored.

The leaching dissolution equilibrium time of copper ion, t , determined from the ICP ion concentration tests was set as the reaction time for the ion adsorption experiment. 2.5 g CuO particles with size less than $74 \mu\text{m}$ were added into various solutions (100 mL as shown in Table 3) with a stirring speed of 100 r/min. After reaction for t minutes, the solid phase and the liquid phase were separated. The liquid phase was sealed and then tested with ICP for the ion concentration. The solid part was dried and then was characterized by X-ray photoelectron spectroscopy (XPS), together with the former solid part which was leached for t minutes.

3. Results and Discussion

3.1. Flotation Analysis. In order to study the influence of S^{2-} , Cu^{2+} , and Fe^{3+} ions on the flotation of copper oxide, the flotation experiments with various pH values and different amount of Na_2S , CuSO_4 , and FeCl_3 were conducted.

TABLE 3: The determination results by XRF (%).

Samples	CuO	Fe ₃ O ₄	Fe ₂ O ₃	Cu	Cu ₂ S	SiO ₂	Al ₂ O ₃	CaO	MgO
1	95.622	0.319	0.334	—	3.324	0.032	0.085	0.020	0.084
2	96.176	0.419	0.164	0.091	2.928	0.100	—	0.073	0.049
3	96.038	0.481	0.282	0.153	2.722	0.217	0.031	—	0.076
4	95.811	0.241	0.091	0.103	3.216	0.282	—	0.061	0.195

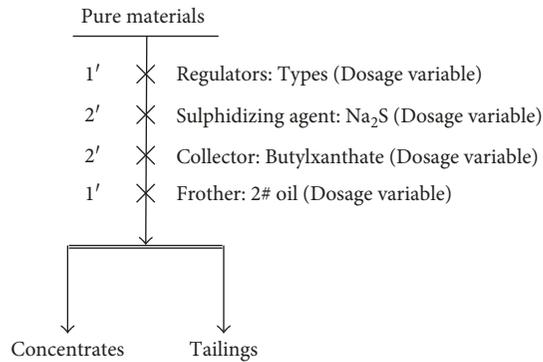


FIGURE 2: Flowsheet of flotation process.

TABLE 4: Various added agents for the experiments.

Condition	1	2	3	4	5	6
Agents	None	Na ₂ S	Cu ²⁺	Na ₂ S Cu ²⁺	Fe ³⁺	Na ₂ S Fe ³⁺

The results of copper oxide flotation are shown in Figure 3. The recovery of CuO under different pH conditions is shown in Figure 3(a). As shown in Figure 3(a), the recovery of copper oxide generally increases with the pH value and reaches the highest value of about 84.8% when the pH value equals 10. The recovery slightly decreases when the pH value reaches 11. The optimum pH value of 10 was applied for the following flotation experiments. As shown in Figure 3(b), the recovery achieved the highest value when Na₂S concentration was 0.156 g/L, indicating that proper concentration of Na₂S could improve the flotation process. Na₂S is widely exploited as an activator of sulfidizing oxide minerals [21], so insufficient sulfidization on the mineral surface cannot render the CuO surface adequately sulfidized. But excess Na₂S could depress the flotation because sulfide ions hold a strong reducing capacity [22], thus the potential of mineral/water interface should be reduced, with which the generation of copper xanthate species on the sulfidized mineral surface will be affected. In addition, excess sulfide-ion species may take place of the formed copper xanthate species on the sulfidized CuO surface because of its lower solubility product constant. Figure 3(c) shows that the maximum recovery of 91.2% was obtained when the concentration of CuSO₄ was 0.025 g/L, suggesting that appropriate concentration of Cu²⁺ could increase the sulphidizing effect of Na₂S. On the other hand, as shown in Figure 3(d), Fe³⁺ has a quite obvious inhibition effect for the recovery of CuO. The recovery of CuO significantly decreased with the increase of Fe³⁺ and ultimately reached about 0%.

3.2. Zeta Potential Analysis. Every ion could attach on the part surface and therefore alter its floatability. The surface electrokinetic potential could reflect the floatability of the material. Therefore, the influence of copper and iron ions on the sulphidizing and floatability of copper oxide can be investigated through the measurements of the surface electrokinetic potential.

Figure 4 shows the effect of different concentrations of Cu²⁺ and Fe³⁺ on the dependence of zeta potential on pH values of CuO. When pure copper oxide was leached in pure water, the pH value of the solution was about 6.5. It can be seen from Figure 4 that the CuO zeta potential is negative in the pH region 3–12 and the isoelectric point (IEP) is about 2.5, but a maximum change was observed when the pH is around 9, and it upraised suddenly where CuO flotation recovery was near its maximum. After Cu²⁺ addition, the potential of CuO in the solution is decreased in value (less negative) and even becomes positive at pH around 10, and the IEP also moved right to nearly 3.5; it may be because the covalent adsorption between Cu²⁺ ion and the CuO surface increases the potential of CuO. When solution was added with Fe³⁺, the potential becomes more positive and remain constant with pH until pH 10. This could be ascribed to the large amount of ferric hydroxide specific adsorption on the CuO surface [23]. Zeta potential of pure CuO was negative, but zeta potential of ferric hydroxide was positive, so there must be specific adsorption occurred, which made the zeta potential positive. Ferric hydroxide begins to precipitate at pH nearly 2.9 [23], and it may precipitate on the CuO surface earlier than precipitating in the solution, so the specific adsorption will continue, and the zeta potential will remain positive until the pH get to the IEP of ferric hydroxide itself (nearly 8).

The effect of Cu²⁺ and Fe³⁺ on the zeta potential of sulfidized CuO is shown in Figure 5. As can be seen from Figure 5, in the presence of Na₂S, the zeta potential became further negative, which indicates that the sulfidization reaction occurred. That is because the S²⁻ and HS⁻ from the hydrolyzation [24] of Na₂S are adsorbed on the CuO surface by chemical adsorption rather than electrostatic attraction [25]. As shown in Figure 5, due to the addition of Na₂S along with Cu²⁺ ions, the CuO potential significantly increased (became more negative) relatively to that of CuO but decreased (became less negative) in relation to CuO + Na₂S. It increased (became more negative) at pH > 9. This phenomenon demonstrated that the Cu²⁺ results in better sulfidization at the region from 9 to 11.5, and more copper-sulfide films were formed on the CuO surface. On the opposite, Fe³⁺ ions have different impact on the adsorption of sulfur ions on CuO surface. It increased (became more negative) relative to that of CuO but decreased (became less negative) in relation to CuO + Na₂S.

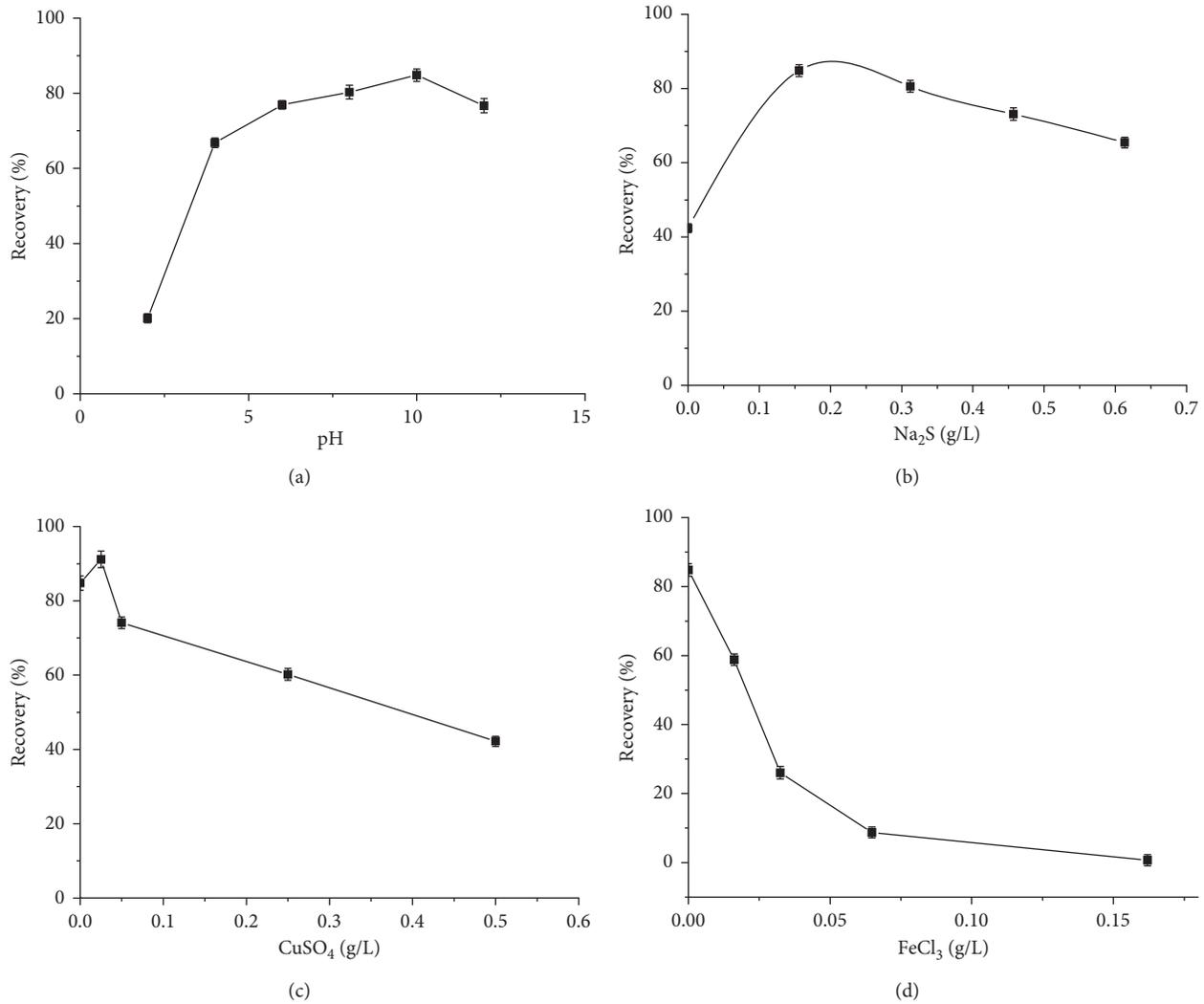


FIGURE 3: Recovery of CuO under different conditions: (a) different pH values (Na_2S 0.156 g/L); (b) different Na_2S concentrations (pH = 10, neither CuSO_4 nor Fe_3Cl addition); (c) different CuSO_4 concentrations (pH = 10, Na_2S 0.156 g/L); (d) different Fe_3Cl concentration (pH = 10, Na_2S 0.156 g/L).

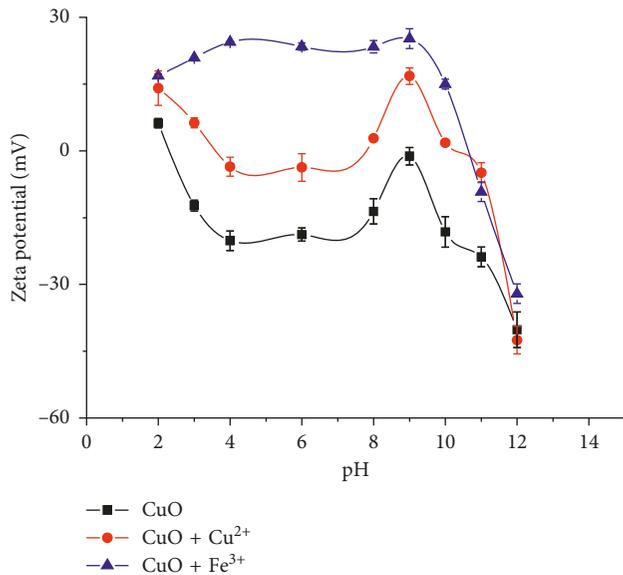
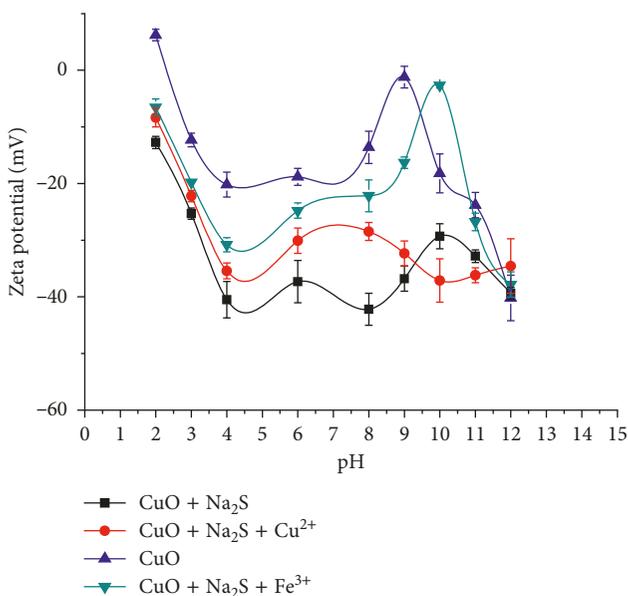
3.3. Adsorption of Cu^{2+} and Fe^{3+} . The solubility of CuO in water is relatively low. It generally takes several hours or even days for CuO to reach the equilibrium of dissolution. Also, with increasing dissolution time, the dissolution rate is gradually reduced. The dissolution rate of CuO was measured to detect the time for obtaining the equilibrium of dissolution, which was then selected as the reaction time for the adsorption experiment.

The time-dependent solubility of CuO in pure water is shown in Figure 6. It can be seen from Figure 6 that the concentration of Cu^{2+} in the CuO solution increased with time, and the dissolution rate became relatively low after dissolving for 30 min, indicating that the dissolution tended to be equilibrium. The concentration of Cu^{2+} after 60 min is similar to that after 1440 min, and therefore, a reaction time of 30–60 min is acceptable.

The ICP results of the CuO solution with adsorbed ions are shown in Figure 7. From the ICP results, it can be concluded that the actual solubility of CuO is higher than the

theoretical reference value [26]. That is because the purity of CuO is hard to reach 100%. Trace substances and the CO_2 in the air could generate salt soluble effect, which increases the solubility and dissolution rate [27, 28].

As shown in Figure 7, with the addition of Na_2S in the CuO solution, the S in the solution was reduced by about 86.2%, indicating that S was well adsorbed on the solid surface. With the presence of Cu^{2+} and Fe^{3+} , the S concentration was further reduced, indicating that Cu^{2+} and Fe^{3+} consumed S or promoted the adsorption of S on the surface of the sample, and the Fe^{3+} ion had a greater effect than Cu^{2+} ion. Further XPS measurements should be conducted to confirm whether it was consumption or adsorption. Regarding the Cu, the concentration of Cu was reduced by 83.4% with the addition of Na_2S in the CuO solution, indicating the existence of covalent adsorption. With further addition of Na_2S , there was an increase in the concentration of Cu^{2+} , suggesting that the Na_2S could consume part of Cu^{2+} and reduce adsorption of Cu^{2+} on the CuO. In addition, Fe^{3+} in the CuO solution was reduced

FIGURE 4: Effect of Cu^{2+} and Fe^{3+} ions on the zeta potential of CuO.FIGURE 5: Effect of Cu^{2+} and Fe^{3+} on the zeta potential of sulfidized CuO.

significantly by about 89.8%. The reduction of Fe^{3+} can be ascribed to not only the adsorption of Fe^{3+} on the solid surface but also the consumption of Fe^{3+} from the redox reaction. With further addition of Na_2S , Fe^{3+} concentration was further reduced to nearly zero. The redox reaction between Fe^{3+} and S^{2-} increased the consumption of Fe^{3+} .

3.4. XPS Analysis. Figure 8 shows the full XPS spectra of CuO surface with and without different additions. The C1s spectrum is used as calibration data in this analysis. As is shown in Table 5, the addition of Na_2S increased the molar percentage of S2p and decreased that of Cu2p and O1s due to

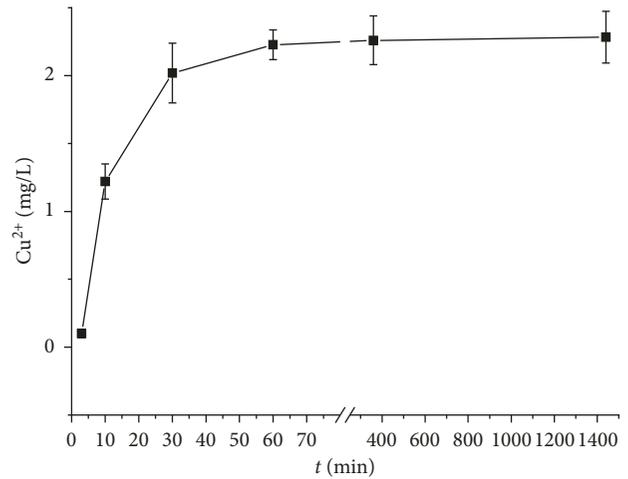


FIGURE 6: Time-dependent solubility of CuO.

the adsorption of S2p. After the addition of CuSO_4 , Cu2p was adsorbed on the surface of CuO, and therefore the mole percentage of Cu2p was increased. After adding both CuSO_4 and Na_2S , the adsorption of S and Cu was increased, indicating that the Cu can promote the adsorption of S on CuO. With the addition of FeCl_3 , Fe adsorption can be clearly observed. When Na_2S and FeCl_3 were both added, the adsorption of S was reduced and a lot of Fe were adsorbed on solid surface possibly because the Fe^{3+} was partially oxidized [29] and Fe-S compounds were produced. The results of XPS full spectra suggest that the copper ions can promote the adsorption and sulphidizing of sodium sulfide while iron ions do the opposite, which are consistent with the conclusion drawn from the flotation experiments.

Figures 9–11 show the fitting of Cu2p, S2p, and Fe2p absorption peaks. In Figure 9, besides two obvious peaks from Cu2p3/2 and Cu2p2/1, two side peaks with energy level splitting were also observed. After the addition of Na_2S , as shown in Figure 10, two doublets fitted the measured spectrum. Sulfur, monosulfides, and polysulfides [14, 21] appeared in S2p peak, reflecting the existence of sulfur-rich environment on the CuO surface. The appearance of sulphate was because Na_2S can be easily oxidized in air, so it could always be detected by XPS. On the other hand, its existence in the figure is to compare with the sample 4, in which CuSO_4 was added, and sample 6, in which the Fe^{3+} should oxidize S^{2-} to sulphate. The presence of polysulfide on the CuO surface was beneficial to CuO hydrophobicity and facilitates the floatability [21,30–33]. In addition, the position of binding energy peak of Cu^+ and Cu^{2+} [34, 35] was displaced, and peak area was changed, suggesting the formation of copper sulfide [36–38]. After the addition of Na_2S and CuSO_4 at the same time, the change of the valence state and binding energy of S2p indicated the occurrence of redox reaction between Cu2p and S2p, which promoted the formation of polysulfide compounds and increased the adsorption of Cu2p on S2p [39–42], leading to the increasing of the sulphidizing of Na_2S . After the addition of FeCl_3 , it can be seen from Figure 11 that the peak of Cu2p appeared among the peaks of Fe2p, which may have some interference

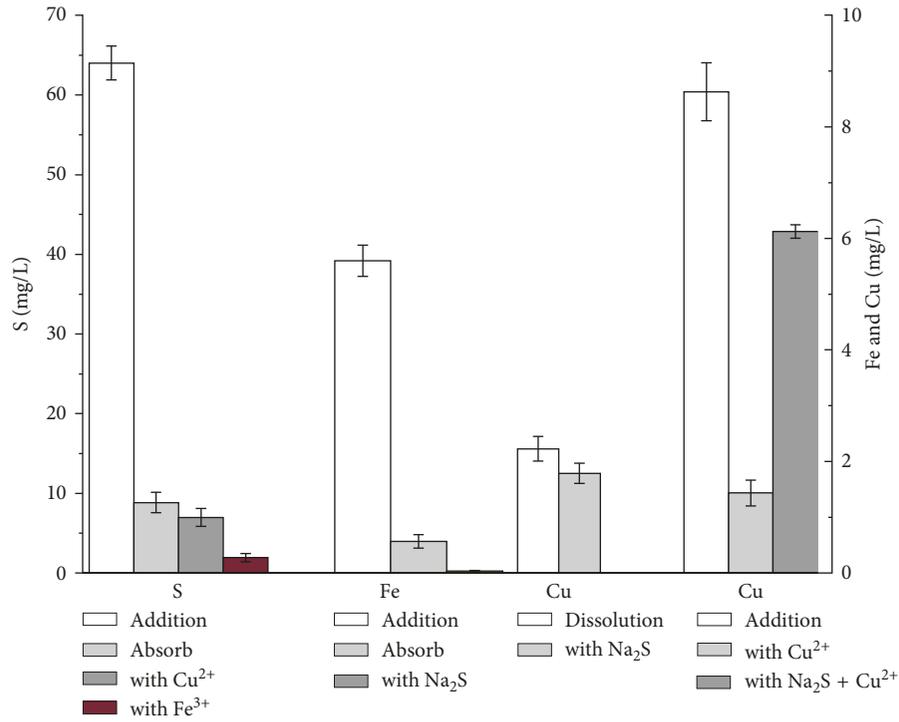


FIGURE 7: ICP results of the CuO solution with adsorbed ions.

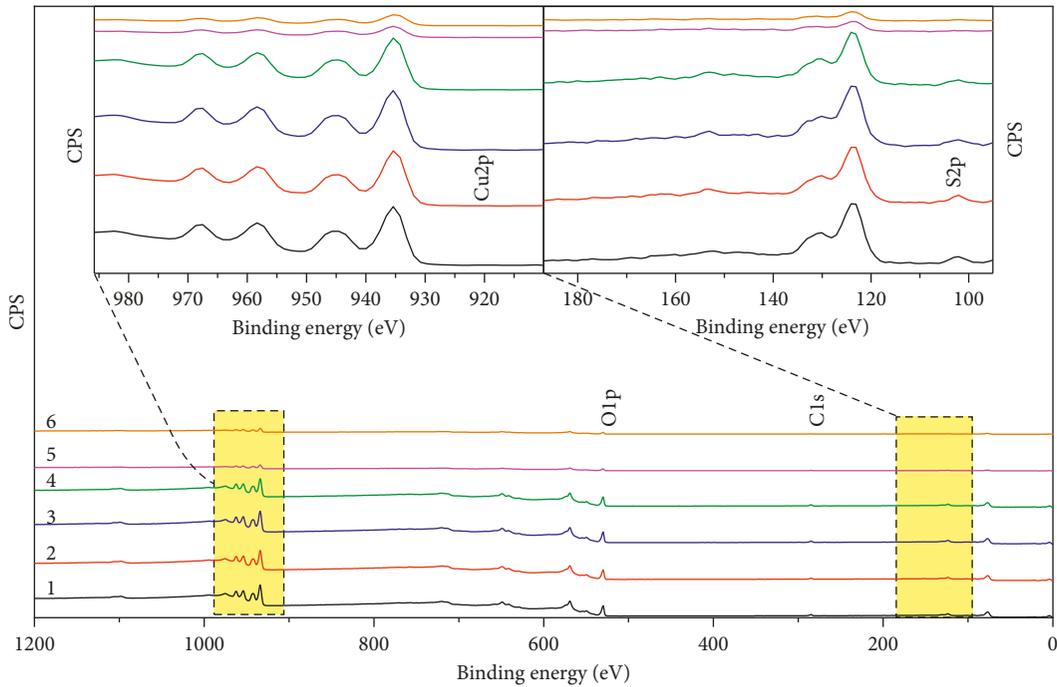


FIGURE 8: Comparison of CuO adsorption with and without different additions.

to the analysis of Fe2p peaks, but it does not influence the estimation of the effect of Fe³⁺ and Fe²⁺. The strong oxidative activity of Fe³⁺ can oxidize the Cu⁺ ion and result in the change of the binding energy of Cu⁺. With the addition of FeCl₃ and Na₂S at the same time, redox reaction occurred between Fe³⁺ and S²⁻ with strong reductivity, leading to the displacement of the binding energy of S2p

with low valence state, and consequently the adsorption of S2p was reduced.

4. Conclusions

- (1) The flotation results show that the Cu²⁺ has a good effect on the sulphidizing of copper oxide and can

TABLE 5: Atomic percentage (%) of elements on CuO surface.

Number	Samples	Cu2p	O1p	S2p	Fe2p
1	CuO	45.01	54.99	0	0
2	CuO + Na ₂ S	44.97	53.76	1.27	0
3	CuO + CuSO ₄	45.80	54.20	0	0
4	CuO + Na ₂ S + CuSO ₄	45.54	53.53	1.92	0
5	CuO + FeCl ₃	43.31	45.73	0	11.62
6	CuO + FeCl ₃ + Na ₂ S	44.68	42.25	1.04	11.43

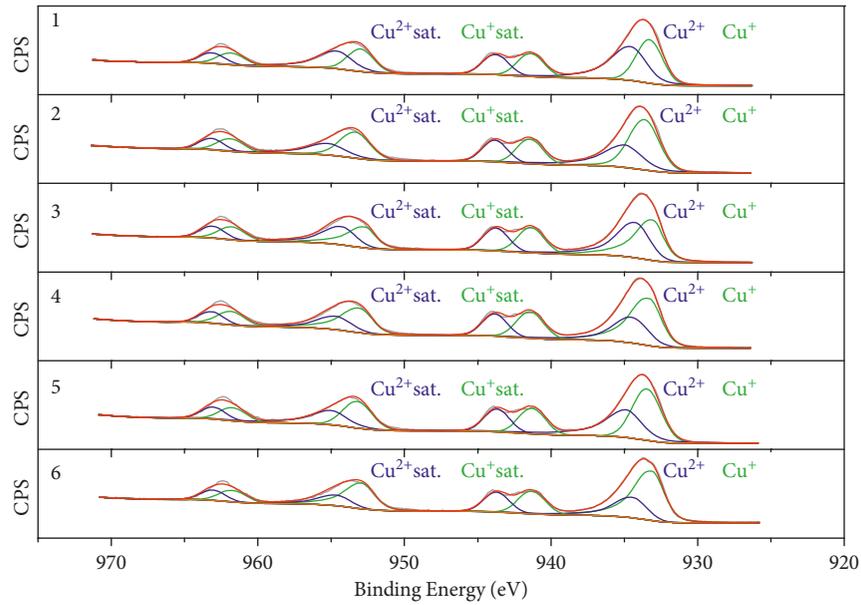


FIGURE 9: Cu2p spectra of CuO adsorption with and without different additions.

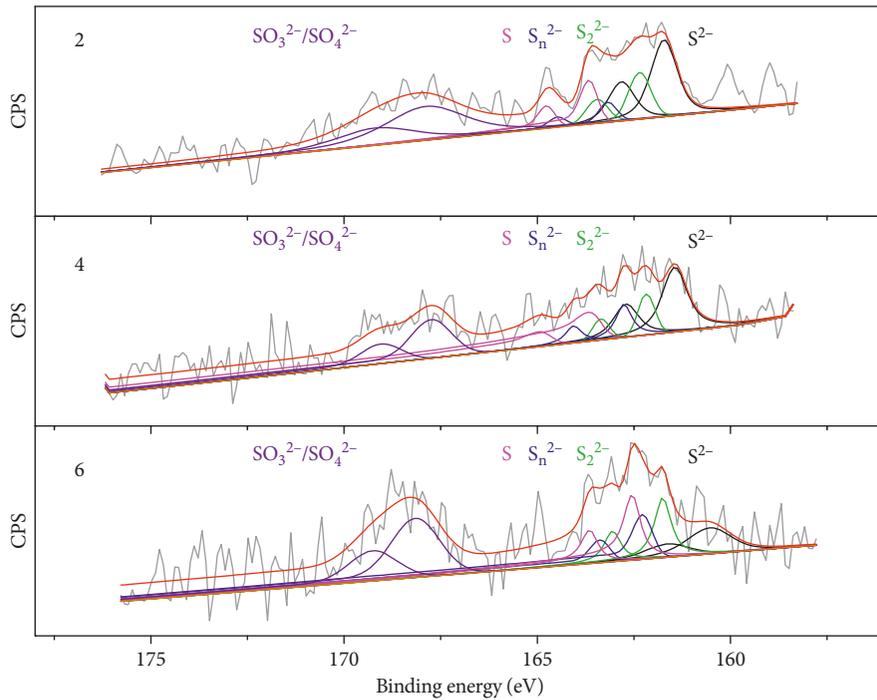


FIGURE 10: S2p Spectra of CuO adsorption with and without different additions.

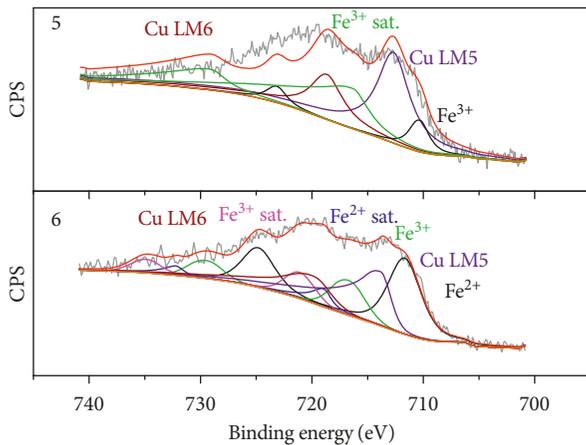


FIGURE 11: Fe2p spectra of CuO adsorption with and without different additions.

improve the recovery with the appropriate concentration. On the contrary, Fe^{3+} has certain depressing effect.

- (2) Zeta potential results show that the Cu^{2+} enhances the surface potential because of covalent adsorption. Fe^{3+} increases the surface potential of CuO significantly because of the large amount of ferric hydroxide which begins to precipitate on the CuO surface earlier than in the solution, so the zeta potential will remain positive until the pH gets to the IEP of ferric hydroxide itself.

When Na_2S was added, the zeta potential became further negative because of sulfidization reaction. Corresponded well with the microflotation tests, addition Na_2S along with Cu^{2+} ions, the potential increased relatively to that of CuO but decreased in relation to $\text{CuO} + \text{Na}_2\text{S}$. This phenomenon demonstrated that the Cu^{2+} results in better sulfidization. On the opposite, Fe^{3+} ions increased relatively to that of CuO but decreased in relation to $\text{CuO} + \text{Na}_2\text{S}$.

- (3) The results of ICP and XPS show that sodium sulfide is adsorbed on the surface in the form of sulfur, monosulfides, and polysulfides, and thus the sulfur-rich environment is formed. The addition of Cu^{2+} changes the binding energy of sulfur and promotes the sulphidizing. The addition of Fe^{3+} can oxidize the sulfur ions and consequently reduce the adsorption. This indicated that the adsorption of iron ions on copper oxide is chemical adsorption.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Qing-qing Pan and Hui-qing Peng conceived and designed the experiments. Qing-qing Pan performed the experiments. Qing-qing Pan and Hui-qing Peng analyzed the data. Qing-qing Pan and Hui-qing Peng wrote the paper.

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