Effects of CaO on Reduction of Copper Slag by Biomass Based on Ion and Molecule Coexistence Theory and Thermogravimetric Experiments

Zongliang ZUO, Qingbo YU,* Junxiang LIU, Qin QIN, Huaqing XIE, Fan YANG and Wenjun DUAN

School of Metallurgy, Northeastern University, NO. 11, Lane 3, Wenhua Road, Heping District, Shenyang, Liaoning, 110819 P. R. China.

(Received on July 1, 2016; accepted on September 28, 2016)

Based on the ion and molecule coexistence theory, the calculation model of action concentration for system of CaO–FeO–Fe2O3–SiO2 copper slags was built up in this article. Effects of CaO, reaction temperature and reduction ratio on reduction of copper slag were discussed. Thermogravimetric experiments of the reduction of copper slag were carried out. As a good potential reductant, biomass was injected and it undertook the task of the reduction of copper slag.

The contents of FeO and Fe2O3 reflect reduction degree in copper slag. The addition of CaO could change the balance of reaction system and promote the separation of Fe and Si from 2FeO·SiO2, which was in favor of copper slag reduction. The effects of temperature on mass action concentration were affected by the addition of CaO. High temperature was in favor of the reduction of Fe3O4 in copper slag. However, excessive addition of CaO (when the content of CaO was over 28% in calculate conditions) caused excessive insoluble solid in slag, increased the viscosity of copper slag and restricted reduction reactions.

The calculation results achieved high conformity with thermogravimetric experiments. The results obtained in this work indicated that biomass would be a good potential reductant for reduction of copper slag. CaO had promotion effects on the reduction reaction. With the increase of CaO, reduction ratio of copper slag increased firstly and reached a peak when CaO/Slag was 0.3:1 and then it declined due to the changes of slag viscosity.

KEY WORDS: copper slag; coexistence theory; biomass; calculation model.

1. Introduction

Copper slag, which is produced during pyrometallurgical production of copper contains large amount of iron. For every ton of copper production about 2.2 tons of slag is generated.1) Therefore, different recovery methods have been studied in order to recover iron from copper slag.2–8) By contrast, reduction method recovers iron by addition of different kinds of reductant and it has the advantages of high Fe recovery and low pollution for the environment. However, reduction method increases energy consumption at the same time.

Considering the acceleration of global warming nowadays, energy saving and CO2 emission reduction in the industry have attracted more and more attention.9) As one of the cheaper sources of clean energy, biomass could be a good potential reductant for the recovery of iron from copper slag. With the variations in chemical compositions of biomass reductant, reduction properties could be changed which influence the recovery of iron from copper slag.

Besides, slag-making material was added in reduction process of copper slag and the structure of copper slag changed as a consequence.10,11)

Based on the coexistence of ion and molecule in slag, Zhang12) developed ion theory and proposed the ion and molecule coexistence theory (IMCT), which enlarged the understanding of the slag structure. After the follow-up studies, IMCT has been successfully applied to the calculation of mass action concentrations, distribution of nonmetallic inclusions and oxidizing capability in different kinds of slag systems.13–16) Copper slag, as a raw material of iron resource, is mainly in the form of fayalite (2FeO·SiO2) and magnetite (Fe3O4). In molten slag system, ferric iron and ferrous iron are in the components of FeO and Fe2O3. Fe3O4 phase in copper slag is the combination of FeO and Fe2O3 in slag system.14,17) When the slag-making material and reductant are added in molten slag, ferric iron and ferrous iron convert to low valence states and silicate is produced. Besides, additives (CaO, MgO, SiO2, Al2O3, MnO, NiO, Cr2O3) had influence on the reduction of Fe2O3, which was investigated in details by Geassy, Nasr, Khedr, Hessein et al.18–21) And in their experiments, CaO had the promotion influence on the reduction of iron oxides.
The calculation model of action concentration for CaO–FeO–Fe₂O₃–SiO₂ copper slag system was built up on the basis of IMCT in this article. The effects of CaO addition, the contents of FeO and Fe₂O₃, and reaction temperature on reduction of copper slag were discussed. Based on the guides of calculation model, thermogravimetric experiments for reduction of copper slag by three typical kinds of biomasses were carried out. By contrast, the calculation results achieved high conformity with thermogravimetric experiments.

2. Model for Calculating Mass Action Concentrations of Structural Units in CaO–FeO–Fe₂O₃–SiO₂ Slags

2.1. Hypothesis

According to IMCT, ion and molecule exist in slags simultaneously. The main assumptions in thermodynamic model for calculation mass action concentrations of structural units are as follows:

(1) The structural units in CaO–FeO–Fe₂O₃–SiO₂ molten slags are composed of simple ions, simple molecules and complex molecules. Each structural unit is independent in slags.

(2) The forming of complex molecules is confirmed by reactions of chemical dynamic equilibrium.

(3) The structural units in slags obey the law of conservation of mass.

(4) The contents of CuO, CuS and CaS in copper slags are lower than 0.5%. The reactions of Cu²⁺ and S²⁻ in copper slags are ignored in this paper.

2.2. Structural Units in Copper Slag System

According to phase diagrams of CaO–SiO₂, FeO–Fe₂O₃, FeO–Fe₂O₄, CaO–FeO–Fe₂O₃, CaO–FeO–SiO₂ from 1 523 K–1 723 K, structural units of CaO–FeO–Fe₂O₃–SiO₂ copper slags are listed in Table 1. Therefore, 5 kinds of simple ions and molecules (Fe²⁺, Ca²⁺, O²⁻, SiO₂ and Fe₂O₃) and 10 kinds of complex compounds (2CaO·Fe₂O₃, CaO·FeO·Fe₂O₃, FeO·SiO₂, CaO·SiO₂, 2FeO·SiO₂, 3CaO·SiO₂, 3CaO·2SiO₂, 2CaO·2SiO₂, 2FeO·2SiO₂, CaO·Fe₂O₃–SiO₂) are determined in CaO–FeO–Fe₂O₃–SiO₂ copper slags.

2.3. Mass Action Concentrations Calculating Model for CaO–FeO–Fe₂O₃–SiO₂ Slags

The definition of the action concentration of the slag system is described in Table 2. Chemical reactions between structural units in slags include Reactions (1)–(9) as shown in Table 3.

Based on conservation of element mass in copper slag system, the balanced relationships are concluded as follows:

\[ (0.5 \times N_1 + 2 \times N_3 + N_6 + N_7 + N_9 + 2 \times N_{10} + 3 \times N_{11} + 3 \times N_{12} + N_{13} ) \times \text{sum}(n) - n_1 = 0 \]  

(1) (mass conservation of Ca)

\[ (0.5 \times N_2 + N_4 + N_8 + 2 \times N_{11} + N_{14} ) \times \text{sum}(n) - n_2 = 0 \]  

(2) (mass conservation of Fe)

Equations (1)–(15) above make up the mass action concentrations calculating model for CaO–FeO–Fe₂O₃–SiO₂ slags. The calculating model is a system of nonlinear multivariable equations. In the equations, \( n_1, n_2, n_3 \) and \( n_4 \) are determined by chemical composition analysis of copper slags.

| Phase diagram | Simple ions and molecules | Complex compounds |
|---------------|---------------------------|-------------------|
| CaO–SiO₂     | Ca²⁺, O²⁻, SiO₂          | CaO·SiO₂          |
| CaO·SiO₂     | CaO·Fe₂O₃, CaO·FeO·Fe₂O₃, FeO·SiO₂, CaO·SiO₂, 2FeO·SiO₂, 3CaO·SiO₂, 3CaO·2SiO₂, 2FeO·2SiO₂, CaO·Fe₂O₃–SiO₂ | CaO·Fe₂O₃, CaO·FeO·Fe₂O₃, FeO·SiO₂, CaO·SiO₂, 2FeO·SiO₂, 3CaO·SiO₂, 3CaO·2SiO₂, 2FeO·2SiO₂, CaO·Fe₂O₃–SiO₂ |

Equations (1)–(15) for calculation of structural units in CaO–FeO–Fe₂O₃–SiO₂ copper slags, 2017 ISIJ
slag. Programming by MATLAB, and using Levenberg-Marquardt calculation method,\(^{23}\) the calculation model was solved.

2.4. Results of Calculated Mass Action Concentrations for Structural Units and Ion Couples in CaO–FeO–Fe\(_2\)O\(_3\)–SiO\(_2\) Slags

2.4.1. Effects of FeO Content on Mass Action Concentrations in Slags

The reduction of hematite was in the sequence of Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), FeO and Fe\(^{2+}\). FeO is an important intermediate product for reduction. Determined by chemical composition analysis of copper slag, in the calculated original slag, mass\%CaO, mass\%SiO\(_2\), mass\%FeO and mass\%Fe\(_2\)O\(_3\) are 0.3\%, 37.9\%, 44.6\% and 17.2\% respectively. The content of FeO reflects the properties of smelting copper slag and had effects on reduction ratio of copper slag. Mass action concentrations of N5(2CaO·FeO\(_2\)), N6(CaO·Fe\(_2\)O\(_3\)), N7(Ca\(_2\)O·Fe\(_2\)O\(_4\)), N10(2CaO·SiO\(_2\)), N11(3CaO·SiO\(_2\)) and N12(3CaO·2SiO\(_2\)) were lower than 10\(^{-3}\) in calculation conditions and the changes of them were not discussed in this paper.

As we can see from Fig. 1, mass action concentrations of structural units in copper slag presented different trends with the change of FeO content. With the increase of FeO, mass action concentration of SiO\(_2\) decreased but mass action concentration of 2FeO·SiO\(_2\) increased. The increase of FeO strengthened the driving force for generation of 2FeO·SiO\(_2\) and promoted the Reaction (8). Mass action concentrations of CaO·SiO\(_2\) and CaO·FeO·SiO\(_2\) remained stable and Fe\(_3\)O\(_4\) declined linearly.

2.4.2. Effects of Fe\(_2\)O\(_3\) Content on Mass Action Concentrations in Slags

According to Fig. 2, with the increase of Fe\(_2\)O\(_3\), the mass action concentrations of SiO\(_2\) and 2FeO·SiO\(_2\) decreased in variously degrees. However, the mass action concentration of FeO\(_2\) increased at first and later slowly flattened. At lower contents of FeO\(_2\) in copper slag, oxygen free ion (O\(^{2-}\)) combined with ferrous (Fe\(^{2+}\)) and ferric (Fe\(^{3+}\)) iron and transform into FeO\(_2\). When the content of FeO\(_2\) reached to 50\%, FeO\(_2\) reached saturation and the increase rate of mass action concentration of FeO\(_2\) was enforced.

---

### Table 2. The definition of the action concentration of the slag system.

| Structural units | Mole number of structural units | Mass action concentrations |
|------------------|--------------------------------|---------------------------|
| Fe\(^{2+}\) + O\(^{2-}\) | n\(_2\)/sum(n) | N\(_1\) = N\(_{CaO}\) = 2n\(_1)/sum(n) |
| Ca\(^{2+}\) + O\(^{2-}\) | n\(_3\)/sum(n) | N\(_1\) = N\(_{CaO}\) = 2n\(_1)/sum(n) |
| SiO\(_2\) | n\(_1\)/sum(n) | N\(_1\) = N\(_{CaO}\) = 2n\(_1)/sum(n) |
| FeO | n\(_2\)/sum(n) | N\(_1\) = N\(_{CaO}\) = 2n\(_1)/sum(n) |

### Table 3. The expressions of chemical reactions, standard Gibbs free energy, equilibrium constants and mass action concentrations.\(^{22}\)

| NO | Reactions | \(\Delta G (J/mol)\) | \(N_i\) |
|----|-----------|-------------------|-----|
| 1  | 2(Ca\(^{2+}\) + O\(^{2-}\)) + FeO\(_2\) = 2CaO·FeO\(_2\) | -53 172.4 - 2.5121 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 2  | (Ca\(^{2+}\) + O\(^{2-}\)) + FeO\(_2\) = CaO·FeO\(_2\) | 51 672.2 - 83.46 × T / 1.37 + 265.21× T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 3  | (Ca\(^{2+}\) + O\(^{2-}\)) + Fe\(^{2+}\) + FeO\(_2\) = CaO·FeO·FeO\(_2\) | -14 653.8 - 27.2142 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 4  | (Fe\(^{2+}\) + O\(^{2-}\)) + Fe\(_2\)O\(_3\) = FeO | -45 845.5 + 10.634 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 5  | Ca\(^{2+}\) + O\(^{2-}\) + SiO\(_2\) = CaO·SiO\(_2\) | -36 425.2 - 30.5636 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 6  | 2(Ca\(^{2+}\) + O\(^{2-}\)) + SiO\(_2\) = 2CaO·SiO\(_2\) | -118 905 - 11.3044 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 7  | 3(Ca\(^{2+}\) + O\(^{2-}\)) + SiO\(_2\) = 3CaO·SiO\(_2\) | -118 905 - 17.197 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 8  | 2(Fe\(^{2+}\) + O\(^{2-}\)) + SiO\(_2\) = 2FeO·SiO\(_2\) | -32 260 - 15.27 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
| 9  | (Ca\(^{2+}\) + O\(^{2-}\)) + (Fe\(^{2+}\) + O\(^{2-}\)) + SiO\(_2\) = CaO·FeO·SiO\(_2\) | -72 996.8 - 29.3169 × T | N\(_1\) = K\(_{CaO}\) N\(_{CaO}\) |
2.4.3. Effects of CaO Addition on Mass Action Concentrations in Slags

Figure 3 reflected the effects of CaO on the mass action concentrations in copper slag. With the increase of CaO, the mass action concentrations of SiO$_2$ and 2FeO·SiO$_2$ decreased gradually. By contrast, the decrease of Fe$_2$O$_3$ and Fe$_3$O$_4$ happened at higher CaO contents.

The mass action concentrations of CaO·SiO$_2$ and CaO·SiO$_2$·FeO presented the same change trends. The addition of CaO strengthened the driving force for the generation of CaO·SiO$_2$ and CaO·SiO$_2$·FeO. When the contents of CaO reached 22% and 28%, mass action concentrations of CaO·SiO$_2$ and CaO·FeO·SiO$_2$ reached to the peak respectively. However, when the addition of CaO increased continuously, the values decreased slowly.

Similarly, with the increase of CaO, the mass action concentrations of FeO and 2CaO·SiO$_2$ presented the same change trends. And the mass action concentrations of them increased at first and slowly flattened later.

By analyzing the relationships of SiO$_2$, 2FeO·SiO$_2$, Fe$_2$O$_3$, Fe$_3$O$_4$, CaO·SiO$_2$, 2CaO·SiO$_2$, and CaO·SiO$_2$·FeO with CaO in Fig. 3, the conversion relationship and reaction sequence of them are obtained.

(1) CaO participated in Reactions (5)–(7) and (9) as shown in Table 3. CaO promoted the generation of FeO, CaO·SiO$_2$, 2CaO·SiO$_2$, and CaO·SiO$_2$·FeO. By consuming SiO$_2$, CaO promoted the separation of Fe and Si from 2FeO·SiO$_2$, which promoted Reaction (8) moved backward.

(2) When the content of CaO was lower than 28%, CaO·SiO$_2$ and CaO·SiO$_2$·FeO were generated by Reactions (5), (9). When the content of CaO was higer than 28%, CaO·SiO$_2$ and CaO·SiO$_2$·FeO transformed to 2CaO·SiO$_2$ and FeO by Reactions (6) and (7).

Figure 4 reflected the changes of mass concentrations of 2FeO·SiO$_2$, relative quantity of CaO, SiO$_2$ and FeO with the increase of CaO. And according to Fig. 4, the mass concentration of 2FeO·SiO$_2$ decreased with the increase of CaO in copper slag. As discussed above, the addition of CaO could change the balance of reaction system, promote the separation of Fe and Si, which was in favor of reduction of copper slag. A rotary viscometer (ND-II type, produced by Northeastern University) was used to measure the viscosity of the copper slag samples based on the rotating cylinder method. The slag compositions are shown in Table 4 in viscosity experiments. As shown in Fig. 5, on the other hand, the addition of CaO can decrease the viscosity of copper slag, which promoted the dynamic reaction condi-
tions. However, excessive addition of CaO caused excessive insoluble solid in slag, increased the viscosity of copper slag and restricted reduction reactions.25,26)

2.4.4. Effects of Reduction Temperature on Mass Action Concentrations in Slags

Temperature affects the equilibrium reactions and the concentrations of ions and molecules in copper slag. The calculated results of mass action concentrations for CaO, FeO, SiO₂, Fe₂O₃, Fe₃O₄, CaO·SiO₂, 2CaO·SiO₂, 2FeO·SiO₂, CaO·FeO·SiO₂ are showed in Fig. 6 respectively. As discussed above, the addition of CaO promoted Reactions (5)–(7) and (9) as shown in Table 3. The change trends for the mass action concentrations of them are the same at different temperatures.

The mass action concentrations of SiO₂, FeO, Fe₂O₃, 2FeO·SiO₂ and CaO·FeO·SiO₂ remained steady with between 1523 K and 1773 K as shown in Figs. 6(b), 6(c), 6(d), 6(h) and 6(i). With the increase of CaO addition, the effects of temperature on mass action concentration of CaO, CaO·SiO₂ and 2CaO·SiO₂ increased gradually. The mass action concentration of Fe₃O₄ decreased linearly with the increase of temperature. It means that high temperature was in favor of the reduction of Fe₃O₄ in copper slag.

3. Thermogravimetric Experiments for Reduction of Copper Slag

3.1. Materials

Before experiment, the copper slag samples were crushed by a crusher, finally sieved to 250 μm and restricted reduction reactions.25,26) Sample B is the mixture of SiO₂ and biomass. The mass of CaO and SiO₂ in sample B and the mass of biomass in sample A is equal to sample B. Sample C is copper slag, and the mass of CaO and copper slag in sample A is equal to the mass of CaO in sample B and CuO in sample A is equal to sample B. Sample C is copper slag, and the mass of copper slag in sample C is equal to sample A. As in Eq. (16), SiO₂ powder in sample B could eliminate diffusion effects of copper slag on reduction. Mass of CaO and SiO₂ remain invariant in experiments.

\[
\rho' = \frac{16}{28} \times \frac{\Delta \rho' - \Delta \rho - \Delta \rho'}{m_C \times \left( \frac{16}{72} \times \text{FeO\%} \times \frac{64}{232} \right) \times 100\%} \quad \text{(16)}
\]

3.2. Apparatus and Methods

A NETZSCH STA409PC thermogravimetric analyzer was employed. The biomass, copper slag and CaO were mixed thoroughly and placed in the high purity aluminum crucible. The protective gas was Ar and the flow rate was 30 mL·min⁻¹ controlled by flow meters. In experiment, about 10 mg of samples were heated from 298 K to 1723 K at a heating rate of 20 K/min and then kept the reaction temperature at 1723 K for 30 min. During the heating process, the pyrolysis reaction of biomass occurred firstly and then reduction reactions of copper slag with fixed carbon occurred. The experimental conditions are showed in Table 7. Biomass/Slag and CaO/Slag are the ratio of mass% and abbreviated as B/S and CaO/S, respectively.

By XRD patterns from Fig. 8, in copper slag, iron was in the phase of fayalite (2FeO·SiO₂) and magnetic (Fe₃O₄). CO and CO₂ were generated in reduction reaction of copper slag by solid carbon and CO gas. Reduction of iron oxides leads to weight loss because the reducible oxygen in the crystal-line structure of iron oxides will escape as CO. Thus, the degree of weight loss reflects the reduction degree of iron ore oxides. Reduction degree of copper slag was calculated as follows:

\[
\Delta \rho' = \text{weight loss of sample A, B and C (as shown in Fig. 8)}
\]

\[
\Delta \rho' = \beta_0 - \beta_d - \beta_c
\]

Fig. 8. XRD patterns of the waste slag before reduction. Table 5 represents XRD patterns of the waste slag before reduction. The CaO sample was calcined from CaCO₃ (AR) at 1273 K and restricted reduction reactions.25,26) Sample B is the mixture of SiO₂ and biomass. The mass of CaO and SiO₂ in sample B and the mass of biomass in sample A is equal to sample B. Sample C is copper slag, and the mass of CaO and copper slag in sample A is equal to the mass of CaO in sample B and CuO in sample A is equal to sample B. Sample C is copper slag, and the mass of copper slag in sample C is equal to sample A. As in Eq. (16), SiO₂ powder in sample B could eliminate diffusion effects of copper slag on reduction. Mass of CaO and SiO₂ remain invariant in experiments.

3.3. Results and Discussion

3.3.1. Influence of the Types of Biomass on Reduction Ratio of Molten Copper Slag

Based on the proximate and components analysis, the
Fig. 6. Concentration curves with the changes of CaO addition and temperature: (a) CaO, (b) FeO, (c) SiO$_2$, (d) Fe$_2$O$_3$, (e) Fe$_3$O$_4$, (f) CaO-SiO$_2$, (g) 2FeO-SiO$_2$, (h) CaO-FeO-SiO$_2$. (mass%CaO = 0.3%, mass%SiO$_2$ = 37.9%, mass%FeO = 44.6% and mass%Fe$_2$O$_3$ = 17.2%).

---

Table 5. The compositions of copper slag, mass%.

|            | FeO  | Fe$_2$O$_3$ | CaO  | Al$_2$O$_3$ | MgFe | SiO$_2$ | Cu   | MgO  | S    | others |
|------------|------|-------------|------|-------------|------|---------|------|------|------|--------|
|            | 37.50| 18.90       | 0.23 | 0.98        | 1.24 | 31.99   | 0.74 | 0.42 | 0.39 | 2.78   | 4.87   |

---

Fig. 7. The picture of X-ray diffraction spectrogram of copper slag.

---

Table 6. Properties of three biomass materials.

| Samples | CN  | PE  | SW  |
|---------|-----|-----|-----|
| Proximate analysis, mass % |
| Moisture | 6.07 | 3.81 | 6.84 |
| Volatiles matter | 73.54 | 79.01 | 67.90 |
| Ash | 3.43 | 2.17 | 9.36 |
| Fixed carbon | 16.96 | 15.01 | 15.90 |
| Components analysis, mass % |
| NDF | 17.93 | 10.99 | 32.02 |
| Hemicellulose | 18.74 | 5.90 | 18.38 |
| Cellulose | 53.69 | 58.88 | 39.68 |
| Lignin | 8.75 | 23.42 | 7.38 |
| Ultimate analysis, mass % |
| Nitrogen | 1.65 | 0.15 | 0.61 |
| Carbon | 41.34 | 48.28 | 45.16 |
| Hydrogen | 5.76 | 6.17 | 5.928 |
| Sulfur | 0.125 | 0.082 | 0.069 |
composition and fiber structure of three kinds of biomass in this experiment were different. According to Fig. 9, with the increase of the addition of biomass, reduction ratio of copper slag increased almost linearly. The results showed that order of reduction ratios from high to low in biomass type were PE > CN > SW. Compared with CN and SW, PE had the largest reduction ratio and the reduction ratios of PE, CN and SW reached to 80.6%, 76.1%, 60.0% respectively when the mass ratio of biomass/slag was 1:2. Based on component analysis, gas yield from lignin is lower than hemicellulose and cellulose, and the lignin was the main component to produce fixed carbon during the pyrolysis process. Compared with CN and SW, the content of lignin in PE was highest. Thus, more fixed carbon was generated in PE, and the ratio of C/O in reduction reaction of copper slag with fixed carbon was higher than that in CN and SW.

3.3.2. Influence of the CaO Addition on Reduction Ratio

Figure 10 reflected the effects of CaO addition on reduction ratio of copper slag. The total development trends of PE, CN and SW were identical. When the mass ratios of CaO/S were 0.15:1, 0.3:1 and 0.45:1, reduction ratios of copper slag were enhanced in varying degrees. With the increase of CaO addition, reduction ratio of copper slag increased and then declined and it reached a peak at 0.3:1. Figure 11 is the comparison of experimental result and thermal analysis result with the addition of CaO. As shown in Fig. 11, the addition of CaO promoted the increase of FeO concentration and it provided a good condition for reduction of copper slag. Based on the coexistence theory of slag structure, CaO participated in Reactions (5)–(9) and promoted Reaction (8) to move backward, which promoted the separation of Fe and SiO₂ sequentially. The separation of them was a favorable condition for reduction of copper slag. However, when the addition of CaO was excessive, CaO existed as insoluble phase and it added the viscosity of molten slag. Consequently, excessive CaO worsened the dynamic conditions of reactions in molten slag.

4. Conclusions

The calculation model of action concentration for CaO–FeO–Fe₂O₃–SiO₂ copper slag system was built up on the basis of IMCT in this article. The main summary remarks can be obtained as follows:

(1) The contents of FeO and Fe₂O₃ reflect the reduction degree in copper slag. And the changes of them affected the characteristics of copper slag. The increase of FeO strengthened the driving force for 2FeO·SiO₂ generation. At lower
contents of Fe₂O₃ in copper slag, oxygen free ion (O²⁻) combined with ferrous (Fe²⁺) and ferric (Fe³⁺) iron and transformed into Fe₃O₄. When the content of Fe₂O₃ reached to 50%, Fe₃O₄ reached saturation and the increase rate of mass action concentration of Fe₂O₃ was enforced.

(2) The addition ofCaO could change the balance of reaction system. By consuming SiO₂, CaO promoted the separation ofFe and Si from 2FeO·SiO₂, which was in favor of the reduction of copper slag. However, excessive addition ofCaO (when the content ofCaO was over 28% in calculate conditions) caused excessive insoluble solid in slag, increased the viscosity of copper slag and restricted reduction reactions.

(3) The effects of temperature on mass action concentration were affected by the addition ofCaO. High temperature was in favor of the reduction of Fe₃O₄ in copper slag.

(4) Thermogravimetric experiments for reduction of copper slag by three typical kinds of biomasses were carried out. By contrast, the calculation results achieve high conformity with thermogravimetric experiments. CaO had promotion effects on reduction reaction in copper slag. With the increase ofCaO, the reduction ratio of copper slag increased firstly and reached a peak when CaO/S was 0.3:1 and then it declined due to the changes of slag viscosity. The results obtained in this work indicated that biomass would be a potential good reductant for reduction of copper slag.

Acknowledgment
This research was supposed by The National Natural Science Foundation of China (51274066, 51304048), The National Science Foundation for Post-doctoral Scientists of China (No. 2015M571322), The National Key Technologies R&D Program of China (2013BA03B03), The Fundamental Research Funds for the Central Universities (N130402019) and Initiative Postdocs Supporting Program (BX201600028).

Nomenclature
sum (n): Total equilibrium mole number of all structure units

\( n_i \): Equilibrium number of structural unit i or ion couple

\( N_i \): Mass action concentrations of structural unit i or ion couple

\( K \): Chemical equilibrium constant of forming component i or structural unit

\( \Delta G \): Standard mole Gibbs free energy of complex molecule, J/mol

\( T \): Absolute temperature, K

\( r_t \): Reduction ratio of copper slag at time of t, %

\( \Delta m_X \): Weight loss of sample X at reduction time of t, mg

\( m_i \): Initial mass of copper slag, mg

\( m_{FeO} \): Chemical content of FeO in copper slag, mass%

\( m_{FeO_2} \): Chemical content of Fe₂O₄ in copper slag, mass%

REFERENCES
1) B. Gorai and R. K. Jana: Resour. Conserv. Recy., 39 (2003), 299.
2) Y. Fan: Mater Trans., 55 (2014), 958.
3) L. N. Zhang, L. Zhang and M. Y. Wang: Trans. Nonferr. Met. Soc. China, 15 (2005), 1.
4) G. Siwiec, B. Oleksiak and L. Matula: Metall. Ital., 53 (2014), 585.
5) J. Zhang, Y. H. Qi and D. L. Yan: J. Iron Steel Res. Int., 22 (2014), 396.
6) B. Sarma, A. W. Cramb and R. J. Fruehan: Metall. Mater. Trans. A, 27 (1993), 717.
7) J. H. Hu, H. Wang and L. Li: 2011 Int. Conf. on Computer, Electrical and Systems Sciences, and Engineering, Information Engineering Research Institute, China, (2011), 541.
8) H. W. Zhang, S. X. Shi and B. Zhang: Metall. Mater. Trans. B, 45 (2013), 382.
9) J. L. Wang, C. F. Zhang and C. R. Tong: J. Cent. South Univ. Technol., 40 (2009), 282, (in Chinese).
10) X. M. Yang, C. B. Shi and M. Zhang: Metall. Mater. Trans. B, 42 (2011), 951.
11) J. L. Wang, X. C. Wen and C. F. Zhang, Trans. Nonferr. Met. Soc. China, 25 (2015), 1633.
12) J. Zhang: J. Univ. Sci. Technol. B, 6 (1984), 21 (in Chinese).
13) J. Zhang, J. Univ. Sci. Technol. B, 13 (1988), 214 (in Chinese).
14) J. L. Wang, C. F. Zhang and C. R. Tong: J. Cent. South Univ. Technol., 40 (2009), 282, (in Chinese).
15) J. L. Wang, C. F. Zhang and C. R. Tong: J. Cent. South Univ. Technol., 40 (2009), 282, (in Chinese).
16) J. L. Wang, C. B. Shi and M. Zhang: Metall. Mater. Trans. B, 42 (2011), 951.
17) J. L. Wang, C. F. Zhang and C. R. Tong: J. Cent. South Univ. Technol., 40 (2009), 282, (in Chinese).
18) A. A. El-Geassy: ISIJ Int., 36 (1996), 1344.
19) A. A. El-Geassy: ISIJ Int., 36 (1996), 1328.
20) M. I. Nasr, A. A. Omar, M. H. Khedr and A. A. El-Geassy: ISIJ Int., 35 (1995), 1043.
21) M. Hessein, Y. Kashawaya and K. Iishi: Ironmaking Steelmaking, 35 (2008), 191.
22) Trans. by J. Wang, Y. Q. Peng and Y. W. Mao: Slag Atlas, Metallurgical Industry Press, Beijing, (1989), 380.
23) Q. Y. Li: Numerical Analysis, Tsinghua University Press, Beijing, (2008), 212.
24) Q. Lin, R. Liu and N. Chen: J. Therm. Anal. Calorim., 58 (1999), 317.
25) D. W. Zeng, G. Z. Li, H. X. Liu and C. F. Zhang: J. Cent. South Univ. Technol., 28 (1997), No. 4, 344, (in Chinese).
26) W. Yan, W. Chen, Y. Yang, C. Lippold and A. Mclean: Ironmaking Steelmaking, 42 (2015), No. 9, 698.
27) Y. Wang, H. H. Wang and F. Zhu: Scientia Silvae Sinicae, 48 (2012), 99, (in Chinese).