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# Distribution Ratio of Sulfur between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-TiO<sub>2</sub> Slag and Carbon-Saturated Iron

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**Abstract:** To explore the feasibility of hot metal desulfurization using red mud, the sulfur distribution ratio ( $L_S$ ) between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-TiO<sub>2</sub> slag and carbon-saturated iron is evaluated in this paper. First, the theoretical liquid areas of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (-Na<sub>2</sub>O-TiO<sub>2</sub>) slag are discussed and the fluxing effects of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and TiO<sub>2</sub> are confirmed. Then,  $L_S$  is measured via slag-metal equilibrium experiments. The experimental results show that  $L_S$  significantly increases with the increase of temperature, basicity, and Na<sub>2</sub>O content, whereas it decreases with the increase of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> content. Na<sub>2</sub>O in the slag will volatilize with high temperatures and reducing conditions. Furthermore, based on experimental data for the sulfur distribution ratio between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-TiO<sub>2</sub> slag and the carbon-saturated iron, the following fitting formula is obtained:  $\log L_S = 45.584\Lambda + \frac{10568.406 - 17184.041\Lambda}{T} - 8.529$

**Keywords:** sulfur distribution ratio; liquid area; carbon-saturated iron

## 1. Introduction

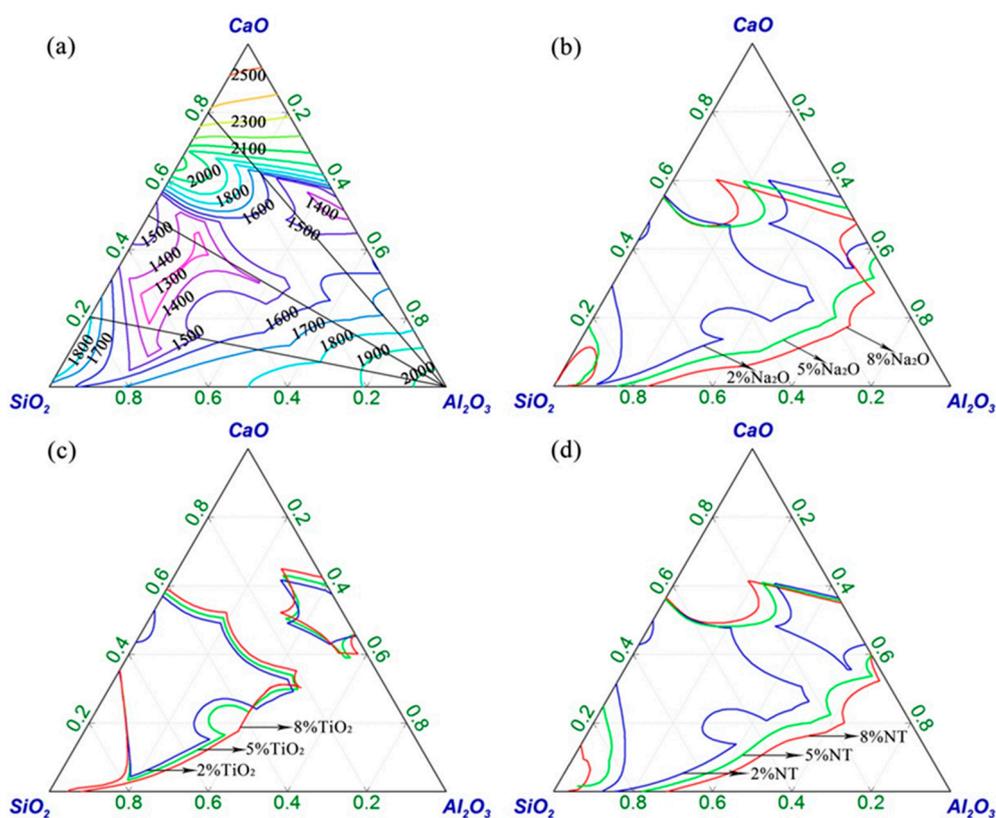
Sulfur often deteriorates metal properties [1,2], especially metals' toughness. To realize the deep desulfurization of steel [3,4], the process of hot metal desulfurization has become an economical and efficient method [2]. During this process, traditional lime-based slag has a high melting point. Therefore, CaF<sub>2</sub> is widely added as an additive to decrease the melting point and improve the solubility of lime [5]. However, because CaF<sub>2</sub> is toxic to the environment and human health, its use has been strictly restricted [6]. Hence, a desulfurizing slag with a much lower melting point, especially under conditions of high basicity, is required. Previous research [5–12] showed that other additives such as Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and TiO<sub>2</sub>, could improve the desulfurization efficiency of lime-based slag. Niekerk and Dippenaar [5] determined that the Na<sub>2</sub>O equivalent of CaO was 0.30, and adding Na<sub>2</sub>O could significantly increase the sulfide capacity of silicate and lime-based slag. Pak and Fruehan [6] reported that the addition of Na<sub>2</sub>O lowered the melting point and improved the fluidity of lime-based slag. Zhang's experiments [7] obtained good slag fluidity and a much better separation between the slag and the melt phases, attributed to the fact that Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O could act as a flux and decrease the melting point of the slag. Yajima et al. [8] found that, with the addition of Al<sub>2</sub>O<sub>3</sub> to the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> slag system at an oxygen partial pressure of  $1.8 \times 10^{-3}$  Pa, the liquid areas were enlarged. Park et al. and Sohn et al. [10,11] confirmed that TiO<sub>2</sub> decreased the viscosity of blast furnace slag by depolymerizing the slag structure.

Red mud is the residue discharged by the aluminum industry after the extraction of alumina. In addition to CaO, there is an abundance of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and TiO<sub>2</sub> in red mud. However, it is piled up, pollutes the environment, and increases the burden on enterprises. The sulfur distribution

ratio between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-TiO<sub>2</sub> slag and carbon-saturated iron is examined in this study to explore the feasibility of hot metal desulfurization using red mud. First, the liquid areas of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag system, along with the effects of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and TiO<sub>2</sub>, are investigated thermodynamically using FactSage7.0 software. Then, the sulfur distribution ratio between these slag systems and carbon-saturated iron is examined using an equilibrium experiment in the laboratory.

## 2. Liquid Areas of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (-Na<sub>2</sub>O-TiO<sub>2</sub>) Slag System

The liquid areas of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag, simulated by the FactSage7.0 software (developed by CRCT, Montreal, QC, Canada and GTT-Technologies, Herzogenrath, Germany), are shown in Figure 1. Figure 1a shows that the liquid areas at 1400 °C, 1500 °C, and 1600 °C account for about 1/11, 1/4, and 1/2 of the whole diagram area, respectively. This indicates that high temperature is beneficial to the melting of slag. In Figure 1a, there are three lines that correspond to the CaO/SiO<sub>2</sub> of 0.25, 1, and 4, respectively. When CaO/SiO<sub>2</sub> is constant, the melting point of the slag decreases at first and then increases with an increase of Al<sub>2</sub>O<sub>3</sub> content, indicating that adding Al<sub>2</sub>O<sub>3</sub> can promote the melting of slag at low concentrations, whereas melting deteriorates above a certain content of Al<sub>2</sub>O<sub>3</sub>. When CaO/SiO<sub>2</sub> is 0.25, 1, and 4, the critical value of Al<sub>2</sub>O<sub>3</sub> content is 13.7–19.3%, 15.3–19.1%, and 36.1–43.4%, respectively. Therefore, Al<sub>2</sub>O<sub>3</sub> has the effect of a flux, but its concentration should be controlled. Figure 1b,c show the effects of Na<sub>2</sub>O and TiO<sub>2</sub> on the liquid areas of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag at 1500 °C, respectively. Figure 1d shows the effect of a Na<sub>2</sub>O and TiO<sub>2</sub> mixture (denoted as “NT”) at a mass ratio of Na<sub>2</sub>O/TiO<sub>2</sub> = 2:1 on the liquid areas of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag at 1500 °C. The liquid areas become enlarged with the increase of Na<sub>2</sub>O, TiO<sub>2</sub>, and NT content, showing that these additives could all promote the melting of the slag. However, Na<sub>2</sub>O and NT could promote the melting of the slag more effectively than TiO<sub>2</sub>.



**Figure 1.** (a) Liquid areas of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag system between 1200 °C and 2600 °C, (b) effect of Na<sub>2</sub>O on the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag system at 1500 °C, (c) effect of TiO<sub>2</sub> on the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag system at 1500 °C, (d) effect of NT on the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag system at 1500 °C.

Therefore, when the temperature is relatively low, it is possible to obtain a good melting effect on slag with the addition of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{TiO}_2$ . For the actual desulfurization capacity of slag systems and the feasibility of hot metal desulfurization using red mud, slag–metal equilibrium experiments were carried out.

### 3. Experimental

#### 3.1. Experimental Materials

Iron was prepared by melting electrolytic iron ( $\text{Fe} > 99.6\%$ ), high-purity  $\text{FeS}$ , and graphite particles in an induction furnace. The final iron contained 4.0% carbon and 0.3% sulfur. The base slag was obtained by mixing analytical-grade reagents (i.e.,  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{SiO}_3$ , and  $\text{TiO}_2$ ), and its composition varied around the composition of red mud.  $\text{Na}_2\text{SiO}_3$  was added as a source of  $\text{Na}_2\text{O}$  [6]. With the help of a muffle furnace,  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  were calcined at  $1000\text{ }^\circ\text{C}$  for 2 h, and  $\text{Na}_2\text{SiO}_3$  was roasted at  $300\text{ }^\circ\text{C}$  for 2 h to remove carbonates and hydroxides prior to use. The base slag was uniformly mixed in an agate mortar and then formed into cylinders with a diameter of 18 mm, at a pressure of 30 MPa for 2 min. The iron samples were shaped into cylinders with a diameter of 18 mm by wire cutting. The weight of the base slag was about 12 g, and that of the iron sample was about 15 g. The mass ratio of slag to metal was 0.8:1. A graphite crucible (OD = 25 mm, ID = 20 mm, H = 30 mm) was employed in the experiment.

#### 3.2. Experimental Scheme

The experiment mainly consisted of two parts. For experiments T1–T3, the effect of temperature, basicity (i.e.,  $\text{CaO}/\text{SiO}_2$ ), and  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{TiO}_2$  content on the sulfur distribution ratio were measured by changing a single factor. For experiments 1–21, we referred to the method of uniform design [12]. Multiple factors were changed simultaneously, including temperature, basicity,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{TiO}_2$  content. The test points were distributed as evenly as possible within the test range, so that each test point could be representative. The slag composition after equilibration is shown in Table 1.

#### 3.3. Experimental Equipment

The experimental equipment included a horizontal resistance furnace, a gas-purification system, and a water-cooling device, whose schematic diagram is shown in Figure 2. A proportional-integral-derivative (PID) controller controlled the furnace with  $\text{MoSi}_2$  heating elements. After being calibrated, a Pt-30%Rh/Pt-6%Rh thermocouple was used to measure the temperature. The temperature control range of the furnace was  $25\text{--}1700\text{ }^\circ\text{C}$ , and the temperature accuracy of the heating zone was  $\pm 2\text{ }^\circ\text{C}$ . The water-cooling device was circulated with cooling water to control the temperature at the end of the furnace tube. The gas-purification system consisted of allochroic silica gel, a molecular sieve for dehydration, and copper and magnesium pieces (heated to  $500\text{ }^\circ\text{C}$ ) for deoxidation. Through the gas-purification system, high-purity argon ( $\text{Ar} > 99.99\%$ ) was introduced into the horizontal furnace tube to protect the samples and graphite crucibles from being oxidized until the experiment's conclusion.

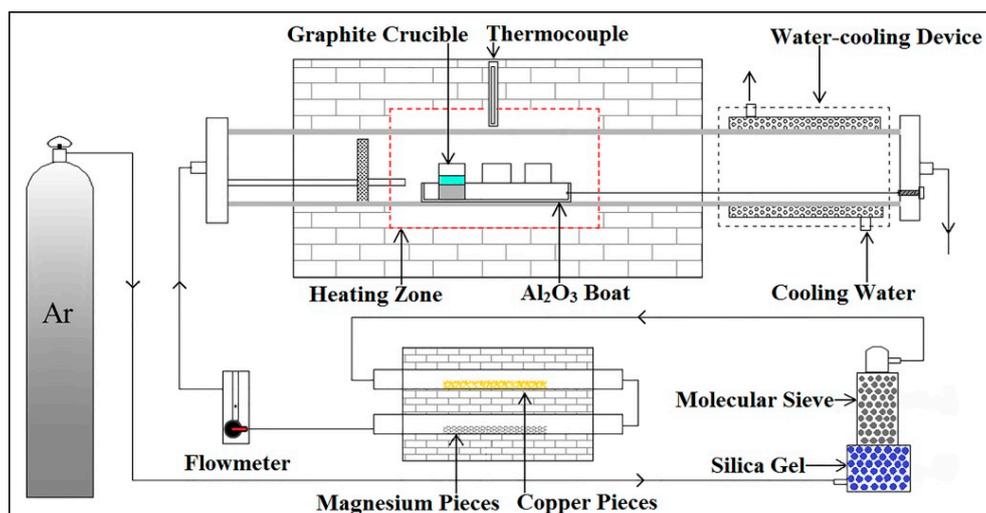


Figure 2. Schematic diagram of the experimental device.

Table 1. Experimental data after equilibration.

| No. | Temp./°C | Slag and Metal-Phase Composition (mass%) |                  |                                |                   |                  |         |        | Basicity | $\Lambda$ | $L_S$ | $\log L_S$ |
|-----|----------|--|------------------|--------------------------------|-------------------|------------------|---------|--------|----------|-----------|-------|------------|
|     |          | CaO                                      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | TiO <sub>2</sub> | [%S]    | (%S)   |          |           |       |            |
| T1  | 1400     | 48.29                                    | 27.87            | 17.84                          | 1.80              | 4.20             | 0.01345 | 0.3788 | 1.73     | 0.7033    | 28.16 | 1.4496     |
| T2  | 1450     | 48.99                                    | 27.99            | 17.92                          | 0.89              | 4.21             | 0.01049 | 0.3784 | 1.75     | 0.7017    | 36.07 | 1.5571     |
| T3  | 1500     | 49.47                                    | 27.70            | 18.13                          | 0.40              | 4.30             | 0.00914 | 0.3817 | 1.79     | 0.7018    | 41.76 | 1.6208     |
| R1  |          | 39.14                                    | 37.17            | 17.47                          | 2.13              | 4.09             | 0.01376 | 0.3769 | 1.05     | 0.6599    | 27.39 | 1.4376     |
| R2  |          | 48.99                                    | 27.99            | 17.92                          | 0.89              | 4.21             | 0.01049 | 0.3784 | 1.75     | 0.7017    | 36.07 | 1.5571     |
| R3  |          | 54.04                                    | 22.29            | 18.78                          | 0.55              | 4.34             | 0.00475 | 0.3815 | 2.42     | 0.7285    | 80.32 | 1.9048     |
| A1  |          | 51.51                                    | 30.22            | 13.11                          | 0.96              | 4.20             | 0.00783 | 0.3778 | 1.70     | 0.7063    | 48.25 | 1.6835     |
| A2  |          | 48.99                                    | 27.99            | 17.92                          | 0.89              | 4.21             | 0.01049 | 0.3784 | 1.75     | 0.7017    | 36.07 | 1.5571     |
| A3  |          | 46.20                                    | 25.97            | 22.11                          | 1.34              | 4.38             | 0.01300 | 0.3820 | 1.78     | 0.6980    | 29.38 | 1.4681     |
| N1  | 1450     | 49.74                                    | 28.38            | 17.38                          | 0.33              | 4.17             | 0.01126 | 0.3727 | 1.75     | 0.7011    | 33.10 | 1.5198     |
| N2  |          | 48.99                                    | 27.99            | 17.92                          | 0.89              | 4.21             | 0.01049 | 0.3784 | 1.75     | 0.7017    | 36.07 | 1.5571     |
| N3  |          | 48.01                                    | 27.44            | 18.79                          | 1.46              | 4.30             | 0.00947 | 0.3695 | 1.75     | 0.7018    | 39.02 | 1.5913     |
| Ti1 |          | 50.06                                    | 28.57            | 18.11                          | 1.19              | 2.07             | 0.00973 | 0.3718 | 1.75     | 0.7049    | 38.21 | 1.5822     |
| Ti2 |          | 48.99                                    | 27.99            | 17.92                          | 0.89              | 4.21             | 0.01049 | 0.3784 | 1.75     | 0.7017    | 36.07 | 1.5571     |
| Ti3 |          | 48.19                                    | 27.39            | 17.27                          | 0.62              | 6.53             | 0.01062 | 0.3763 | 1.76     | 0.6995    | 35.43 | 1.5494     |
| 1   |          | 45.36                                    | 27.11            | 18.66                          | 2.85              | 6.02             | 0.01205 | 0.3762 | 1.67     | 0.6997    | 31.22 | 1.4946     |
| 2   |          | 53.86                                    | 23.43            | 13.88                          | 3.41              | 5.42             | 0.00671 | 0.3854 | 2.30     | 0.7386    | 57.44 | 1.7591     |
| 3   |          | 42.81                                    | 31.01            | 19.46                          | 2.03              | 4.69             | 0.01461 | 0.3797 | 1.38     | 0.6809    | 25.99 | 1.4147     |
| 4   | 1400     | 53.22                                    | 26.69            | 15.78                          | 0.74              | 3.57             | 0.01066 | 0.3733 | 1.99     | 0.7177    | 35.02 | 1.5444     |
| 5   |          | 36.00                                    | 34.27            | 22.51                          | 3.50              | 3.72             | 0.01864 | 0.3801 | 1.05     | 0.6598    | 20.39 | 1.3095     |
| 6   |          | 47.94                                    | 27.35            | 19.13                          | 2.51              | 3.07             | 0.01180 | 0.3831 | 1.75     | 0.7058    | 32.47 | 1.5114     |
| 7   |          | 56.74                                    | 24.49            | 14.77                          | 1.78              | 2.22             | 0.00704 | 0.3778 | 2.32     | 0.7388    | 53.66 | 1.7294     |
| 8   |          | 43.07                                    | 30.69            | 19.17                          | 1.14              | 5.93             | 0.01328 | 0.3785 | 1.40     | 0.6790    | 28.50 | 1.4549     |
| 9   |          | 50.80                                    | 25.66            | 16.76                          | 0.92              | 5.86             | 0.01083 | 0.3774 | 1.98     | 0.7127    | 34.85 | 1.5420     |
| 10  |          | 36.43                                    | 33.92            | 22.06                          | 2.32              | 5.27             | 0.02115 | 0.3793 | 1.07     | 0.6576    | 17.93 | 1.2536     |
| 11  | 1450     | 48.99                                    | 27.99            | 17.92                          | 0.89              | 4.21             | 0.01049 | 0.3784 | 1.75     | 0.7015    | 36.07 | 1.5571     |
| 12  |          | 58.63                                    | 23.87            | 13.15                          | 0.74              | 3.61             | 0.00671 | 0.3873 | 2.46     | 0.7427    | 57.72 | 1.7613     |
| 13  |          | 46.35                                    | 31.45            | 18.91                          | 0.68              | 2.61             | 0.01175 | 0.3827 | 1.47     | 0.6856    | 32.57 | 1.5128     |
| 14  |          | 54.27                                    | 25.09            | 15.83                          | 2.29              | 2.52             | 0.00746 | 0.3865 | 2.16     | 0.7310    | 51.81 | 1.7142     |
| 15  |          | 39.55                                    | 32.00            | 21.95                          | 0.74              | 5.76             | 0.01783 | 0.3789 | 1.24     | 0.6644    | 21.25 | 1.3274     |
| 16  |          | 49.71                                    | 27.19            | 16.98                          | 0.68              | 5.44             | 0.00814 | 0.3731 | 1.83     | 0.7050    | 45.84 | 1.6611     |
| 17  |          | 57.58                                    | 24.03            | 13.39                          | 0.26              | 4.74             | 0.00672 | 0.3696 | 2.40     | 0.7367    | 55.00 | 1.7401     |
| 18  | 1500     | 44.20                                    | 30.36            | 19.98                          | 0.46              | 5.00             | 0.01606 | 0.3719 | 1.46     | 0.6803    | 23.16 | 1.3645     |
| 19  |          | 54.97                                    | 25.67            | 15.06                          | 0.21              | 4.09             | 0.00827 | 0.3744 | 2.14     | 0.7237    | 45.27 | 1.6560     |
| 20  |          | 44.44                                    | 31.18            | 21.14                          | 0.39              | 2.85             | 0.01289 | 0.3811 | 1.43     | 0.6790    | 29.57 | 1.4708     |
| 21  |          | 54.60                                    | 27.13            | 15.77                          | 0.12              | 2.38             | 0.00708 | 0.3662 | 2.01     | 0.7187    | 51.72 | 1.7138     |

### 3.4. Experimental Procedure

Pre-prepared slag and iron were placed in the graphite crucible. At the same temperature, an  $\text{Al}_2\text{O}_3$  boat can hold five graphite crucibles simultaneously. They were positioned in the heating zone of the furnace with the help of a molybdenum bar. Ar gas was introduced into the furnace tube at the flow rate of 500 mL/min. The furnace was then switched on. Before this, an experiment had been carried out to determine the equilibrium time. Figure 3 shows the change of sulfur content with time. (i.e., in experiment T1, the mass ratio of slag to metal was 0.3:1.) It was found that the sulfur content was almost unchanged after 4 h. Therefore, an equilibrium time of 4.5 h was chosen to ensure a complete reaction [13,14]. When equilibrium was reached, the  $\text{Al}_2\text{O}_3$  boat was pulled out of the furnace tube immediately for quenching. After being cooled, the slag and iron were separated. The slag was dried and then crushed into 200 mesh particles. The iron was washed with a steel brush and ultrasonically cleaned to remove surface residues. The sulfur content in slag and iron was detected by a carbon-sulfur analyzer (EMIA-920V2, HORIBA, Kyoto, Japan), and the composition of the slag was determined by an X-Ray fluorescence spectrometer (XRF-1800, Shimadzu, Kyoto, Japan). All experimental results are listed in Table 1.

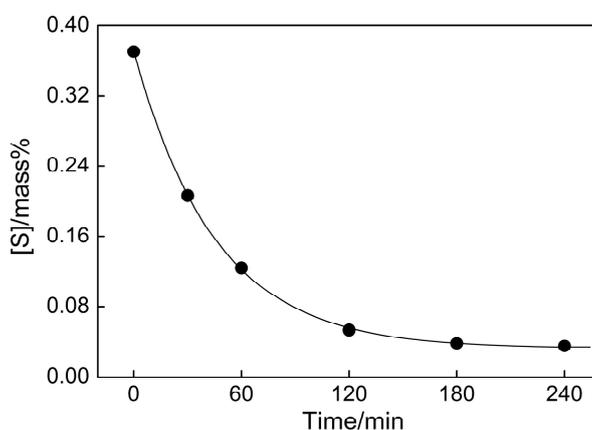


Figure 3. The change of sulfur content in the metal with time.

## 4. Results and Discussion

### 4.1. Effect of Temperature

The temperature dependence of  $\log L_S$  is shown in Figure 4. The data in Figure 4a are the results of experiments T1–T3, shown in Table 1. For these experiments, the slag compositions were similar. Figure 4b shows the dependence of  $\log L_S$  on the temperature for all five components of the slag system ( $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$ ), whose compositions varied significantly (i.e., experiments 1–21 in Table 1). As it can be seen from Figure 4a,  $\log L_S$  increased from 1.45 to 1.62 when the temperature increased from 1400 °C to 1500 °C, for similar slag compositions. The desulfurization reaction is endothermic. Thus, the high temperature promotes the migration of sulfur from the metal into the slag phase. Simeonov et al. [13] investigated the sulfur distribution ratio between  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$  slag and carbon-saturated iron from 1450 °C to 1600 °C and learned that  $\log L_S$  increased with the increase in temperature. The value of  $\log L_S$  in Simeonov's experiment was much larger than that in this paper, mainly because of the higher basicity in their study. (The basicity in their study was 4.4, whereas, here, it was only about 1.75). Lin et al. [15] measured the sulfur distribution ratio between  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$  slag and carbon-saturated iron from 1450 °C to 1550 °C. The value of  $\log L_S$  in Lin's experiment was much larger than that in this paper, because of the low content of weak acid oxides ( $\text{Al}_2\text{O}_3 = 10\%$ ,  $\text{TiO}_2 = 0\text{--}8\%$ ).

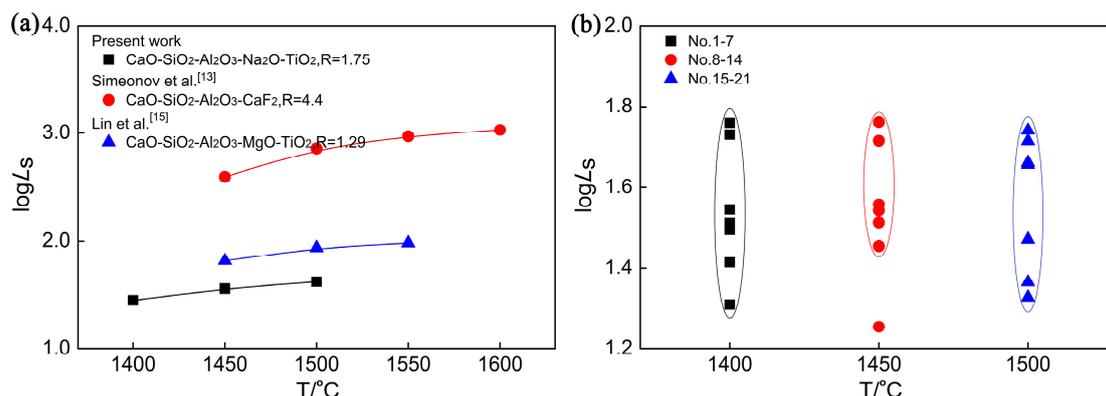


Figure 4. Effect of temperature on  $\log L_S$ .

However, this trend did not hold for the data shown in Figure 4b, which suggests that the temperature has no significant effect on  $\log L_S$  when the slag compositions vary significantly. Despite the different requirements of temperature, a similar tendency was observed in the research [16] on the phosphorus distribution ratio between the  $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$  slag and the carbon-saturated iron, which suggests that the phosphorus distribution ratio showed much greater dependency on the slag composition, such as on basicity rather than on temperature. Together, these results indicate that, for hot metal pretreatment, slag compositions tend to have significant effects on the desulfurization/dephosphorization efficiency.

#### 4.2. Effect of Basicity

Figure 5a shows the effect of basicity (i.e.,  $\text{CaO/SiO}_2$ ) on  $\log L_S$ . The data are the results of experiments R1–R3, for which the other factors of the slag are similar, but the basicity is different. The value of  $\log L_S$  increased from 1.44 to 1.90 with an increase in basicity from 1.05 to 2.42. This trend is in accordance with previous research [17–20]. The value of  $\log L_S$  in Huang’s experiments [17] (shown in Figure 5a) was relatively low, mainly because of the high content of weak acid oxides ( $\text{Al}_2\text{O}_3 = 15\%$ ,  $\text{TiO}_2 = 25\%$ ). The increase of basicity implies the disintegration of the silicate network structure [18] and the increase of the free  $\text{O}^{2-}$  concentration in the slag. A high concentration of free  $\text{O}^{2-}$  thermodynamically promotes the desulfurization reaction [11].

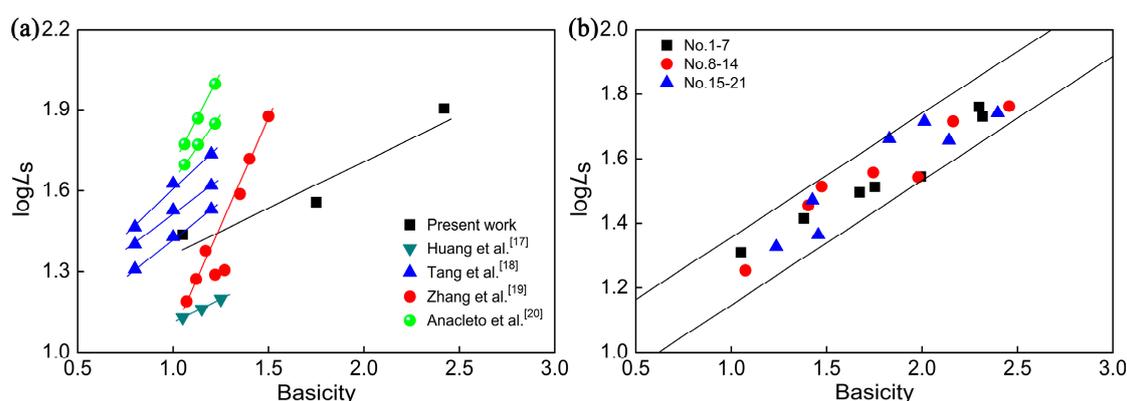


Figure 5. Effect of basicity on  $\log L_S$ .

The data in Figure 5b are the results of experiments 1–21. The temperature had three gradients, and the composition of slag was changed simultaneously at each temperature. Irrespective of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{TiO}_2$  content and temperature,  $\log L_S$  showed a strong dependence on the basicity of the slag, which linearly increased with the increase in basicity. This suggests that basicity has a much stronger effect on  $\log L_S$  than other influencing factors, such as temperature, under this experimental condition.

### 4.3. Effect of $\text{Al}_2\text{O}_3$

Figure 6a shows the effect of  $\text{Al}_2\text{O}_3$  content on  $\log L_S$ . The data are the results of experiments A1–A3, for which all slag factors were similar, with the exception of  $\text{Al}_2\text{O}_3$  content. As can be seen, the value of  $\log L_S$  decreased from 1.68 to 1.47 with an increase in  $\text{Al}_2\text{O}_3$  content from 13.11% to 22.11%. This was due to the fact that  $\text{Al}_2\text{O}_3$  acted as an acidic oxide in the basic slag.  $\text{Al}_2\text{O}_3$  consumed the free  $\text{O}^{2-}$  to form  $[\text{AlO}]_4^{5-}$ -tetrahedron, which decreased free  $\text{O}^{2-}$  concentration and weakened the desulfurization capacity of the slag [21]. The same experimental trend was observed by Zhang et al. [19]. They obtained a much lower sulfur distribution ratio, even at a higher temperature (1500 °C), than the present work (1450 °C), mainly because of the lower basicity (1.17) of the slag in their study.

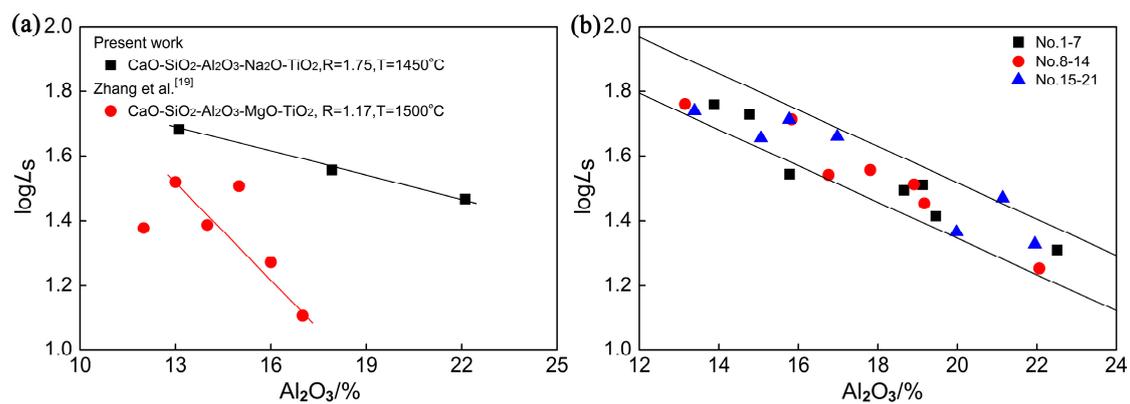


Figure 6. Effect of  $\text{Al}_2\text{O}_3$  on  $\log L_S$ .

The data in Figure 6b are the results of experiments 1–21. The temperature had three gradients, and the composition of slag was changed simultaneously at each temperature. Irrespective of basicity,  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$  content, and temperature,  $\log L_S$  also showed a strong dependence on  $\text{Al}_2\text{O}_3$  content. This suggests that  $\text{Al}_2\text{O}_3$  is also an important factor affecting the sulfur distribution ratio under this experimental condition.

### 4.4. Effect of $\text{Na}_2\text{O}$

Figure 7a shows the effect of  $\text{Na}_2\text{O}$  content on  $\log L_S$ . The data are the results of experiments N1–N3, for which the other factors of the slag are similar. As can be seen,  $\log L_S$  linearly increased from 1.52 to 1.59, with an increase in  $\text{Na}_2\text{O}$  content from 0.33% to 1.46%. This was because  $\text{Na}_2\text{O}$  is a strong basic oxide, and  $\text{Na}^+$  tends to have a strong affinity for  $\text{S}^{2-}$ . Niekerk et al. [5] pointed out that the addition of  $\text{Na}_2\text{O}$  significantly increased the sulfide capacity of silicate and lime-based slag. Additionally, the  $\text{Na}_2\text{O}$  equivalent of  $\text{CaO}$  was determined to be 0.30. Pak and Fruehan [6,22] suggested that  $\text{Na}_2\text{O}$  could lower the melting point of a lime-based slag, reduce the consumption of acid oxides to  $\text{CaO}$ , and significantly increase the activity of  $\text{CaO}$ . Subsequently, the desulfurization capacity of the slag was enhanced.

The data in Figure 7b are the results of experiments 1–21. The temperature had three gradients, and the composition of the slag was changed simultaneously at each temperature. When other factors (e.g., temperature) changed,  $\text{Na}_2\text{O}$  content in the slag had no significant effect on  $\log L_S$ . This could be due to the experimental conditions. Because of the strong reduction potential of hot metal,  $\text{Na}_2\text{O}$  can be reduced to metal  $\text{Na}$ , which can easily evaporate into the gas phase, especially at a high temperature. Therefore, the higher the temperature, the more  $\text{Na}$  vaporizes into the gas phase, and less residual  $\text{Na}_2\text{O}$  content remains in the slag. As shown in Figure 7b, the  $\text{Na}_2\text{O}$  content was 0.74–3.50% (square symbols in Figure 7b) at the lower temperature (1400 °C), while at a high temperature (1500 °C), the  $\text{Na}_2\text{O}$  content was only 0.12–0.74% (triangular symbols in Figure 7b). The promoting effect on desulfurization of higher  $\text{Na}_2\text{O}$  content was eventually counteracted by lower temperatures, as in

the case where the negative influence of lower  $\text{Na}_2\text{O}$  content tended to be neutralized by higher temperatures. Comprehensively,  $\text{Na}_2\text{O}$  content showed no significant effect on  $\log L_S$  under this experimental condition.

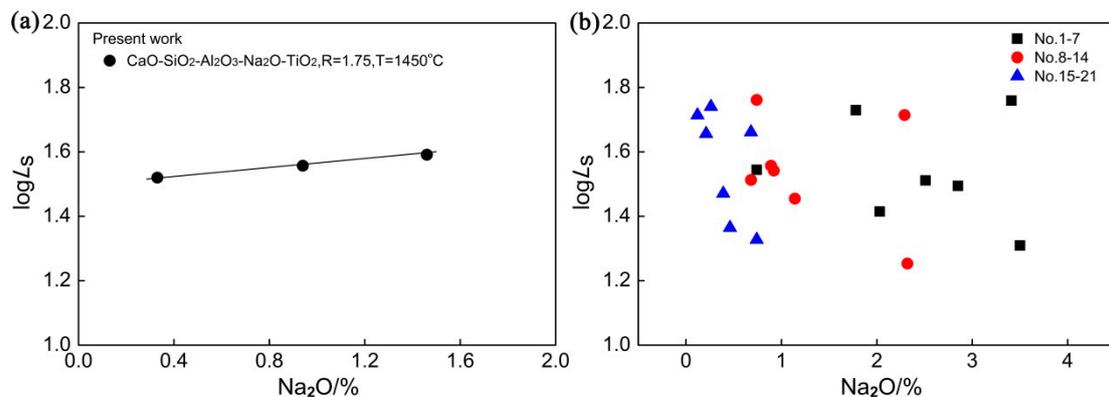


Figure 7. Effect of  $\text{Na}_2\text{O}$  on  $\log L_S$ .

However, a different tendency was observed in the case of hot metal dephosphorization. The results of hot metal dephosphorization by Li [16] showed that, when changing various factors, such as temperature and slag compositions, the distribution ratio of phosphorus between the slag and iron-saturated iron ( $L_P$ ) increased significantly with the increase of  $\text{Na}_2\text{O}$  content. This was mainly because hot metal dephosphorization was carried out in an oxidizing atmosphere, and  $\text{Na}_2\text{O}$  in the slag was hard to be reduced to metal Na. The volatilization of  $\text{Na}_2\text{O}$  is much weaker than that of metal Na. Finally, more  $\text{Na}_2\text{O}$  is maintained, and it plays the role of a strong basic oxide in the slag phase. Consequently, hot metal dephosphorization is promoted by high  $\text{Na}_2\text{O}$  content.

#### 4.5. Effect of $\text{TiO}_2$

Figure 8a shows the effect of  $\text{TiO}_2$  content on  $\log L_S$ . The data are the results of experiments Ti1–Ti3, for which all factors of the slag were similar except for  $\text{TiO}_2$  content. As can be seen, the value of  $\log L_S$  decreased slightly from 1.58 to 1.55 with an increase in  $\text{TiO}_2$  content from 2.07% to 6.53%. This is in accord with the results of Lin et al. and Tang et al. [15,18], who investigated the sulfur distribution ratio between  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$  slag and carbon-saturated iron at 1500 °C. The electrostatic potential of  $\text{Ti}^{4+}$  (5.88) is lower than that of  $\text{Si}^{4+}$  (9.76). Therefore, the Ti-O bond is weaker than the Si-O bond, which causes  $\text{TiO}_2$  to exist as  $[\text{TiO}]_6^{8-}$ -octahedron in a basic slag. Sommerville et al. [23] also suggested that  $\text{TiO}_2$  acted as an acidic oxide in a basic slag and existed in the form of  $[\text{TiO}]_6^{8-}$ -octahedron, which decreased the amount of free  $\text{O}^{2-}$  and weakened the desulfurization capacity of the slag.

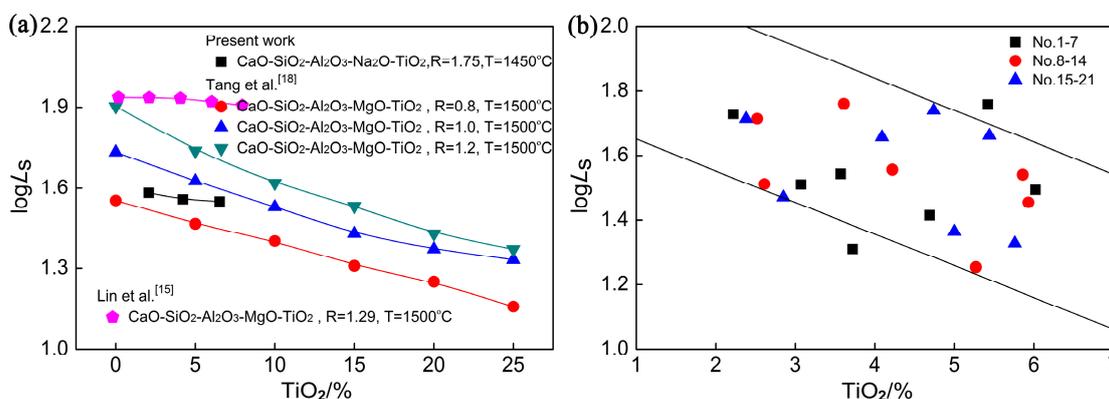


Figure 8. Effect of  $\text{TiO}_2$  on  $\log L_S$ .

The data in Figure 8b are the results of experiments 1–21. The temperature had three gradients, and the composition of the slag was changed simultaneously at each temperature. Although a relatively large fluctuation was observed, the total  $\log L_S$  decreased with an increase in the  $\text{TiO}_2$  content. This indicates that  $\text{TiO}_2$  in the slag has also a thermodynamically negative effect on the desulfurization capacity of the slag.

#### 4.6. Regression Analysis of $\log L_S$

To further study the relationship between  $\log L_S$ ,  $\Lambda$ , and  $T$ , based on the data of experiments 1–21 in Table 1, the following regression equation was obtained by using the SPSS (Statistical Product and Service Solutions) software (SPSS10.91, SPSS Inc., Chicago, IL, USA) [24]. A comparison between the experimental values and the calculated values of  $\log L_S$  is shown in Figure 9, which shows good agreement.

$$\log L_S = 15.584\Lambda + \frac{10568.406 - 17184.041\Lambda}{T} - 8.529, \quad (r = 0.963) \quad (1)$$

where  $L_S$  is the sulfur distribution ratio;  $T$  is the temperature, °C;  $\Lambda$  is the optical basicity of the slag [25];  $r$  denotes the correlation coefficient.

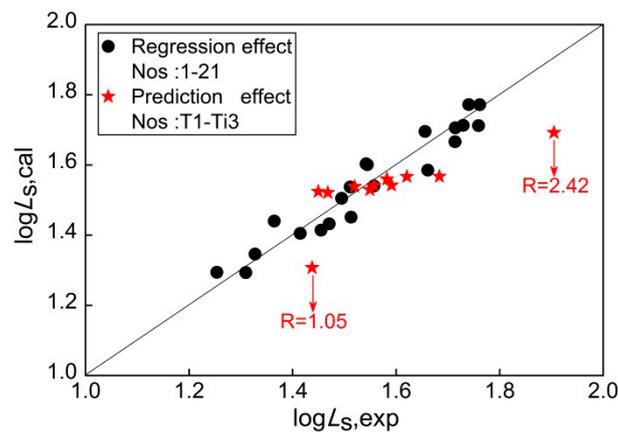


Figure 9. Comparison of experimental values and calculated values.

When the temperature was 1400–1500 °C, basicity was 1.0–2.5,  $\text{Al}_2\text{O}_3$  content was 12–22%,  $\text{Na}_2\text{O}$  content was 0–3%, and  $\text{TiO}_2$  content was 2–6%. The equation could be helpful in predicting the sulfur distribution ratio between  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$  slag and carbon-saturated iron.

## 5. Conclusion

The sulfur distribution ratio between  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$  slag and carbon-saturated iron was re-evaluated in this study. Based on the theoretical calculation and equilibrium experiments, the conclusions are summarized as follows.

- (1) The thermodynamic calculation shows that high temperature helps the melting of the slag.  $\text{Al}_2\text{O}_3$  is beneficial as a flux. However, the content should be controlled.  $\text{Na}_2\text{O}$  can promote the melting effect on the slag more effectively than  $\text{TiO}_2$ .
- (2) The experimental data suggest that the distribution ratio of sulfur between the slag and the carbon-saturated iron strongly increases with the increase of temperature, basicity, and  $\text{Na}_2\text{O}$  content, whereas it decreases with the increase of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  content.  $\text{Na}_2\text{O}$  in the slag will volatilize because of the high temperature and the reducing conditions.

- (3) Based on the experimental data, for the distribution ratio of sulfur between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-TiO<sub>2</sub> slag and carbon-saturated iron, the following fitting formula is obtained:

$$\log L_S = 15.584\Lambda + \frac{10568.406 - 17184.041\Lambda}{T} - 8.529$$

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