The Iron Removal in Marmatite Concentrate Pressure Leaching Process

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Abstract. To modify the pressure leaching technology of horizontal autoclave using marmatite concentrate, an appropriate increase in the pulp’s residence time in the horizontal autoclave is required. This increase will provide sufficient time for leaching to be completed in the first three chambers of the horizontal autoclave. Adding zinc oxide ore and potassium sulfate in the fourth chamber of the horizontal autoclave is needed to complete preliminary neutralization and iron precipitation in the horizontal autoclave. The pilot plant experimental results of the proposed technology are satisfactory, further shortening the process of pressure leaching and improving its economic efficiency.

1. Introduction
Currently available mineral resources are mostly low-grade and complex with multi-metal mixing because of the depletion of high-quality mineral resources \cite{1}. Marmatite concentrate is a zinc mineral that is categorized into the low-grade and complex class of resources. The iron element in marmatite is embedded in the sphalerite crystal through isomorphous substitution. As a result, general beneficiation methods cannot effectively separate zinc from iron in marmatite. Proven reserves of this mineral in Yunnan province, China, are as high as 7 million tons and accounts for one-third of the proven zinc resource reserves in the province \cite{2,3}.

The traditional zinc hydrometallurgy process requires the iron content to be as low as possible, because iron-containing zinc concentrate generates copious zinc ferrite during roasting, which reduces the efficiency of zinc leaching. Although utilizing hot acid leaching can destroy zinc ferrite and increase the efficiency of zinc leaching, iron is also leached into the solution. The subsequent removal of iron is a lengthy process that results in a larger amount of leach residue, low zinc recovery rate, and other limitations \cite{4-6}. Using a single-stage pressure leaching technology results in approximately 60% precipitation of the iron into the residues, although the iron content in the leachate can be as high as 5 ~ 15 g/L and the acid concentration is generally 30 g/L or higher \cite{2,3}. The resulting leachate must undergo the jarosite process to remove the irons. In a two-stage pressure leaching technology of marmatite concentrate, the irons and acids contents of the leachate are low, although the iron content is still 3 ~ 5 g/L, which does not meet the requirements of neutral supernatant. Additionally, the capital investment required for the two-stage pressure leaching is very substantial \cite{7}. In the current study, the removal of iron from marmatite via single-stage horizontal autoclave pressure
leaching is described. This process removes iron from the leaching solution while maintaining the requirements for a neutral supernatant.

2. Experimental

2.1. Raw Materials
The concentrated sulfuric acid and potassium sulfate used in experiment were industrial grade, the chemical composition of single-stage pressure leaching liquor was shown in Table 1, chemical composition of zinc oxide ore used for neutralization was shown in Table 2.

Table 1. Chemical composition of single-stage pressure leaching liquor.

| Component | Zn\(^{2+}\) | Fe\(^{3+}\) | Fe\(^{2+}\) | H\(_2\)SO\(_4\) | As\(^{3+}\) | Cd\(^{2+}\) | Co\(^{2+}\) | Ni\(^{2+}\) | Cu\(^{2+}\) |
|-----------|--------------|------------|------------|----------------|-----------|-----------|-----------|-----------|-----------|
| Content(g/L) | 128.37 | 13.21 | 2.93 | 42.58 | 0.087 | 0.382 | 0.014 | 0.022 | 0.115 |

Table 2. Chemical composition of zinc oxide ore (mass fraction, %).

| Component | Zn | Pb | Fe | CaO | SiO\(_2\) | As | F | Cl |
|-----------|----|----|----|-----|---------|----|---|----|
| Content(%, \(\omega\)) | 19.64 | 3.45 | 8.51 | 7.13 | 10.087 | 0.18 | 0.027 | 0.006 |

2.2. Experiment Programs
The horizontal autoclave has four chambers. In the experiments, the autoclave system reduced the flow rate of slurry. Thus, the marmatite concentrate was completely leached in the first three chambers. In the fourth chamber, zinc oxide ore and potassium sulfate were added. Under high temperature, the zinc ore and potassium sulfate inside the horizontal autoclave resulted in a high-pressure and oxidizing atmosphere. The iron was quickly precipitated in the form of jarosite salt\(^9\)-\(^{11}\). As a result of leaching, the neutralization and iron removal of the marmatite concentrate were completed in a horizontal autoclave. The experiment process flow chart is presented in Figure 1.
The pressure leaching process of marmatite concentrate is a routine technology, and thus the process will no longer be described here. In these experiments, a single-stage pressure leachate of marmatite concentrate was used as raw materials. The experiment to remove iron was conducted in the 2 L autoclave. The influence of various reaction parameters on iron removal was investigated through a series of carefully controlled experiments. The parameters included final PH value, reaction time, potassium sulfate dosage, temperature, and other factors.

3. Results and Discussion

3.1. Effects of Final pH Value

Through the process of pre-grinding zinc oxide ore the size of particles less than 0.074 mm accounted for 95%. Experiment conditions: pressure leaching liquor = 500 mL, potassium sulfate = 3g, temperature = 130 ℃, reaction time = 30 min, air pressure= 1.2 MPa, stirring speed = 600 rpm. The results are shown in Figure 2.

The figure indicates that the precipitation rate of irons and the main impurities of copper, cadmium, and cobalt increased, and the leaching rate of zinc decline with the final pH value of the reaction. This result occurred because the precipitation rate of irons increased with the final pH value, whereas, the quantity of impurities of copper, cadmium, and cobalt increased in the leach residue as a result of hydrolysis precipitation or adsorbed in the iron precipitation. Simultaneously, the filtration rate of slurry decreased with the increase in pH value. To ensure the highest precipitation rate of iron, the final pH value of the slurry should be 5.0.

3.2. Effects of Temperature

Experiment conditions: pressure leaching liquor = 500mL, potassium sulfate = 3g, final pH value = 5.0, reaction time = 30 min, air pressure = 1.2 MPa, stirring speed = 600 rpm. The results are shown in Fig. 3.
The figure shows that the precipitation rate of iron increased with the temperature of the reaction, whereas the impurities of copper, cadmium, and cobalt gradually decrease, and the leaching rate of zinc increases slowly. The reason for this outcome was the leaching residue at high temperature has better crystal shape. Thus, as temperature increased, the amount of absorbed metal impurities decreased in the iron precipitation residue. At the same time, the filtration rate of the slurry increased with temperature. Thus, the optimum operating temperature for this reaction should be near 150 °C.

3.3. Effects of Potassium Sulfate Addition

Experiment conditions: pressure leaching liquor = 500 mL, reaction temperature = 150 °C, final pH value = 5.0, reaction time = 30 min, air pressure = 1.2 MPa, stirring speed = 600 rpm. The results are shown in Fig. 4.

The figure indicates that the precipitation rate of iron was essentially the same as that with the increased amount of the potassium sulfate to the reaction mixture. In comparison, the precipitation rate of copper, cadmium, cobalt, and other impurities decline at first and remained constant after, the leaching rate of zinc increase at first and constant after. The leaching residue has better crystal shape and the filtration rate of the slurry increased with the amount of potassium sulfate added. Thus, the amount of potassium sulfate added 3g is appropriate.
3.4. Effects of the Reaction Time
Horizontal autoclave has four reaction chambers, sphalerite pressure leaching time is generally 1 ~ 2.5 h, so each chamber of the residence time is 15 ~ 40 min, due to the iron precipitating process performed in the fourth chamber, therefore the investigated time range is 15 ~ 40 min. Experiment conditions: pressure leaching liquor = 500 mL, reaction temperature = 150 ℃, final PH value = 5.0, potassium sulfate = 3 g, air pressure = 1.2 MPa, stirring speed = 600 rpm. The results are shown in Fig. 5.

![Figure 5. Effects of the reaction time](image)

The figure indicates that the precipitation rate of iron is essentially the same as that with the increased pressure time. In comparison, the precipitation rate of copper, cadmium, cobalt, and other impurities slowly decline, the leaching rate of zinc slowly increase. Thus, the iron removal time should be longer, 30 ~ 40 min is appropriate.

3.5. Horizontal Autoclave Pilot Plant Experiment
The precipitating iron experiment conditions were chosen as follows: temperature = 150 ℃, final pH = 5.0, pressure = 1.2 MPa, reaction time = 30 min, and stirring speed = 600 rpm, potassium sulfate = 3 g. The experimental results are presented in Table 3.

| Order number | Composition of leachate (g/L) |
|--------------|------------------------------|
|              | Zn  | Fe  | Cu  | Cd  | Co  | Ni  | As  |
| 1            | 142.53 | 0.134 | 0.032 | 0.064 | 0.006 | 0.013 | 0.016 |
| 2            | 148.65 | 0.107 | 0.042 | 0.066 | 0.005 | 0.009 | 0.013 |
| 3            | 141.24 | 0.158 | 0.033 | 0.072 | 0.006 | 0.011 | 0.019 |
| 4            | 152.69 | 0.132 | 0.045 | 0.076 | 0.008 | 0.014 | 0.023 |

The chemical composition of the leachate from horizontal autoclave pressure leaching in Table 3 demonstrates that the content of harmful impurities in the leachate was relatively low. Thus, the product could be sent directly to the zinc-leaching solution purification process.
4. Conclusions

(1) The optimum conditions of the pressure leaching iron removal were as follow: reaction temperature = 150 °C, end-point PH = 5.0, potassium sulfate = 3 g, pressure = 1.2 MPa, the reaction time = 30 min, stirring speed = 600 rpm. The iron removal process was performed in the fourth chamber of the horizontal autoclave at high temperature and high pressure under strong oxidizing circumstance within the autoclave. Just 30 min to complete the process, and the iron removal effect is obvious.

(2) Compared with the traditional zinc pressure leaching process, the proposed method disregards the jarosite iron-removal process outside the horizontal autoclave steps, shortens the process, and reduces the amount of zinc powder in zinc-leaching solution purification, because of the lower contents of harmful impurities in the leaching solutions. The economic benefits of the proposed process are significant.

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