Experimental and Mechanism Analysis of Chlorination and Reduction of Copper Slag

Shuchen Sun², Qingchun Yu¹,*, Yong Deng¹, Xiumin Chen¹, Jing Chen³, and Liang Zhou¹

¹State Key Laboratory of Complex Nonferrous Metal Resources Clear Utilization, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, P.R. China.
²School of Metallurgy, Northeastern University, Shenyang, 110819, P.R. China.
³Faculty of Public Safety and Emergency Management, Kunming University of Science and Technology, Kunming 650093, P.R. China

*Corresponding author

Abstract. Waste copper slag contains large amounts of iron. Carbothermic reduction of the copper slag to recover iron inevitably results in the co-production of copper, which causes brittleness and poses a significant cost to remove. In this work, the method of medium-temperature (MT) chlorination by sodium chloride and high-temperature (HT) reduction by carbon is used to remove copper selectively before the recovery of iron. The composition of raw materials and the products were analyzed by X-ray diffraction (XRD), and chemical analysis. It was found that excessive carbon and high temperature were unfavorable to the removal of copper from the copper slag. Cu₂S and Cu can be chlorinated by sodium chloride and evaporates in the form of CuCl gas. Meanwhile, chlorination mechanism of copper slag was discussed.

Keywords: Copper slag; chlorination; sodium chloride; carbothermic reduction; mechanism.

1. Introduction

Lots of copper slag is produced in a typical pyrometallurgical process for copper production. Most of the copper slag generated is discarded at dump sites, which causes severe environmental pollution. However, the waste slag, depending on the definite process employed, contains about 35-45% wt% of iron that can be recovered if treated suitably.

Iron in copper slag is mostly in the form of fayalite (2FeO•SiO₂), with a small amount in the form of magnetite. High temperature oxidation – room temperature magnetic separation process [1] process was used to recover iron from copper slag. The component of ferrous oxide in fayalite is firstly changed into magnetite phase (Fe₃O₄), then, it is recovered through magnetic separation process. Yang [2] proposed a method with lignite-based direct reduction followed by magnetic separation. The fayalite and magnetite in copper slag reduced to metallic iron with a particle size more than 30 μm on the surface of slag particles. The dissociated metallic iron particles are recovered via magnetic separation method. Different from the two-step process, iron in slag can be reduced directly to metallic iron, i.e., one-step process. An iron-rich alloy with copper content in the range of 0.6-0.8% can be obtained by reduction [3] of a smelting copper slag with 150% of the stoichiometric carbon. Corbari [4] found injecting carbon into slag results into the reaction of the carbon with FeO dissolved in the slag generates gas (CO) that causes the
slag to foam. The addition of CaCO$_3$ [5] improved the ratio of CO among reaction atmosphere and enhanced the reduction rate of iron oxide as well as the metallization rate of iron. Products from HT oxidation and RM magnetic separation are iron concentrates, which require a secondary reduction. Meanwhile, the viscosity of copper slag increases in stage of HT oxidation, which inhibits the oxidation reaction and the growth of the magnetite phase. Carbothermic reduction of copper slag directly to recover iron inevitably results in the co-reduction of large amounts of iron together with copper. High copper content in the pig iron causes the brittleness [6], and makes the iron worthless. Thus, it is felt appropriate to make an attempt to recover iron from copper slag with copper content as low as possible. In this work, MT chlorination and HT reduction of copper slag is used to remove copper before the recovery of iron from the copper slag. The chlorination and the reduction of copper slag were investigated, and the chlorination mechanism was discussed.

2. Experimental

2.1. Materials

The copper slag used in the experiment was a waste product from the Yunnan Copper (Group) Co. Ltd. The slag is dark gray with hard texture and uneven particle size. The slag was first crushed to a fine particle size by a ball grinder, then it was sifted through a 200 mesh sieve and the fraction with particle size under 200 meshes was used in the experiment. The chemical composition, mineral phases were evaluated using chemical analysis and X-ray diffraction (XRD), respectively. As can be seen in Table 1, the slag contained significant levels of iron (41.96wt%), whereas the contents of copper and sulfur were low, approximately to 0.69wt% and 0.85wt%, respectively.

| composition | Fe   | Cu   | SiO$_2$ | Al$_2$O$_3$ | CaO  | MgO  | S   | C   | Others |
|-------------|------|------|---------|-------------|------|------|-----|-----|--------|
| content (wt%)| 41.96| 0.69 | 29.54   | 4.99        | 4.75 | 2.41 | 0.85| 0.02| 14.79  |

2.2. Experimental Methods

The experiments were carried out in a high-frequency induction furnace. Sodium chloride and carbon was used as chlorinating agent and reducing agent, respectively. Sodium chloride and copper slag were mixed uniformly. The mixture was pressed into pellets with 25mm in diameter and 30mm in height under pressure of 15MPa. After the pellets were dried in bake oven at 150 °C for 8 hours, they were charged into the induction furnace. The pellets were subjected to chlorination at 850°C, then following carbothermic reduction after a rapid heating up to 1500°C. After experiment the product was cooled and examined by chemical analysis and XRD. Rc is the removal ratio of copper. The removal ratio of copper is defined as follows:

\[ R_c = \frac{w(c_0) - w(c_1)}{w(c_0)} \times 100\% \]

Where, R$_c$ (%) is the removal ratio of copper, w (c$_0$) and w (c$_1$) are the mass of copper in the initial sample and the product, respectively.

3. Results and Discussion

3.1. Effect of Carbon and Sodium Chloride

The effect of the carbon addition on the chlorination of copper slag is shown in Fig. 1(a). It can be found from Fig. 1(a) that the removal rate of copper increases, then decreases sharply, finally increases again at a normal state. Meanwhile the content of copper appears an opposite change comparing with that of the removal rate of copper, which reaches a maximum of 55.10% with C/Fe molar ratio 1.5, and the copper content in the product is 89.48%. Excessive carbon may inhibit the dissociation of sodium chloride, consequently the removal ratio of copper declines.

The effect of the sodium chloride addition on the chlorination of copper slag is shown in Fig. 1(b). As shown in Fig. 1(b), the copper content increases in a curved shape as the sodium chloride addition
increases, and the removal ratio of copper shows an opposite change within the whole range of sodium chloride addition. The maximum removal ratio of copper is 46.94% with addition of 15% sodium chloride. The lowest copper content in the product is 1.04%, meanwhile, the iron content is 89.80%.

![Graph](a) Carbon addition  (b) Sodium chloride

**Figure 1.** Effect of carbon addition and sodium chloride on the removal of copper.

### 3.2. Effect of Temperature and Time

The effect of temperature on the chlorination of copper slag is shown in Fig. 2(a). It is found that the removal ratio of copper decreases sharply in the temperature range of 850-1050°C in Fig. 2(a). A slightly increase occurs at 1150°C, but decreases again at 1250°C. This indicates that high temperature is unfavorable to the removal of copper from the copper slag. The results are consistent with the phenomenon that the saturated vapor pressure of chlorides increases with increasing temperature [7]. The maximal removal ratio of copper is 52.55% at the temperature of 850°C. Meanwhile, the iron content in the product is 85.85%. The removal rate of copper decreases with increasing temperature, which means the chlorination of copper slag is an exothermic process.

The change of copper content and removal ratio of copper in metal at different times is shown in Fig. 2(a). It can be found that the copper content in the product is between the minimum 0.83% and the maximum 1.12%. The iron content in the product varies little with an average more than 90%. It is obvious that the copper content remarkably decreases. The maximal removal ratio of copper is 57.65% with copper content of 83%. Compared with theoretical copper content 1.96%, the copper content decreases much with the product produced with MT chlorination and HT reduction process.

![Graph](a) Temperature  (b) Time

**Figure 2.** Effect of temperature and time on the removal of copper.

### 3.3. Mechanism Analysis

The phase compositions of the product and the residue is shown in Fig. 3 (a) and (b), respectively. It is found that the phase composition is metallic iron and iron carbide. Carburization of iron occurred because of excessive carbon during the carbothermic reduction process, but excessive carbon can be removed by decarburization in the following steel-making process. The phase composition of the residue is CaO, SiO₂, Al₂O₃, and MgO. FeO or Fe₂O₃ are not found in the residue.
Figure 3. XRD analysis of the product and the residue.

Figure 4. The correlation of Gibbs free energy with temperature for reactions (1) – (8).

Regarding the thermodynamic analysis and the experimental observations above, a possible explanation of the chlorination and carbothermic reduction mechanism pertaining to the slag containing copper and iron is given. The chlorination of copper slag is conducted at 850°C. Sodium chloride is a chlorination agent that can provide gaseous chlorine. SO₂ and SO₃ mainly come from the oxidation of sulfides and the decomposition of sulfates as shown in Fig. 4. The chemical reactions are as follows:

\[
\begin{align*}
2\text{NaCl} + \frac{1}{2} \text{O}_2 (g) &= \text{Na}_2\text{O} + \text{Cl}_2 (g) \quad (1) \\
\text{Na}_2\text{O} + \text{SO}_3 (g) &= \text{Na}_2\text{SO}_4 \quad (2) \\
\text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) &= \text{SO}_3 (g) \quad (3) \\
\end{align*}
\]

(1) + (2) + (3), the additive reaction (4) is obtained.

\[
2\text{NaCl} + \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) = \text{Na}_2\text{SO}_4 + \text{Cl}_2 (g) \quad (4)
\]

It can be seen from the Fig. 4 that \(\Delta G\) of the reaction (1) is far above zero, which indicates the reaction (1) is not thermodynamically feasible. Under the coupling effect of the reaction (2) and (3), the additive reaction (4) becomes feasible at 1123K and Cl₂ is obtained.

\[
\begin{align*}
\text{Cu}_2\text{S} + \text{O}_2 (g) &= 2\text{Cu} + \text{SO}_2 (g) \quad (5) \\
2\text{Cu} + \text{Cl}_2 (g) &= 2\text{CuCl} (g) \quad (6) \\
\text{Cu}_2\text{O} + \text{Cl}_2 (g) &= 2\text{CuCl} (g) + \frac{1}{2}\text{O}_2 (g) \quad (7) \\
\end{align*}
\]

(5) + (6), the additive reaction (8) is obtained.

\[
\text{Cu}_2\text{S} + \text{Cl}_2 (g) + \text{O}_2 (g) = 2\text{CuCl} (g) + \text{SO}_2 (g) \quad (8)
\]
The initial reaction temperature of the reaction (6) is 1035K. Under the coupling effect of reaction (5), the initial temperature of additive reaction (8) drops to -421K. The decrease of the initial reaction temperature enforced removal capability of copper. It can be seen from the Fig. 4, the Gibbs free energy of the reaction (8) is far below zero, which means the reaction (8) can proceed spontaneously under experimental conditions. However, Gibbs free energy of the reaction (4) increases with the increase of temperature, causing the decrease of chlorine amount, which affects the chlorination of Cu2S. This trend is in accordance with the experimental results shown in Fig. 2(a). The initial reaction temperature of the reaction (7) is 1416K, indicating that the reaction (7) will not occur at 1123K. That is why a small amount of copper has been left in the product.

Iron in copper slag mainly exists in the form of fayalite (2FeO•SiO2) and a small amount in the form of ferric oxide (Fe2O3). Meanwhile, the un-chlorinated Cu2O can also be reduced into copper. The chemical reactions during carbothermic reduction of copper slag after chlorination are as follows:

\[ 2\text{FeO} \cdot \text{SiO}_2 + 2\text{C} = 2\text{Fe} + \text{SiO}_2 + 2\text{CO} \ (g) \]  
\[ 2\text{FeO} \cdot \text{SiO}_2 + 2\text{CO} = 2\text{Fe} + \text{SiO}_2 + 2\text{CO}_2 \ (g) \]  
\[ \text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO} \ (g) \]  
\[ \text{Fe}_2\text{O}_3 + 3\text{CO} = 2\text{Fe} + 3\text{CO}_2 \ (g) \]  
\[ \text{Cu}_2\text{O} + \text{C} = \text{Cu} + \text{CO} \ (g) \]  
\[ \text{Cu}_2\text{O} + \text{CO} = \text{Cu} + \text{CO}_2 \ (g) \]  
\[ \text{C} + \text{CO}_2 = 2\text{CO} \ (g) \]  

The reduction of Cu2O by C and CO starts parallel with, and it continues along with the reduction of fayalite and ferric oxide. Reductive product CO2 is transformed into CO again by Boudouard reaction Eq. (15). Many previous works have reported that the carbothermic reduction of fayalite, ferric oxide \[11,12\], and the Boudouard reaction \[13\]. Hence, the details about that will not be demonstrated in current study. In general, MT chlorination and HT reduction is an effective way to reduce copper from copper slag, but more efforts should be done to improve the removal rate of copper.

4. Conclusions
(1) Excessive carbon and high temperature is unfavorable to the removal of copper from copper slag during the chlorination process.
(2) The copper content in metal iron decreases from 1.96% to 0.83%, and the maximum iron content in the product is 92.18%.
(3) Cu2S and Cu can be chlorinated by sodium chloride and evaporates in the form of CuCl gas.

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