An innovative process for extracting boron and simultaneous recovering metallic iron from ludwigite ore

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A B S T R A C T

Ludwigite ore has not yet been utilized on an industrial scale due to its complex mineralogy and fine mineral dissemination in China. Boron–iron separation and dissolution activity of boron-bearing minerals in alkaline liquor are the two key issues in the utilization of ludwigite ore, governing the boron recovery as well as operating cost. This paper proposes an innovative process for extraction of boron and iron from ludwigite ore based on coal-based direct reduction process with sodium carbonate (Na2CO3). The novel process involves reduction roasting, combined leaching and grinding of reduced ludwigite ore, followed by magnetic separation of leach residue, and experimental validation for each of the processing steps is demonstrated. Alkali-activation of boron and metallization of iron were synchronously achieved during carbothermic reduction of ludwigite ore in the presence of Na2CO3. Consequently, boron was readily extracted in the form of sodium metaborate (NaBO2) with water at room temperature during ball mill grinding, and metallic iron powder was recovered from the leaching-filtering residue by magnetic separation. Boron extraction of 72.1% and iron recovery of 95.7% with corresponding iron grade of 95.7% in the magnetic concentrate were achieved when ludwigite ore was reduced with 20% sodium carbonate at 1050 °C for 60 min.

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1. Introduction

Boron and boron compounds, with properties such as fire retardant, heat resistance, high hardness, high strength, wear resistance and catalytic performance, are widely used in the industrial and agricultural sectors (Zheng, 2008). Chinese boron resources are of low quality, averaging about 8.4% B2O3, in comparison to the Turkish and America reserves, which average about 26–31% and 25.3–31.9% B2O3, respectively (Angulo and Crabgle, 2011). Ludwigite ore is abundant in Liaoning province of China, accounting for 57% boron resources of the country, containing 28.43 Mt B2O3 resources (Liu et al., 2006). However, it has not yet been utilized on an industrial scale due to its complex mineralogy and fine mineral dissemination in China (Wang et al., 2012).

Generally, boron–iron separation and dissolution activity of boron-bearing minerals in alkaline liquor are the two key issues in the utilization of ludwigite ore, governing the boron recovery as well as operating cost (Chen et al., 1996). Current processes for boron–iron separation of ludwigite ore involves a blast furnace or a solid pre-reduction followed by electric arc furnace melting and bears the advantage of mature technology for iron production. However, both of these two current routes face the same crucial problem that the molten boron-rich slag has to be cooled slowly (cooling rate less than 2 °C/min in the temperature range of 1200–900 °C) to obtain the alkali-dissolution activity of boron, which limits the utilization of boron resource (Wang et al., 2012; Zhan et al., 2007).

Direct reduction process is an effective way for the treatment of complex iron ores (Jiang et al., 2007). Aiming at comprehensive utilization of ludwigite ore based on direct reduction roasting process, sodium carbonate was employed to activate boron and simultaneously intensify the reduction of iron oxides. A technological route of combined metallic reduction roasting, leaching, and grinding followed by magnetic separation is proposed in this paper. Moreover, effects of sodium carbonate on boron extraction, as well as grade and recovery of iron in the magnetic concentrate are investigated. The new method does not require slow cooling and therefore may be more economic in comparison with the existing methods.

2. Experimental

2.1. Materials

The sodium carbonate used in this work was of analytical grade. Pulverized lignite with fixed carbon content of 59.42 wt.% and volatile content of 29.25 wt.% was used as the reductant.
Ludwigite ore was taken from Liaoning province of China, and ground to 80 wt.% passing 0.074 mm. The chemical composition of the ludwigite ore is shown in Table 1. XRD results (as shown in Fig. 1) indicates that the ludwigite ore is mainly composed of magnetite (Fe$_3$O$_4$) and szajbelyite (Mg$_2$(OH)[B$_2$O$_4$(OH)]), as well as (Mg$_3$Si$_2$O$_5$(OH)$_4$) and magnesite (MgCO$_3$).

### 2.2. Methods

The overall experimental flow sheet is presented in Fig. 2. The ludwigite sample was thoroughly mixed with or without 20% sodium carbonate for green ball production. The green balls with diameter of 12–16 mm were dried at 120 °C for 2 h. Carbothermic reduction of the dried balls was conducted in a vertical resistance furnace of which more details were given in our previous work (Li et al., 2012). After roasting, the reduced balls were cooled to room temperature in a stainless steel pot isolated from atmospheric oxygen. A sub-sample of the cooled, reduced balls was ground to less than 0.074 mm for metallic iron and total iron content determination by chemical titration method, as well as boron content by inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. Thus, the metallic iron ratio of iron was calculated according to the following equation:

$$\eta = \left( \frac{\text{Fe}_{\text{metallic}}}{\text{Fe}_{\text{total}}} \right) \times 100\%$$  \hspace{1cm} (1)

where $\eta$ is the metallic iron ratio of the reduced sample; $\text{Fe}_{\text{total}}$ is the total iron content of the reduced sample and $\text{Fe}_{\text{metallic}}$ is the metallic iron content of the reduced sample.

Another sub-sample of the reduced balls was crushed to the particle size less than 1 mm, and then charged into an XMQ φ 240 × 90 ball mill for grind-leaching test with a liquid to solid mass ratio of 1 at room temperature. After filtration of the slurry, the filter liquor was assayed for boron content. Filter residue was further pulped and separated in an XCGS-73 Davis Tube using a magnetic field intensity of 0.1 T. Subsequently, the magnetic material of metallic iron was obtained. The extraction of boron was calculated as shown in the following equation:

$$\gamma = \left( \frac{V \times C}{m_0 \times x} \right) \times 100\%$$ \hspace{1cm} (2)

where $\gamma$ is the extraction of boron; $x$ is the boron content in reduced sample, %; $C$ is the concentration of boron of filter liquor, g/L; $m_0$ is the mass of reduced sample before grind-leaching, g; and $V$ is the volume of filter liquor, L. Meanwhile, iron recovery was obtained according to the following equation:

$$\varepsilon = \left( \frac{m_2 \times \delta}{m_1 \times \beta} \right) \times 100\%$$ \hspace{1cm} (3)

where $\varepsilon$ is the recovery of iron; $m_1$ is the feed mass of magnetic separation, g; $\beta$ is the iron content in the feed, %; $m_2$ is the mass of magnetic concentrate, g; and $\delta$ is the iron content in the magnetic concentrate, %.

### 3. Results and discussion

#### 3.1. Boron extraction and iron recovery from reduced ludwigite ore in the absence/presence of sodium carbonate

The grind-leaching and magnetic separation results of reduced ludwigite ore obtained at varying temperatures in the absence/presence of Na$_2$CO$_3$ are shown in Table 2. As can be seen from Table 2 that boron extraction is extremely low (less than 2%). With reducing temperature increased from 900 °C to 1100 °C, the iron grade and recovery in the magnetic concentrate increased from 80.5% to 84.0% and 63.0% to 92.1%, respectively.

The results show that both the extraction of boron and recovery of iron were enhanced by the addition of Na$_2$CO$_3$. Compared with

### Table 1

Main chemical composition of the ludwigite ore sample/wt.%.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Fe$_{\text{total}}$</th>
<th>FeO</th>
<th>B$_2$O$_3$</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>S</th>
<th>P</th>
<th>LOI</th>
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<tbody>
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<td>Content</td>
<td>52.11</td>
<td>24.65</td>
<td>5.25</td>
<td>13.05</td>
<td>5.36</td>
<td>0.39</td>
<td>0.62</td>
<td>1.21</td>
<td>0.014</td>
<td>2.45</td>
</tr>
</tbody>
</table>

*LOI: loss on ignition.*