Optimal Combination of Calcination and Reduction Conditions as well as Na$_2$SO$_4$ Additive for Carbothermic Reduction of Limonite Ore

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The optimal carbothermic reduction temperature of limonite ore and the influence of calcining on these were investigated. In addition, the impact of the addition of Na$_2$SO$_4$ on limonite ore which had been calcined before reduction at optimal carbothermic conditions was also investigated. XRD analysis, BET-specific surface area analysis, bromine methyl alcohol solution analysis, and chemical compositional analysis were used in order to obtain the associated parameters.

The best nickel grade and recovery rate of the 673 K-calcined limonite ore can reach >30 mass% and 90.2 mass%, respectively, when the reduction temperature is 1373 K, with a reduction time of 30 min, and a carbon-oxygen ratio of 0.6. This is because the 673 K-calcined limonite ores have the highest specific surface area of 46.8 m$^2$/g with pores in the size of 29.7 Å. The addition of Na$_2$SO$_4$ by 5 mass% resulted in the best nickel grade of >30 mass% and the best recovery rate of 93.8 mass% at the same reduction temperature, time and carbon-oxygen ratio.

Keywords: limonite, calcination, carbothermic reduction, additive

1. Introduction

Nickel (Ni) is a ferromagnetic element with a high melting point at 1728 K and thermal endurance, excellent corrosion-resistance and antioxidation, good mechanical properties, superior malleability and chemical stability. Its major application is for the smelting of steel and iron, especially for the manufacturing of stainless steel, which accounts for 61% of the total consumption of metallic nickel. The nickel that has been explored in the world are approximately 160 million tons, of which 30–40% is nickel sulfide ore and 60–70% is nickel oxide ore. Since the technology used to extract nickel from the nickel sulfide ore is more mature, 60–70% of nickel production comes from this. However, the amount of nickel sulfide ore which can be exploited is limited, and the reserves of nickel oxide ore are still rather high and the mining cost is relatively low. As such, the use of nickel oxide ore has become an important issue.

An oxidized-type of laterite nickel ore is formed from the mass nickel-containing serpentine in tropical or subtropical zones through long-term weathering and erosion effects. It is an oxidized-type of silicate mineral with a loose clay soil appearance containing hydrous oxides of iron, aluminum and silicon. The mineral vein of laterite nickel ore can generally be divided into two layers: the upper layer is limonite-type laterite nickel ore, which contains more iron and less nickel (about 0.8–1.5%); the lower layer is saprolite-type magnesium silicate nickel ore, which contains less iron and more nickel, and the nickel content is about 1.5–2.5%.

At present, there are three categories of refining processes for nickel: the hydrometallurgical process, re-refining process and hybrid hydrometallurgical-fire refining process. Two types of hydrometallurgical processes are used in industrial production, reduction roasting-ammonia leaching (AL) and high pressure acid leaching (HPAL). Although the recovery rate is high, this process is now used less than previous days because of its low economic benefits and the large amount of toxic waste it produces, thus causing serious pollution if piled in unsheltered conditions. The smelting technologies include a rotary kiln-electric furnace (RKEF) process, a sintering-blast furnace sulfidation smelting process and a sintering-blast furnace smelting process. The industrial application of hybrid hydrometallurgical-fire refining technology can be found in the Nippon Yakin Company’s Oheyama smelting plant. Laterite nickel ore has many applications, and can be used to produce intermediate products like nickel oxide, nickel-sulfur or nickel iron alloy, of which the nickel-sulfur and nickel oxide can be used by nickel refineries to solve the problem of insufficient nickel sulfide. A nickel-iron alloy can also be used as a substitute for pure nickel addition in the manufacturing of stainless steel and low-nickel alloy steel.

According to the Gibbs free energy of the Ellingham diagram, the lower the coordinate in the diagram, the lower and more stable the free energy, which indicates that the oxides in the lower part of the diagram will stably exist, and thus be difficult to reduce. In contrast, in the upper range of the Ellingham diagram the existence of oxides causes higher free energy in the reaction, which then destabilizes the oxides, making them more readily reduced. This concept can be applied to the selected reduction of oxides, where manufacturers can allow certain oxides to be reduced by controlling the temperature and reducing atmosphere, based on the associated Ellingham diagram. By applying this mechanism to laterite nickel ore in a carbothermic reduction experiment, the reduction of the nickel oxide will take place before the iron oxide starts to be reduced. In addition, by adjusting the amount of reductant that is added, as well as the reduction temperature and reduction time, one can control the reduction level of selected oxides.
With the addition of reductants, and with the appropriate control of temperature and time, the carbothermic reduction process of laterite nickel ore can be conducted in order to extract the metal phases of nickel and iron from the mineral phase.\(^{16-20}\) Many studies on the thermal analysis of laterite nickel ore report that the free water is removed at temperatures between 333 K and 383 K, dehydration occurs at 553 K, the serpentine phase transforms into enstatite and olivine at 898 K, and the recrystallization reaction happens at 1093 K.\(^{21}\)

Zevgolis et al.\(^{22}\) pointed out that a higher specific surface area is helpful to the carbothermic reduction of laterite nickel ore, and the limonite-type laterite nickel ore has a lower reduction rate. As indicated by previous study,\(^{23}\) the mineral phase of limonite-type laterite nickel ore can be simplified by calcining at 1173 K. Therefore, after being calcined in advance, the following carbothermic reduction process (at a re-action temperature of 1373 K) could enhance the nickel grade of the laterite nickel ore, accompanied by a lower recovery rate. Yang et al.\(^{24}\) proposed that garnieritic-type laterite nickel ore has a phase transformation at the calcining temperature of 873–973 K, and the accompanying increase in surface area and the generation of fine pores are also helpful to the carbothermic reduction. At a calcining temperature of 973–1123 K, laterite nickel ore will start its recrystallization, reducing its specific surface area and generating bigger pores, which are detrimental to the following carbothermic reduction. Therefore, for garnieritic-type laterite nickel ore, the calcining temperature beneficial to the carbothermic reduction is 873–973 K.

Sodium salts or other alkaline additives can react with minerals containing aluminum oxide and silicates, thus forming sodium aluminate or sodium aluminum silicates. Moreover, the sodium salts can intensify the reduction of iron oxides, resulting in the separation of iron from aluminum and silicon.\(^{25}\) As indicated by Li et al.,\(^{26,27}\) the addition of Na\(_2\)SO\(_4\) to the carbon-bearing pellets of laterite nickel ore is beneficial to the reduction of nickel, resulting in a better nickel grade and recovery rate. Sun et al.\(^{28}\) studied the influence of four additives (Na\(_2\)SO\(_4\), Na\(_2\)CO\(_3\), CaCO\(_3\) and CaSO\(_4\)) on the carbothermic reduction of low-nickel high-iron laterite nickel ore. Their results showed that Na\(_2\)SO\(_4\) suppressed the reduction of iron, and that the dissolution of Na\(_2\)SO\(_4\) could generate sulfur which would reduce the surface energy and melting point of the nickel-iron pellets, prompting the growth of the pellets and inducing their separation from other oxide-phase compositions. After being dissolved, Na\(_2\)SO\(_4\) could generate alkaline oxides and sulfur. The sulfur would then react with iron to produce iron sulfide, suppressing the reduction of iron. Meanwhile, the alkaline oxides could improve the reduction effect on the carbothermic reduction.

By studying the reduction of 1173 K-calcined limonite-type laterite nickel ore under different reaction times and carbon-oxygen ratios, this study has obtained the optimal carbothermic reduction conditions. The influence of calcining temperatures (673, 873 and 1173 K) on the ore’s nickel grade and recovery rate when it was reduced under fixed carbothermic reduction conditions was also examined. Since the added Na\(_2\)SO\(_4\) can improve the nickel grade and recovery rate of laterite nickel ore, this research studied the optimal addition level that could yield the best nickel grade and recovery rate to meet industrial standards: 15–16 mass% for nickel grade and 85 mass% for the recovery rate.

2. **Experimental Procedure**

The experimental flow chart of this research is shown in Fig. 1. The first step was to prepare the samples for the experiment. In order to conduct the calcination experiment, Indonesian limonite-type laterite nickel ores undergone heat treatment at 673, 873 and 1173 K, each for 2 h, in advance. The ores and reductants (graphite powder) were then separately ground into fine powders, which could pass through a 200-mesh sieve, and these were dried at 378 K until they had no free water. Next, the powders were mixed based on the calculated carbon-oxygen ratio (C/O), and the additive (Na\(_2\)SO\(_4\)) and binding agent (Bentonite) were then added. Finally, the powders were manually rolled into small pellets with a diameter of about 12 mm.

The procedures of the high temperature carbothermic reduction experiment are as follows: Let the inert gas (N\(_2\), 500 cc/min) flow into the muffle furnace; start the furnace and let the temperature rise to 1373 K. Put the sample pellets into the furnace; conduct the carbothermic reduction process and then, take the sample out of the furnace after the preset reaction time is completed. Place the hot sample into a nitrogen-flowing cooling box until it is chilled to room temperature. A schematic diagram of the furnace is shown as Fig. 2.

The optimal carbothermic reaction parameters with the best nickel grade and recovery rate were investigated through the carbothermic reduction process of 1173 K-calcined limo-
nite ore while its reaction time varied between 10 to 40 min and the carbon-oxygen ratio ranged between 0.4 and 0.9. In addition, the influence of different calcining temperatures (673, 873, and 1173 K) on the nickel grade and recovery rate under fixed carbothermic reduction conditions was also probed. The impact of the addition of Na2SO4 (5, 10 mass%) on the carbothermic reduction of limonite ore calcined at different temperatures (673, 873 and 1173 K) was studied.

Analysis of the iron samples was carried out as follows: 1. Compound analysis of the reduction products through the X-ray diffraction method; 2. Analysis of the nickel content by bromine methyl alcohol solution analysis; 23) 3. Chemical analysis of the content of each element by the Inductively Coupled Plasma (ICP-OES) method to calculate the nickel grade and recovery rate; 4. Measurement of the specific surface area of the pellets and the average size of their pores before reduction through BET specific surface area analysis (using a Surface Area & Mesopore Analyzer).

The nickel grade and recovery rate were calculated using the following equations:

\[ N_{\text{grade}}(\%) = \frac{M_{\text{Ni}}(\%)}{M_{\text{Ni}}(\%) + M_{\text{Fe}}(\%)} \times 100 \]  
\[ N_{\text{recovery}}(\%) = \frac{M_{\text{Ni}}}{T_{\text{Ni}}} \times 100 \]

\( M_{\text{Ni}} \): Content of metal Ni  
\( M_{\text{Fe}} \): Content of metal Fe  
\( T_{\text{Ni}} \): Total content of Ni

For chemical analysis, the major elements of limonite ore calcined under different temperatures are shown in Table 1. The contents of nickel, Fe2O3, and FeO in the uncalcined limonite ore were 1.18 mass%, 59.7 mass% and 23.4 mass%, respectively. For the 673 K-calcined limonite ore, the contents of nickel, Fe2O3 and FeO were 1.41 mass%, 59.3 mass% and 3.72 mass%, respectively. For the 673 K-calcined limonite ore, the contents of nickel, Fe2O3 and FeO were 1.37 mass%, 67.2 mass% and 0.37 mass%, respectively. For the 1173 K-calcined limonite ore, the contents of nickel, Fe2O3 and FeO were 1.28 mass%, 70.0 mass% and 0.12 mass%, respectively.

As the temperature rose, the iron oxide phase was oxidized into Fe2O3. After calcination, the mass fractions of nickel and iron increased because of the removal of water and other impurities. Table 2 shows the chemical composition of bentonite, which is used as the binding agent for pelleting.

Table 1 Chemical analysis of limonite ores calcined at different temperatures, unit: mass%.

<table>
<thead>
<tr>
<th>Calcining Temp. (T/K)</th>
<th>Ni</th>
<th>Co</th>
<th>CaO</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>Fe2O3</th>
<th>FeO</th>
<th>TFe</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>1.18</td>
<td>0.16</td>
<td>0.15</td>
<td>4.41</td>
<td>4.50</td>
<td>10.2</td>
<td>59.7</td>
<td>23.4</td>
<td>41.1</td>
</tr>
<tr>
<td>673</td>
<td>1.41</td>
<td>0.13</td>
<td>0.25</td>
<td>5.64</td>
<td>4.78</td>
<td>11.1</td>
<td>59.3</td>
<td>3.72</td>
<td>44.4</td>
</tr>
<tr>
<td>873</td>
<td>1.37</td>
<td>0.13</td>
<td>0.26</td>
<td>6.10</td>
<td>5.17</td>
<td>11.9</td>
<td>67.2</td>
<td>0.37</td>
<td>47.3</td>
</tr>
<tr>
<td>1173</td>
<td>1.28</td>
<td>0.01</td>
<td>0.20</td>
<td>6.11</td>
<td>5.24</td>
<td>11.9</td>
<td>70.0</td>
<td>0.12</td>
<td>49.0</td>
</tr>
</tbody>
</table>

H2O). When the temperature reached 794 K, the crystal water was removed, the goethite (including limonite rich in iron phase) was pyrolyzed into magnetite and the serpentine was pyrolyzed into olivine and enstatite. Recrystallization took place at 1059 K.

Figures 3(a) and 3(b) show the XRD analysis results of limonite ore (a) calcined at 673 K and (b) calcined at 873 K.

Table 2 Chemical composition of bentonite, unit: mass%.

<table>
<thead>
<tr>
<th>Elemental</th>
<th>P</th>
<th>S</th>
<th>CaO</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>K2O</th>
<th>Na2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>0.03</td>
<td>0.37</td>
<td>4.63</td>
<td>1.25</td>
<td>12.9</td>
<td>62.8</td>
<td>0.62</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Fig. 3 XRD analysis results of limonite ore (a) calcined at 673 K and (b) calcined at 873 K.
3. Results and Discussion

3.1 Optimal reduction conditions versus reduction results of 1173 K-calcined limonite ores

Previous study indicated that the best reduction temperature was 1373 K for calcined limonite ore. However, this earlier research focused on the optimal carbothermic reduction parameters for limonite-type laterite nickel ore by examining reactions under various reduction times and carbon-oxygen ratios. Table 3 shows the chemical composition of limonite ore which was calcined at 1173 K for 2 h in advance, and then reduced for different reduction times under a temperature of 1373 K with a carbon-oxygen ratio of 0.7. The results indicate that the content of nickel and iron increases as the reduction time is prolonged; the iron content increased from 0 to 3.51 mass%, and the nickel content increased from 0.25 to 0.98 mass%.

During the reduction process, the carbon combined with iron oxide and nickel oxide to form a metallic iron-nickel phase, reducing the reacted content of carbon from 8.30 to 5.87. Figure 4 shows a bar diagram displaying the nickel grade and recovery rate of the limonite ore which had been calcined at 1173 K for 2 h in advance, and then reduced for different reduction times under a temperature of 1373 K with a carbon-oxygen ratio of 0.7. As the reduction time was prolonged, the nickel grade first declined from 100 mass% to 21.8 mass% and then, remained constant. This was because metallic iron gradually formed from the reduction process as time passed, thus reducing the nickel grade.

The nickel recovery rate first increased and then declined. As time passed, the rate increased from 18.5 mass% to 75 mass%, which meant the ore was gradually reduced to metallic iron, consequently lowering the nickel grade. Along with the rising carbon-oxygen ratio, the nickel recovery rate first rose from 60.3 mass% to 79.5 mass% and then stayed constant. According to Table 3 and Fig. 4, a 30-min reduction time could generate the best nickel grade (20.6 mass%) and recovery rate (75.0 mass%). However, it is noted that a lot of carbon remained in the pellets after reduction for 30 min; therefore, further investigation regarding the best carbon-oxygen ratio was needed to find the optimal reduction parameters.

Table 4 shows the chemical analysis results of calcined (1173 K, 2 h) limonite ore which was reduced for 30 min at 1373 K under different carbon-oxygen ratios. From the table, it is noted that as the carbon-oxygen ratio went up, the contents of the metallic iron and nickel also increased from 0.18 mass% to 7.46 mass% and from 0.76 mass% to 1.01 mass%, respectively. With the increase in carbon-oxygen ratio, the content of carbon increased from 5.12 mass% to 9.04 mass%. Figure 5 shows a bar diagram of the nickel grade and recovery rate of calcined (1173 K, 2 h) limonite ore which was reduced for 30 min at 1373 K under different carbon-oxygen ratios.

The results show a declining trend for the nickel grade from 80.85 mass% to 11.9 mass%, accompanied by an increase in the carbon-oxygen ratio, as sufficient carbon content could reduce the associated content of ore into metallic iron, consequently lowering the nickel grade. Along with the rising carbon-oxygen ratio, the nickel recovery rate first rose from 60.3 mass% to 79.5 mass% and then stayed constant. According to Table 4 and Fig. 5, both the best nickel grade (22.1 mass%) and recovery rate (78.6 mass%) were obtained when the carbon-oxygen ratio was 0.6.

Integrating these discoveries regarding reduction time and carbon-oxygen ratio, the best nickel grade (22.1 mass%) and recovery rate (78.6 mass%) of calcined (1173 K for 2 h) limonite-type laterite nickel ore could be obtained under a reduction temperature of 1373 K, a reduction time of 30 min and a carbon-oxygen ratio of 0.6. In order to meet industrial standards: a 15–16 mass% for nickel grade and 85 mass% recovery rate. Table 4 provides a reference for selecting the optimal combination of calcination and reduction conditions as well as Na2SO4 additive for carbothermic reduction of limonite ore.

![Fig. 4](image-url) Relationship between reduction time and nickel grade and recovery rate of calcined (1173 K, 2 h) limonite ore reduced under 1373 K with C/O ratio of 0.7, unit: mass%.

![Fig. 5](image-url) Relationship between nickel grade and recovery rate of calcined (1173 K for 2 h) limonite ore reduced at 1373 K for 30 min with different C/O ratios.

Table 3 Reduction time vs. chemical composition of calcined (1173 K, 2 h) limonite ore reduced under 1373 K with C/O ratio of 0.7, unit: mass%.

<table>
<thead>
<tr>
<th>Time (t/min)</th>
<th>TFe</th>
<th>FeO</th>
<th>Fe</th>
<th>TNi</th>
<th>Ni</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>44.2</td>
<td>23.8</td>
<td>/</td>
<td>1.37</td>
<td>0.25</td>
<td>8.30</td>
</tr>
<tr>
<td>20</td>
<td>46.0</td>
<td>45.7</td>
<td>0.24</td>
<td>1.39</td>
<td>0.87</td>
<td>7.18</td>
</tr>
<tr>
<td>30</td>
<td>47.4</td>
<td>53.6</td>
<td>3.67</td>
<td>1.27</td>
<td>0.95</td>
<td>6.17</td>
</tr>
<tr>
<td>40</td>
<td>47.3</td>
<td>50.9</td>
<td>3.51</td>
<td>1.44</td>
<td>0.98</td>
<td>5.87</td>
</tr>
</tbody>
</table>

Table 4 C/O ratio vs. chemical composition of calcined (1173 K, 2 h) limonite ore reduced under 1373 K with C/O ratio of 0.7, unit: mass%.

<table>
<thead>
<tr>
<th>C/O</th>
<th>Fe</th>
<th>TNi</th>
<th>Ni</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.18</td>
<td>1.26</td>
<td>0.76</td>
<td>5.12</td>
</tr>
<tr>
<td>0.5</td>
<td>0.40</td>
<td>1.26</td>
<td>0.84</td>
<td>5.86</td>
</tr>
<tr>
<td>0.6</td>
<td>3.49</td>
<td>1.26</td>
<td>0.99</td>
<td>6.08</td>
</tr>
<tr>
<td>0.7</td>
<td>3.67</td>
<td>1.27</td>
<td>0.95</td>
<td>6.17</td>
</tr>
<tr>
<td>0.8</td>
<td>4.46</td>
<td>1.27</td>
<td>0.96</td>
<td>7.62</td>
</tr>
<tr>
<td>0.9</td>
<td>7.46</td>
<td>1.27</td>
<td>1.01</td>
<td>9.04</td>
</tr>
</tbody>
</table>
Table 5  Chemical composition results of limonite ore calcined at different temperatures and reduced under optimal reduction conditions, unit: mass%.

<table>
<thead>
<tr>
<th>Calcining Temp. (T/K)</th>
<th>TNi</th>
<th>Ni</th>
<th>TFe</th>
<th>FeO</th>
<th>Ni grade</th>
<th>Ni recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>1.43</td>
<td>1.29</td>
<td>47.9</td>
<td>46.0</td>
<td>&gt;30</td>
<td>90.2</td>
</tr>
<tr>
<td>873</td>
<td>1.44</td>
<td>1.05</td>
<td>47.9</td>
<td>46.2</td>
<td>&gt;30</td>
<td>72.9</td>
</tr>
<tr>
<td>1173</td>
<td>1.26</td>
<td>0.99</td>
<td>47.7</td>
<td>52.6</td>
<td>22.1</td>
<td>78.6</td>
</tr>
</tbody>
</table>

Table 6  BET analysis results of limonite ore calcined at different temperatures.

<table>
<thead>
<tr>
<th>Calcining Temp. (T/K)</th>
<th>Surface Area (m²/g)</th>
<th>Average pore radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>25.5</td>
<td>31.0</td>
</tr>
<tr>
<td>673</td>
<td>46.8</td>
<td>29.7</td>
</tr>
<tr>
<td>873</td>
<td>30.7</td>
<td>44.9</td>
</tr>
<tr>
<td>1173</td>
<td>12.5</td>
<td>61.5</td>
</tr>
</tbody>
</table>

and above for the recovery rate, and to make up for an insufficient recovery rate, this research also examined other parameters. From Fig. 3, it is noted that three reactions happened around 657 K, 794 K and 1059 K. Therefore, the corresponding effects of the calcining temperatures of 673 K, 873 K and 1173 K on the optimal reduction parameters of limonite-type laterite nickel ore were investigated.

3.2  Calcining temperatures versus carbothermic reduction results

According to previous research,26,28) the reduction efficiency of laterite nickel ore calcined at 873–1273 K is good, while that for limonite-type laterite nickel ore is still not suitable for reduction even after being calcined. Therefore, this research investigated the effects of calcining temperatures (673, 873 and 1173 K) on the optimal reduction parameters. Table 5 shows the chemical composition of limonite ore calcined at three temperatures and reduced under optimal reduction conditions. The table shows that the metallic nickel content declined from 1.29 mass% to 0.99 mass% as the calcining temperature increased. Therefore, when the calcined temperature was 673 K, the best nickel recovery rate was obtained and relatively less metallic iron was produced. Meanwhile, the nickel grade decreased in the range of 22.1–30 mass% as the calcined temperature increased because the metallic iron was gradually reduced from its oxides leading to a decline in the nickel grade. The nickel recovery rate first declined from 90.2 mass% to 72.9 mass% and then rose to 78.6 mass% along with the rising temperature. Table 6 shows the results of the BET analysis of the carbon-containing pellets of limonite ore calcined at three temperatures. These indicate that as the calcining temperature rose, the specific surface area first increased from 25.5 m²/g to 46.8 m²/g and then, decreased to 12.5 m²/g; and the average pore size first decreased from 31.0 Å to 29.7 Å and then, increased to 61.5 Å.

The results show that the lattice of the uncalcined limonite ore whose specific surface area was smaller, contained free water, crystal water and hydrogen cations. When the calcining temperature was 673 K, dehydroxylation occurred, removing some crystal water and hydrogen cations, leaving pores with similar sizes and thus increasing the specific surface area. Under a calcining temperature of 873 K, phase transformation of limonite ore began, and its serpentine phase transformed to olivine and enstatite, decreasing the specific surface area and slightly enlarging the pore size. Recrystallization started at 1173 K, and a sintering effect occurred in the interior of the pellets, making the pore size bigger and resulting in a large loss of specific surface area. The whole process is illustrated in Fig. 6.

According to the reaction formula 2

\[ 2αFeOOH → αFe_3O_4 + H_2O \]

and 30 min and a carbon-oxygen ratio of 0.6). In order to improve limonite ore calcined at 873 K and 1173 K and to make the nickel grades and recovery rates reach 15–16 mass% and 85 mass%, respectively, as required by industrial standards, the previous researchers25–28) proposed the addition of Na₂SO₄, which could effectively increase the reduction of metallic nickel. This study thus probed the effects of the addition of different amounts of Na₂SO₄ on the nickel grade and recovery rate of limonite ore which was calcined at different temperatures in advance and then reduced under optimal reduction parameters.

3.3  Impact of different amounts of additives

Table 7 shows the chemical analysis results of calcined (673, 873 and 1173 K) limonite ore which was reduced under optimal reduction parameters. The results indicate that the metallic nickel content of 673 K-calcined limonite ore increased from 1.29 mass% to 1.40 mass%, as the amount of...
Na$_2$SO$_4$ added rose during the reduction process. For 873 K-calcined limonite ore, the metallic nickel content grew from 1.05 mass% to 1.50 mass% along with the increase of Na$_2$SO$_4$ during the carbothermic reduction process. Furthermore, the increase of Na$_2$SO$_4$ during the carbothermic reduction process of 1173 K-calcined limonite ore caused the metallic nickel content to rise from 0.99 mass% to 1.48 mass%. Generally speaking, the metallic nickel content of limonite ore (calcined at 673 K, 873 K and 1173 K) grew along with the increase in Na$_2$SO$_4$ in the carbothermic reduction process. Therefore, it is deduced that the addition of Na$_2$SO$_4$ in the reduction process could effectively reduce the ore back to a metallic nickel phase.

The results also show that the nickel grade of 673 K-calcined limonite ore increased to 21.6 mass% with an increase in the amount of Na$_2$SO$_4$ added during the reduction process. 873 K-calcined limonite ore displayed a similar trend, as its nickel grade increased to 16.5 mass% as the amount of Na$_2$SO$_4$ added increased. However, the 1173 K-calcined limonite ore presented a different pattern; its nickel grade first rose from 22.1 mass% to 23.1 mass% and then, descended to 17.4 mass% as the amount of Na$_2$SO$_4$ added increased. When the amount of additive increased, it was easier to reduce the ore to a metallic iron phase, causing the nickel grade to decline.

After being reduced, the nickel recovery rate of 673 K-calcined limonite ore increased from 90.2 mass% to 97.2 mass% as the added amount of Na$_2$SO$_4$ increased. The 873 K-calcined limonite ore showed a similar trend; its nickel recovery rate after reduction rose from 72.9 mass% to 100 mass% as the addition of Na$_2$SO$_4$ increased. This was also the case for the 1173 K-calcined limonite ore, whose nickel recovery rate grew from 78.6 mass% to 100 mass% with a rise in the amount of Na$_2$SO$_4$ added during the reduction process. It is thus concluded that Na$_2$SO$_4$ could prompt effective displacement of the metallic nickel, increasing its content and recovery rate.28

Figure 7 shows the XRD analysis results of limonite ore calcined at different temperatures (673, 873 and 1173 K) and then, reduced under optimal reduction parameters and with different amounts of additive. Figure 7(a) indicates that after being reduced, the major phases of the 673 K-calcined limonite ore were Fe$_2$SiO$_4$, Fe$_{0.9712}$O, FeMg$_{0.03}$SiO$_4$, Fe$_{0.9712}$O, FeMg$_{0.03}$SiO$_4$. However, XRD peaks corresponding to the Fe-phase appeared as the amount of Na$_2$SO$_4$ increased. Figures 7(b)(c) also show a similar pattern in which the peaks corresponding to the metallic iron increased as the amount of Na$_2$SO$_4$ increased.

The results of the experiment show that the addition of Na$_2$SO$_4$ could aid in the reduction of calcined limonite ore to metallic nickel and iron, increasing the nickel recovery rate.
This is because the sodium salts combined with the aluminum and silicon in the mineral phase, forming aluminum-silicon-sodium salts and displacing the metallic nickel and iron phases, while the sulfur combined with the iron to form iron sulfide, suppressing the reduction of the metallic iron.\(^{(28)}\)

From experimental results and the discussion outlined above, our study found that the optimal reduction conditions of 1173 K-calcined limonite ore are 1373 K for the reduction temperature, 30 min for reduction time and 0.6 for the carbon-oxygen ratio, which contribute to the best nickel grade of 22.1 mass\% and recovery rate of 78.6 mass\%. Through the carbothermic reduction process of limonite ore calcined at different temperatures (673, 873 and 1173 K), it was discovered that 673 K-calcined limonite ore experienced a dehydroxylation, creating a higher specific surface area and smaller pores, which represent better activity beneficial to the spread of gas during the following carbothermic reduction process. They could consequently cause a better reduction of metallic iron and nickel, effectively cutting energy consumption. 673 K-calcined limonite ore, after being reduced, had a nickel grade better than 30 mass\%, and its nickel recovery rate could reach 90.2 mass\%.

From the study of the impact of the addition of different amounts of Na\(_2\)SO\(_4\) on limonite ore calcined at different temperatures (673, 873 and 1173 K), it was noted that when the amount of Na\(_2\)SO\(_4\) was increased, the nickel grade decreased and the recovery rate rose, meeting the requirements of industrial standards: 15–16 mass\% for nickel grade and >85 mass\% for recovery rate. In the future, different reduction methods for limonite ore could be selected according to the associated manufacturing process.

4. Conclusion

There are three parts to this research. First, the optimal carbothermic reduction parameters for the limonite ore and their impact on the nickel grade and recovery rate were investigated. Then, for limonite ore calcined at different temperatures in advance, their nickel grade and recovery rate after being reduced under optimal reduction parameters were also probed. Finally, additives were used to improve the nickel recovery rate. The conclusions obtained in this work are as follows:

1. 673 K-calcined limonite ore obtained the best nickel grade of >30 mass\% and the best recovery rate of 90.2 mass\% under a reduction temperature of 1373 K, a reduction time of 30 min and a carbon-oxygen ratio of 0.6.

2. 673 K-calcined limonite ore possesses a higher specific surface area of 48.8 m\(^2\)/g, and an average pore size of 29.7 Å, which provide better activity for reduction.

3. 673 K-calcined limonite ore with the addition of Na\(_2\)SO\(_4\) (5 mass\%) can obtain the best nickel grade of >30 mass\% and the best recovery rate of 93.8 mass\% when the reduction temperature is 1373 K, the reduction time is 30 min, and the carbon-oxygen ratio is 0.6.

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