Comprehensive Recovery of Multisource Metallurgical Wastes: Recycling Nickel Slag by Aluminum Dross with Converter-Slag Addition

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Recovery of multisource metallurgical wastes can facilitate the recovery of valuable metals, and achieve the full utilization of slag. Recycling nickel slag by aluminum dross with converter-slag addition was studied. Based on the element mapping of slags, mineral phases in the modified slag were reconstructed under the interaction of nickel and converter slags, and FeO could be separated from the relevant structures of the two slags. Element mapping and chemical analysis of the metal phase after reduction indicated that the reduced product was Fe–Cu-based alloy. Element mapping and XRD detection of the secondary slag indicated a complex characterization. The influence of factors, including the basicity of the modified slag, the reduction temperature and the Al/FeO ratio on the recovery degree of Fe, Cu, Mn and P, was discussed and the optimal technical parameter was determined as 1.0, 1773 K and 0.67, respectively.

KEY WORDS: nickel slag; converter slag; Al/FeO ratio; recycling; recovery degree.

1. Introduction

Rapid developments in metallurgical industry have resulted in undesirable but unavoidable waste slags. Innovative processing is essential to relieve pressure faced by the industry, especially under current global environmental constraints. If processing can be conducted to recycle valuable metals and achieve full slag utilization, it will favor the sustainable development of the metallurgical industry.1) The comprehensive recovery of multisource metallurgical wastes is likely to be one of the most effective methods to achieve this goal.

Nickel slag is a metallurgical solid waste from the nickel smelting industry. It contains iron (typically, the iron content can reach up to 50 wt%) and copper and can be recycled as an excellent secondary source. According to the U.S. Geological Survey on identified land-based resources, at least 40% of nickel reserves reside in sulfide deposits and the remainder exists in laterites.2) Because the treatment of hydroxysilicate in nickel laterites is difficult, 60%–70% of the current global nickel production is derived from nickel sulfides, and extensive nickel slag is generated as a result.3) For example, Jinchuan Group Co. Ltd (Yinchuan, China) has accumulated more than 33 million tons of nickel slag thus far. Most slag is discharged directly into heaps or exposed in the open air, which wastes valuable resources and yields environmental problems.4–7)

Since FeO in the nickel slag exists mainly in the form of silicates, and SiO2 is the network former in a slag structure according to related works,8–12) A network-modification process is essential to separate FeO from the silicate structure. Appropriate modification would benefit the recovery process and the transition of secondary slag into value-added materials. As studied by Zhao et al., constituent regulators such as CaO, CaCO3, CaF2 and other composite additives were essential to modify the slag properties during recycling.13–16) In our previous work, CaO was treated as the modifier in recycling nickel slag.17) However, converter slag was adopted as the substitution in this work to avoid the CO2 emissions during CaO production. Converter slag is a basic slag (the basicity changes typically in the range of 3.0–4.0) produced from steelmaking industries, and accounts for 15%–20% of the total final volume of crude steel.18) As studied by Li et al., converter slag is unsuitable for use besides in road construction and cement production, and its utilization ranges from 10% to 30%. Converter slag masses that are abandoned or backfilled cause enormous value losses and environmental concerns.19–21) In view of the fact that iron in these two slags exists in a relevant network structure, converter-slag addition into nickel slag is speculated to promote them to act as modifiers for each other, achieve phase reconstruction in the modified slag (the mixture of nickel and converter slags) and yield a higher activity of ‘FeO’ from the interaction of these two slags. What’s more, converter slag is also iron-bearing slag, converter-slag addition to nickel slag during pyrometallurgical recycling can make it possible to recover iron and other valued components, such as Mn, from multisource metallurgical wastes.
In recent years, extensive researches have been conducted to recycle nickel slag, converter slag and other iron-bearing metallurgical solid wastes using hydrometallurgical, pyrometallurgical and physical processes. We used the aluminothermic reduction method that is treated as a self-sustaining technique in this work. During the reduction process, considerable heat can be supplied to the slag bath with the exothermic property of aluminothermy. To reduce the processing cost, aluminum dross as the waste residue of the aluminum industry was selected as the reductant. The content of Al in aluminum dross can typically reach 30 wt%–35 wt%, which signifies an exciting new alternative source of aluminum.

Based on above background, recycling nickel slag by aluminum dross with converter-slag addition was investigated in this work. The modification behavior between nickel slag and converter slag was studied. Also, the reduction behavior of nickel slag by aluminum dross with converter-slag addition was investigated. Element mapping of the modified slag after reduction was studied to elucidate the mechanism of aluminum in the current recycling process. Factors that affect the recovery degree of Fe, Cu, Mn and P, including the basicity of the modified slag, the reduction temperature and the Al/FeO ratio, were discussed to obtain the optimal technical parameters.

2. Experimental

2.1. Materials

Nickel and converter-slag raw material was collected from a domestic nickel-smelting enterprise and a steel company, respectively. The chemical compositions of the two metallurgical solid wastes are listed in Table 1. The total Fe (TFe) contents in nickel and converter slags are 39.91 wt% and 17.88 wt% and the basicities of the two slags were 0.11 and 3.55, respectively. Aluminum dross used in this study was provided by an aluminum enterprise, the compositions of which are also shown in Table 1. The Al content in the aluminum dross is 33.14 wt%, and the lower contents of hazardous elemental F, K and Cl (~0.14%) are ignored due to the process conditions without soluble-salt addition.

Mineral phases in raw materials were detected by using X-ray diffraction (XRD, D8 Advance, Bruker AXS GmbH, Germany). Patterns were obtained at 40 kV and 40 mA with Cu–Kα radiation, and the data were collected in the 2-theta range from 10° to 90°. The results in Fig. 1(a) indicate that nickel slag is characterized by fayalite (2FeO·SiO₂) and hortonolite (2(MgO, FeO)·SiO₂). Converter slag consists mainly of dicalcium ferrite (2CaO·Fe₂O₃), tricalcium silicate (3CaO·SiO₂), dicalcium silicate (2CaO·SiO₂), free CaO (f-CaO), RO (solid solution of FeO, MnO and MgO) and calcium phosphate (3CaO·P₂O₅). Simultaneously, the characterization of aluminum dross is shown in Fig. 1(b). The XRD patterns show that the dominant phases in aluminum dross are metallic Al, SiO₂, AlN and other oxides. Based on the particle size distribution measured by Master sizer 2000 (Malvern, England), the mean size of aluminum dross is 839.36 μm.

2.2. Experimental Procedure

Figure 2 shows a schematic diagram of the experimental setup (Fig. 2(a)) and a flowsheet of the reduction process (Fig. 2(b)). Before the reduction experiment, nickel slag and converter slag were mixed in an agate mortar, and the proportion of converter slag was determined to obtain a CaO/SiO₂ ratio of 1.0 in the modified slag (mixture of nickel and converter slags). Approximately 20 g of the samples was charged into a 30 mm × 24 mm × 45 mm (outer diameter ×

<table>
<thead>
<tr>
<th>Compositions</th>
<th>TFe</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>Al</th>
<th>AI</th>
<th>Na₂O</th>
<th>Ni</th>
<th>Co</th>
<th>Cu₂O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel slag</td>
<td>39.91</td>
<td>3.58</td>
<td>8.41</td>
<td>31.60</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.16</td>
<td>0.08</td>
<td>0.25</td>
<td>1.20</td>
</tr>
<tr>
<td>Converter slag</td>
<td>17.88</td>
<td>45.89</td>
<td>8.12</td>
<td>12.94</td>
<td>5.88</td>
<td>1.77</td>
<td>1.95</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Aluminum dross</td>
<td>–</td>
<td>2.04</td>
<td>6.97</td>
<td>10.12</td>
<td>40.83</td>
<td>–</td>
<td>–</td>
<td>33.14</td>
<td>4.85</td>
<td>2.05</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

![Fig. 1](image-url). (a) XRD patterns of nickel and converter slags and (b) characterization of aluminum dross. (Online version in color.)
inner diameter \times \text{height}) magnesia crucible. The crucible was kept in the high-temperature zone of the furnace, which was equipped with six MoSi$_2$ heaters and controlled by a PtRh30-PtRh6 thermocouple with a deviation of \(\pm 2\) K. After heated to 1 773 K, the mixture was held for 30 min to make the slag homogenous. The crucible was removed from the furnace and quenched into prepared liquid nitrogen for subsequent examinations.

During the reduction experiment, the temperature range of 1 673–1 873 K was determined according to a pre-thermodynamic calculation for the current reduction process. For the molten modified slag at 1 573–1 673 K, an increasing temperature range of 450–467 K could be supplied to the slag bath with the heat input from the aluminothermic reaction and with the heat output containing the heat loss during the reduction process and the dissolution consumption of aluminum dross. When the modified slag was homogenous, a certain proportion of aluminum dross was added into the slag system. After reduction for a predetermined time (5, 10, 30 and 60 min), the crucible was removed from the furnace and quenched in liquid nitrogen for microstructure examination and chemical analysis. High-purity argon atmosphere was maintained throughout the experiment to avoid the slag-component oxidation.

The microstructure of the modified slag was examined by scanning electron microscopy (SEM; Zeiss ULTRA 55, Zeiss Microscope Co., Germany) equipped with energy-dispersive spectrometry (EDS). Initially, the sample was inlaid with epoxy resin and ground with different grades of abrasive papers. After grinding and polishing, the sample was set up on a conductive support and coated with a thin layer of gold–palladium alloy by using a sputter coater. The mineral phases of the modified slag were detected using XRD. Element mapping of the modified slag after reduction was also achieved by SEM. After the reduced product and secondary slag had been separated, their compositions were analyzed by X-ray fluorescence (XRF, ZSX100e, Rigaku, Japan), and the mineral phases in the secondary slag were detected by using XRD.

3. Results and Discussion

3.1. Element Mapping of Modified Slag

To elucidate the characterization of the modified slag, the microstructure and element mapping were examined and compared with the original nickel and converter slags. Figures 3(a), 3(b) and 3(c) show the results for the nickel slag, converter slag and modified slag, respectively.

As shown in Fig. 3(a), a layered and clumpy structure is dispersed randomly in the matrix. The EDS results of points A, B and C are shown in Table 2. The atomic ratio of elements confirms that the main phases in the nickel slag are fayalite (2FeO·SiO$_2$) and hortonolite (2(MgO, FeO)·SiO$_2$), which corresponds well with the XRD pattern. Based on element mapping, the obvious enrichment in elemental Fe and Si indicates that the matrix of nickel slag is 2FeO·SiO$_2$ and the overlapped distribution of elemental Fe, Mg and Si implies a phase of 2(MgO, FeO)·SiO$_2$.

As shown in Fig. 3(b), the microstructure of minerals in the converter slag is characterized by a reticular structure. Combined with the XRD pattern, the EDS results of points D and E in Table 2 illustrate the existence of ferrites and silicates. Different from the element mapping of nickel slag, elemental Fe in the converter slag is connected mainly with elemental Ca, which suggests a 2CaO·Fe$_2$O$_3$ phase. Some elemental Ca coexists with elemental Si apart from the combination with elemental Fe, which indicates the presence of 3CaO·SiO$_2$ and 2CaO·SiO$_2$ phases.

As shown in Fig. 3(c), element mapping in the modified slag is well defined. Compared with the original nickel slag, the characterization of modified slag has evolved significantly. The distribution of elemental Fe and Si and the EDS result of point F in Table 2 indicate that FeO has been separated from the 2FeO·SiO$_2$ and 2(MgO, FeO)·SiO$_2$ silicate network under the effect of a converter slag. Therefore, more free FeO would exist in the molten slag, which benefits the subsequent reduction process. Alternatively, the coexistence of elemental Ca and Si and the EDS result of point G in Table 2 demonstrate the effect of nickel slag on converter slag. From this perspective, converter-slag addition into nickel slag could achieve the interaction of these two slags. To achieve further confirmation, the reconstructed phases in the modified slag were firstly calculated by FactSage 7.0,$^{34}$ a cooling sequence for the phases of Oxides (FeO, Fe$_2$O$_3$ and MgO), Merwinite (Ca$_3$Mg$_2$Si$_2$O$_7$), Akermanite (Ca$_2$MgSi$_2$O$_7$) and Gehlenite (Ca$_2$Al$_2$Si$_2$O$_9$) was obtained. Considering the less amount of MgO (8.65 wt%) and Al$_2$O$_3$ (2.82 wt%) and the element mapping of modified slag, it can be predicted the existence of Wollastonite (CaSiO$_3$) and Calcium orthosilicate (Ca$_2$SiO$_3$). In conjunction with the XRD detection,

[Fig. 2. (a) Schematic diagram of experimental setup and (b) flow sheet of the reduction process. (Online version in color.)]
the phases of CaO·SiO\(_2\), Ca\(_3\)MgSi\(_2\)O\(_6\), FeO·Fe\(_2\)O\(_3\), Fe\(_2\)O\(_3\), FeO, CaMgSi\(_2\)O\(_6\), Ca\(_2\)MgSi\(_2\)O\(_7\), 2CaO·SiO\(_2\) and MgO were determined.

### 3.2. Element Mapping of Modified Slag after Reduction

Figure 4 shows the element mapping of the modified slag after reduction at 1773 K for 10 min under a fixed Al/FeO’ ratio of 0.67. The produced metal droplets tend to aggregate and grow. The dimensions of the larger particles reach 150 \(\mu\)m, indicating a good coalescence behavior of the metal droplets under the current conditions.

The element distribution of the metal phase indicates that the reduced product may be Fe–Cu-based alloy, which was confirmed by EDS detection and chemical analysis. The EDS result of point H in Fig. 5 shows that the average

<table>
<thead>
<tr>
<th>Point</th>
<th>Fe</th>
<th>Mg</th>
<th>Si</th>
<th>O</th>
<th>Ca</th>
<th>Al</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24.59</td>
<td>3.01</td>
<td>21.98</td>
<td>50.42</td>
<td>0</td>
<td>0</td>
<td>Hortonolite, 2(MgO, FeO)·SiO(_2)</td>
</tr>
<tr>
<td>B</td>
<td>13.44</td>
<td>20.55</td>
<td>16.03</td>
<td>49.98</td>
<td>0</td>
<td>0</td>
<td>Hortonolite, 2(MgO, FeO)·SiO(_2)</td>
</tr>
<tr>
<td>C</td>
<td>16.76</td>
<td>13.15</td>
<td>16.17</td>
<td>53.92</td>
<td>0</td>
<td>0</td>
<td>Fayalite, 2FeO·SiO(_2)</td>
</tr>
<tr>
<td>D</td>
<td>15.93</td>
<td>3.26</td>
<td>52.50</td>
<td>26.75</td>
<td>1.56</td>
<td>0</td>
<td>Calcium ferrite, 2CaO·Fe(_2)O(_3)</td>
</tr>
<tr>
<td>E</td>
<td>2.95</td>
<td>0.56</td>
<td>11.49</td>
<td>54.90</td>
<td>28.43</td>
<td>1.56</td>
<td>Silicates, 3CaO·SiO(_2), 2CaO·SiO(_2)</td>
</tr>
<tr>
<td>F</td>
<td>32.67</td>
<td>15.71</td>
<td>0.19</td>
<td>51.26</td>
<td>0.11</td>
<td>0.06</td>
<td>Oxides, Fe(Mg)O, Fe(_2)O(_3), etc.</td>
</tr>
<tr>
<td>G</td>
<td>0.23</td>
<td>7.21</td>
<td>18.56</td>
<td>53.76</td>
<td>20.14</td>
<td>0.10</td>
<td>Complete silicates, CaO·SiO(_2), etc.</td>
</tr>
</tbody>
</table>

Fig. 3. Element mapping of (a) nickel slag; (b) converter slag and (c) modified slag. (Online version in color.)
mass ratio of elemental Fe and Cu is 97.60% and 3.08%, respectively. To achieve a further understanding of the metal phase, chemical analysis was carried out. Although the metal droplets that dispersed randomly in slag were difficult to collect, the visible droplets were collected with the iron ingots that were deposited on the bottom of crucible by using magnetic separation. Along with the results after a reaction time of 5, 30 and 60 min, the reduced product compositions are listed in Table 3. It can be found that the reduced product is dominated by elemental Fe and Cu.

Fig. 4. Element mapping of modified slag after reduction at 1773 K for 10 min. (Online version in color.)

Fig. 5. EDS results of points H, I and J in the modified slag after reduction. (Online version in color.)
In addition, the contents of elemental Mn and P increase gradually with the reaction time, which shows that these two elements are inevitably reduced during the reduction process. Agreement is maintained with the element mapping examination and with chemical analysis.

As studied by Weng et al., weathering steel containing elemental Cu, Ni, Cr, Mn, P, Ni and S (the content of these elements differs in the range of 0.10–0.55, 0.20–2.0, 0.0024–0.15, 0.12–1.15 and 0.0031–0.05, respectively) is used for anti-corrosion materials because of the good corrosion resistance.35–39) Where Cu and Ni are the main alloying elements that affect the corrosion resistance, where Cu and Ni are the main alloying elements that affect the corrosion resistance.35–39)

The chemical compositions of commonly used weathering steel in the related references are shown in Table 4. It’s perceptible that the contents of elemental Cu, Mn, Ni and S in this work meet the chemical requirement of weathering steel except for the higher P content. Although it can’t be applied directly to industry in its current chemistry, the produced alloy has the potential to be used as a raw material in making weather-resistant steel after a refining process. Furthermore, considering the potential harms from the elemental Al and O, the content of these two elements in the reduced alloy produced after 60 min is determined as ~34 ppm and ~19 ppm by Inductively coupled plasma spectrometer (ICP-5000, Focused Photonics Inc., China) and Oxygen, nitrogen and hydrogen combined analyzer (ONH836, LECO, USA), respectively. Since the Al content may vary from 0.03 to 3.5 wt% in Al-containing weathering steel, the less amounts of elemental Al and O would not have a significant effect on the alloy purity.35,38)

### 3.3. Influence of Factors on the Recovery Degree of Fe, Cu, Mn and P

#### 3.3.1. Influence of Basicity of Modified Slag

The recovery degree of Fe, Cu, Mn and P are calculated from Eqs. (1)–(4).

\[
R_{\text{Fe}} = \frac{M_{\text{Fe}^\text{P}} \times w(\text{Fe})}{M_{\text{NS}} \times w(\text{TFe})_{\text{NS}} + M_{\text{CS}} \times w(\text{TFe})_{\text{CS}}} \times 100\% \quad \ldots \ldots (1)
\]

**Table 3.** Chemical compositions of the reduced product (wt%).

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>P</th>
<th>Ni</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>99.46</td>
<td>0.46</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>99.36</td>
<td>0.44</td>
<td>0.10</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
<td>99.00</td>
<td>0.44</td>
<td>0.27</td>
<td>0.27</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>60</td>
<td>98.81</td>
<td>0.43</td>
<td>0.34</td>
<td>0.39</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Table 4.** Chemical compositions of commonly used weathering steel in references (wt%).

<table>
<thead>
<tr>
<th>Refs.</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>P</th>
<th>Ni</th>
<th>Al</th>
<th>Si</th>
<th>C</th>
<th>Cr</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weng et al.</td>
<td>0.351</td>
<td>0.99</td>
<td>0.099</td>
<td>0.005</td>
<td>0.03</td>
<td>0.29</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morcillo et al.</td>
<td>≥0.20</td>
<td>≤1.0</td>
<td>≤0.15</td>
<td>≤0.05</td>
<td>≤0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25–0.40</td>
<td>0.8–1.25</td>
<td>≤0.04</td>
<td>≤0.05</td>
<td>0.3–0.5</td>
<td>0.085–0.15</td>
<td>0.005–0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liang et al.</td>
<td>0.1–0.19</td>
<td>0.30–0.60</td>
<td>0.035–0.050</td>
<td>≤0.01</td>
<td>0.3–0.5</td>
<td>0.085–0.15</td>
<td>0.005–0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Song et al.</td>
<td>0.25–0.45</td>
<td>0.30–2.15</td>
<td>0.0024–0.0090</td>
<td>0.0014–0.0031</td>
<td>0.24–1.15</td>
<td>0.7–3.5</td>
<td>0.10–0.95</td>
<td>0.021–0.053</td>
<td>0.5–2.4</td>
<td></td>
</tr>
<tr>
<td>GB/T 4171-2008</td>
<td>0.20–0.55</td>
<td>0.20–2.0</td>
<td>0.025–0.12</td>
<td>≤0.03</td>
<td>0.12–0.65</td>
<td>0.1–0.75</td>
<td>≤0.16</td>
<td>0.3–1.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

35,38) Balance

where \( R_{\text{Fe}} \), \( R_{\text{Cu}} \), \( R_{\text{Mn}} \) and \( R_{\text{P}} \) are the recovery degree of Fe, Cu, Mn and P, respectively (%); \( M_{\text{Fe}^\text{P}} \) is the mass of reduced product (kg); \( w(\text{Fe}) \), \( w(\text{Cu}) \), \( w(\text{Mn}) \) and \( w(\text{P}) \) are the mass fractions of Fe, Cu, Mn and P in reduced product (%), respectively; \( M_{\text{NS}} \) and \( M_{\text{CS}} \) are the masses of nickel slag and converter slag (kg), respectively; \( w(\text{TFe})_{\text{NS}} \) and \( w(\text{Cu})_{\text{NS}} \) are the mass fractions of TFe and Cu in the nickel slag (%), respectively; \( w(\text{TFe})_{\text{CS}} \), \( w(\text{Mn})_{\text{CS}} \) and \( w(\text{P})_{\text{CS}} \) are the fraction of TFe, Mn and P in the converter slag (%), respectively.

Figure 6 shows the dependence of the recovery degree of Fe, Cu, Mn and P (Fig. 6(a)) after a reaction time of 60 min and \( \alpha(\text{FeO})_{\text{eq}} \) (Fig. 6(b)) on the basicity of the modified slag, respectively. To obtain the optimal basicity of the modified slag, the reaction temperature of 1 773 K and Al/%FeO ratio of 0.67 was fixed, respectively. With an increase in slag basicity from 0.50 to 1.50, the recovery degree of iron increases initially and then decreases, and a maximum value of 85.26% is obtained around the basicity of 1.0. The tendency of the curve should be originated from the activity of equivalent ‘FeO’ (\( \alpha(\text{FeO})_{\text{eq}} \)) in the slag, which is calculated based on the ion and molecule coexistence theory.40–43) Taking the valence state of iron ions into consideration, the equivalent mass fraction of ‘FeO’ (\( w(\text{FeO})_{\text{eq}} \)) is expressed in Eq. (5).

\[
w(\text{FeO})_{\text{eq}} = w(\text{FeO}) + 2 \cdot \frac{M_{\text{FeO}}}{M_{\text{Fe}_2\text{O}_3}} - w(\text{Fe}_2\text{O}_3) \quad \ldots \ldots (5)
\]

where \( w(\text{FeO}) \) and \( w(\text{Fe}_2\text{O}_3) \) represent the mass fractions of FeO and Fe2O3, respectively (%); and \( M_{\text{FeO}} \) and \( M_{\text{Fe}_2\text{O}_3} \) are the molar masses of the two oxides (g·mol⁻¹).

The variation of \( \alpha(\text{MeO}, \text{Me}=\text{Cu, Fe, Mn and P}) \) with basicity of modified slag is shown in Table 5. Combined with Fig. 6(b), \( \alpha(\text{FeO})_{\text{eq}} \) increases from 0.542 to 0.659 as the basicity increases from 0.5 to 1.0, which suggests that converter-slag addition would lead to a separation of FeO and Fe2O3 from the silicates in the nickel slag and the ferrates in the converter slag, respectively. Therefore, the recovery degree of iron increases. A larger basicity of the modified slag induces a lower \( \alpha(\text{FeO})_{\text{eq}} \) and results in a decreasing recovery degree. For the other three oxides,
the logic for relationship between reduction degree and the basicity of modified slag is available. Although $a(Cu_2O)$ decreases from $9.88 \times 10^{-4}$ to $7.07 \times 10^{-4}$, the change in recovery degree of Cu can be ignored, and values higher than 91.22% suggest its priority during reduction. Simultaneously, the recovery degree of Mn and P increase, which indicates a higher activities of these two elements with converter-slag addition. It should be mentioned that $a(P_2O_5)$ is characterized by the form of original compound $Ca_3P_2O_8$ ($a(Ca_3P_2O_8)$), and $a(MnO)$ and $a(Ca_3P_2O_8)$ increases from $4.1 \times 10^{-3}$ to $2.4 \times 10^{-2}$, $3.02 \times 10^{-6}$ to $5.94 \times 10^{-5}$, respectively. From the perspective of a higher recovery degree of iron, the optimal basicity of the modified slag is determined to be 1.0.

### 3.3.2. Influence of Reduction Temperature

Based on the optimal basicity of the modified slag (1.0), the influence of reduction temperature was investigated under a fixed Al/$'FeO'$ ratio of 0.67. Figure 7 shows the dependence of the recovery degree on the reduction temperature. A temperature increase from 1 673 to 1 773 K results in an increase in recovery degree of Fe, Cu, Mn and P from 74.48% to 85.26%, 87.32% to 92.68%, 15.11% to 25.62% and 7.65% to 14.16%, respectively. However, further temperature increases lead to a slight ascension. The influence of reduction temperature on the recovery degree should be correlated with the slag viscosity, which is a function of composition and temperature. An increase in temperature will decrease the viscosity and improve the kinetic condition of the molten slag, accelerate the reaction rate and mass-transfer rate and increase the recovery degree.

For instance, viscosity of the modified slag after reduction are calculated as 0.758 and 0.386 Pa·s by FactSage at 1 673 and 1 773 K, respectively. Because of the exothermic effect of the aluminothermic reaction and the negligible evolution of slag viscosity at temperature higher than 1 773 K, a further increase in temperature does not increase the recovery degree significantly. Therefore, the reduction temperature of 1 773 K is recommended.

**Table 5.** Variation of $a(MeO, Me = Cu, Fe, Mn and P)$ with basicity of modified slag.

<table>
<thead>
<tr>
<th>Basicity of modified slag</th>
<th>$a(Cu_2O)$</th>
<th>$a('FeO')_{eq}$</th>
<th>$a(MnO)$</th>
<th>$a(Ca_3P_2O_8)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>$9.88 \times 10^{-4}$</td>
<td>0.542</td>
<td>$4.10 \times 10^{-3}$</td>
<td>3.02\times 10^{-6}</td>
</tr>
<tr>
<td>0.75</td>
<td>$9.43 \times 10^{-4}$</td>
<td>0.619</td>
<td>$6.80 \times 10^{-3}$</td>
<td>6.02\times 10^{-6}</td>
</tr>
<tr>
<td>1.00</td>
<td>$9.03 \times 10^{-4}$</td>
<td>0.659</td>
<td>$9.60 \times 10^{-3}$</td>
<td>9.00\times 10^{-6}</td>
</tr>
<tr>
<td>1.25</td>
<td>$8.22 \times 10^{-4}$</td>
<td>0.579</td>
<td>$1.69 \times 10^{-2}$</td>
<td>1.86\times 10^{-5}</td>
</tr>
<tr>
<td>1.50</td>
<td>$7.07 \times 10^{-4}$</td>
<td>0.535</td>
<td>$2.40 \times 10^{-2}$</td>
<td>5.94\times 10^{-5}</td>
</tr>
</tbody>
</table>

Fig. 6. Dependence of (a) recovery degree of Fe, Cu, Mn and P and (b) $a('FeO')_{eq}$ on basicity of the modified slag. (Online version in color.)

Fig. 7. Dependence of recovery degree of Fe, Cu, Mn and P on the reduction temperature. (Online version in color.)

Fig. 8. Dependence of recovery degree of Fe, Cu, Mn and P on the Al/$'FeO'$ ratio. (Online version in color.)
3.3.3. Influence of Al/’FeO’ Ratio

Based on the optimal basicity of the modified slag of 1.0 and the reduction temperature of 1773 K, the influence of Al/’FeO’ ratio on the recovery degree was also studied. Figure 8 shows the results after a reaction time of 60 min. The recovery degree of Fe and Cu increases monotonously with an increase in Al/’FeO’ ratio from 0.27 to 0.67, which accounts for the reaction degree for different dosages of aluminum dross. Excessive aluminum-dross addition does not promote significant evolution, and the recovery degree of Fe and Cu changes slightly from 85.26% to 91.76% and 92.68% to 93.60%. It can also be found, however, the recovery degree of Mn and P increases gradually before the Al/’FeO’ ratio of 0.67, accompanied by an abrupt evolution then. This can be explained as that the elemental Mn and P would be reduced by aluminum dross when the residual contents of FeO and Cu2O are lower. Because of the worse slag kinetic condition that is observed during the later reduction process by excessive aluminum-dross addition, the optimal Al/’FeO’ ratio was determined to be 0.67.

3.4. Evolution of Slag Compositions and Mineral Phases

Figure 9 shows the evolution of the slag compositions and mineral phases in the current process, where Fig. 9(a) represents the CaO–SiO2–FeO–Al2O3 (−10.5 wt% MgO) slag system and Fig. 9(b) shows the mineral phases in modified and secondary slags. Compared with the CaO addition in our previous work, converter-slag addition induces a higher MgO content of 10.23%, causes a higher viscosity and a lower recovery degree of Fe and Cu. However, converter-slag addition can also achieve the separation of ‘FeO’ from the relevant structures in nickel and converter slags and favor the following reduction process, as shown in Fig. 9(b). The main phases in secondary slag are calculated as spinel (MgAl2O4), CaMg2Al16O27, anorthite (CaAl2Si2O8), gehlenite (Ca₂Al₂SiO₇) and akermanite (CaMg₅Si₂O₇) by FactSage, which is similar to that modified by CaO.17,34) Nevertheless, MgAl12O19 and CaMg₂Al₁₆O₃₇ are the dominant phases by XRD detection. It can be attributed to the precipitation of MgAl12O19 upon the mole ratio of atom Mg and Al, inducing that other minerals have insufficient time to precipitate during the quenching process.

3.5. Suggestions for the Industrial Practice

To promote the applications of current recycling into industrial practice, the following suggestions can be made based on the present experimental results.

(1) The optimal basicity of the modified slag, reduction temperature and Al/’FeO’ ratio are 1.0, 1773 K and 0.67, respectively, and the recovery degree of Fe, Cu, Mn and P is 85.26%, 92.68%, 14.16% and 25.62%, respectively, under optimal conditions.

(2) Based on the optimal conditions, material and heat balance calculations indicate that 53.63 kilograms of aluminum dross and 85.07 kilograms of converter slag will be consumed for treating 100 kilograms of nickel slag. Additionally, an increment of slag temperature varies from −73 to 342 K with the reduction process in assumptions of the output temperature of the nickel slag as 1573 K and the heat loss as 10% of the physical heat of the whole slag system. Therefore, before the self-sustaining period of the reduction process, external energy should be supplied into the slag system.

4. Conclusions

Recycling nickel slag by aluminum dross with converter-slag addition is studied, and the following conclusions can be drawn based on the experimental results.

(1) Element distribution in the element mapping of modified slag indicates converter-slag addition can achieve the separation of ‘FeO’ from the relevant structures in nickel and converter slags. Based on XRD detection, phases in the modified slag are dominated by CaO·SiO₂, Ca₃MgSi₂O₆, FeO·Fe₂O₃, Fe₂O₃, FeO, CaMgSi₂O₆, Ca₂MgSi₂O₆, 2CaO·SiO₂ and MgO. Compared with the original nickel and converter slags, phase reconstruction in the modified slag is caused by the interaction of these two slags.

(2) Element mapping and chemical analysis indicate that the reduced product is Fe–Cu-based alloy, and the contents of elemental Mn and P increase gradually with reduction process, indicating that elemental Mn and P are inevitably reduced during the reduction process. The overlapped distribution of elemental Ca, Si, Mg, Al and O signifies the generation of complex compounds, which is confirmed as MgAl12O19 and CaMg₂Al₁₆O₃₇ by XRD detection.

(3) The optimal basicity of the modified slag, reduction
temperature and Al/FeO’ ratio is 1.0, 1.773 K and 0.67, respectively. The recovery degree of Fe, Cu, Mn and P is 85.26%, 92.68%, 14.16% and 25.62%, respectively, under the optimal conditions.

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