Article

 Proper MgO/Al₂O₃ Ratio in Blast-Furnace Slag: Analysis of Proper MgO/Al₂O₃ Ratio Based on Observed Data

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Abstract: With the gradual depletion of high-quality iron-ore resources, ironmaking blast furnaces have gradually shifted to using high-content Al₂O₃ iron ore. Under this condition, the addition of MgO in the slag is adopted to alleviate operation problems caused by the high content of Al₂O₃. However, the proper value of the MgO/Al₂O₃ ratio for blast-furnace slag systems (Al₂O₃ = 8–25%) is not systematically studied. In this paper, we discuss the proper MgO/Al₂O₃ ratio on the basis of blast-furnace slag systems under different Al₂O₃ contents. On the basis of thermodynamics and phase-diagram analysis, it could be concluded that: (1) the MgO/Al₂O₃ ratio is not limited when Al₂O₃ in slag is less than 14%, (2) the MgO/Al₂O₃ ratio is required to be in the range of 0.40–0.50 when Al₂O₃ in the slag is 15–17%, and (3) the MgO/Al₂O₃ ratio should be 0.45–0.55 when Al₂O₃ in the slag is larger than 18%. The proper MgO/Al₂O₃ ratio value has been established in various industries, and it has achieved significant economic and social benefits.

Keywords: three-segment control; MgO/Al₂O₃ ratio; BF slag; high Al₂O₃

1. Introduction

The massive use of Al₂O₃-enriched iron ore inevitably leads to the increase in Al₂O₃ content in blast-furnace (BF) slag; thus, there exist the two following problems in BF production: First, the increase in slag viscosity. Figure 1 shows the isoviscosity diagram of the CaO–SiO₂–Al₂O₃ ternary slag system at 1500 °C, where the straight line is the isobasicity line, and the curve is the isoviscosity line [1]. Industry practices request that slag viscosity be below 0.4 Pas [2]; thus, slag basicity (CaO/SiO₂, wt %) should be about 1.1, and Al₂O₃ content in slag should be 9–13%. Meanwhile, slag viscosity exceeds 0.4 Pas as Al₂O₃ content in the slag increases at constant slag basicity, leading to difficult BF operation. Therefore, on the basis of phase-diagram analysis, we see that, while maintaining BF temperature and slag basicity, an increase in slag viscosity caused by the high content of Al₂O₃ in the slag is one of the reasons that make BF operations difficult [3–6].

The second problem is the relative decrease in the desulfurization ability of slag. Keeping slag basicity constant, CaO content in the slag decreases as the content of Al₂O₃ in the slag increases, worsening the slag’s desulfurization ability [7,8]. In addition, the poor kinetic conditions of desulfurization caused by increased slag viscosity are another reason for the weakened desulfurization. Therefore, in view of thermodynamics and kinetics, high Al₂O₃ content has a
negative impact on slag desulfurization. In fact, overall, the operational problem of high-Al₂O₃ BF slag is mainly related to the increase in slag viscosity.

![Isoviscosity diagram of the SiO₂–CaO–Al₂O₃ ternary slag system (1500 °C, Pas) [1].](image)

BF operation problems of high-Al₂O₃ slag stem from the increase in slag viscosity; thus, it is necessary to reduce slag viscosity while maintaining the proper melting point of slag. Although increasing slag basicity helps to improve slag viscosity, it significantly increases the melting point of the slag [9]. However, lowering slag basicity helps to reduce its melting point, further deteriorating its desulfurization ability of slag [10]. The addition of proper MgO can increase the liquid-phase region, reduce the melting point of slag, and improve its fluidity. T. Paananen [11] found that MgO significantly accelerates the reduction of magnetite to iron. M. Matsumura et al. [12], J. Chang [13], and X. Qin et al. [14] found that proper MgO can decrease the melting temperature and increase the desulfurization ability of slag. Therefore, the current popular method for adjusting the metallurgical properties of high-Al₂O₃ BF slag is to add MgO into the slag.

Regarding the influence of MgO on slag viscosity, Figure 2 shows the isoviscosity diagram of the CaO–SiO₂–Al₂O₃–MgO quaternary slag system with a SiO₂ content of 35% [1]. With the addition of MgO, slag viscosity is reduced. For BF slag with a basicity of about 1.15, adding a certain amount of MgO gives a proper slag viscosity within the range of 0.3 to 0.4 Pas.
In addition, MgO is an alkaline substance. Under the condition of constant binary basicity, CaO content is reduced by about 0.4% for each added 1% of MgO. Since the desulfurization ability of MgO is about 0.7 times that of CaO [15], the addition of MgO can maintain the desulfurization ability of slag, keeping it unchanged from a thermodynamic point of view. If the MgO were added with an appropriate simultaneous increase in basicity, the desulfurization ability of the slag would be improved. In addition, as mentioned above, the addition of MgO can improve slag fluidity and the kinetic conditions of slag desulfurization. Therefore, the addition of MgO is an effective measure for high-Al2O3 BF slag operations.

According to the above analysis, in order to ensure a proper viscosity for the high Al2O3 BF slag, it is necessary to add MgO. This topic, apart from the studies mentioned above, has also been studied by many other researchers [16–18]. H. He et al. [16], and Y. Liu [17] obtained that slag viscosity decreases with the increase in MgO content in a definite range. T. Talapaneni [3] and Tingle. L [18] found that slag viscosity increases with an increase in the Al2O3 content, and decreases with an increase in MgO content, by using FTIR and Raman spectroscopy. However, most studies are only qualitative analyses, and rarely mention the addition method of MgO under different Al2O3 contents in production. In fact, MgO is also proper for BF slag with a lower content of Al2O3. However, what is the proper amount of MgO addition, or what is the proper MgO/Al2O3 ratio? So far, there has been no clear answer. In this paper, phase-diagram analyses with laboratory experiments and production practices were conducted to determine the proper MgO/Al2O3 ratio and formulate operational guidelines.

2. Analysis of Proper MgO/Al2O3 Ratio

The proper MgO/Al2O3 ratio should be considered in two aspects, that is, fluidity (viscosity) and the melting point of BF slag.

2.1. BF Slag Viscosity

An experiment was carried out to study the effect of MgO/Al2O3 on viscosity. Slag was prepared from a mixture of reagent-grade CaO, SiO2, Al2O3, and MgO. Slag compositions are listed in Table 1. A vertical-resistance furnace was used. Slag of 140 g was placed in a graphite crucible into the hot zone of the furnace. The sample was heated to 1500 °C and maintained at 1500 °C for 30 min to sufficiently ensure complete melting and homogenization. A rotating Mo spindle connected to a viscometer was employed in the high-temperature viscosity measurement. Figure 3 shows the variation of slag viscosity with basicity (R) of 1.1 and 1.2, and Al2O3 content of 12%, 15%, and 18% at 1500 °C under laboratory conditions. The present results showed the same trend as that of T.Iida et
al [19]. When the Al₂O₃ content in the slag was less than 15%, slag viscosity increased slightly with the decrease in the MgO/Al₂O₃ ratio. However, when Al₂O₃ content in the slag reached 18%, for the slag with lower basicity (R = 1.1), slag viscosity increased rapidly with the decrease in the MgO/Al₂O₃ ratio, due to the melting point rapidly rising (see Section 3.3 for specific discussion). When the MgO/Al₂O₃ ratio was 0.25, slag viscosity reached 0.5 Pas. Therefore, according to Figure 3, for high-Al₂O₃ BF slag, the lower limit of the MgO/Al₂O₃ ratio should not be less than 0.25.

Table 1. Experimental viscosity scheme.

| NO. | CaO% | SiO₂% | MgO% | Al₂O₃% | w(MgO)/w(Al₂O₃) | R₂ |
|-----|------|-------|------|--------|----------------|----|
| 1   | 44.52| 40.48 | 3.00 | 12     | 0.25           |    |
| 2   | 43.90| 39.91 | 4.20 | 12     | 0.35           |    |
| 3   | 43.27| 39.33 | 5.40 | 12     | 0.45           |    |
| 4   | 42.56| 38.69 | 3.75 | 15     | 0.25           |    |
| 5   | 41.77| 37.98 | 5.25 | 15     | 0.35           |    |
| 6   | 40.99| 37.26 | 6.75 | 15     | 0.45           |    |
| 7   | 40.60| 36.91 | 4.50 | 18     | 0.25           |    |
| 8   | 39.65| 36.05 | 6.30 | 18     | 0.35           |    |
| 9   | 38.71| 35.19 | 8.10 | 18     | 0.45           |    |
| 10  | 46.36| 38.64 | 3.00 | 12     | 0.25           |    |
| 11  | 45.71| 38.09 | 4.20 | 12     | 0.35           |    |
| 12  | 45.06| 37.55 | 5.40 | 12     | 0.45           |    |
| 13  | 44.32| 36.93 | 3.75 | 15     | 0.25           |    |
| 14  | 43.50| 36.25 | 5.25 | 15     | 0.35           |    |
| 15  | 42.68| 35.57 | 6.75 | 15     | 0.45           |    |
| 16  | 42.27| 35.23 | 4.50 | 18     | 0.25           |    |
| 17  | 41.29| 34.41 | 6.30 | 18     | 0.35           |    |
| 18  | 40.31| 33.59 | 8.10 | 18     | 0.45           |    |
2.2. Melting Point of BF Slag

Figure 4 is a phase diagram of a CaO–SiO₂–Al₂O₃–MgO quaternary slag system when Al₂O₃ is 20% [1]. If the content of MgO in BF slag exceeds 16% (in this case, MgO/Al₂O₃ = 0.80), the melting point of BF slag is as high as 1500 °C (dashed line in Figure 4), reaching or even exceeding the slag temperature during BF production (1500–1550 °C), which leads to the incomplete melting of slag in the BF hearth. To ensure the safety of BF production, the melting point of slag is usually controlled to below 1400 °C [20]. Therefore, the upper limit of the MgO/Al₂O₃ ratio of BF slag should not be larger than 0.80 according to the melting point of BF slag. In addition, the content of Al₂O₃ in BF slag is not higher than 20% in most cases. Because the liquid phase decreases with the increase in Al₂O₃ at a fixed temperature, it is feasible to take 20% Al₂O₃ as the upper limit and separately discuss it.

As mentioned above, considering various constraints, such as the viscosity and melting point of slag, the MgO/Al₂O₃ ratio of BF slag should be controlled within the range of 0.25–0.80.
3. Discussion (Three-Segment Control of Proper MgO/Al₂O₃ Ratio)

According to the above analysis, the MgO/Al₂O₃ ratio of BF slag and of high-Al₂O₃ slag should be controlled between 0.25 and 0.80. However, the above range is too wide and thus needs to be refined. In addition, in order to comprehensively investigate the mechanism of the MgO/Al₂O₃ ratio, the proper MgO/Al₂O₃ ratio for low-Al₂O₃ slag should also be demonstrated. The following is the respective discussion.

3.1. Less Than 14% Al₂O₃ in Slag

According to the phase diagram of the CaO–SiO₂–MgO–Al₂O₃ quaternary system when SiO₂ is 35% (Figure 5) [1], if the Al₂O₃ content in the slag is 12–14% and even less, the melting point of BF slag is below 1400 °C with MgO less than 20% (shadow in Figure 5). Then, there is no limitation to the amount of added MgO, and it can be added depending on resource and production-cost conditions. Table 2 shows the composition of the BF slag of a European steel company. Although the MgO content in the BF slag is as high as 17.5%, its melting point is around 1390 °C (elliptical area in the figure), that is, this BF production can still normally proceed because the Al₂O₃ content in the slag is only 13%. Therefore, the MgO/Al₂O₃ ratio of BF slag is not limited when Al₂O₃ in the slag is less than 14%.

Table 2. Composition of the blast-furnace (BF) slag of a European steel company (%).

|       | CaO  | SiO₂ | MgO  | Al₂O₃ | K₂O  | S    | others | R = CaO/SiO₂ |
|-------|------|------|------|-------|------|------|--------|-------------|
|       | 30.7 | 33.5 | 17.5 | 13.0  | 0.46 | 1.38 | 3.46   | 0.92        |
3.2. \( \text{Al}_2\text{O}_3 \) in Slag Equals to 15–17% 

Figure 6 is an isoviscosity diagram of a CaO–SiO\(_2\)–MgO–Al\(_2\)O\(_3\) quaternary system where the SiO\(_2\) content is 35% \([1]\), where the hexagon area (enclosed by bold lines) is \( R \) of 1.0–1.2, Al\(_2\)O\(_3\) of 12.5–20.0\%, and MgO of 5.0–15.0\%; and the light-gray region represents a slag viscosity of 0.3–0.4 Pas. After adding the corresponding MgO/Al\(_2\)O\(_3\) ratio isolines into the figure, when the Al\(_2\)O\(_3\) content was 15–17%, the production requirement of slag viscosity to be 0.3–0.4 Pas could be satisfied under the condition of the MgO/Al\(_2\)O\(_3\) ratio being within the range of 0.35–0.8 (Al\(_2\)O\(_3\) = 15–17% and light-gray area in the figure). However, from the perspective of minimizing cost, slag volume, and energy consumption, it is desirable to choose the MgO/Al\(_2\)O\(_3\) area while adding as little MgO as possible. Therefore, for slag containing Al\(_2\)O\(_3\) of 15–17%, a proper MgO/Al\(_2\)O\(_3\) ratio should be 0.40–0.50 (dark-gray area in the figure).

For slag containing 15–17% Al\(_2\)O\(_3\), attention should be paid to slag sensitivity on temperature during operation. According to the study of T. Koshida et al. \([21]\), for slag containing 15–17% Al\(_2\)O\(_3\), viscosity is acceptable when slag temperature is high, but viscosity rises rapidly when the slag temperature is lower than around 1425 \( ^\circ \text{C} \). That is to say, slag containing 15–17% Al\(_2\)O\(_3\) is very sensitive to temperatures of around 1425 \( ^\circ \text{C} \); thus, attention should be paid to changes in slag temperature. It is necessary to ensure that slag temperature is sufficient to prevent poor BF performance caused by a sudden increase in slag viscosity.

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**Figure 6.** Isoviscosity diagram of the SiO\(_2\)–CaO–Al\(_2\)O\(_3\)–MgO quaternary slag system (SiO\(_2\) = 35%, 1500 \( ^\circ \text{C} \), Pas) \([1]\).
3.3. Higher Than 18% \( \text{Al}_2\text{O}_3 \) in Slag

Similarly, the MgO/\( \text{Al}_2\text{O}_3 \) ratio should be 0.45–0.55 to keep viscosity in the range of 0.3–0.4 Pas for slag containing 18–20% \( \text{Al}_2\text{O}_3 \). Therefore, a proper MgO/\( \text{Al}_2\text{O}_3 \) ratio is 0.45–0.55 for slag containing more than 18% \( \text{Al}_2\text{O}_3 \). In addition, from the perspective of the melting point of slag, the relationship between the MgO/\( \text{Al}_2\text{O}_3 \) ratio and \( \text{Al}_2\text{O}_3 \) content of slag can also be obtained as shown below. Figure 7 shows the effect of the MgO/\( \text{Al}_2\text{O}_3 \) ratio on the melting point for slag containing different \( \text{Al}_2\text{O}_3 \) contents [1].

![Figure 7. Correlation of the MgO/\( \text{Al}_2\text{O}_3 \) ratio and melting point for slag containing different contents of \( \text{Al}_2\text{O}_3 \) [1].](image)

For slag containing 10% \( \text{Al}_2\text{O}_3 \), an MgO/\( \text{Al}_2\text{O}_3 \) ratio of less than 2.0 can maintain the melting point below 1425 \( ^\circ \text{C} \). That is, there is no limitation on the MgO/\( \text{Al}_2\text{O}_3 \) ratio under this condition, and MgO can be added according to raw-material conditions and production costs. For slag containing 20% \( \text{Al}_2\text{O}_3 \), the MgO/\( \text{Al}_2\text{O}_3 \) ratio should be controlled to not exceed 0.6 to keep the melting point of slag lower than 1425 \( ^\circ \text{C} \). The proper MgO/\( \text{Al}_2\text{O}_3 \) ratio obtained on the basis of the melting point of BF slag was highly consistent with that obtained on the basis of viscosity analysis. That is, both viscosity and melting-point analysis gave the same scientific theoretical basis for controlling a proper MgO/\( \text{Al}_2\text{O}_3 \) ratio.

In summary, the three-segment control of proper MgO/\( \text{Al}_2\text{O}_3 \) ratio for BF slag obtained by thermodynamics and phase-diagram analysis is listed in Table 3.

| Proper MgO/\( \text{Al}_2\text{O}_3 \) ratio for BF slag (three-segment control) | Conditions |
|---|---|
| (a) \( \text{Al}_2\text{O}_3 \leq 14\% \), MgO can be added according to production needs. |
| (b) \( \text{Al}_2\text{O}_3 = 15–17\% \), MgO/\( \text{Al}_2\text{O}_3 \) ratio should be 0.40–0.50. |
| (c) \( \text{Al}_2\text{O}_3 = 18–20\% \), MgO/\( \text{Al}_2\text{O}_3 \) ratio should be 0.45–0.55. |

The emphasis here is that the MgO/\( \text{Al}_2\text{O}_3 \) ratio is "proper". Above the proper value, it is not impossible to carry out BF operations, but it would lead to a substantial increase in production costs.
A higher MgO/Al₂O₃ ratio not only increases the consumption of slag, energy, and magnesium resources, but also affects sintering production and quality. Conversely, if the MgO/Al₂O₃ ratio were too low, the furnace condition would be unstable. In addition, the above-mentioned proper MgO/Al₂O₃ ratio was optimized on the basis of the CaO–SiO₂–Al₂O₃–MgO slag system. If other components, such as TiO₂, MnO, and FeO, are added to the system, this proper MgO/Al₂O₃ ratio may still work, but slightly differently.

4. Practical Example of Proper MgO/Al₂O₃ Ratio

Table 4 shows the production data for a steel company to implement the proper MgO/Al₂O₃ ratio. In 2013, the company’s BF slag contained 15.5% Al₂O₃ and an MgO/Al₂O₃ ratio of 0.51. To reduce production costs, and energy and MgO consumption, on the basis of the three-segment control theory of the proper MgO/Al₂O₃ ratio, the company gradually reduced MgO content in the sinter from 1.8% in 2013 to 1.5% in 2017. As a result, the MgO content in BF slag was decreased from 7.96% in 2013 to 7.02% in 2017. The fuel ratio fell to an average of 492.5 kg/tHM in 2017, a decrease of 1.5 kg/tHM from the fuel ratio in the first half of 2014. At the same time, BF production was stable and smooth, and the quality of pig iron was excellent, with an (S) decrease from 0.4 to less than 0.025 in the hot metal. Reducing the MgO/Al₂O₃ ratio not only reduces the fuel ratio, but also saves resources, reduces costs, and decreases CO₂ emissions. The carbon content of fuel is calculated to be 85%, and CO₂ emissions can be reduced by 4.7 kg/tHM per ton of iron. The annual output of iron in 2017 was 7.2 million tons, and CO₂ emissions could be reduced by 34,000 tons per year. A proper MgO/Al₂O₃ ratio has significant economic and social benefits.

| Year | Sinter | BF Slag |
|------|--------|---------|
|      | MgO, % | Al₂O₃, % | MgO, % | Al₂O₃, % | MgO/Al₂O₃ |
| 2013 | 1.80   | 1.81     | 7.96   | 15.50   | 0.51       |
| 2014 | 1.79   | 1.85     | 7.70   | 15.65   | 0.49       |
| 2015 | 1.64   | 1.87     | 7.26   | 15.73   | 0.46       |
| 2016 | 1.62   | 1.82     | 7.06   | 16.32   | 0.43       |
| 2017 | 1.50   | 1.79     | 7.02   | 16.17   | 0.43       |

5. Conclusions

On the basis of thermodynamics and phase-diagram theory, analysis was conducted on production practices regarding the proper MgO/Al₂O₃ ratio of BF slag, and the following conclusions were obtained:

(1) A quantitative three-segment control theory of the proper MgO/Al₂O₃ ratio was obtained regarding BF slag containing Al₂O₃ of 10–25%.

(A) The MgO/Al₂O₃ ratio is not limited when the Al₂O₃ in the slag is less than 14%, and MgO can be added according to resource and production-cost conditions.

(B) The MgO/Al₂O₃ ratio is required to be between 0.40–0.50 when the Al₂O₃ in the slag is 15–17%, but the temperature should be closely monitored due to slag sensitivity to temperature.

(C) The proper MgO/Al₂O₃ ratio should be 0.45–0.55 when the Al₂O₃ in the slag is larger than 18%.

(2) Industrial practices showed that a proper MgO/Al₂O₃ ratio can help to achieve great economic and social benefits when used.
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