Experimental study on the separation of a shred copper slag

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Abstract. An experimental study on copper separation from a shred copper slag in Yunnan province was carried out. The test contents included: grinding curve test, grinding process determination test, comparison tests of different flotation processes. The results shown that: the main ingredients of shred copper slag were iron, silicon and the main valuable metallic elements were Cu, Fe, grade of 0.70%, 40.14%, consistent with the main components of the copper smelting slag. When the grinding time exceeded 35 minutes, the grinding fineness curve tended to flatten, indicating that the grinding effect was not obvious after the time exceeded 35 minutes, and the grinding fineness did not change much, which may be the shrend copper slag crystallized into a dense structure during the cooling process. Finally, the two stages grinding and regrinding process was adopted. Under the fineness of -0.074 mm 70% on the first grinding, the fineness of -0.037 mm 100% on the second grinding, and the fineness of -0.026 mm 85% on the regrinding, the process of regrinding and recleaning for combined cleaning middling of sulfide copper with roughing and scavenging middling of oxidized copper was suitable for the shrend copper slag.

1. Preface
The world’s copper production was rapidly growth in recent years and copper production in China had surpassed the Chilean leaped to the world. Now the world’s copper production adopted pyrometallurgy was more than 80%, the remaining 20% used hydrometallurgy production. More than 97% of China’s copper production was produced with pyrometallurgy [1]. The pyrometallurgy process produced a large number of bearing-iron copper slag occupied lots of land, and had an impact on the surrounding environment [2]. Prodution of 1 ton copper by pyrometallurgy would produce 2.2 tons copper slag, and the annual output of copper slag in China was as high as 15 million tons [3]. Although the composition of copper slag produced by different smelting methods was different, the content of iron and copper was generally higher (the content of Fe and Cu was usually up to 30-40 % and 0.5-2.1 %) [4], which reached or even exceeded the recoverable grade of natural iron ore and copper ore in China. Therefore, it had a high recycling value. The cooling of copper slag was the basis of flotation, and its cooling rate directly determines the crystal density of copper ore. The slower the cooling rate of slag, the better the migration and aggregation of copper phase particles will be. In the process of slow cooling, the primary evolution of slag melt could be carried out uniformly, forming good automorphic crystal or semi-automorphic crystal, and continuously gathering to form several independent phases, which was conducive to the later separation and recovery [5]. If the furnace slag was cooled at a high speed, it was difficult to form crystalline structure with fine and dispersed grains, and it was difficult to distinguish various crystals, that is, it was difficult to carry out flotation recovery.
Therefore, in the cooling process of copper smelting slag, most manufacturers chose the thermal insulation cooling and shred method, rather than the natural cooling or shred method alone [6].

In this study, the copper separation experiment of a copper slag shred alone was carried out, which had certain guiding significance for the utilization of this type of copper slag.

2. Experimental materials and preparation

2.1 Chemical properties of ore samples

Chemical multi-element analysis was carried out on the sample of shred slag, provided by a company in Yunnan. The main quantitative analysis results of chemical multi-element were shown in Table 1.

| Chemical composition | Cu  | Pb  | Zn  | Fe  | S   | SiO₂ |
|----------------------|-----|-----|-----|-----|-----|------|
| Contents, %          | 0.70| 0.36| 1.04| 40.14| 0.90| 26.20|

| Chemical composition | Al₂O₃ | CaO  | MgO  | Na₂O | K₂O | Au   |
|----------------------|-------|------|------|------|-----|------|
| Contents, %           | 3.80  | 2.52 | 2.35 | 0.57 | 0.77|      |

From the results of multi-element analysis, it could be seen that the main compositions of the shred slag were iron and silicon, which was consistent with that of the copper smelting slag. The main valuable metal elements were Cu and Fe, with grade of 0.70% and 40.14% respectively. Due to the low sulfur content, it could be roughly inferred that the occurrence state of Pb and Zn was in the form of oxide, which had no recovery value.

2.2 Reagents, instruments and equipments

Reagents: collector: Z-200, butyl xanthate, ammonium butadiene black, LP-01, BK905, MAC, amyl xanthate, etc; inhibitor: Lime; activator: copper sulfate, sodium sulfide; dispersant: sodium silicate, sodium hexametaphosphate; frother: 2# oil.

Instruments and equipments: PE 60×100 jaw crusher, 200×150 double-roll crusher, XSE-73 300×600 vibrating screen machine, XMQ-240×90 cone ball mill, XFD, XFG series flotation machine.

The test water was tap water for civil use.

3. Experiments

3.1 Grinding curve test

The weight of each batch of ore samples was 1 kg, and the grinding concentration was 75%. The grinding fineness test was carried out for the grinding time variable, and the results were shown in Figure 1.
3.2 Determination experiment of grinding process
It was found from the exploration experiment that the grade of copper in the middling was about 1%, and after two or three times of cleaning, it could only be enriched to about 2-3%, indicating that there were a lot of symbionts in the middling, so it should be considered to regrind and reclean for the middling. Among them, the fineness of first stage grinding was controlled at -200 mesh accounting for 70%, the fineness of second stage grinding was controlled at -400 mesh about 100%, and the fineness of regrinding was controlled at -600 mesh above 85%. Therefore, the two-stage grinding and middling regrinding process was adopted as the final process.

3.3 Regrinding and reselecting for combination of copper sulfide and roughing concentrate of copper oxide
The test conditions were as followed: the fineness of first stage grinding was controlled at -200 mesh accounting for 70%, the fineness of second stage grinding was controlled at -400 mesh above 90%, and the fineness of regrinding was controlled at -400 mesh above 95%. CuSO₄ and Na₂S were not added before the grinding. Sodium silicate was added before the floatation of copper sulfide and copper oxide respectively. The copper sulfide and the roughing concentrate of copper oxide were combined for regrinding and recleaning. The results were shown in Table 2.

3.4 Separate regrinding of copper oxide middling and copper sulfide roughing concentrate combined for selecting
The test conditions were as followed: CuSO₄ and Na₂S were not added before the grinding and the floatation of copper sulfide and copper oxide was respectively. The copper oxide was reground and reselecting, and the roughing concentrate of sulfide copper was incorporated into the concentrate 2 carried out four cleanings. Copper sulfide entered the second-stage grinding after the first roughing without the second roughing. The results were shown in Table 3.

| Table 2. Results of regrinding and reselecting for combination of copper sulfide and roughing concentrate of copper oxide/% |
|-----------------|-------|-------|-------|-------|
| Title           | Weight/g | Yield  | Grade | Recovery |
| KCu             | 15.7    | 1.57   | 10.32 | 23.15   |
| n₁              | 11.0    | 1.10   |       |         |
| n₂              | 9.4     | 0.94   | 0.93  | 14.37   |
| n₃              | 66.3    | 6.63   |       |         |
| n₄              | 21.5    | 2.15   |       |         |
| X               | 876.1   | 87.61  | 0.50  | 62.58   |
| Ore             | 1000    | 100    | 0.70  | 100     |

| Table 3. Results of separate regrinding of copper oxide middling and copper sulfide roughing concentrate combined for selecting/% |
|-----------------|-------|-------|-------|-------|
| Title           | Weight/g | Yield  | Grade | Recovery |
| KCu             | 3.9     | 0.39   | 27.13 | 15.11   |
| n₁              | 121.1   | 12.11  | 1.08  | 18.68   |
| n₂              | 52.6    | 5.26   | 1.15  | 8.64    |
| n₃              | 4.3     | 0.43   | 2.18  | 1.34    |
| n₄              | 2.1     | 0.21   | 4.82  | 1.44    |
| X               | 816     | 81.6   | 0.47  | 54.79   |
| Ore             | 1000    | 100    | 0.70  | 100     |
3.5 Regrinding and reselecting for combination of the copper sulfide cleaning middling and copper oxide roughing and scavenging middling

The test conditions were as followed: copper sulfide ore was preferential floated and separate selection. The combination of copper sulfide cleaning middling and copper oxide roughing and scavenging middling was reground and reselected with CuSO₄ activator. The results were shown in Table 4.

Table 4. Results of regrinding and reselecting for combination of the copper sulfide cleaning middling and copper oxide roughing and scavenging middling/%

| Title   | Weight/g | Yield | Grade | Recovery |
|---------|----------|-------|-------|----------|
| KCu₁    | 5.9      | 0.59  | 22.51 | 18.30    |
| KCu₂    | 2.2      | 0.22  | 19.50 | 5.91     |
| n₁      | 109.1    | 10.91 | 0.75  | 11.27    |
| n₂      | 39.8     | 3.98  | 1.20  | 6.58     |
| n₃      | 5.2      | 0.52  | 1.63  | 1.17     |
| n₄      | 4        | 0.40  | 2.94  | 1.62     |
| X       | 833.8    | 83.38 | 0.48  | 55.15    |
| Ore     | 1000     | 100   | 0.726 | 100      |

4. Results and discussions

As shown in Figure 1, when the grinding time exceeded 35 min, the grinding fineness curve tended to be flat, indicated that the grinding effect was not obvious after the grinding time exceeded 35 min, and the grinding fineness did not change much, which may be due to the compact structure formed by the crystallization of the shred copper slag in the cooling process.

It could be seen from Table 2, the process failed to obtain qualified concentrate grade which was not suitable for this copper slag. In addition, the copper recovery rate was not high, and the tailing grade reached 0.50%.

It could be seen from Table 3 that the mixed concentrate could be achieved through four cleanings, and the final concentrate grade reached 27.13%, but the copper recovery rate was too low, only 15.11%.

It could be seen from Table 4 and Figure 4, the copper concentrate with a yield of 0.59%, a grade of 22.51% and a recovery of 18.30% could be obtained by cleaning separately for copper sulfide ores. The copper concentrate with a yield of 0.22%, a grade of 19.50% and a recovery of 5.91% could also be obtained by combining the cleaning middling of copper sulfide with the roughing and scavenging concentrate of copper oxide. The copper grade of the tailing was 0.48%, which was similar to the previous test results, indicated that the copper particles in the tailing were very fine and wrapped by iron, which was difficult to reduce. The process was an ideal process for the shred copper slag.

5. Conclusions

(1) From the results of multi-element analysis, it could be seen that the main compositions of the shred slag were iron and silicon, which was consistent with that of the copper smelting slag. The main valuable metal elements were Cu and Fe, with grade of 0.70% and 40.14% respectively. Due to the low sulfur content, it could be roughly inferred that the occurrence state of Pb and Zn was in the form of oxide, which had no recovery value.

(2) When the grinding time exceeded 35 min, the grinding fineness curve tended to be flat, indicated that the grinding effect was not obvious after the grinding time exceeded 35 min, and the grinding fineness did not change much, which may be due to the compact structure formed by the crystallization of the shred copper slag in the cooling process.

(3) The two stages grinding and regrinding process was adopted. Under the fineness of -200 mesh 70% on the first grinding, the fineness of -400 mesh 100% on the second grinding, and the fineness of -600 mesh 85% on the regrinding, the process of regrinding and recleaning for combined cleaning
middling of sulfide copper with roughing and scavenging middling of oxidized copper was suitable for the shred copper slag.

Acknowledgements
We gratefully acknowledge the financial assistance of Yunnan Provincial Education Department Project (No: 2019J0738), National Natural Science Foundation (No: 51964044), Yunnan Local Colleges Applied Basic Research Projects (No: 2018FH001-051), Yunnan University Students Innovation and Entrepreneurship Training Program (No: 2019B20, 2020B28).

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