The Flotation Modification Test of Chrysocolla Research on RSM

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Abstract. This study is focused on the flotation of a cooper mineral. Chrysocolla is poor flotability, surface porous, high porosity, nonuniform property, so it has strong hydrophilic and difficult dissolution. XRD and SEM were used to detect the properties and surface morphology of chrysocolla. The paper make an experiment, it contain modified polymer adsorption - intermediate metal copper ion connection - collector adsorption testing program. The experiment can exchange mineral surface property which enhancing mineral flotation and hydrophobicity. With the conclusion, the results have a trend that increasing the agents can increase mineral recovery, then mineral recovery reach the stable trend. In the simulation of RSM, mineral recovery is based on 3 factors ammonium, xanthate and agent, those factors interact with each other, simulation find the main factor is agent. RSM response surface method has the function of optimizing test results, improving test efficiency, inputting test influence factors and results, and getting the best test factors and results through test simulation.

Keywords. Chrysocolla; flotation; RSM.

1. Introduction
Copper is an important production raw material in the national economy main products, with good electrical conductivity, ductility and easy to form alloys, so it is widely used in electronic, national defense, construction, machinery, light industry and other industries. With the continuous exploitation of copper resources, relatively easy beneficiation has been reduced year by year and the shortage of resources has worsened. Therefore, great attention has been paid to the application research and development of low-grade oxidized copper ores [1]. This type of minerals generally have the characteristics of high oxidation rate, high binding rate, fine dissemination particle size, large mud content, polymetallic symbiosis, etc., so it is difficult to obtain better technical and economic indexes with conventional processing and smelting technology. Study on beneficiation of oxidized copper ore in China has a history of more than 50 years, and its processing technology has made great progress [2-5]. The copper mines of the world are mined for a long time and grade decreased.

However, the copper demand is increasing, and the mining cost is getting higher and higher. The copper in the refractory complex copper oxide ore can be deeply developed and utilized, and it is significant to study the complex refractory copper oxide ore [6]. The malachite studied in this paper generally occurs in the copper-lead-zinc ore, which belongs to the refractory, complex and high oxidation rate copper, it is difficult to be floatated by conventional collector. On the one hand, chrysocolla surface porous and high porosity, the nature of the change is uneven, belongs to the typical strong hydrophilicity, refractory, difficult to float mineral [7]. The hydrophobic differences of various minerals are enhanced by the selective adsorption of flotation reagents according to the physical and
chemical properties of the mineral surfaces, so that the target minerals are selectively separated from the gangue minerals [8]. Oxidized ore due to the strong hydrophilicity, specific surface area (128 m$^2$/g), soluble and surface copper ion diffusivity is poor, collector is hard to copper oxide ore recovery, on the other hand because of chrysocolla predecessors research content is less. It is a kind of copper oxide ore with scientific research significance. In order to overcome these challenges, it is necessary to further understand the activation properties of the activator adsorbed on the mineral and to design more efficient activators for chrysocolla. Found that ammonium sulfate and ethylenediamine phosphate had certain activation effect on malachite, and sodium sulfide [9-11] would inhibit the floatability of malachite. In this study, an appropriate amount of copper sulfate was added to activate malachite, and then the polymer agent reacted with the surface of malachite through surface organic modification. After the surface modification of malachite, the added copper ions are combined with the outer layer of the modified polymer agent, and finally the amyl xanthate is added to combine with the copper ions outside the modified polymer agent.

2. Mineral Experiment Research

2.1. Experiment Raw Mineral

The composition of malachite is CuSiO$_3$ 2H$_2$O. The test material was taken from the ore of malachite in Wuhan, Hubei Province, and the purity was over 90% after manual selection. The manually selected pure mineral of malachite is ground to less than 200 mesh through a three-headed agate grinder. Under the grinding of agate grinding machine, pure minerals keep their original composition, and no impurities will be entrapped after grinding.

| Element | Cu | SiO$_2$ |
|---------|----|---------|
| Content | 35.82 | 34.25 |

As shown in the table 1, the Cu and SiO$_2$ content is 35.82% and 34.25% in the pure mineral sample by multi-element analysis.

Figure 1 shows the SEM spectrum. (a), (b), (c) and (d) respectively show the surface morphology of ore under the detection distance of 1 mm, 200 um, 100 um and 20 um by SEM. CuSiO$_3$ is the main component of malachite. There are some white points raised on the surface of malachite. The ore is fragile and fragmented after crushing grinding. The atomic contents of O, Cu and Si were 40.90%, 8.74% and 10.89%, respectively, and the ratio of atomic content of Cu: Si: O was approximately 1:1:4.

Due to the strong hydrophilicity and poor floatability of malachite, it is of research significance to understand the modification mechanism of activator to improve the flotation efficiency of valuable minerals recovered from ores, and to develop more powerful activator. The combined application of SEM, XRD, ATR-FTIR, X-ray photoelectron spectroscopy (XPS), DFT calculation and solution chemistry can accurately clarify the activation properties of the activator on the surface of malachite, and provide a new way to understand the modification configuration and hydrophobicity mechanism of the activator on mineral surface.
2.2. Experiment Agent
The main agents used in the test are anhydrous copper sulfate, sodium hydroxide, ammonium sulfate, surface-modified polymer agents, ethylenediamine phosphate, amyl xanthate, No.2 oil. Polyacrylamide is a broad spectrum of flocculant, for the majority of the microgranular mineral grain has the very good flocculation effect, to transform, to remove oxygen atoms with strong hydrophilic, join the sulfur atom of copper ion selective adsorption ability, can obtain the surface with a surface modification effect of chrysocolla more atoms polymer reagents. The modified polyacrylamide is an organic modified polymer agent, and the modified polymer agent in this paper uniformly uses the GFZ code.

2.3. Experiment Method
The test was carried out in XFGC laboratory aerated flotation tank with a volume of 60ml. First, 2g of 200 mesh pure mineral silachite was weighted, and 40ml of deionized water was injected into the flotation tank. 2g of pure mineral silachite was added. The spindle speed of flotation machine is set at 1800r/min. The flotation reagent amyl xanthate concentration test, the activator ammonium sulfate concentration test, the activator ethylenediamine phosphate and ammonium sulfate concentration test and the ammonium sulfate GFZ reagent test were carried out successively. After flotation, each product will be placed in a conical funnel for natural filtration, drying, weighing, sample preparation and testing to obtain the corresponding weight and finally calculate the recovery rate.

3. Experiment Project and Results Analysis

3.1. GFZ Agent Experiment Theory
As shown in the equations (1), (2), (3), CuSiO₃ in the water is dissolving to Cu and SiO₃²⁻, then SiO₃²⁻ react with H₂O to HSiO₃ and OH⁻, finally HSiO₃ react with H₂O to H₂SiO₃ and OH⁻.

\[
Cu\text{SiO}_3 \rightarrow Cu^{2+} + SiO_3^{2-}
\]  \hspace{1cm} (1)
\[ SiO_3^{2-} + H_2O \rightarrow HSiO_3^- + OH^- \]  
\[ HSiO_3^- + H_2O \rightarrow H_2SiO_3 + OH^- \]  

3.2. RSM Analysis Experiment Results

Design-expert is the world's top experimental Design software. As shown in the figure 2 RSM recovery of ammonium and xanthate diagram can intuitively see the influence of two factors on the dependent variable, and can intuitively find out the optimal range. With the increase of ammonium and addition amount of xanthate, the recovery will correspondingly increase, and finally the recovery reaches the maximum value of 81.5%, then the recovery tends to be stable [12-14].

Figure 2. RSM recovery of ammonium and xanthate.

As shown in the figure 3 RSM recovery of GFZ agent and xanthate, with the increase of GFZ agent and xanthate addition, the recovery gradually increases to the maximum value.

Figure 3. RSM recovery of GFZ agent and xanthate.

As shown in the table 2 above, the p values of recovery is 0.0001 respectively, and the significance test of the model was p < 0.05, indicating that the model had statistical significance. If the regression equation is favorable to the model, there is no defect, so the regression equation can be used to replace the real point of the experiment to analyze the experimental results.

Table 2. RSM model results analysis.

| Source   | Sum of squares | Freedom | F value | p-value prob>F | Significance |
|----------|---------------|---------|---------|----------------|--------------|
| Model    | 4.52          | 9       | 45.34   | 0.0023         | Significant  |
| A-xanthate | 3.62          | 1       | 72.5    | 0.0031         |              |
| B-ammonium sulfate | 2.41        | 1       | 8.50    | 0.0012         |              |
| C-GFZ agent | 2.63          | 1       | 81.98   | 0.0014         |              |
| AB       | 0.76          | 1       | 1.29    | 0.2941         |              |
| AC       | 0.21          | 1       | 13.75   | 0.0076         |              |
| BC       | 0.74          | 1       | 0.043   | 0.8411         |              |
| A^2      | 0.72          | 1       | 0.43    | 0.5309         |              |
| B^2      | 0.43          | 1       | 0.025   | 0.8788         |              |
| C^2      | 0.67          | 1       | 1.27    | 0.2973         |              |
| Residual | 0.35          | 7       |         |                |              |

In this example, as shown in the table 2 above, the p values of recovery is 0.0001 respectively, and the significance test of the model was p < 0.05, indicating that the model had statistical significance. If the regression equation is favorable to the model, there is no defect, so the regression equation can be used to replace the real point of the experiment to analyze the experimental results.

Final Equation in Terms of Coded Factors:
Recovery = 43.26 + 18.64*A + 3.82*B + 12.47*C + 2.20*A*B + 7.20*A*C + 0.46*B*C + 1.46*A^2 + 0.39*B^2 + 2.62*C^2

(4)

As shown in equation (4), multiple quadratic response surface regression models were obtained through quadratic response surface regression analysis with the design-expert software.

As shown in the table 3 RSM prediction of concentration recovery, quadratic response surface regression analysis was carried out by design-expert software, and the predicted value calculated based on the obtained multivariate quadratic response surface regression model was compared with the actual value. The prediction effect is good, which indicates that the modeling is of good quality.

| Actual value | Predicted value | Error | Residual |
|--------------|----------------|-------|----------|
| 30.00        | 28.08          | 1.92  | 0.869    |
| 38.00        | 39.84          | -1.84 | -0.504   |
| 87.00        | 85.66          | 1.34  | 0.449    |
| 35.00        | 37.16          | -2.16 | -0.946   |
| 40.00        | 43.26          | -3.26 | -1.213   |
| 75.00        | 69.77          | 5.23  | 2.446    |
| 35.00        | 30.44          | 4.56  | 2.395    |
| 56.00        | 57.73          | -1.73 | -0.733   |
| 62.00        | 58.36          | 3.64  | 1.139    |
| 45.00        | 46.31          | -1.31 | -0.580   |
| 26.00        | 24.85          | 1.15  | 0.406    |
| 25.00        | 23.43          | 1.57  | 0.587    |
| 32.00        | 33.97          | -1.97 | -0.876   |
| 55.00        | 54.47          | 0.53  | 0.206    |
| 46.00        | 47.47          | -1.47 | -0.416   |
| 20.00        | 22.66          | -2.66 | -0.947   |
| 89.00        | 92.53          | -3.53 | -1.707   |

**Table 3. RSM prediction of concentration recovery.**

As shown in the figure 4, the best flotation agent dosage, based on the response surface design experiment and the central combination test design principle of box-benhnken, three factors that have significant influence on the grade and recovery of copper concentrate were selected: xanthate A,
ammonium sulfate B and GFZ agent C. Three factors and three levels of response surface analysis test were conducted. Finally, the best process was obtained: xanthate 3, ammonium sulfate3, GFZ agent C 3, concentrate recovery rate 92.52\% [15-17].

4. Conclusion
In this paper, the flotation mechanism and the flotation results optimization are studied.

(1) Due to the experiment results, with GFZ agent and xanthate increase, recovery also increase, so GFZ agent has a certain activation effect on malachite.

(2) RSM is a great experiment tool, it contains data analysis function, and the RSM model p value is reliable.

(3) RSM surface response method has the function of optimizing the test results, improving the test work efficiency, and inputting the influence factors and results of the test, the optimized experimental results are improved to a certain extent compared with the actual test results.

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