Decomposition test study on short-process mechanical strengthening equipment of alkali decomposition of tungsten ore

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Abstract: The traditional alkali decomposition process and equipment of tungsten ore are limited by the situation that the grade of tungsten ore resources is decreasingly and the impurity content is getting higher and higher. A set of high-efficiency alkali decomposition process equipment of tungsten ore based on mechanical strengthening is researched and developed in this paper. Fourteen groups of mechanical strengthening decomposition tests were carried out on three particle sizes of ore samples, which verifies the feasibility and reliability of strengthening the alkali decomposition of tungsten ore by the test prototype.

1 Introduction
In May, 2009, according to the general requirements of "Guiding Opinions on Promoting the Construction of Strategic Alliance of Industrial Technology Innovation" by six departments including Ministry of Science and Technology and "Building Strategic Alliance of Industry, University and Research Technology Innovation in Key Nonferrous Metals Fields" by China Nonferrous Metals Industry Association, Ruilin Company initiated and jointly established the "Strategic Alliance of Technology Innovation of Nonferrous Heavy Metals Short Process Energy Saving Metallurgical Industry" with 15 units\textsuperscript{[1]}. The establishment of this "alliance" shows that "short process" will become the research direction of enterprises, universities and scientific research units in smelting industry.

On the basis of previous studies, it is the goal of this subject to study the equipment for alkali decomposition of tungsten ore with short process of grinding, alkali cooking, soaking and grinding by mechanical strengthening. In this paper, the equipment is tested and studied.

2 Materials and Methods

2.1 Test raw materials, reagents and equipment
(1) Ore sample:
   tungsten ore are provided by a mineral product company.
   There are wolframite containing more than 25% WO\textsubscript{3}, mixed ore, and scheelite containing more than 33% WO\textsubscript{3} particle size less than 1000\textmu m of all.
   The wolframite with particle size of 250\textmu m (60 mesh) is magnetically separated.
   The particle size of 75\textmu m (200 mesh) is flotation scheelite.
The grain size of 45µm (325 mesh) is finely ground wolframite and scheelite.

(2) Reagents: Sodium hydroxide: flake caustic soda (NaOH≥98%)

(3) Equipment: Test equipment for alkali decomposition of mechanically strengthened tungsten ore is shown in Figure 1.

![Figure 1 Test equipment for alkali decomposition of mechanically strengthened tungsten ore](image)

2.2 Test principle

In order to decompose tungsten concentrate, sodium hydroxide is used, which is a common method in tungsten smelting industry, at home and abroad. But when the calcium content of wolframite concentrate is greater than 1%, the decomposition rate will be greatly reduced, among which scheelite is the most difficult, followed by high calcium wolframite\(^2\). Its reaction formula can be expressed as follows:

\[
\text{(Fe, Mn)}\text{CaWO}_4(\text{s}) + 2\text{NaOH}_{(\text{aq})} = \text{Na}_2\text{WO}_4(\text{aq}) + \text{Fe(OH)}_2(\text{s})[\text{or Mn(OH)}_2(\text{s})]
\]

(1)

\[
\text{CaWO}_4(\text{s}) + 2\text{NaOH}_{(\text{aq})} = \text{Na}_2\text{WO}_4(\text{aq}) + \text{Ca(OH)}_2(\text{s})
\]

(2)

2.3 Factors and levels of decomposition reaction

It is unrealistic to carry out multi-factor and multi-level comprehensive tests, so the orthogonal test method is adopted here according to the ore samples provided by a Mineral Products Co., Ltd.

In order to verify the treatment capacity of mechanically enhanced tungsten ore alkali decomposition equipment for decomposing tungsten minerals, determine the main influencing factors of five factors (grade, calcium content, particle size, alkali dosage and holding time), determine the primary and secondary relationship of each factor affecting the decomposition rate of tungsten minerals, and finally determine the optimal process operation conditions, 14 groups of experiments were designed for verification.

| Table 1 Test Operation Data | level | Sample ore | WO₃ (%) | Ca (%) | Granularity (µm) | Ore input (kg) | Water (l) | Alkali (kg) | Holding time (min) |
|-----------------------------|-------|------------|---------|-------|-----------------|----------------|-----------|-------------|------------------|
| 1                           | 1     | Wolframite | 38.3    | 1.0   | 1000            | 20.23          | 16.22     | 4.01        | 90               |
| 2                           | 2     |            | 25.2    | 1.3   | 1000            | 20.23          | 17.06     | 3.16        | 100              |
| 3                           | 3     |            | 38.3    | 1.0   | 250             | 20.23          | 16.22     | 4.01        | 70               |
| 4                           | 4     |            | 25.2    | 1.3   | 250             | 20.23          | 17.06     | 3.16        | 90               |
| 5                           | 5     |            | 38.3    | 1.0   | 45              | 20.23          | 16.49     | 3.74        | 70               |
| 6                           | 6     |            | 25.2    | 1.3   | 45              | 20.23          | 17.42     | 2.81        | 80               |
| 7                           | 7     | Scheelite  | 42.5    | 13.5  | 1000            | 19.71          | 15.09     | 4.62        | 90               |
| 8                           | 8     |            | 33.8    | 11.0  | 1000            | 19.71          | 15.35     | 4.37        | 110              |
After checking all switches, valves, instruments and meters of the test prototype are in good condition, put sample ore, reagents and clean water into the test prototype as shown in Table 1, close the feed valve, start the heating device and motor, set the operating values, upper limit values, lower limit values and design values of temperature and pressure, set the decomposition time and adjust the rotating speed, and automatically start timing after the temperature reaches the operating values. Pay attention to observe and record the changes of temperature and pressure and the running status of the equipment. After the reaction, the test prototype automatically turns off the heating device and motor, cuts off the power supply, starts the cooling device, opens the discharge valve after the temperature in the reactor drops to 80°C to obtain the reaction product, and calculates the decomposition rate.

3 Results & Discussion

3.1 Test results
The above test records and analysis data are tabulated, and the results are shown in Table 2.

| level | Sample ore     | WO₃ (%) | Ca (%) | Granularity (µm) | Alkali (multiple) | Holding time (min) | Pressure (Mpa) | Mixing speed (r/min) | Decomposition rate (%) |
|-------|----------------|---------|--------|------------------|-------------------|-------------------|----------------|----------------------|------------------------|
| 1     | Wolframite     | 38.3    | 1.0    | 1000             | 1.5               | 90                | 0.8            | 500                  | 99.09                  |
| 2     |                | 25.2    | 1.3    | 1000             | 1.8               | 100               | 0.7            | 500                  | 98.36                  |
| 3     |                | 38.3    | 1.0    | 250              | 1.5               | 70                | 0.8            | 150                  | 99.19                  |
| 4     |                | 25.2    | 1.3    | 250              | 1.8               | 90                | 0.7            | 150                  | 98.15                  |
| 5     |                | 38.3    | 1.0    | 45               | 1.4               | 70                | 0.8            | 50                   | 99.40                  |
| 6     |                | 25.2    | 1.3    | 45               | 1.6               | 80                | 0.7            | 50                   | 98.36                  |
| 7     |                | 42.5    | 13.5   | 1000             | 1.6               | 90                | 0.8            | 450                  | 99.11                  |
| 8     |                | 33.8    | 11.0   | 1000             | 1.9               | 110               | 0.8            | 450                  | 98.58                  |
| 9     | Scheelite      | 42.5    | 13.5   | 75               | 1.6               | 85                | 0.8            | 100                  | 99.18                  |
| 10    |                | 33.8    | 11.0   | 75               | 1.9               | 90                | 0.8            | 100                  | 98.72                  |
| 11    |                | 42.5    | 13.5   | 45               | 1.5               | 85                | 0.8            | 50                   | 99.32                  |
| 12    |                | 33.8    | 11.0   | 45               | 1.8               | 90                | 0.8            | 50                   | 98.78                  |
| 13    | Scheelite (1/6)| 42.5    | 13.5   | 1000             | 1.8               | 90                | 0.8            | 480                  | 99.18                  |
|       | Wolframite (5/6)| 25.2    | 1.3    |                  |                   |                   |                |                      |                        |
| 14    | Scheelite (5/6)| 42.5    | 13.5   | 1000             | 2.0               | 110               | 0.8            | 480                  | 99.05                  |
|       | Wolframite (1/6)| 25.2    | 1.3    |                  |                   |                   |                |                      |                        |
3.2 Analysis and discussion

The amount of alkali used in treating tungsten ore by traditional alkali digestion leaching method is about 2.4 times of the theoretical amount. For example, the WO$_3$ content in the slag after treating wolframite (Ca > 2\%) is as high as 10\% in a factory\[^3\], and that in a Cemented Carbide Factory after treating wolframite concentrate containing Ca 2\% ~ 3\% is as high as 6\% ~ 8\%\[^4\].

Fourteen groups of mechanical strengthening decomposition tests were carried out on three particle sizes of ore samples.

1) wolframite results

According to the results of six groups of tests on wolframite, the content of WO$_3$ and Ca in ore samples are 25.2\% ~ 28.3\% and 1.0\% ~ 1.3\%, respectively. Under the conditions that the amount of alkali is 1.4 ~ 1.8 times the theoretical amount and the decomposition time is 70 ~ 100 min, the decomposition rate is over 98.15\%, with an average decomposition rate of 98.76\%. The fifth group has the best decomposition effect, and the decomposition rate reaches 99.40\% under the loosest decomposition conditions such as alkali dosage, decomposition temperature and decomposition time, because its particle size is 45 \textmu m grade, the content of WO$_3$ is the highest, and the content of Ca is only 1\%, so the effect of mechanical strengthening decomposition is more obvious. The effect of group 4 is a little worse. Although its particle size grade is not the highest, the Ca content is relatively higher by 0.3\%. It can be considered to increase the decomposition rate by appropriately prolonging the decomposition time and increasing the amount of alkali.

2) Scheelite results

According to the results of six groups of scheelite tests, the content of WO$_3$ and Ca in ore samples are 33.8\% ~ 42.5\% and 11.0\% ~ 13.5\%, respectively. Under the conditions that the amount of alkali is 1.5 ~ 1.9 times the theoretical amount and the decomposition time is 85 ~ 110 min, the decomposition rate is over 98.72\%, with an average decomposition rate of 98.95\%. The 11th group has the best effect. Similar to the above wolframite group, the decomposition rate reaches 99.32\% under the most relaxed decomposition conditions, such as alkali dosage, decomposition temperature and decomposition time. It is also because its particle size is 45 \textmu m, and the content of WO$_3$ is the highest and the content of Ca is the lowest, so the effect of mechanical strengthening decomposition is the most obvious. The effect of group 8 is a little worse, its particle size grade is 1000\textmu m, and the content of Ca also reaches 11\%. By prolonging the decomposition time and increasing the amount of alkali, the decomposition rate also reaches 98.58\%.

3) Black and Alite mixed tungsten ore

According to the experimental results of two groups of wolframite mixed ore, the decomposition rate can be increased to more than 99\% under the conditions that the amount of alkali is 1.8 ~ 2.0 times of the theoretical amount and the decomposition time is 90 ~ 110 min, and the decomposition effect of the thirteenth group is slightly better, mainly because the proportion of wolframite is 5/6 of the mixed ore and scheelite is 1/6.

It can be seen that small particle size is the key factor of alkali decomposition of tungsten ore, and calcium content is also one of the sensitive factors.

4. Conclusions

Compared with the traditional process, the results show that:

1) the fine grinding process can be omitted, and the adaptability of mechanically strengthened tungsten ore alkali decomposition equipment to the granularity of tungsten ore raw materials can be improved from 45\textmu m to 75\textmu m ~ 250\textmu m or even 1000\textmu m.

2) Thermodynamic conditions such as temperature, pressure and time of decomposition reaction are relatively low.

3) For wolframite, scheelite and wolframite mixed ore with WO$_3$ content of 25.2\% ~ 42.5\% and Ca content of 1.0\% ~ 13.5\%, the decomposition time is 70 ~ 110 min, the decomposition temperature is 165\degree C ~ 170\degree C, and the decomposition pressure is 0.7\text{MPa} ~ 0.7\text{MPa}.
It can be seen that the experiment is successful and has the value of further expansion and popularization.

Due to the limitation of test conditions and professional fields, the ore samples are in two grades of wolframite and scheelite and the mixed ore made of these two grades of wolframite and scheelite. The range of factors such as particle size grade, grade, calcium content, alkali consumption, decomposition time, decomposition temperature and decomposition pressure is also relatively small. The above tests only stay in the scope of verification, and have not been extended to the multi-factor and multi-level tests that meet the requirements of scientific experiments, so comprehensive test data have not been obtained for statistics. Especially, three factors, such as ore sample position, alkali dosage and decomposition time, should be expanded to carry out orthogonal test.

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