Article

Reduction of Copper Smelting Slag by Carbon for Smelting Cu-Fe Alloy

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Abstract: An innovative technology for the direct reduction of copper slag was studied while smelting Cu-Fe alloy by carbon to recover the main valuable elements from the copper smelting slag. The melting temperature of samples first decreased, followed by an increase in Fe₃O₄ content in slag. The melting temperature reached the minimum temperature of 1157 °C once the Fe₃O₄ content was about 8 wt%. The recovery rate of copper and iron first increased gradually, followed by a rapid increase in the modifier (CaO). Subsequently, the rise in the recovery rate slowed down. The reduction rate of copper and iron only increased by 1.61% and 1.05% from 5 wt% CaO to 10 wt% CaO, but significantly increased by 8.89% and 14.21% from 10 wt% CaO to 25 wt% CaO, and remained almost unchanged beyond 25 wt% CaO. This could be attributed to the reaction between modifier (CaO) and silicate in acidic copper slag to generate low melting point composite oxide while replacing free iron oxides, improving the melting properties and reduction reaction. Meanwhile, the recovery rates of copper and iron increased with the increase of reaction time, reaction temperature, and reduction agent in a certain range. To obtain good element yield, the optimum conditions for reducing copper and iron from the molten copper slag were determined to be 1500 °C, 14 wt% C, 20–25 wt% CaO, and 60–80 min. The recovery rates of iron and copper reached about 90% and 85%, and the contents of iron and copper in alloy reached about 91–93 wt% and 5–7 wt%, respectively. The tailing was mainly composed of Ca₃Si₃O₉, Ca(Mg,Al)(Si,Al)₂O₆, and SiO₂, which could be used as a raw material for cement and pelletizing.

Keywords: copper smelting slag; Cu-Fe alloy; recovery; direct reduction

1. Introduction

Resource and environmental factors have become major forces in the mining and metallurgy industries driving research for sustainability purposes [1–3]. The concept of zero-waste processing is rapidly spreading across the world. The scant availability of high-quality raw materials and stringent environmental regulations has forced researchers to focus on recycling waste and exploring new frontiers of minimizing/eliminating waste generation [2–4]. This study is aimed at addressing the aspects of recycling copper slag to generate wealth and produce utilizable materials at the same time as restoring the ecosystem [5–8]. Copper ore is rich in copper metal and is often accompanied by iron, gold, silver, and other elements [9–11]. At present, 80% of the world’s copper production follows the pyrometallurgy procedure [4,11,12]. One ton of copper smelting by pyrometallurgy procedure generates about 2.2 tons of copper slag, accounting for an annual output of up to 42.2 million tons worldwide [12–15]. Most of the slag is stored except for a small amount which is used for mine filling, cement batching, and construction materials [13,15–27]. The worldwide cumulative amount exceeded 500 million tons, which not only occupies a large
amount of land but also causes serious environmental problems such as the introduction of heavy metal (Pd, As, Zn et al.) into the water bodies and soil [14,23–28]. Moreover, the copper slag contains many valuable metals, such as copper and iron, indicating the need for recycling and utilization of its valuable secondary resource [27–30]. The typical composition of converter copper slag consists of 35–50 wt% TFe, 30–40 wt% SiO₂, 0.5–2.5 wt% Cu, CaO ≤ 10%, and Al₂O₃ ≤ 10%, as listed in Table 1 [31–34]. The contents of copper and iron could exceed the exploitable grade of the corresponding ores, which is an artificial, rich ore with high development potential. Therefore, there is a high demand in the metallurgical industry to efficiently recycle and utilize these resources, while improving their comprehensive added value and reducing environmental pollution.

Table 1. Chemical multielement analysis results of converter copper slag % (note: with “*” unit: g/t).

<table>
<thead>
<tr>
<th>Composition</th>
<th>TFe</th>
<th>Cu</th>
<th>Zn</th>
<th>S</th>
<th>Pb</th>
<th>As</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>35.0–50.0</td>
<td>0.5–2.5</td>
<td>0.8–1.8</td>
<td>0.3–0.82</td>
<td>0.1–0.3</td>
<td>0.01–0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Composition</td>
<td>SiO₂</td>
<td>CaO</td>
<td>MgO</td>
<td>Al₂O₃</td>
<td>MnO</td>
<td>Ag *</td>
<td>Au *</td>
</tr>
<tr>
<td>Content</td>
<td>30.0–40.0</td>
<td>2.5–6.5</td>
<td>1.5–3.5</td>
<td>1.5–2.5</td>
<td>0.3–0.6</td>
<td>16.47</td>
<td>0.26</td>
</tr>
</tbody>
</table>

In addition, the tapping temperature of copper slag is 1200–1250 °C and its physical sensible heat is about 1.32 GJ/ton [32–36]. Each year, approximately 42.2 million tons of copper slag is produced worldwide. The residual heat of copper slag that can be recycled stands at 5.570 × 10⁷ GJ and can nearly save 1.9 million tons of standard coal [32–36]. However, waste heat could not be continuously recovered and utilized due to the discontinuous slag production. The high-temperature copper slag, at about 1200 °C, is mostly treated by water quenching. This results in a large amount of white water mist, which not only wastes a large amount of physical sensible heat but also creates water pollution and worsens the working environment [32–36]. To efficiently and comprehensively utilize copper slag, it is necessary to consider the bulk treatment and the deep recovery of resources as well as energy (waste heat).

According to the literature, the recovery of valuable metals from copper slag is mainly focused on the recovery of single metals, such as copper or iron concentrate. However, only a few studies have been conducted on the recovery of Cu-Fe alloy. The Cu-Fe alloy can be used as the raw material for weathering steel [37–40]. The weathering steel demonstrates good weather resistance and excellent mechanical and welding properties while being widely used in rail transit, bridge engineering, and containers [37–40]. In addition, due to the expensive price of pure copper, the use of cheap copper-containing iron (Cu-Fe alloy) instead of pure copper can significantly reduce production costs. Therefore, the Cu-Fe alloy as raw material for weathering steel has broad market prospects [37–40]. The high value-added Cu-Fe alloy can be reduced by modifying the high-temperature molten copper slag to effectively recover the valuable elements (Fe, Cu) and physical sensible heat. In addition, silicate tailing can be used as a raw material for cement and pelletizing preparation, which ultimately achieves the comprehensive recovery and utilization of copper slag resources [37–40]. Compared to other recovery processes, the smelting of Cu-Fe alloy using copper slag is a simple technology and generates less pollution. Therefore it has potential technological, economic, and environmental advantages.

Based on the copper slag secondary resource recovery process, this study carried out the direct reduction smelting of Cu-Fe alloy while utilizing molten copper slag. Moreover, the influence of modifiers, reducing agents (graphite), temperature reduction, and time reduction on the recovery of copper and iron were investigated. The alloy composition concerning the formulation parameters of Cu-Fe alloy smelting was studied while utilizing copper slag.
2. Experimental Section

The slag sample was obtained from a copper plant in China. Its general chemical composition was investigated by X-ray fluorescence spectroscopy (XRF). The specific contents of various oxides present in the samples were calculated using the mass of corresponding elements obtained from inductively coupled plasma atomic emission spectrometry (ICP-OES) test results (Table 2). The mineralogical phases of copper slag were examined by X-ray powder diffraction (XRD) using Cu Ka1 radiation (λ = 1.5406 Å) with a step of 0.02° (2θ) and scanning rate of 2° min⁻¹ in a range of 10° to 90° C. The microstructures, as well as a compositional analysis of the phases in the samples, were determined by a scanning electron microscope (SEM) with an attached energy dispersive X-ray analyzer (EDS) (with operating condition EHT = 15.00 kV, WD = 7.9~10 mm, Time = 20~30 s).

Table 2. Multi-element analysis of converter copper slag, wt%.

<table>
<thead>
<tr>
<th>Component</th>
<th>TFe</th>
<th>TCu</th>
<th>Zn</th>
<th>S</th>
<th>Pb</th>
<th>As</th>
<th>P</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>41.46</td>
<td>2.52</td>
<td>1.23</td>
<td>0.32</td>
<td>0.31</td>
<td>0.01</td>
<td>0.02</td>
<td>1.22</td>
</tr>
<tr>
<td>Component</td>
<td>FeO</td>
<td>SiO₂</td>
<td>CaO</td>
<td>MgO</td>
<td>Al₂O₃</td>
<td>MnO</td>
<td>Cu₂S</td>
<td>Others</td>
</tr>
<tr>
<td>Content</td>
<td>39.98</td>
<td>31.45</td>
<td>4.53</td>
<td>3.38</td>
<td>2.35</td>
<td>0.36</td>
<td>1.26</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Reagent-grade powders of CaO (>99.90 wt%) and Fe₃O₄ (>99.90 wt%) were used as raw materials to adjust the composition of copper slag. High-purity graphite (>99.99 wt%) was used as a reducing agent. To homogenize the material composition, the copper slag was finely grounded to 200 mesh before batching. The ground copper slag and CaO or Fe₃O₄ were dried at 105 °C for 4 h in a drying oven to remove moisture and were mixed thoroughly in a ball mill according to the required proportion. The purpose of using magnetite as a raw material was to investigate the influence of magnetite on the melting property of copper slag. Subsequently, the mixed powders were pressed into tablet samples and heated at 1450 °C for 120 min in a corundum crucible to ensure complete melting before preparing pre-melted slag under Ar gas in a resistance furnace. After heating, the sample was cooled to room temperature in a furnace with Ar gas to avoid the oxidation of elements during the cooling process.

After completion of the pre-melting process, the pretreated slag was also grounded to about 200 mesh. Subsequently, the pretreated slags were investigated for their melting properties by the hemisphere method under the Ar gas atmosphere. Meanwhile, the pretreated slags and reducing agents were thoroughly mixed in a ball mill according to the required proportion. The mixture was poured into a corundum crucible to study the reduction of copper and iron in slag. Moreover, the composition in metal was determined under different amounts of reducing agent, temperature, and time in a resistance furnace with Ar gas. The samples obtained under different reduction conditions were also cooled to room temperature in a furnace with Ar gas. The chemical components of alloy and slag were determined by XRF and ICP-OES. The various oxide contents in samples were converted by the mass of the corresponding elements obtained from ICP-OES analysis. Conclusively, the recovery rate of iron and copper was calculated based on Equation (1).

\[
\eta_M = \frac{m_0 \times w_0 - m_1 \times w_1}{m_0 \times w_0}
\]

where \(\eta_M\) denotes the recovery rate of elements (iron or copper) in copper slag and \(m_0\) and \(m_1\) represent the mass of slag and tailings, respectively. The \(w_0\) and \(w_1\) denote the mass fractions of oxides in slag and tailing, respectively.
3. Results and Discussion

3.1. Mineralogical Phases of Converter Copper Slag

It is widely known that converter copper slag is mainly composed of iron and copper. The XRD result of the actual converter copper slag is shown in Figure 1. The main mineral compositions of actual converter copper slag consisted of copper phase (Cu), chalcocite phase (Cu$_2$S), magnetite phase (Fe$_3$O$_4$), and fayalite phase (Fe$_2$SiO$_4$), which was derived from the oxidation of matte melt in the converter.

![Figure 1. XRD pattern of actual converter copper.](image)

The SEM photomicrograph illustrating the morphology of the actual converter copper slag is presented in Figure 2. Figure 2a demonstrates that the phases of the actual converter copper slag are mainly composed of four mineral phases, i.e., phase 1 (point 1-bright white), phase 2 (point 2-white grey), phase 3 (point 3-light grey), and phase 4 (point 4-dark grey). According to energy dispersive spectroscopy (EDS), the bright white phase and the white-grey phase represented the copper phase (Cu) and chalcopyrite (Cu$_2$S), respectively. These were the main copper-bearing phases dispersed in the matrix. In addition, the light grey phase and dark grey phase represented magnetite and fayalite, respectively. In addition, it can be seen from Figure 2a that the morphology of each phase was different. The white Cu-bearing phases (Cu, Cu$_2$S) had similar morphology, which was mainly irregular circle or oval. The morphology of Fe$_3$O$_4$ was irregular quadrilateral, and its crystals were linked to each other to form larger aggregates. Dark gray Fe$_2$SiO$_4$ had no fixed shape due to its low melting point, and it was mainly filled with other crystallized phases during condensation. Both of them were the main iron-bearing phases in slag and their content directly affected the viscosity as well as the melting point of slag [10,31,41]. In particular, magnetite with a high melting point mainly exists in the solid phase under the condition of copper smelting in the converter [10,31,32,41]. It can sharply increase the viscosity of slag and reduce the fluidity, leading to a large number of copper-containing phases wrapped in slag that cannot be effectively separated [10,17,25,41]. In addition, the recovery of copper from copper slag by pyro-depletion is key to reducing the content of magnetite, improving the fluidity of slag, and achieving copper enrichment [10,17,25]. However, the recovery of copper by pyro-depletion isn’t ideal according to the actual results [10,31]. In addition, a large amount of iron in the slag can not be effectively recycled and utilized.
In order to effectively recover and utilize copper and iron in converter copper slag, the melting properties of slag were investigated. On this basis, the effects of reducing agent, temperature, and duration on the reduction of copper and iron were studied to obtain suitable reducing conditions.

3.2. Effect of Fe₃O₄ on Melting Property of Copper Slag

In order to study the effect of Fe₃O₄ on its melting characteristics, the copper slag with different Fe₃O₄ content was synthesized by the addition of magnetite according to the required proportion. Figure 3 shows the influence of Fe₃O₄ content on the melting temperature of copper slag. A rapid decline in the melting temperature of samples was observed, followed by a significant increase in Fe₃O₄ content in slag. The melting temperature reached the minimum value of 1157 °C once the Fe₃O₄ content reached 8 wt%. This could be attributed to the easy formation of Fe₃O₄ low melting point composite oxides with SiO₂ and CaO in the copper slag [6,18,26]. However, Fe₃O₄ precipitated from the slag once its content exceeded a certain value, demonstrating a sharp increase in the melting temperature of the slag [6,18,26]. This phenomenon deteriorated the fluidity of the slag, which ultimately affected the reduction reaction, the coalescence, and the growth of metal droplets as well as slag-metal separation. The loss of copper during converter smelting was mainly due to the existence of a large amount of high melting point solid Fe₃O₄ (about 1594 °C) that caused the increase of slag viscosity [6,18,26]. Therefore, copper and its compounds in the molten pool were entrained into the copper slag, resulting in the loss of valuable element copper. In addition, the recovery of copper from copper slag by pyro-depletion is key to reducing the content of magnetite, improving the fluidity of slag and achieving copper enrichment [6,18,33].
3.3. Reduction of Elements in Copper Slag

Figure 4 shows the compositions of the alloy after the reduction process with 14 wt% carbon and 20 wt% CaO at 1550 °C for 80 min. It can be seen that there were mainly two phases in the metal, namely grey phase 1 (point 1) and white phase 2 (point 2). The grey phase 1 was mainly an Fe-containing phase with an iron content of 96.39%, copper content of 0.38%, and silicon contents of 3.23%, respectively. In white phase 2, the content of copper was up to 5.53%, which was the main copper-containing phase, in which the contents of silicon and iron were 2.35% and 92.12%, respectively. Meanwhile, the white phase was striped and evenly distributed in the gray matrix. In addition, it can be seen from the distribution of elements that iron was basically evenly distributed throughout the region. However, the distribution of copper was higher in the white region than in the gray area, but it was not obvious. Silicon, like iron, was relatively evenly distributed in the region.

Figure 5 shows the distribution of elements in the tailing. It can be seen from the figure that the main elements in the tailing were calcium, silicon, and oxygen. There was a small amount of magnesium and aluminum in the tailing, and their respective contents were less than 3%. The contents of copper and iron were almost negligible, which indicated that the valuable elements in copper slag were almost completely reduced. According to the distribution of elements, it can be seen that the distribution of silicon, calcium, and...
oxygen elements overlapped with each other, which indicated that the main mineral of the tailing was silicate mineral (wollastonite). In addition, from the mineralogical analysis of the tailing, it could be seen that the tailing was mainly composed of \( \text{Ca}_3\text{Si}_3\text{O}_9 \), \( \text{Ca(}\text{Mg, Al})\text{(Si, Al)}_2\text{O}_6 \), and \( \text{SiO}_2 \), which were mainly silicates and quartz, as shown in Figure 6. In addition, it can be seen from Figure 6 that there were no mineral phases of iron or copper in the tailing, which further proved that the reduction of the main valuable elements of iron and copper in the slag was relatively complete.

![Element distribution of the reduced tailing.](image)

**Figure 5.** Element distribution of the reduced tailing.

![XRD pattern of the tailing.](image)

**Figure 6.** XRD pattern of the tailing.

### 3.4. Effect of Reduction Conditions on Recovery of Copper and Iron from Copper Slag

To effectively separate and enrich metal, the reducing temperature was controlled between 1500–1600 °C. To investigate the recovery rate of Fe and Cu, 100 g of the copper slag was reduced under different conditions. Table 3 shows the reducing amount of alloy as well as the recovery rate of Fe and Cu under different conditions. The quality of the alloy was 35.47 g at 1400 °C, 39.89 g at 1500 °C, and 41.11 g at 1600 °C, respectively. The recovery rates of Fe and Cu increased with the increase in temperature while standing at
78.23% for Fe and 76.41% for Cu at 1400 °C, 89.31% for Fe and 84.98% for Cu at 1500 °C, 92.13% for Fe and 86.52% for Cu at 1600 °C. The results indicated that the quality of alloy and recovery rate increased rapidly for the temperature range of 1400–1500 °C. Whereas it increased slowly for a temperature range of 1500–1600 °C, indicating temperature at 1500 °C to be unsuitable for the reduction of Fe and Cu in copper slag. Figure 7 shows the macrographs of the alloy under different conditions. Although the copper slag was reduced and enriched into many small particles at 1400 °C. The small particles that were not coarsened and were dispersed into slag to increase the separation difficulty of metal. Once the temperature reached 1500 °C, the reduction metal was enriched into a large particle and a small number of small particles. Once the temperature reached 1600 °C, the reduced metal was completely coarsened into a large particle and small particles in the slag were not discovered. To effectively separate and enrich metal, the reducing temperature was controlled between 1500–1600 °C.

Table 3. Recovery rate of Fe and Cu with 14 wt% C and 20 wt% CaO at different temperatures for 60 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Quality of Alloy (g)</th>
<th>Recovery Rate of Fe (%)</th>
<th>Recovery Rate of Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1400</td>
<td>35.47</td>
<td>78.23</td>
<td>76.41</td>
</tr>
<tr>
<td>2</td>
<td>1500</td>
<td>39.89</td>
<td>89.31</td>
<td>84.98</td>
</tr>
<tr>
<td>3</td>
<td>1600</td>
<td>41.11</td>
<td>92.13</td>
<td>86.52</td>
</tr>
</tbody>
</table>

Figure 7. Macrographs of the samples after reduction at different conditions: (a) 1400 °C; (b) 1500 °C; (c) 1600 °C.

According to the above analysis, appropriate reduction conditions were found to be important for the coalescence of metals and the reduction of copper and iron because the appropriate temperature could improve the fluidity of the melt and reduce the activation
energy of the reaction, and the appropriate reducing agent and reaction time might be conducive to the reduction of elements. Therefore, the effect of technological conditions such as the amount of modifier, amount of reducing agent, reducing temperature, and holding time on the recovery of copper and iron as well as compositions of the alloy were investigated to obtain the optimal reducing results.

Figure 8 shows the recovery results of copper and iron in the copper slag obtained by modifier (CaO content) at 1500 °C with a holding time of 60 min and 14 wt% C. As shown in Figure 8a, the recovery rate of copper and iron first increased gradually, followed by a rapid rise with the increase in modifier, and scarcely increased during the end. The reduction rate of copper and iron only increased by 1.61% and 1.05% from 5 wt% CaO to 10 wt% CaO, but significantly increased from 10 wt% CaO to 25 wt% CaO and increased by 8.89% and 14.21%, and almost unchanged beyond 25 wt% CaO. This could be attributed to the fact that the addition of CaO reacted with SiO$_2$ in acidic copper slag ($R = (\text{MgO} + \text{CaO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.19$) to generate low melting point composite oxide (CaO-SiO$_2$, 3CaO·2SiO$_2$, CaO·FeO·SiO$_2$, et al.) while improving the melting properties of slag and reaction kinetics [4,10,25,31,41]. In addition, the reaction between CaO and silicate can replace free-FeO, while decreasing the reduction activation energy to improve the reaction of iron. Once the CaO content in slag exceeds a certain amount, the composite oxides with the low melting point can change into high melting point oxides (2CaO·SiO$_2$, 3CaO·SiO$_2$, 2CaO·Al$_2$O$_3$·SiO$_2$, et al.). Moreover, the process may generate free-CaO, which can reduce the fluidity of slag and deteriorate the kinetics of the chemical reaction. In addition, it can be known from Figure 8b that the copper content in metals decreased slightly with the increase of CaO, while the iron content increased slightly. As shown in Figure 8c, even though there was an increase in iron and copper amount with the increase in modifier. However, when the amount of CaO exceeded 25 wt%, the change trends of recovery rate, reduction amount, and metal content of copper and iron could be almost ignored. Overall, CaO as a flux can improve the fluidity of slag and chemical reactions and reduce the nucleation barrier while promoting the rapid nucleation and growth of metal grains [10,31,41]. However, excessive addition of CaO can generate a large number of high melting point phases, which increases the viscosity of slag. Therefore, the mass transfer diffusion of components is not feasible, resulting in difficulties for chemical reaction occurrence [10,31,41]. Moreover, the metal nucleation as well as recovery rate can hinder [10,31,41]. Therefore, the optimum amount of CaO in the slag was found to be 20–25 wt%.

![Figure 8](image-url)

**Figure 8.** Effect of modifier on recovery of copper and iron from copper slag. (a) Recovery rate of Cu and Fe, (b) Content of Cu and Fe in the alloy, (c) Reduction amount of Cu and Fe.
Figure 9 shows the recovery of copper and iron in slag at varying temperatures with 20 wt% CaO and 14 wt% C for 60 min. As illustrated in Figure 9a, the recovery rate of Cu and Fe increased rapidly initially with the increase in temperature, followed by a scarce increase for temperature beyond 1500 °C. The recovery of Cu and Fe reached 85% and 90% at 1500 °C. This could be attributed to the reduction reactions that took place thoroughly while achieving optimum copper and iron reduction rates. Meanwhile, the reducing amount of Fe and Cu increased with the temperature rise, as shown in Figure 9c. Following the trend, the iron content present in the alloy increased gradually, whereas the copper content first increased followed by a decline at the end, as shown in Figure 9b. As the reducing amount of Fe was much greater than that of copper, the copper content declined. From an economic point of view, the suitable temperature could be identified as 1500 °C.

![Figure 9](image-url)  
Figure 9. Effect of reducing temperatures on recovery of copper and iron from copper slag. (a) Recovery rate of Cu and Fe, (b) Content of Cu and Fe in the alloy, (c) Reduction amount of Cu and Fe.

Figure 10 shows the effect of reducing agents on the recovery of copper and iron from copper slag with 20 wt% CaO at 1500 °C for 60 min. It can be seen from Figure 10a that the recovery rate of copper changed slightly with the increase in reducing agents. For iron oxidation, the recovery rate increased with the increase in reducing agent, followed by a scarce increase beyond 14 wt% C. Meanwhile, the content of Fe in alloy increased gradually. On the contrary, the copper content in the alloy decreased as shown in Figure 10b. After complete reduction, the copper and iron content in the alloy was found to be almost unchanged. The reduction amount of copper and iron increased with the increase of the reduction agent, followed by a scarce increase beyond 14 wt% C, which was similar to that of the recovery rate, as shown in Figure 10a,c. This is mainly because copper is more reducible than iron oxide according to the oxygen potential diagram [4,31,32]. Therefore, copper was almost reduced for the low carbon content, whereas iron was partially reduced. Overall, the amount of carbon has a significant impact on the reduction effect of Fe with a reducing agent below 14 wt%. Therefore, the optimum reducing agent was found to be 14 wt% C. Moreover, the recovery of copper and iron reached about 85% and 90%, respectively.
Figure 10. Effect of reducing agent on recovery of copper and iron from copper slag. (a) Recovery rate of Cu and Fe, (b) Content of Cu and Fe in the alloy, (c) Reduction amount of Cu and Fe.

Figure 11 shows the effect of reducing time on the recovery of copper and iron in the copper slag at 1500 °C with 20 wt% CaO and 14 wt% C. As shown in Figure 11a,c, both recovery rate and reducing amount of iron first increased significantly with the extension of reduction time, followed by a scarce increase after 60 min and reaching a constant value for time beyond 80 min, which was because the reduction of copper and iron was basically complete. Meanwhile, the recovery rate and reduction amount of copper increased slightly with the extension of reduction time. In addition, as illustrated in Figure 11b the change trend of iron content in the alloy was opposite to that of copper. However, the contents of copper and iron changed slightly. In general, the appropriate reduction time was found to be 60–80 min, with the recovery rate of iron and copper reaching 90% and 85%, respectively.

Figure 11. Effect of reducing times on recovery of copper and iron from copper slag. (a) Recovery rate of Cu and Fe, (b) Content of Cu and Fe in the alloy, (c) Reduction amount of Cu and Fe.
In general, Cu-Fe alloy was smelted by direct reduction of copper slag to effectively recycle the valuable elements in copper slag, obviously decreasing the amount of waste discharge and storage. The tailing was mainly composed of \( \text{Ca}_3\text{Si}_3\text{O}_9 \), \( \text{Ca}(	ext{Mg, Al})(\text{Si, Al})_2\text{O}_6 \), and \( \text{SiO}_2 \), which could be used as a raw material for cement and pelletizing preparation. Meanwhile, modifier and reduction temperature have the same effect on the recovery of copper and iron. Also, reductant and reduction time have the same effect on the recovery of copper and iron. The recovery rates of copper and iron under suitable conditions could reach over 80% and 90%, respectively. This is mainly due to that there is a proportion of elements in metal and slag at a certain temperature, which leads to the lowest content of copper and iron in the slag. At the same time, as the copper content in the slag was far lower than iron and the reduction amount of iron was much greater than copper, the resulting recovery rate of copper was lower than iron. Overall, the contents of copper and iron in alloy under different conditions were slightly changed. The contents of iron and copper in alloy reached about 91–93 wt% and 5–7 wt%. Based on the above analysis, the optimum condition for reducing copper and iron from the molten copper slag was found to be 1500 °C, 14 wt% C, 20–25 wt% CaO, and 60–80 min.

4. Conclusions

According to the characteristics of copper slag, this study directly used converter copper slag to smelt Cu-Fe alloys, recycling the valuable elements in copper slag, and decreasing the amount of waste discharge. The main conclusions are summarized as follows:

1. The melting temperature of samples first decreased, followed by an increase in \( \text{Fe}_3\text{O}_4 \) in slag. The melting temperature reached a minimum value once the \( \text{Fe}_3\text{O}_4 \) content reached 8 wt%. This could be attributed to the easy formation of \( \text{Fe}_3\text{O}_4 \) low melting point composite oxides with \( \text{SiO}_2 \) and \( \text{CaO} \) in the copper slag.

2. The recovery rate of copper and iron first increased gradually, followed by a rapid increase in the modifier. Finally, the recovery rate scarcely increased, which could be attributed to the reaction between modifier and silicate in acidic copper slag. The reduction rate of copper and iron only increased by 1.61% and 1.05% from 5 wt% \( \text{CaO} \) to 10 wt% \( \text{CaO} \), but significantly increased by 8.89% and 14.21% from 10 wt% \( \text{CaO} \) to 25 wt% \( \text{CaO} \) and almost unchanged beyond 25 wt% \( \text{CaO} \). Meanwhile, the recovery rate of copper and iron increased with the increase in reaction time, reaction temperature, and reduction agent. The increase in iron recovery was obvious, the increase in the copper recovery rate was small.

3. To obtain good element yield, the optimum condition for reducing copper and iron from the molten copper slag was found to be 1500 °C, 14 wt% C, 20–25 wt% CaO, and 60–80 min. The recovery rates of iron and copper reached about 90% and 85%, respectively. Moreover, the contents of iron and copper in alloy reached about 91–93 wt% and 5–7 wt%, respectively. The tailing was mainly composed of \( \text{Ca}_3\text{Si}_3\text{O}_9 \), \( \text{Ca}(	ext{Mg, Al})(\text{Si, Al})_2\text{O}_6 \), and \( \text{SiO}_2 \), which could be used as a raw material for cement and pelletizing preparation.


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