CAUSTIC DECOMPOSITION OF SCHEELITE AND SCHEELITE-WOLFRAMITE CONCENTRATES THROUGH MECHANICAL ACTIVATION

Li Honggui  Liu Maosheng  Sun Peimei  Li Yunjian

(Department of Nonferrous Metallurgy, Central South University of Technology, Changsha, 410083, China)

Abstract Based on physicochemical study of the reaction between scheelite and NaOH, a new decomposition process for scheelite and scheelite-wolframite concentrate, i.e., mechanically activating caustic decomposition has been developed, and it has been successfully used on a commercial scale in 11 tungsten plants in our country. Industrial practice has shown that a tungsten recovery higher than 98% for scheelite concentrate and 99% for scheelite-wolframite mixed concentrate is obtained, under the conditions of NaOH/WO₃ mole ratio of 3.6~4.8, 160~170 °C, and it is suitable to treat almost any sort of tungsten ore concentrates, including low grade complex concentrate, and it is more effective than the traditional soda ash digestion process.

Key words  mechanical activation; scheelite concentrate; caustic decomposition

NaOH digestion process is the most conventional method for the decomposition of wolframite concentrate to extract WO₃ from it. As for scheelite concentrate, on account of the difficulty for CaWO₄ to react with NaOH solution, many metallurgists working in these fields considered that the decomposition of scheelite concentrate by NaOH solution is impossible in commercial conditions. Even in the case of wolframite concentrate, the tungsten recovery will decrease obviously with the increase of the calcium content in it, and a calcium content lower than 1% is required in order to get a tungsten recovery of 97%~98%.

In recent years, we have carried out a series of fundamental study about the following reaction:

\[ \text{CaWO}_4(s) + 2\text{NaOH(aq)} = \text{Ca(OH)}_2(s) + \text{Na}_2\text{WO}_4(aq) \]  \hspace{1cm} (1)

including the determination of its equilibrium constant \(K_a\), its apparent equilibrium constant \(K_r\) and the solubility of Na₂WO₄ in NaOH-H₂O system, and the study of the influence of mechanical activation on the decomposition process. Based on these studies, we have developed a new technology --- mechanically activating decomposition process \(^{1,2}\), and it has been

† Project supported by the Nonferrous Metals Industry Corporation of China

Synopsis of the first author  Li Honggui, professor. Born in 1934. Research areas are: metallurgy of rare metals, hydrometallurgy, mechanico-chemistry. Main awards are: Invention Prize of the National Scientific and Technological Committee of China (2nd class) (1993); Scientific and Technological Achievement Prize of Guangxi Zhuang Autonomous Region (2nd class) (1990); Chinese Excellent Patent Prize of People's Republic of China (1993); Best Patent Prize of the Patent Office of Hunan Province (1990), Excellent Scientists of Hunan Province (1990).

Manuscript received April 8, 1995
adopted in 11 tungsten plants in our country to replace the traditional digestion process, which can only be used to treat wolframite concentrate with less than 0.5%Ca. Industrial practice of these plants has shown that it is suitable to treat almost any sort of tungsten concentrates, such as scheelite concentrate, scheelite-wolframite mixed concentrate, or low grade complex concentrate, and a tungsten recovery of higher than 98% is easily obtained with relatively low NaOH consumption.

1 FUNDAMENTAL STUDY

In order to master the required thermodynamic condition for reaction (1), a lot of experiments have been completed.

1.1 Determination of the Equilibrium Constant $K_a$ and Aparent Equilibrium Constant $K_s$ of Reaction (1)\(^{[3,4]}\)

The apparent equilibrium constant $K_s$ of reaction (1) is defined as:

$$K_s = \frac{c_{NaWO_4}}{c^{3}_{NaOH}}$$

where $c_{NaWO_4}$ and $c_{NaOH}$ are the equilibrium concentrations of Na$_2$WO$_4$ and NaOH, respectively. $K_s$ is related not only to temperature but also to concentration of given system, and it is more effective than $K_a$ when used to characterize the equilibrium condition of the actual decomposition process at high NaOH and Na$_2$WO$_4$ concentrations. From the $K_s$ value we can directly estimate the required NaOH concentration and NaOH/WO$_4$ ratio for the given reaction.

Through a lot of experiments, we determined the $K_s$ value of reaction (1) from both forward and reverse reactions. The relationship between $K_s$ and $c_{NaOH}$ at different temperatures is shown in Fig. 1, from which it is found that $K_s$ increases remarkably with the increase of $c_{NaOH}$ and temperature. For example, at 150°C and $c_{NaOH}$ of 4.06 mol/L, the $K_s$ value increases to $2.06 \times 10^{-4}$, and accordingly the equilibrium concentration of Na$_2$WO$_4$ reaches a value of 0.34 mol/L. Therefore, reaction (1) will occur spontaneously at higher temperature and higher NaOH concentration.

On account of $K_s \sim K_a$, when concentration is nearing zero, we extrapolated the curves in Fig. 1 to $c_{NaOH}=0$, and obtained the $K_s$ value of reaction (1) at different temperatures as shown in Table 1.

<table>
<thead>
<tr>
<th>$t$/°C</th>
<th>$70$</th>
<th>$90$</th>
<th>$130$</th>
<th>$150$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_s \times 10^2$</td>
<td>$1.2$</td>
<td>$2.0$</td>
<td>$5.8$</td>
<td>$10.0$</td>
</tr>
</tbody>
</table>

1.2 Solubility of Na$_2$WO$_4$ in NaOH-H$_2$O System\(^{[5]}\)

In a rotatory equilibrium reactor, we determined the solubility of Na$_2$WO$_4$ in NaOH-H$_2$O system at 60~175°C. The results are summarized in Fig. 2. From Fig. 2, it is shown obviously that the solubility of Na$_2$WO$_4$ decreases sharply with the increase of NaOH concentration. At 150°C and NaOH concentration of 6.0 mol/L, it is only 1.28 mol/L. This indi-
cates that the produced Na₃WO₄ will become saturate and its concentration will no more increase when reaction (1) proceeds with an excess of NaOH. The produced Na₃WO₄ of the further reaction will crystallize as solid. This will be favorable to the decomposition process thermodynamically.

3 Influence of Mechanical Activation on the Decomposition Process

By means of electron spin resonance (ESR), we have studied the structure of both activated (in planetary mills) and not activated scheelite crystals. The ESR spectrums show that the half width $\Delta b$ from 883 Gs for not activated sample increase to 1014 Gs of activated one, which indicated that lattice defect such as paramagnetic centres is increased in mechanical activating process, and correspondingly the activity and the caustic decomposition velocity of activated sample will also increase.

For wolframite, a similar result has been obtained, and it is found that the apparent activation energy of the following reaction

$$(\text{Fe,Mn})\text{WO}_4(s) + 2\text{NaOH(aq)} = \text{FeO(MnO)}(s) + \text{Na}_3\text{WO}_4(aq) + \text{H}_2\text{O}$$

(2)

decreases from 77.33 kJ/mol for not activated samples to 58.94 kJ/mol of activated one.

It must be pointed out that mechanical activation favors the decomposition reaction not only kinetically but also thermodynamically. For example, by means of mechanical activation, the scheelite in reaction (1) will be in the state of high energy level, and its Gibb’s free energy will be higher than that in the standard state, i.e.,

$$G^* - G^o = \Delta G^*$$

$$\Delta G^* > 0$$

where $G^*$ and $G^o$ are the Gibb’s free energy of scheelite in activated state and standard state respectively.

Then the relationship between the Gibb’s free energy change $\Delta G$ in activated state and that $\Delta G^o$ in standard state for the reaction (1) may be expressed as follows:

$$\Delta G = \Delta G^o - \Delta G^*$$

$$\Delta G < \Delta G^o$$

Accordingly, with activated scheelite, reaction (1) may proceed more easily.

From the result of the above study, we have come to a conclusion that the decomposition of scheelite by NaOH solution is possible and the key to success in this process is to create the required thermodynamic and kinetic conditions.

2 INDUSTRIAL PRACTICE

Based on the above fundamental study, we have developed a new technology—mechanically activating decomposition, i.e. tungsten concentrate and NaOH solution are added into a mechanically activating reactor, in which the required physicochemical condition for decomposition is created and the mineral is activated mechanically, so that chemical reactions of decomposition are organically combined with the grinding and mechanical activation of
mineral. Therefore, an effective decomposition is realized.

In this process we have finished laboratory experiments about the decomposition of various tungsten concentrates (including low-grade scheelite concentrate) with NaOH solution, and the optical condition for decomposition is found. Then, in collaboration with Sanhu Mine, we have completed pilot experiments and achieved good results. This new process was immediately adopted by South-East Tungsten Metallurgical Co. Ltd., and other ten tungsten plants to replace their traditional NaOH digestion process. The industrial practice of the present process in these plants is summarized as follows[4].

The main equipment used is mechanically activating reactor designed by us which has a dimension of $\Phi$900 mm $\times$ 1500 mm and a capacity of 600 $\sim$ 650 kg concentrate per batch. The reactor is heated electrically and the maximum working temperature is 180 $^\circ$C, corresponding to a pressure of 1.0 MPa.

The flowsheet is shown in Fig. 3.

Tungsten concentrate with a particulate size of $<$5 mm is added into the reactor directly without grinding. A calculated amount of NaOH may be added as solid or solution. At a given temperature, the tungsten concentrate can be activated and decomposed by NaOH in the reactor for about 1.5 h, then pulp will be discharged and the Na$_2$WO$_4$ solution will be separated from it by filtration.

By means of the new technology, most sorts of tungsten concentrates, especially scheelite concentrate and low-grade mixed scheelite-wolframite concentrate, have been decomposed with a high tungsten recovery and low leaching efficiency of impurities. The average targets of industrial practice in several plants are shown in Table 2 and Table 3. The comparison of the present process with the soda digestion process, which is widely used in the world for the decomposition of scheelite concentrate, is shown in Table 4.

From Table 4, it is obvious that the present process is more effective than the traditional soda digestion process.

Table 2 The results of caustic decomposition of tungsten concentrates by mechanical activation

<table>
<thead>
<tr>
<th>raw materials</th>
<th>decomp. conditions</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>kinds</td>
<td>NaOH/WO$_3$ (mole ratio)</td>
<td>$t$/C</td>
</tr>
<tr>
<td>scheelite</td>
<td>4.4</td>
<td>170</td>
</tr>
<tr>
<td>conc.</td>
<td>4.5</td>
<td>170</td>
</tr>
<tr>
<td>mixed</td>
<td>4.4</td>
<td>170</td>
</tr>
<tr>
<td>conc.</td>
<td>4.4</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>3.6$^{\ast}$</td>
<td>148$^{\sim}$164</td>
</tr>
<tr>
<td>low-grade</td>
<td>7.0</td>
<td>170</td>
</tr>
<tr>
<td>mixed conc.</td>
<td>5.97</td>
<td></td>
</tr>
</tbody>
</table>

Notes: $^\dagger$ Average value of 5 results; $^\dagger\dagger$ Average value of 7 results
Table 3  Leaching efficiency of impurities in the present process

<table>
<thead>
<tr>
<th>kinds</th>
<th>WO_3 (%)</th>
<th>Ca (%)</th>
<th>Sn (%)</th>
<th>As (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixed conc.</td>
<td>70.51</td>
<td>3.42</td>
<td>10.33</td>
<td>5.57</td>
<td></td>
</tr>
<tr>
<td>low-grade mixed conc.</td>
<td>34.57</td>
<td>5.97</td>
<td>1.83</td>
<td>4.47</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Table 4  The comparison of caustic mechanically activating decomposition (CMAD) with soda digestion (SD)

<table>
<thead>
<tr>
<th>working condition</th>
<th>grinding</th>
<th>t/℃</th>
<th>P/MPa</th>
<th>consumption of NaOH or Na_2CO_3 kg/kg•WO_3</th>
<th>recovery of WO_3 (%)</th>
<th>specific capacity of reactor V (WO_3/M²•Batch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAD without pregrinding</td>
<td>160~170</td>
<td>0.4~0.5</td>
<td>NaOH:1.7~0.8</td>
<td>≥98</td>
<td>0.35~0.4</td>
<td></td>
</tr>
<tr>
<td>SD pregrinding to 0.045 mm</td>
<td>225~235</td>
<td>2.5</td>
<td>Na_2CO_3:1.35~1.40</td>
<td>95~98</td>
<td>0.2~0.25</td>
<td></td>
</tr>
</tbody>
</table>

3 CONCLUSION

Based on fundamental study, a new caustic decomposition process—mechanically activating decomposition process has been developed and its industrial practice has indicated that it is suitable to treat most sorts of tungsten concentrates and is more effective than traditional soda digestion process.

References