Calculation Model for Activity of FeO in Quaternary Slag System SiO$_2$-CaO-Al$_2$O$_3$-FeO

Zhi Li $^{1,2,3}$, Guojun Ma $^{1,2,3,*}$, Mengke Liu $^{1,2,3}$ and Jingjing Zou $^{1,2,3}$

$^1$ State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China; zhili@wust.edu.cn (Z.L.); liumengke@wust.edu.cn (M.L.); zjj980125@icloud.com (J.Z.)

$^2$ Hubei Provincial Engineering Technology Research Center of Metallurgical Secondary Resources, Wuhan University of Science and Technology, Wuhan 430081, China

$^3$ Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan 430081, China

* Corresponding author: gma@wust.edu.cn; Tel.: +86-27-68862810

Received: 17 August 2018; Accepted: 6 September 2018; Published: 12 September 2018

Abstract: According to the coexistence theory of slag structure, a calculation model for the activity of FeO in the quaternary system SiO$_2$-CaO-Al$_2$O$_3$-FeO of depleted copper slag was established. The model was used to calculate and analyze the effects of temperature (T), basicity (B), and Al$_2$O$_3$ content on the activity of FeO ($N_{FeO}$). The results show that temperature has little impact on $N_{FeO}$. With increased basicity, $N_{FeO}$ first increased slightly, then increased sharply, and finally decreased. It is easier for CaO to combine with SiO$_2$ than FeO to form calcium silicate, which replaces FeO in 2FeO·SiO$_2$ and increases $N_{FeO}$. However, when basicity is higher than 2.0, CaO not only reacts with SiO$_2$, but also combines with FeO to form calcium ferrate compounds to decrease $N_{FeO}$. In addition, the activity of FeO decreases with increased Al$_2$O$_3$ content because of the reaction between CaO and Al$_2$O$_3$. The results can be used as a theoretical basis to guide the carbothermal reduction process of copper slag.

Keywords: copper slag; activity of FeO; calculation model for activity

1. Introduction

In the last 50 years, copper consumption has tripled because of rapid industrial development [1]. The production of refined copper was 23.33Mt in 2016, and the quantity of copper increases year by year [1]. According to a prediction by the International Copper Study Group (ICSG), the global supply of refined copper slightly increased by 0.9% in 2017, far below the average growth rate of 3% in the previous 10 years due to the fact that the depletion of global mines is more and more serious, and the grade of newly discovered mines is low. Considering the huge consumption and lack of supply, it is extremely urgent to make full use of copper production and other Cu-containing wastes.

Copper slag is one of the byproducts of the copper production process. Typically, about 2.2–3 t of copper slag are generated per ton of matte produced [2,3], which indicates that the annual output of copper slag was at least 51.33 Mt in 2016. There are abundant metals in copper slag, in which the grades of copper and iron are close to or even higher than corresponding ores of copper and iron. There are several main processes of recycling copper and iron in copper slag, such as beneficiation, oxidation-magnetic separation, smelting reduction, and carbothermal reduction at high temperature. It is generally believed that smelting reduction and carbothermal reduction at high temperature are effective ways to reutilize copper slag, which can obtain carbon-saturated molten iron containing less than 0.4% copper [4–7]. Zhang et al. [8] reported on copper slag and iron-bearing slag as flux to recover iron and separate phosphorus, where the recovery of iron could be as high as 90%. According to the
results of Xing et al. [9], temperature has a great effect on the recovery of iron and zinc, but has little effect on the recovery of copper. The recovery of iron and copper can reach 91% and 99%, respectively. However, there is a high level of Cu in the recovered iron-bearing product, and it restricts these products from being used in the steelmaking process. Tang et al. [10] reported that the oxidizing ratio of copper in CuO-FeCl₂ can reach 62.5% with an argon flow of 50 mL/min at 973 K, based on the fact that it is easier for Cu to react with Cl than Fe and CuCl₂ can be volatilized easily. However, the high cost of the recycling process hinders the recycling of copper slag. Therefore, large amounts of copper slag are simply stockpiled or placed in landfills. The residual elements in copper slag, such as Zn, Pb, and As, are potentially leached with rainwater, resulting in excessive levels of heavy metals in groundwater and spread of small particles of copper slag in the air, causing health hazards for nearby people and animals [11, 12]. In order to make full use of copper slag and improve the ratio of recycling, the thermodynamics of the carbothermal reduction of copper slag should be further studied.

As the main iron-containing phase of copper slag is fayalite (2FeO-SiO₂), the activity of FeO has a significant effect on the reduction process. The activity of FeO in blast furnace slag has been investigated by O’Neill et al. [13], Taniguchi et al. [14], and Arotu et al. [15], and has been shown to have relatively low FeO content (<5 wt. %). Zhang [16] utilized the coexistence theory of slag structure to calculate the activity of FeO in the ternary slag system SiO₂-CaO-FeO, and compared with other studies [17], the results are similar. However, the FeO content in copper slag is higher than that in steel slag. Wang et al. [18] employed the coexistence theory of slag structure for the ternary slag system SiO₂-CaO-FeO to calculate the activity of FeO with different basicity in order to recovery iron in copper slag. However, Al₂O₃ in the slag was ignored during the calculation, which led to errors in the results.

The coexistence theory of slag structure was initially proposed by Chuiko [19] and developed by Zhang [16]. The coexistence theory is based on the relevant phase diagrams, thermodynamic relations, and the law of mass balance of ions and molecules coexisting in molten slag, and establishes some equations to calculate the concentrate of components, by which the activity of components is characterized. The theory has already been used in some slag systems, such as CaO-FeO-Fe₂O₃-SiO₂-Cu₂O and MnO-FeO-SiO₂-Al₂O₃ [20, 21].

In this paper, a calculation model for the activity of FeO in the quaternary slag system SiO₂-CaO-Al₂O₃-FeO is established according to the coexistence theory of slag structure, in order to analyze the variation of FeO activity with the effect of temperature (T), basicity (B), and Al₂O₃ content and provide a theoretical basis to guide the carbothermal reduction process of copper slag.

2. Calculation Model of Activity

According to the coexistence theory of slag structure and relevant phase diagrams [22] such as CaO-SiO₂, Al₂O₃-CaO, SiO₂-Al₂O₃, SiO₂-FeO, Al₂O₃-FeO, SiO₂-CaO-Al₂O₃, and SiO₂-CaO-FeO, the structural units were determined at 1573–1773 K, shown in Table 1.

<table>
<thead>
<tr>
<th>Simple Ions</th>
<th>Ca²⁺, Fe²⁺, O²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO-SiO₂, 2CaO-SiO₂, 3CaO-SiO₂, 3CaO-2SiO₂, 3Al₂O₃-2SiO₂, 3CaO-Al₂O₃, 12CaO-7Al₂O₃, CaO-2Al₂O₃, CaO-6Al₂O₃, CaO-Al₂O₃, 2FeO-SiO₂, FeO-Al₂O₃, CaO-Al₂O₃, 2SiO₂, 2CaO-Al₂O₃-SiO₂, CaO-FeO-SiO₂, Al₂O₃, SiO₂</td>
<td></td>
</tr>
</tbody>
</table>
obtained first based on specific temperature and the standard Gibbs free energy. Then, the equilibrium constants in Table 2, and the components of slags in Table 3. The equilibrium constants $\Delta G_{m1}^{o} = -81416 - 10.498T$ $N_3 = k_1N_2N_3$

$\Delta G_{m1}^{o} = -160431 + 4.160T$ $N_6 = k_2N_2N_3$

$\Delta G_{m3}^{o} = -93366 - 23.03T$ $N_7 = k_2N_2N_3$

$\Delta G_{m4}^{o} = -236973 + 9.63T$ $N_8 = k_3N_2N_3$

$\Delta G_{m5}^{o} = 8589.9 - 17.39T$ $N_9 = k_3N_2N_3$

$\Delta G_{m6}^{o} = -17000 - 32.0T$ $N_{10} = k_4N_2N_4$

$\Delta G_{m7}^{o} = -86100 - 205.17T$ $N_{11} = k_5N_2N_5$

$\Delta G_{m8}^{o} = -16400 - 26.87T$ $N_{12} = k_6N_2N_6$

$\Delta G_{m9}^{o} = -17430 - 37.2T$ $N_{13} = k_6N_2N_7$

$\Delta G_{m10}^{o} = -18120 - 16.82T$ $N_{14} = k_6N_2O_4$

$\Delta G_{m11}^{o} = -28986 + 3.349T$ $N_{15} = k_4N_2N_5$

$\Delta G_{m12}^{o} = -33272.8 + 6.1028T$ $N_{16} = k_4N_2N_6$

$\Delta G_{m13}^{o} = 28006 - 74.795T$ $N_{17} = k_4N_2N_7$

$\Delta G_{m14}^{o} = -17092 + 8.778T$ $N_{18} = k_4N_2N_8$

$\Delta G_{m15}^{o} = -72996.8 - 29.3169T$ $N_{19} = k_4N_2N_9$

The ternary phase diagram of $SiO_2$-$CaO$-$Al_2O_3$ is depicted in Figure 1 using FactSage software (Version 7.0, GTT-TECHNOLOGIES, Herzogenrath, Germany). According to the phase diagram, two kinds of slags are suitable to recover iron for less energy consumption, better liquidity, and less viscosity. The major chemical composition of the initial copper slag and the composition of the two kinds of slag are shown in Table 3. Considering high FeO content, the quaternary slag system of $SiO_2$-$CaO$-$Al_2O_3$-$FeO$ has been established.

The activity calculation program was developed based on Equations (6) to (9), the equilibrium constants in Table 2, and the components of slags in Table 3. The equilibrium constants $k_i$ ($i = 1\rightarrow 15$) were obtained first based on specific temperature and the standard Gibbs free energy. Then, the equilibrium constants and the composition of slags in Table 3 were substituted into Equations (6) to (9), and the contents of the composition in the $SiO_2$-$CaO$-$Al_2O_3$-$FeO$ slag system were calculated. According to the variation of temperature and compositions of slag, the effect of temperature, basicity, and $Al_2O_3$ content were obtained.

$$\sum_{i=1}^{19} N_i = 1$$

$$x_1 = (0.5N_1 + 2N_{15} + N_{16} + N_{19})\sum n$$

$$x_2 = (0.5N_2 + N_5 + 2N_6 + 3N_7 + 3N_9 + 3N_{10} + 12N_{11} + N_{12} + N_{13} + N_{14} + N_{17} + 2N_{18} + N_{19})\sum n$$

$$x_3 = (N_3 + N_5 + N_7 + 2N_8 + 2N_9 + 2N_{15} + 2N_{17} + N_{18} + N_{19})\sum n$$

$$x_4 = (N_4 + 3N_9 + N_{10} + 7N_{11} + 2N_{12} + 6N_{13} + N_{14} + N_{16} + N_{17} + N_{18})\sum n$$

$$N_1 + N_5 + N_8 + k_1N_2N_3 + k_2N_2N_3 + k_3N_2N_3 + k_4N_2N_3 + k_8N_2N_3 + k_9N_2N_3 + k_{10}N_2N_3 + k_{11}N_2N_3 + k_{12}N_2N_3 + k_{13}N_2N_3 + k_{14}N_2N_3 + k_{15}N_2N_3 = 1$$

$$x_5 (0.5N_2 + 3k_3N_2N_3 + 12k_8N_2N_3 + k_9N_2N_3 + k_{10}N_2N_3) - x_3 (N_3 + 2N_5N_2N_3 + k_1N_2N_3) + (k_3N_2N_3 + k_5N_2N_3)(x_3 - x_2) + (k_2N_2N_3 + k_4N_2N_3)(2x_3 - x_2) + k_8N_2N_3(3x_3 - x_2) + k_9N_2N_3(3x_3 - 2x_2) + k_{10}N_2N_3(3x_3 - 2x_2) = 0$$

$$x_6 (N_4 + 3k_3N_2N_3 + k_{14}N_2N_3) - x_4 (0.5N_2 + k_1N_2N_3 + 2k_2N_2N_3 + 3k_8N_2N_3 + 3k_9N_2N_3 + k_{14}N_2N_3) - k_9N_2N_3(x_3 - x_4) + k_{10}N_2N_3(7x_2 - 12x_4) + k_8N_2N_3(2x_2 - x_4) + k_9N_2N_3(6x_2 - x_4) + (k_{10}N_2N_3(x_2 - x_4) + 14k_8N_2N_3(x_2 - x_4) = 0$$

$$x_7 (0.5N_1 + k_{12}N_1N_4) - x_3 (N_3 + k_1N_2N_3 + k_2N_2N_3 + k_3N_2N_3 + 2k_4N_2N_3 + 2k_5N_2N_3 + 2k_3N_2N_3 + k_{14}N_2N_3) + k_{11}N_2N_3(3x_3 - x_1) + k_{15}N_1N_2N_3(x_3 - x_1) = 0$$

$$x_8 (0.5N_1 + k_{12}N_1N_4) - x_3 (N_3 + k_1N_2N_3 + k_2N_2N_3 + k_3N_2N_3 + 2k_4N_2N_3 + 2k_5N_2N_3 + 2k_3N_2N_3 + k_{14}N_2N_3) + k_{11}N_2N_3(3x_3 - x_1) + k_{15}N_1N_2N_3(x_3 - x_1) = 0$$

$$x_9 (0.5N_1 + k_{12}N_1N_4) - x_3 (N_3 + k_1N_2N_3 + k_2N_2N_3 + k_3N_2N_3 + 2k_4N_2N_3 + 2k_5N_2N_3 + 2k_3N_2N_3 + k_{14}N_2N_3) + k_{11}N_2N_3(3x_3 - x_1) + k_{15}N_1N_2N_3(x_3 - x_1) = 0$$

Table 2. Chemical equilibria of structural units.
3. Results and Discussion

3.1. Effect of Temperature on Activity of FeO

To consider the effect of temperature on the activity of FeO ($N_{FeO}$), $N_{FeO}$ was calculated in the different slags shown in Table 3 and at a temperature range of 1573–1823 K. The results are shown in Figure 2. It was found that $N_{FeO}$ in the two slags increased slightly with increased temperature. Figure 3 shows the activity of some components in slag 2 at different temperatures. F, S, C, and A represent FeO, SiO$_2$, CaO, and Al$_2$O$_3$, respectively.

### Table 3. Chemical composition of copper slag (wt. %).

<table>
<thead>
<tr>
<th>Slag Type</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>FeO</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>39.96</td>
<td>7.21</td>
<td>3.35</td>
<td>49.47</td>
<td>0.08</td>
</tr>
<tr>
<td>1</td>
<td>34.91</td>
<td>7.61</td>
<td>14.27</td>
<td>43.22</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>27.50</td>
<td>11.90</td>
<td>26.55</td>
<td>34.05</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Figure 1. Phase diagram of SiO$_2$-Al$_2$O$_3$-CaO.

Figure 3. Chemical composition of copper slag (wt. %).
3.2. Effect of Basicity on Activity of FeO

To calculate the effect of basicity on $N_{FeO}$, the contents of $Al_2O_3$ and FeO were kept constant at 7.61% and 43.36% in slag 1, respectively. In slag 2, the contents of $Al_2O_3$ and FeO were 11.90% and 33.68%, respectively. From Figure 2, it can be seen that temperature had little effect on $N_{FeO}$, thus the study was carried out at 1723 K, and basicity was used with binary basicity $R = w(CaO)/w(SiO_2)\%$. The results are shown in Figure 4, indicating that the tendency of $N_{FeO}$ was the same with different contents of $Al_2O_3$ and FeO. $N_{FeO}$ first increased slightly, then increased sharply, and finally decreased. In slag 1, the maximum activity was 0.64 at basicity of 1.7, while the maximum was 0.55 in slag 2 with basicity of 2.0. From Table 2, it can be seen that $\Sigma n$, the sum of moles of ions and molecules in the slag system, decreased because of the reactions between CaO and SiO$_2$. According to the equation $N_{FeO} = 2x_{FeO}/\Sigma n$, $N_{FeO}$ would increase as the reactions between CaO and SiO$_2$ proceed. On the other
hand, FeO would react with CaO, Al₂O₃, or SiO₂, which would decrease the content of FeO. Since these two are opposite factors, the activity of FeO would appear at the maximum value.

In Figure 5, the measured $\gamma_{FeO}$ results are plotted for slag systems of SiO₂-CaO-Al₂O₃-FeO and SiO₂-CaO-FeO by Taniguchi et al. [14], Arato et al. [15], and Wang et al. [18]. It is found that the present work is in good agreement with the results of Taniguchi et al. and Arato et al., while it is within the wide variation range reported by Wang et al. This is possibly because Al₂O₃ was not considered by Wang et al. Comparing the results of Taniguchi et al., Arato et al., and the present work, the results here are very small, which probably means that the effect of Al₂O₃ on $\gamma_{FeO}$ is inert in the system.

Figure 6 shows the activity of some components in slag 2 at 1723 K. When basicity was below 0.8, the activity of Al₂O₃ and SiO₂ declined and the activity of CFS (CaO-FeO-SiO₂) increased. As basicity increased to 0.8, there was little activity of 2CaO-SiO₂ and 2FeO-SiO₂ disappeared gradually, which means that CaO reacts with 2FeO-SiO₂ first to form CaO-FeO-SiO₂, instead of forming 2CaO-SiO₂. It proves that while the content of CaO is low, it is hard to replace the FeO from
2FeO-SiO$_2$. During the process, $\Sigma r$ decreased and $N_{FeO}$ increased. Therefore, although the content of FeO decreased, $N_{FeO}$ increased slowly.

![Figure 6](image-url) 

**Figure 6.** Activity of some components in slag 2 with different basicity, C$_2$S, F$_2$S and CFS, represent 2CaO-SiO$_2$, 2FeO-SiO$_2$ and CaO-FeO-SiO$_2$ respectively.

From Figure 6, it can be seen that the tendency of the activity of 2CaO-SiO$_2$ is same as that of FeO when basicity is higher than 0.8, and the activity of CaO increases while the activity of CaO-FeO-SiO$_2$ declines. This indicates that CaO reacted with CaO-FeO-SiO$_2$ to form FeO and 2CaO-SiO$_2$ with increased basicity, making the activity of FeO and 2CaO-SiO$_2$ increase. The formation of 2CaO-SiO$_2$ in copper slag has two steps, shown in Equations (10) and (11): first CaO reacts with 2FeO-SiO$_2$ to form CaO-FeO-SiO$_2$ and FeO, and then CaO reacts with CaO-FeO-SiO$_2$ to form 2CaO-SiO$_2$ and FeO. CaO is alkaline oxide and can dissociate O$^{2-}$ and Ca$^{2+}$ easily. Meanwhile, CaO has higher alkalinity than FeO. On the contrary, SiO$_2$ is acidic oxide, which reacts more easily with CaO. FeO bound with SiO$_2$ in the form of 2FeO-SiO$_2$ would be free to increase the $N_{FeO}$.

\[
(Ca^{2+} + O^{2-}) + 2FeO\cdot SiO_2 = CaO\cdot FeO\cdot SiO_2 + FeO \quad (10)
\]

\[
(Ca^{2+} + O^{2-}) + CaO\cdot FeO\cdot SiO_2 = 2CaO\cdot SiO_2 + FeO \quad (11)
\]

When basicity reaches near 2.0, maximum $N_{FeO}$ as the affinity of CaO for SiO$_2$ reaches the maximum value at the ratio of $N_{CaO}/N_{SiO_2} = 2$ [14]. When the value of Si/O is smaller, the structure of silicate is more stable and simpler. With basicity higher than 2.0, the CaO content still increases. By this, all the silicate exists as SiO$_2$$^4$-, which is the most stable structure (Si/O = 1/4) [23], and O$^{2-}$ cannot continue to be consumed to form silicate. Residual O$^{2-}$ reacts with Fe$^{2+}$ to form FeO$_2$$^2_-$, decreasing the FeO content; in the meantime, residual CaO reacts with FeO to form calcium ferrate compounds. With these two results, the activity of FeO decreases [24].

3.3. Effect of Al$_2$O$_3$ on Activity of FeO

$N_{FeO}$ was calculated in different contents of Al$_2$O$_3$ for slag 1 and slag 2 with basicity of 1.7 and 2.0, respectively, at 1723 K, as shown in Figure 7. It can be seen that the value of $N_{FeO}$ slightly decreased with increased Al$_2$O$_3$ content, but the variation was very small. To study the variation further, the activity of some components in the slag system were calculated and are shown in Figure 8.

From Figure 8, it can be seen that the value of the activity of FA (FeO-Al$_2$O$_3$) is very small, just like the value of the activity of S (SiO$_2$). Although the activity of FeO-Al$_2$O$_3$ increased with increased Al$_2$O$_3$ content, the value of activity of FeO-Al$_2$O$_3$ was so small to be ignored, which means it is hard for Al$_2$O$_3$ to react with FeO in this slag system. On the other hand, the activity of CaO-Al$_2$O$_3$ increased, indicating that the Al$_2$O$_3$ reacted with CaO and decreased its activity. With such a decrease, it is
difficult for CaO to replace FeO from $2\text{FeO} \cdot \text{SiO}_2$, which decreases the $N_{\text{FeO}}$ [24]. CaO can only react with $2\text{FeO} \cdot \text{SiO}_2$ to form $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$, as in Equation (10). Therefore, the activity of $2\text{CaO} \cdot \text{SiO}_2$ decreases and the activity of $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$ increases when the content of $\text{Al}_2\text{O}_3$ increases.

![Figure 7. Effect of $\text{Al}_2\text{O}_3$ on activity of FeO.](image)

![Figure 8. Activity trend of some components in slag 2. $\text{C}_2\text{S}$, $\text{CA}$, $\text{F}_2\text{S}$, $\text{FA}$ and $\text{CFS}$ represent $2\text{CaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{FeO} \cdot \text{SiO}_2$, $\text{FeO} \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$, respectively.](image)

4. Conclusions

1. The calculation model can predict the activity of components generated in the quaternary slag system $\text{SiO}_2$-$\text{CaO}$-$\text{Al}_2\text{O}_3$-$\text{FeO}$ with different temperatures, basicity, and $\text{Al}_2\text{O}_3$ content. Temperature influences the activity of $N_{\text{FeO}}$ slightly at 1573–1773 K.

2. Basicity is the major factor affecting the activity of FeO. With basicity ranging from 0.4 to 0.8, $N_{\text{FeO}}$ increased slightly due to the formation of $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$. When basicity reaches near 2.0, there is maximum $N_{\text{FeO}}$, as CaO can react with SiO$_2$ to form the most stable and simplest structure, SiO$_{\frac{1}{4}}^-$ (Si/O = 1/4). When basicity is higher than 2.0, CaO not only reacts with SiO$_2$, but also combines with FeO to form calcium ferrate compounds to decrease $N_{\text{FeO}}$.

3. The value of $N_{\text{FeO}}$ slightly decreases with increased $\text{Al}_2\text{O}_3$ content, as CaO reacts with $\text{Al}_2\text{O}_3$, which limits the free FeO generated from $2\text{FeO} \cdot \text{SiO}_2$. 

Author Contributions:


Funding: This research was funded by Hubei Provincial Special Project on Technology Innovation (Foreign Scientific and Technological Cooperation), grant number: 2017AHB042.

Conflicts of Interest: The authors declare no conflict of interest.

References
7. Sarfo, P.; Wyss, G.; Ma, G.J.; Das, A.; Young, C. Carbothermic reduction of copper smelter slag for recycling into pig iron and glass. Miner. Eng. 2017, 107, 8–19. [CrossRef]


© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).