Comprehensive utilization of paigeite greening and efficient

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Abstract. In the paper, according to the chemical composition of paigeite and mineral structure, designing a clean, efficient and comprehensive utilization process. Through roasting paigeite with ammonium sulfate, magnesium, iron, aluminum, boron in paigeite changes into water soluble products, silicon exists in the form of silica, insoluble in water. Roasting product is dissolved by water, filtration. The magnesium, iron, aluminum and boron are separated from silicon dioxide. Magnesium, iron, aluminum, boron is formed precipitation on the difference value of pH, adding alkaline material such as NH₃ solution to adjust the pH value of solution, such as magnesium, iron, aluminum, boron fractional precipitation and separation. Sulfuric acid root into ammonium sulfate, evaporation crystallization returned after roasting. Chemical raw materials recycling.

Key words: Paigeite, Ammonium sulfate, Roasting, Recycling.

China's Boron reserves are large, accounting for 18% of the world's boron. Among them, the boron resources in Liaoning Province account for 56% of China's total reserves [2]. There are two types of boron ore in Liaoning Province, namely, magnesium borate ore and Ludwigite, which are collectively referred to as Ludwigite. Among them, 20% of the reserves of Ludwigite have high boron grade, which has been exhausted after years of exploitation and utilization. In the traditional process, boron concentrate is obtained after magnetic separation, and then the target product is produced continuously. However, due to the low content of boron, a large amount of waste residue is accumulated in the production, which occupies land and pollutes the environment [3].

There are also a large number of magnesium silicate minerals in boron ore [4]. Making full use of them can prepare silicon, magnesium, iron, aluminum and other products, which not only improves the utilization of high added value of boron ore, but also reduces the discharge of waste, meeting the requirements of circular economy, clean production and improving the comprehensive utilization rate of mineral resources.

In view of the current situation that bornite can not be reasonably treated, this paper carried out the research on high value-added green comprehensive utilization process of bornite. It is planned to use ammonium sulfate method to roast bornite. Iron, magnesium, aluminum and boron in minerals react with ammonium sulfate to form water-soluble substances, and silicon in bornite generates water-insoluble silicon dioxide. The roasted clinker is dissolved with water and filtered. The silica residue mainly containing silica is separated from the filtrate. Calcium silicate and quartz products are obtained...
from silicon slag by sodium hydroxide treatment. Adjust the pH value to make the iron, magnesium and aluminum in the filtrate under different pH values to prepare iron hydroxide, magnesium oxide and aluminum hydroxide products for separation. Using solubility difference, ammonium borate and ammonium sulfate were separated [5 ~ 7]. Ammonium sulfate and ammonia are recycled. In this process, the chemical raw materials are recycled without waste residue, waste water and waste gas emission, and the whole process is green, which meets the requirements of developing circular economy and building a resource-saving and environment-friendly society.

1. Process design

1.1. Raw materials
The raw material is bornite from a certain area of Liaoning Province. The chemical composition is shown in Table 1.

| B$_2$O$_3$ | MgO  | CaO   | Al$_2$O$_3$ | Fe$_2$O$_3$ | SiO$_2$ |
|------------|------|-------|------------|-------------|--------|
| 8.34       | 22.4 | 0.522 | 1.41       | 48.3        | 18.5   |

The XRD spectrum of bornite is shown in Figure 1.

![Figure 1. XRD pattern of bornite](image)

The ammonium sulfate used in the experiment is industrial grade with purity ≥ 96%; liquid ammonia, ammonium carbonate and ammonium bicarbonate are analytical grade; water is deionized water.

1.2. Process design principle
According to the chemical composition and mineral phase composition of bornite, the technological process is designed to mix bornite and ammonium sulfate for roasting. The products of magnesium, iron, aluminum and boron are dissolved in water. Silicon exists in the form of silicon dioxide and is insoluble in water. The calcined product is dissolved out with water and filtered. Separate magnesium, iron, aluminum, boron from silica. The pH value of the precipitate produced by reusing magnesium, iron and aluminum in the solution is different. By adjusting the pH of the solution, magnesium, iron and aluminum can be separated and extracted. At this time, the filtrate is alkaline solution, and there are a lot of NH$_4^+$, SO$_4^{2-}$ and B$_4$O$_7^{2-}$ in the solution. When the filtrate is heated and evaporated, the solution gradually becomes saturated solution, and then the saturated solution gradually becomes supersaturated solution. At this time, the solute begins to precipitate from the supersaturated solution. Ammonium
sulfate is crystallized, and the remaining concentrated solution of ammonium borate is crystallized by adjusting the temperature. The separated ammonium sulfate is recycled.

2. Process introduction

2.1. Roasting
The bornite was dried, crushed and ground to below 80 μ M. The ground bornite and ammonium sulfate are proportioned and mixed. The amount of ammonium sulfate consumed in the complete reaction of magnesium, iron, aluminum and boron in bornite is calculated as 1:1. The ratio of ammonium sulfate to bornite is 2.5:1. When the temperature rises to 450 ℃ and roasts for 2 hours, the ammonia and sulfur dioxide produced are recovered to make liquid ammonia and ammonium sulfate. Ammonia is used to adjust the pH value, separate and extract magnesium, iron and aluminum, and then evaporate and crystallize the solution to obtain ammonium sulfate, which is returned to the batching process. The main chemical reactions [8-10] in the roasting process are as follows:

\[
\begin{align*}
4Fe_3O_4 + O_2 + 24(NH_4)_2SO_4 & = 12NH_4Fe(SO_4)2 + 18H_2O \uparrow + 36NH_3 \uparrow \\
Mg_3[Si_2O_5](OH)_4 + 6(NH_4)_2SO_4 & = 3(NH_4)_2Mg(SO_4)_2 + 5H_2O \uparrow + 2SiO_2 + 6NH_3 \uparrow \\
2MgBO_2(OH) + 4(NH_4)_2SO_4 & = 2(NH_4)_2Mg(SO_4)_2 + B_2O_3 + 4NH_3 \uparrow + 3H_2O \uparrow \\
2(Mg,Al)_3[(Si,Fe)_2O_5](OH)_4 + 5.5O_2 & = 6MgO + 2Fe_2O_3 + 3Al_2O_3 + 2SiO_2 + 4H_2O \uparrow \\
Al_2O_3 + 4(NH_4)_2SO_4 & = 2NH_4Al(SO_4)_2 + 6NH_3 \uparrow + 3H_2O \uparrow \\
MgO + 2(NH_4)_2SO_4 & = (NH_4)_2Mg(SO_4)_2 + H_2O \uparrow + 2NH_3 \uparrow
\end{align*}
\]

2.2. Preparation of silicon products by alkali leaching of silicon slag
The calcined clinker was dissolved with water at the ratio of 3:1. The dissolution temperature is 60-80 ℃. Dissolve while stirring. The dissolution time was 1 hour. The sulfate in clinker dissolves in water, but SiO₂ does not. The main component of filter residue (silicon residue) is silicon dioxide. After three times of washing, it is silicon product. It can also be further processed into wollastonite or silica.

The filtrate is a solution containing magnesium sulfate, ferric sulfate and aluminum sulfate.

The silicon slag and alkali liquor were mixed according to the liquid-solid ratio of 3:1. The temperature of alkali leaching was controlled at 130 ℃ for 1 h. The filtrate is sodium silicate solution and the filter residue is quartz powder. Filter to remove residue.

2.2.1. Preparation of calcium silicate. Lime milk was added to the filtrate (sodium silicate solution) and reacted at 90 ℃ for 2 h to obtain calcium silicate precipitation. The calcium silicate product is obtained by filtration, washing and drying. After evaporation and concentration of NaOH solution, it is returned to alkali leaching to dissolve the silicon residue for recycling.

2.2.2. Preparation of silica. The following chemical reaction occurs when CO₂ is introduced into the filtrate (sodium silicate solution).

\[
Na_2SiO_3 + CO_2 + H_2O = H_2SiO_3 \downarrow + Na_2CO_3
\]

After filtration and washing, metasilicic acid is obtained, and white carbon black is obtained by heating decomposition.

\[
H_2SiO_3 = SiO_2 + H_2O \uparrow
\]

Adding Ca(OH)₂ into the filtrate, the chemical reaction is as follows

\[
Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3 \downarrow
\]

The temperature of desilication solution was kept below 40 ℃, and hydrogen peroxide was added to the solution to oxidize Fe²⁺ into Fe³⁺. Then raise the solution temperature above 40 ℃, pass NH₃ gas, and control the pH value to 3. Or (NH₄)₂CO₃ or NH₄HCO₃ is added and stirred to form FeOOH. After
the reaction, the filter residue is iron hydroxide, which is used as raw material for ironmaking after washing and drying. The optimum conditions were pH 3, temperature 60 ℃ and reaction time 2 h.

A stage of overburning can also be added in the roasting process. When the temperature is above 750 ℃, ammonium ferric sulfate decomposes. The chemical reactions are as follows:
\[
\text{NH}_4\text{Fe(SO}_4\text{)}_2 = \text{Fe}_2\text{O}_3 + 2\text{NH}_3 \uparrow + 4\text{SO}_3 \uparrow + \text{H}_2\text{O} \uparrow
\]

The generated NH₃, SO₃ and H₂O enter into the flue gas and are absorbed by dust to obtain (NH₄)₂SO₄.

After digestion and filtration, Fe₂O₃ and SiO₂ become filter residue. It can be separated from SiO₂ by mineral processing. Or alkali solution, filtration, Fe₂O₃ as filter residue and SiO₂ separate.

2.3. Refined aluminum hydroxide

Ammonia (or (NH₄)₂CO₃ or NH₄HCO₃) is introduced into the solution after iron precipitation, and the pH value of the solution is adjusted to 5. The aluminum in the solution generates aluminum hydroxide precipitation:
\[
\text{NH}_4\text{Al(SO}_4\text{)}_2 + 3\text{NH}_3 + 3\text{H}_2\text{O} = \text{Al(OH)}_3 \downarrow + 2(\text{NH}_4)_2\text{SO}_4
\]

The results show that the optimal process conditions of aluminum precipitation are temperature 30 ℃, pH 5, and the solution after aluminum precipitation is filtered to obtain aluminum slag. Aluminum slag is used to prepare alumina. The filtrate is refined magnesium sulfate solution.

When aluminum slag is added into NaOH solution, the following chemical reaction occurs:
\[
\text{Al(OH)}_3 + \text{NaOH} = \text{NaAlO}_2 + 2\text{H}_2\text{O}
\]

Filter to remove residue. Al(OH)₃ crystal seeds were added to the solution, Al(OH)₃ crystal was precipitated, and Al(OH)₃ product was obtained by filtration. The filtrate is returned to the digestion process for recycling.

2.4. Separation and extraction of magnesium

After removing silicon, iron and aluminum, ammonia is added to the refined magnesium sulfate solution, the pH value of the solution is adjusted to 11, and the temperature is maintained at 40-60 ℃. Magnesium hydroxide precipitation is generated by reaction, and magnesium hydroxide product and filtrate are obtained by filtration and washing. The optimum conditions of magnesium precipitation were obtained as follows: temperature 30 ℃, reaction time 2 h, pH value 11, stirring intensity 400 R·min⁻¹.

2.5. Evaporation crystallization ammonium sulfate and ammonium borate

The filtrate after magnesium precipitation is heated, evaporated and crystallized to obtain ammonium sulfate product, which is returned to ingredients for recycling. Distilled water recovery.

At the same time, ammonium borate in filtrate is concentrated. The ammonium borate in the filtrate was controlled to reach the maximum solubility. No more evaporation and crystallization. The concentrated solution uses the difference of solubility of ammonium borate and ammonium sulfate with temperature by controlling the temperature. After concentration, ammonium borate is obtained by controlling the temperature and crystallization. The remaining ammonium sulfate solution is returned to the mixing process for recycling.

| T/℃  | 0  | 20  | 40  | 60  | 80  | 90  | 100 |
|------|----|-----|-----|-----|-----|-----|-----|
| Solubility of ammonium borate /g | 4.00 | 7.07 | 11.4 | 18.2 | 26.4 | 30.3 | -   |
| Solubility of ammonium sulfate /g | 70.1 | 75.4 | 81.2 | 87.4 | 94.1 | -   | 102 |

3. Conclusion

(1) Magnesium, iron, aluminum and boron in bornite can be converted into water soluble products by roasting bornite with ammonium sulfate. Silicon is converted into water-insoluble silicon dioxide, dissolved, filtered, separated and further processed into wollastonite or silica.
(2) By adding NH$_3$ gas (or (NH$_4$)$_2$CO$_3$ or NH$_4$HCO$_3$) and adjusting pH, the magnesium, iron and aluminum dissolved in water are precipitated, filtered, separated and further made into products.
(3) Ammonium sulfate was crystallized by evaporation crystallization and recycled.
(4) The process can separate and extract the valuable components from the bornite and recycle the chemical raw materials without causing environmental pollution. It is a green and high value-added process.

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