Effect of copper and iron ions on the sulphidizing floatation of copper in copper smelting slag

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Abstract. This study investigates the influence of Na2S, CuSO4 and FeCl3 on sulphidizing floatation of copper in copper smelting slag. The results show that copper has a good floatability, independent of the addition of Na2S and Cu2+ ions, while Fe3+ inhibits the floatation. In the pH range between 2 and 4, in conditions with Na2S and Cu2+ ions addition, the recovery rate of metal copper rapidly increased and maintained the high level. But the inhibition effect of Fe3+ was enhanced with the increasing of the concentration. Further analysis shows that the Cu2+ and Fe3+ both enhance the surface potential, but with addition of Na2S, Fe3+ and Cu2+ get an opposite effect. Sodium sulfide would formed polysulfide, Monosulfides and polysulfides on solid surface. The addition of Cu2+ would not increase the adsorption amount of S2p on Cu surface and Fe3+ would not only oxidized sulfur ions thus reduce the adsorption and change the valence state of sulfur, but also oxidized metallic copper.

1. Introduction

Nowadays, more than 97% of the world's copper 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 matte, 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 floatation [7,8]. In the past, most of the researches about the recycle and utilization of the copper slag were conducted to optimize the floatation agents, processes and procedures in the floatation process of copper recycling [9-11]. However, the composition of copper smelting slag differs from that of ordinary copper minerals and the floatation mechanism of copper in the process has been rarely reported in the existing literature.

The researches on the floatation 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 Ca2+, Mg2+, Fe2+, Fe3+, Cu2+, Zn2+ and Al3+ etc.) 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 impact 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 copper ions of self-activation. The same group also studied the types, structures, and compositions in natural pure chalcopyrite, and measured the total concentrations of Cu (CCuT) and Fe (CFeT) released from the inclusions [18-20]. 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[21].

In this study, the effects of Cu2+ and Fe3+ on the sulphidizing and flotation of copper 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 Cu2+ and Fe3+ on the copper surface is illuminated.

2. Experimentals

2.1. Materials 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,

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

| Cu  | Fe   | S    | Zn  | Pb  | SiO₂ | Al₂O₃ | 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 Oxide | Diffluent copper salt | Other copper compounds | Total |
|----------------|--------------|-----------------------|------------------------|-------|
| 3.003          | 0.827        | 0.204                 | 0.002                  | 0.0334| 4.07 |

The raw slag was crushed and ground, particles with a size of around 0.1 to 0.074 mm were filtered out. Metal 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 according to the JCPDS cards. Although the material contains other impurities, the concentration was relatively low. The chemical test confirms the copper grade was above 96.22, and the purity of copper should be more than 95%. The obtained metal copper was used in the following experiments.
2.2. Flotation experiments

ARK / FGC-35mL groove type flotation machine was used for the flotation experiments. 2 g of Cu was first weighed and then added into 25 mL Na2S (0.156 g / L) aqueous solution at different pH values. The flotation temperature was room temperature. The stirring speed was 1000 r/min, the concentration of the collector butylxanthate and frother 2# oil was 0.167g/L and 0.027g/L, respectively. The pH value which earned 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 0.025g/L CuSO4, 0.156g/L Na2S and 0.0162g/L FeCl3. Cu particles were milled to obtain a particle size less than 38 μm. 0.05 g particles were added in a 100 mL beaker. Deionized water, CuSO4, Na2S and FeCl3 were added according to Table 3, and diluted with deionized water to 50mL. HCl and NaOH aqueous solutions were used to adjust the pH value. After that, the solutions was magnetically stirred for about 5 minutes for the Zeta potential measurements.

Table 3. Various added agents for the experiments

| Condition | 1  | 2     | 3     | 4     | 5     | 6     |
|-----------|----|-------|-------|-------|-------|-------|
| Agents    | None | Na2S  | Cu2+  | Na2S  | Fe3+  | Na2S  |
|           |     |       |       | Cu2+  |       | Fe3+  |
2.4. ICP and XPS measurements
The Cu particles were ground into small particles with size less than 74μm. 2.5g particles was added to 100mL solution to conduct the leaching experiments. The stirring speed was 100r/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. 2.5g Cu particles with size less than 74μm were added into various solutions (100 mL as shown in Table 3) with a stirring speed of 100r/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 S2-, Cu2+ and Fe3+ ions on the flotation of copper, the flotation experiments with various pH values and different amount of Na2S, CuSO4 and FeCl3 were conducted.

The results of copper flotation are shown in Figure 3. The recovery of Cu under different pH conditions is shown in Fig.3(a). As shown in Fig.3 (a), the recovery rapidly increases with the pH in range 2-4 and reaches the high value of about 93.13% when pH is 4. Then the recovery remains high level around 95%. As shown in Fig.3 (b), Na2S is widely exploited as an activator of sulfidizing copper slag [21], and may depress the flotation because sulfide ions hold a strong reducing capacity [22]. But the recovery remains at around 95% no matter how much the Na2S added is. Fig.3(c) also shows that the recovery remains at about 95% whatever the Cu2+ was added or not. On the contrary, as shown in Fig.3 (d), Fe3+ has a quite obvious inhibition effect for the recovery of Cu. The recovery of Cu significantly decreased with the increase of Fe3+, and ultimately reached nearly 0%. It maybe because Fe3+ has strong oxidizing properties and the metal copper was oxidized into copper ions, oses its excellent floatability.
3.2. Zeta potential analysis
No matter what ion is, once adsorbed on the material surface, it may change the material’s floatability. The surface electrokinetic potential could reflect the floatability of the material. Therefore, we can observe the sulphidizing and floatability changes of copper through the measurements of the surface electrokinetic potential.

Figure 4. Zeta potential and pH value curve under different addition of Cu2+, Fe3+ and Na2S
Fig 4 shows the effect of different concentration of Cu2+ and Fe3+ on the dependence of Zeta potential on pH values of Cu. When pure copper was leached in pure water, the pH value of the solution was about 6.7. The isoelectric point (IEP) is about 4, but a maximum change was observed when the pH around 6. After Cu2+ addition, the potential of Cu in the solution is increased in value
and even remains positive at pH less than 9, the IEP also moved right to nearly 10, it may be because the covalent adsorption between Cu2+ ion and the Cu surface increases the potential of Cu. 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 Cu surface [23]. Zeta potential of pure Cu was nearly 0 and even negative, but zeta potential of ferric hydroxide was positive, so there must be specific adsorption occurred, which made the zeta potential is positive. Ferric hydroxide begins to precipitate at pH nearly 2.9[23], it may precipitate on the Cu surface earlier than precipitate 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).

![Figure 5. Zeta potential and pH value curve of Cu sulphidization](image)

The effect of Cu2+ and Fe3+ on the Zeta potential of sulfidized CuO is shown in Fig 5. As seen from Fig 5, in the presence of Na2S, the zeta potential became further negative, which indicates that sulfidization reaction occurred. That is because the S2- and HS- from the hydrolyzation [24] of Na2S are adsorbed on the Cu surface by chemical adsorption rather than electrostatic attraction [25]. As shown in Fig 5, addition Na2S along with Cu2+ ions, the Cu potential significantly increased (became more negative) relatively to that of Cu but decreased (became less negative) in relation to Cu + Na2S. This phenomenon demonstrated that the Cu2+ have no influence in sulfidization of Cu. On the opposite, Fe3+ ions have different impact on the adsorption of sulfur ions on Cu surface. It increased (became more negative) relative to that of Cu but decreased (became less negative) in relation to Cu+Na2S.

### 3.3. Adsorption of Cu2+ and Fe3+

The solubility of Cu in water is relatively low. It generally takes several hours or even days for Cu to reach the equilibrium of dissolution. Also, with increasing dissolution time, the dissolution rate is gradually reduced. The detected dissolution rate of Cu to obtain the time reaching the dissolution equilibrium, which was then selected as the reaction time for the adsorption experiment.

The time-dependent solubility of Cu is shown in Fig.6. It can be seen from Fig.6 that the dissolution rate concentration of Cu2+ became relatively low after dissolving for 60 min, indicating that the dissolution tended to be equilibrium after 60 min. Therefore, the reaction time was set at 60 min.
Figure 6. Time-dependent solubility of Cu

The ICP results of the solution after the copper adsorbed ions are shown in Fig.7. From the ICP results, it can be concluded that the actual solubility of Cu is higher than the theoretical reference value[26]. That is because the purity of Cu is hard to reach 100%. Trace substances and the CO2 in the air could generate salt soluble effect, which increases the solubility and dissolution rate [27,28].

Figure 7. ICP results of the Cu solution with adsorbed ions

As shown in Fig.7, with the addition of Na2S in the Cu solution, the S in the solution was reduced by about 78.56%, indicating that S was well adsorbed on the solid surface. With the presence of Cu2+ and Fe3+, the S concentration was further reduced, indicating that Cu2+ and Fe3+ consumed S or promoted the adsorption of S on the surface of the sample, and the Fe3+ ion had a greater effect than Cu2+ ion. Further XPS measurements should be conducted to confirm whether it was consumption or adsorption. Regarding the Cu2+ ion, the concentration of Cu2+ was reduced by 96.21% with the addition of Na2S in the Cu solution, indicating the existence of covalent adsorption. With further addition of Na2S, there was an increase in the concentration of Cu2+, suggesting that the Na2S could consume part of Cu2+ and reduce adsorption of Cu2+ on the Cu. In addition, Fe3+ in the Cu solution was reduced significantly by about 97.61%. The reduction of Fe3+ can be ascribed to not only the adsorption of Fe3+ on the solid surface but also the consumption of Fe3+ from the redox reaction. With further addition of Na2S, Fe3+ concentration was further reduced to nearly zero. The redox reaction between Fe3+ and S2- increased the consumption of Fe3+. Therefore, it can be observed that
the ICP results are in accordance with the above Zeta potential results.

3.4. XPS analysis

![XPS graph]

Figure 8. Comparison of Cu adsorption with and without different additions

Table 4. Atomic percentage (%) of elements on Cu surface

| Number | Samples          | Cu2p  | O1p   | S2p   | Fe2p  |
|--------|------------------|-------|-------|-------|-------|
| 1      | Cu               | 57.26 | 42.74 | 0     | 0     |
| 2      | Cu+Na2S          | 56.66 | 37.56 | 5.78  | 0     |
| 3      | Cu+CuSO4         | 58.69 | 41.31 | 0     | 0     |
| 4      | Cu+Na2S+ CuSO4   | 57.95 | 39.10 | 2.95  | 0     |
| 5      | Cu+FeCl3         | 56.33 | 28.76 | 0     | 14.91 |
| 6      | Cu+FeCl3+ Na2S   | 53.66 | 30.34 | 2.48  | 13.51 |

Fig. 8 shows the full spectra of Cu solutions with and without different additions. The C1s spectrum is used as calibration data in this analysis. The metal copper is tend to be oxidized at room temperature, so it generally takes only 2 minutes to form a layer of Cu2O film with a thickness less than the detection depth of the electron spectrum (about 5-15 nm). Also, trace CuO may still exist in copper after the metal copper is separated from copper smelting slag, so in the energy spectrum, the signals of copper and its oxide both exist, and the test results contain a certain proportion of O1s, but this does not affect the analysis of S2p, Cu2p and Fe2p adsorption trend on copper surface. As is shown in Table 4, the addition of Na2S increased the molar percentage of S2p and decreased that of Cu2p and O1s due to the adsorption of S2p. After the addition of CuSO4, Cu2p was adsorbed on the surface of copper, therefore the mole percentage of Cu2p was increased. After adding CuSO4 and Na2S simultaneously, the molar percentage of S2p decreased and the adsorption of Cu2p was increased, but this proves that the Cu2p did not promote the adsorption of S2p on Cu surface, which was consistent with the former flotation experiments. With the addition of FeCl3, Fe2p adsorption can be clearly observed. When Na2S and FeCl3 were both added, the adsorption of S2p was reduced due to a lot of S2- ions was partially oxidized by Fe3+ [29] and Fe-S compounds and sulfur were produced.
Figure 9. Cu2p spectra of Cu adsorption with and without different additions

Figure 10. S2p Spectra of Cu adsorption with and without different additions
Figure 11. Fe2p spectra of Cu adsorption with and without different additions

Figs 9-11 show the fitting of Cu2p, S2p and Fe2p absorption peaks. In Fig.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 Na2S, 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 solid surface. The appearance of sulphate was because Na2S 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 CuSO4 was added, and sample 6, in which the Fe3+ should oxidize S2- to sulphate. In addition, the position of binding energy peak of Cu+ and Cu2+ [30, 31] was displaced and peak area was changed, suggesting the formation of copper sulfide [32-34]. After the addition of Na2S and CuSO4 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[35-38]. After the addition of FeCl3, it can be seen from Fig.11 that the peak of Cu2p appeared among the peaks of Fe2p, which may have some interference 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 floatation results show that the Na2S and Cu2+ barely has any effect on the recovery of copper, which has a great floatability. Fe3+ has certain depressing effect on the floatation of copper. With the increase of Fe3+ concentration, the recovery of copper decreased.

2) Zeta potential results show that the Cu2+ enhances the surface potential is because of covalent adsorption. Fe3+ increase the surface potential of Cu significantly is because of the large amount of ferric hydroxide which begins to precipitate on the Cu surface earlier than in the solution, so the the zeta potential will remain positive until the pH get to the IEP of ferric hydroxide itself. Because of the excellent floatability, added Na2S or Na2S along with Cu2+ ions, the potential increased( more negative) but have no influence in recovery compared to the flotation result . On the opposite, Fe3+ ions increased relatively to that of Cu but decreased in relation between Cu and Na2S.

3) The results of ICP and XPS show that sodium sulfide is adsorbed on the surface of copper in the form of polysulfide, Monosulfides and polysulfides and the sulfur-rich environment is formed on the
solid surface. The addition of Cu2+ would not increase the adsorption amount of S2p on Cu surface, which has no effect on the adsorption of sulfur ions and metal copper. The addition of Fe3+ not only oxidized sulfur ions and change the valence state of sulfur, but also oxidized metallic copper in the surface, changing the binding energy and molar percentage of copper, and thus suppress the metal copper flotation process.

References
[1] Zhang J, QI YH, YAN DL, XU HC 2015 J Iron Steel Res, Intl, 22(5) 396-401.
[2] Gan HC 2004 Hunan Metall 32(4) 28-34
[3] Huang HJ 2012 Nonferr Metal (Miner Process) 6 16-9, 24
[4] Jiang F, Huang HJ, Sun W, Liu RQ, Xiong Y 2013 Nonferr Metal (Miner Process) 6 60-3
[5] Liu L, Yan HJ, Zhou JM, Gao Q, Zhang ZY, Liu FK, Cui ZX 2012 Chinese J Nonferr Metal 22(7) 2116-24
[6] Chai LY, Wu JX, Wu YJ, Tang CB, Yang WC 2015 T Nonferr Metal SO C 25 3429-35
[7] Rozendaal A, Horn R 2013 Miner Eng 52 184-90
[8] Corin KC, Kalichini M, O'Connor CT, Simukanga S 2017 Miner Eng 102 15-7
[9] Wang PR, Dai RX, Hu QH 2012 Min Metall 21(1) 15-7, 30
[10] Roy S, Datta A, Rehani S 2015 Int J Miner Process 143 43-9
[11] Jarosikova A, Ettler V, Mihaljevi M, Kribek B, Mapani B 2017 J Environ Manage 187 178-86
[12] James RO, Healy TWJ 1972 J Colloid Interf Sci 40(1) 42−52
[13] Fornasiero D, Ralston J 2005 Int J Miner Process 76(1/2) 75−81
[14] Feng QC, Zhao WJ, Wen SM, Cao,QB 2017 J Ind Eng Chem 48 125−32
[15] Wei MA, Sun CY 2008 Nonferr Metal 60(2) 92-5
[16] Yuan ZT, Zhang QD, Liu JT 2016 J North East Univ C(Nat Sci) 37(7) 1013-16
[17] Deng JS, Wen SM, Liu J, Wu DD, Feng QC 2014 T Nonferr Metal SO C 24 3955−63
[18] Deng JS, Wen SM, Xian YJ, Liu J, Bai.SJ 2013 Miner Eng 42 22-8
[19] Feng QC, Wen SM, Zhao WJ, Deng JS, Xian YJ 2016 Appl Surf Sci 360 365−72
[20] Zhang J, Wang WQ, Liu J, Huang Y, Feng QM, Zhao H 2014 Miner Eng 61 16-22
[21] Feng QC, Wen SM 2017 J Alloy Compd 709 602−8
[22] Feng QC, Wen SM, Deng JS, Zhao WJ 2017 Appl Surf Sci 396 920−5
[23] Feng QM, Liu GS, Yu ZJ, Lu YP, Ou LM, Zhang GF 2006 J Cent South Univ Sci T 37(3) 476-80
[24] Zhang GF, Jiang SP, Feng QM, Zhang BF 2017 J Cent South Univ Sci T 48(4) 851−9
[25] Feng QC, Wen SM, Zhao WJ 2015 Miner Eng 83 128-35
[26] Wang DZ, Hu YH 1988 Hunan Sci T Pres
[27] Yan ZW, Liu HL, Li SX 2013 Shandong Land Resour 29(10-11) 103-66
[28] Yan ZW, Zang ZW 2009 Hydrogeol Eng Geol 1 113-8
[29] Wu X, Lv L, Xu DY 2009 Chinese J Chem Educ5 66-7
[30] Li FX, Zhong H, Xu HF, Jia H, Liu GY 2015 Miner Eng 71 188-93
[31] Liu QY, Huang YG, Qu XY, Xiao JJ, Yang XL, Xu ZH 2016 Colloid Surfaces A 503 34-42
[32] Rober GA, Sarah LH, David AB 2010 Miner Eng 23(11-13) 928-36
[33] Mielczarski J 1987 J Colloid Interf Sci 120(1) 201-9
[34] Skinner WM, Prestidge CA, Smart RSC 1996 Surf Interface Anal 24 620-6
[35] Liu S, Liu QY, Zhong H, Yang XL 2017, J Ind Eng Chem 52 359-68
[36] Velasquez P, Ramos-Barrado JR, Cordova R, Leinen D 2000 Surf Interface Anal 30 149-53
[37] Sarah LH, ET Joan, Daniel F, Andrea RG 2006 Geochim Cosmochim Acta 70(17) 4392-402
[38] Termes SC, Buckley AN, Gillard RD 1987 Inorg Chimica Acta 126(1) 79-82