Effect of Magnesium and Aluminum Oxides on Fluidity of Final Blast Furnace Slag and Its Application

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Generally, decreasing slag volume of blast furnace operation can lead to the lower fuel ratio and higher productivity. For high sinter ratio operation, one of effective ways to obtain a lower slag volume is to reduce the gangue content of sinter. Basically, lowering the amount of serpentine in the sinter mix is a feasible way to produce suitable sinter with the lower gangue content. However, this method may result in lower magnesium oxide content in the final slag that may affect its fluidity. Hence, the objective of this study was to understand the effect of MgO and Al_2O_3 on the fluidity of final slag. The liquidus temperature and viscosity of semi-synthetic slag were measured using optical softening temperature device and viscometer, respectively, and the data were treated to develop the multiple-regression formula of $SiO_2-Al_2O_3-CaO-MgO-TiO_2$ semi-synthetic slag for liquidus temperature, viscosity equations and iso-fluidity diagrams.

The experimental results indicated that the lower liquidus temperature and the better viscosity stability lay in the area of $MgO = 5.4\%$, $Al_2O_3 = 10-15\%$, $TiO_2 = 0.5\%$ and $C/S = 1.2$ for the range of composition studied. Several observations in the iso-fluidity diagrams of blast furnace final slag have shown that liquidus temperature decreased with decreasing MgO content and the viscosity of slag could be regarded as being independent of MgO content in the range of $MgO = 5-9\%$, $Al_2O_3 = 15\%$, $C/S = 1.0-1.2$. And, slag fluidity became worse with increasing Al_2O_3 content under the conditions of $MgO = 5.4\%$, $C/S = 1.2$. This study suggested the MgO contents could be lowered from current 6.5 to 5.4% in the conditions of $Al_2O_3 = 15\%$, $C/S = 1.2$ under the stable blast furnace operation with high thermal level. Furthermore, this recipe of lower MgO content (5.4%) had been implemented in CSC's BF operation to reduce the slag volume, and the formula of fluidity developed in this study had been installed in the process computer of all CSC's BFs to present slag fluidity in real time.

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1. Introduction

The blast furnace final slag is made from the meltdown liquid of sinter, lump ore, coke and flux at high temperature, and can be approximately considered as a mixture of the five oxides, SiO_2 , Al_2O_3 , CaO , MgO and TiO_2 . There are four kinds of slags with distinct compositions produced at different regions inside the blast furnace via a series of reduction reactions. That is, primary slag, bosh slag, tuyere slag and final slag are respectively generated in the cohesive zone, dripping zone, raceway and hearth. As well known, good tapping is primarily based on the fluidity of the final slag (low liquidus temperature and low viscosity).

Generally, the major operating region of blast furnace slag for good fluidity in the quinary system ($SiO_2-Al_2O_3-CaO-MgO-TiO_2$) liquidus diagram is the melilites phase (solid solutions of akermanite, $Ca_2MgSi_2O_7$, and gehlenite, $Ca_2Al_2SiO_7$). And, decreasing the slag volume of the blast furnace operation can obtain the lower fuel ratio and higher productivity. For the high sinter ratio operation, one effective way to reach the lower slag volume is to reduce the gangue content of sinter. Basically, lowering the amount of serpentine in the raw mix is a feasible way to produce the qualified sinter with lower gangue. However, this method may result in the lower content of MgO and the higher content of Al_2O_3 in the final slag. The average data of China Steel Corporation (CSC) BF final slag in 2007 are summarized in Table 1. It can be seen that this MgO content ranged from 6.4 to 6.7%, the Al_2O_3 and TiO_2 content was around 15 and 0.55%, C/S was controlled within 1.18 to 1.20, and the hot metal temperature (HMT) was around 1500°C.¹⁾

Table 1 Average data of MgO, Al_2O_3 , TiO_2 , C/S and HMT for CSC's BF final slag in 2007.

Items	1BF	2BF	3BF	4BF
MgO (%)	6.7	6.5	6.4	6.5
Al_2O_3 (%)	14.8	15.2	15.0	15.2
TiO_2 (%)	0.50	0.50	0.67	0.57
C/S (—)	1.18	1.19	1.20	1.20
HMT, T/°C	1504	1504	1497	1495

Therefore, the objective of this study was to evaluate the effect of MgO on the fluidity of the blast furnace final slag and find the appropriate MgO level for better BF performance. A final slag fluidity database will be built for reference on burden preparation of blast furnace by using the experimental results and calculated iso-fluidity diagrams.

2. Experimental Method

2.1 Experimental apparatus

The measurements of the liquidus temperature and viscosity of semi-synthetic slag were made by using an optical softening temperature device and a viscometer, respectively.

2.1.1 Optical softening temperature device

The experimental set-up was used for measuring the softening temperature of the slag by observing the deformation of the sample. Its schematic diagram is shown in Fig. 1. A horizontal tube furnace that can be heated up to a maximum temperature of 1700°C was used. Each end of the reaction tube was properly sealed by water-cooling metal

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Fig. 1 The schematic diagram of experimental apparatus for the measurement of the softening temperature.

Fig. 2 The schematic diagram of experimental apparatus for the viscosity measurement.

caps to prevent air entering into the system, and closed by a quartz window allowing the CCD camera to follow the experiments visually. A thermocouple was inserted into the furnace through the quartz window, and the reaction tube was purged with Ar gas throughout the duration of experiment. In this experiment, approximately 0.07 g of cylindrical slag sample (outside diameter: 3 mm, height: 3 mm) was placed on the MgO substrate kept in the ceramic reaction tube.

2.1.2 Viscometer

A rotating cylindrical method was adopted to measure the viscosity of the molten slag. The apparatus is schematically shown in Fig. 2. A viscometer is connected to a graphite spindle through a graphite rod. The spindle consists of a bob and a shaft, of which the dimensions are also shown Fig. 2. The graphite crucible has a 50 mm internal diameter, 140 mm height, and 10 mm thickness of wall and base. The graphite crucible containing the slag sample (about 120 g of mixed powder) was placed in a given position of the heated furnace where the temperature distribution was uniform. The slag samples were kept molten for more than 2 h, and the rotating spindle was then completely immersed into the molten samples. The holding time for reaching equilibrium state was more than 20 min at each experimental temperature. A metal flange was used to fill the gap between the ceramic reaction tube and the viscometer, and Ar gas was introduced into the reaction chamber at 0.4 L/min. The viscometer was calibrated by using Brookfield standard solutions with 0.5–49 poise (1 poise = 0.1 Pa·s) at room temperature.

Fig. 3 The experimental approach for fluidity measurement in this study.

2.2 Experimental procedure

The experimental approach with above apparatus for the fluidity measurement in this study is given in Fig. 3. At the beginning, the semi-synthetic slag samples were the water-quenched slag obtained from the blast furnace, and prepared with different MgO contents and C/S by adding pure oxide powers (reagent grade). In order to prepare a uniform slag, 110–120 g of mixed SiO₂–CaO–Al₂O₃–MgO–TiO₂ slag was pre-melted in a graphite crucible under the atmosphere of Ar gas (0.4 L/min) at 1500°C. Afterward, the melt was cooled to form solid (slag), and the solid milled into fine powder. Subsequently, three kinds of measurements on the slag samples were conducted at the same time: (1) preparation of briquette samples, followed by heating the samples to measure the slag softening temperatures by observing their deformation as shown in Fig. 4; (2) analysis of the slag chemical compositions; (3) measuring the slag viscosity by using a viscometer at high temperature. Finally, the measured data for liquidus temperature and viscosity was processed by the multiple regression method to get mathematic equations, and the iso-fluidity diagrams could be developed by combining the equation: SiO₂ + CaO + Al₂O₃ + MgO + TiO₂ = 100%.

The original form of a briquette sample is shown in Fig. 4(A). It started deforming as given in Fig. 4(B), the temperature at this time was defined as the deformation temperature. The temperature, as the sample was heated to a semi-sphere form, shown in Fig. 4(D), was defined as the liquidus temperature. Finally, Fig. 4(E) shows the sample form spreading gradually with the increasing temperature, and this point was named as flow temperature.

3. Results and Discussions

In the experimental design, MgO, Al₂O₃ and C/S ranged from 0 to 15%, 10 to 20% and 1.10 to 1.40, respectively, and the highest operation temperature for slag viscosity measurement was above 1500°C, and totally forty tests were conducted among these ranges.

3.1 Softening temperatures of final slag

3.1.1 Observation

Figure 5 indicates the variation of the softening temperatures measured by observing the deformation of the slag

Fig. 4 The softening temperatures based on the deformation of the slag samples.

Fig. 5 The variation of the softening temperatures as a function of the MgO content (0–15 mass%) at $C/S = 1.2$, $Al_2O_3 = 15 \text{ mass\%}$ and $TiO_2 = 0.5 \text{ mass\%}$. Fig. 6 The dependence of softening temperature on C/S at $MgO = 5.4 \text{ mass\%}$, $Al_2O_3 = 15 \text{ mass\%}$ and $TiO_2 = 0.5 \text{ mass\%}$.

sample as a function of the MgO content (0–15 mass%) for each slag composition at a basicity of $C/S = 1.2$, 15 mass% Al_2O_3 and 0.5 mass% TiO_2 . In this plot, there are four different softening temperatures, comprising the above-defined flow, liquidus, sphere and deformation temperature from high to low temperature. The curves in Fig. 5 show that the softening temperatures increased gradually then decreased with increasing MgO content, and that the lower liquidus temperature ($<1430^\circ\text{C}$) could be obtained in the range of MgO content from 2.4 to 5.7 mass%. Figure 6 shows the dependence of softening temperature on C/S at 5.4 mass% MgO and 15 mass% Al_2O_3 , where the softening temperatures increased gradually with the increasing C/S . From the results in Fig. 6, the lower liquidus temperature ($<1430^\circ\text{C}$) could be obtained in the range of C/S from 0.95 to 1.20. It is shown in Fig. 7 that the dependence of softening temperature on Al_2O_3 at a basicity of $C/S = 1.2$, 5.4 mass% MgO and 0.5 mass% TiO_2 , where the softening temperatures increased gradually with increasing Al_2O_3 content. From the results in Fig. 7, the higher liquidus temperature ($>1430^\circ\text{C}$) could be obtained in the range of Al_2O_3 from 17 to 20%.

Fig. 7 The variation of the softening temperatures as a function of the Al_2O_3 content (10–20 mass%) at $C/S = 1.2$, $MgO = 5.4 \text{ mass\%}$ and $TiO_2 = 0.5 \text{ mass\%}$.

Fig. 8 The liquidus isotherms diagram for SiO_2 - CaO - Al_2O_3 - MgO - TiO_2 semi-synthetic slag at $\text{Al}_2\text{O}_3 = 15 \text{ mass\%}$ and $\text{TiO}_2 = 0.5 \text{ mass\%}$.

3.1.2 Multiple regression

The data for both liquidus temperature (1349 – 1490°C) and composition of the slags (31.2 – $40.3 \text{ mass\% SiO}_2$, 38.7 – $46 \text{ mass\% CaO}$, 10.3 – $20.4 \text{ mass\% Al}_2\text{O}_3$ and 0 – $5 \text{ mass\% TiO}_2$) were multiple-regression to get an equation with $R^2 = 0.98$ as eq. (1):

$$T_{\text{liquidus}} = a\text{SiO}_2^2 + b\text{CaO}^2 + c\text{MgO}^2 + d\text{Al}_2\text{O}_3^2 + e\text{TiO}_2^2 + f\text{SiO}_2 + g\text{CaO} + h\text{MgO} + i\text{Al}_2\text{O}_3 + j\text{TiO}_2 \quad (1)$$

Then, the liquidus isotherms diagram could be obtained by combining the normalized sum of five oxides with the formula with $\text{SiO}_2 + \text{CaO} + \text{Al}_2\text{O}_3 + \text{MgO} + \text{TiO}_2 = 100\%$ (as shown in Fig. 8) at $15 \text{ mass\% Al}_2\text{O}_3$. Each curve in Fig. 8 indicates the distribution of liquidus temperature as a function of slag composition. Based on the distribution of the different liquidus temperatures in this diagram, two distinct regions can be specified. The first region (as blue-colored) is specified for the slag where the liquidus temperature decreases with decreasing MgO content (when $C/S < 1.3$, $\text{MgO} < 9 \text{ mass\%}$). The second region (as red-colored) is specified for the slag where the liquidus temperature is not affected by MgO content (when $C/S > 1.3$). From the result described in the distinct regions of the liquidus isotherms diagram, it is known that the liquidus temperature is favorable for the slag while decreasing the MgO content under a wide range of C/S . In terms of the BF operation range ($1.18 < C/S < 1.20$, $6.4 \text{ mass\%} < \text{MgO} < 6.7 \text{ mass\%}$) for CSC, the liquidus temperature ranges from 1420 to 1440°C and the slag composition is located in the first region, which means that a lower liquidus temperature could be obtained when the MgO content is reduced.

3.2 Viscosities of final slag

3.2.1 Observation

Figure 9 shows the effect of MgO content on the viscosities of SiO_2 - CaO - Al_2O_3 - MgO - TiO_2 semi-synthetic slag as a function of temperature under the conditions of $C/S = 1.2$, $15 \text{ mass\% Al}_2\text{O}_3$ and $0.5 \text{ mass\% TiO}_2$, and these

Fig. 9 The effect of MgO content on the viscosities of SiO_2 - CaO - Al_2O_3 - MgO - TiO_2 semi-synthetic slag as a function of temperature at $C/S = 1.2$, $\text{Al}_2\text{O}_3 = 15 \text{ mass\%}$ and $\text{TiO}_2 = 0.5 \text{ mass\%}$.

experimental results indicated that the slag viscosity increases with decreasing slag temperature. However, the curves in Fig. 9 are too complex to easily distinguish the preferable conditions for BF tapping. For instance, from the curve which stands for the case at $15 \text{ mass\% MgO}$, the viscosity is lower in the high slag temperature range but it becomes higher rapidly in the low temperature range; while for the case of $5.9 \text{ mass\% MgO}$, the viscosity is lower in high temperature range and it increases slowly in the low temperature range. Therefore, in order to determine the better viscosity stability, two criteria were set up. The first criterion for evaluating the stable viscosity was the lower melting temperature ($< 1400^\circ\text{C}$). The melting temperature means the turning point of the curves in Fig. 9, and the results show that most of melting temperatures are lower than 1400°C except for the cases of 6.8 and $9.0 \text{ mass\% MgO}$. The second criterion was made to choose the lower viscosity from the lower melting temperatures for the MgO content in the first criterion. Among the cases of MgO content lower than the BF operation range at CSC ($\text{MgO} = 6.4$ – $6.7 \text{ mass\%}$), it was found that the MgO content for the most stable viscosity in this work was $5.4 \text{ mass\%}$ under the above criteria.

The tendency is observed in the temperature-viscosity curves of slag with different C/S values (1.1 – 1.3) under the conditions of $\text{MgO} = 5.4 \text{ mass\%}$ and $\text{Al}_2\text{O}_3 = 15 \text{ mass\%}$ (as shown in Fig. 10). Figure 10 shows that a lower melting temperature for slag is observed at $C/S = 1.2$ by using the above criteria. Therefore, the more stable viscosity in this work is $C/S = 1.2$. It is also shown that the BF operation condition for CSC ($C/S = 1.18$ – 1.20) is located in the suitable range in this study. It is shown in Fig. 11 that the viscosity variation tendency in the temperature-viscosity curves of slag with different Al_2O_3 content (10 – $20 \text{ mass\%}$) under the conditions of $\text{MgO} = 5.4 \text{ mass\%}$, $0.5 \text{ mass\% TiO}_2$ and $C/S = 1.2$. Figure 11 shows that a higher viscosity for slag is observed at the range of $\text{Al}_2\text{O}_3 = 17$ – $20 \text{ mass\%}$ by using the above criteria.

Fig. 10 The effect of C/S on the viscosities of SiO₂-CaO-Al₂O₃-MgO-TiO₂ semi-synthetic slag as a function of temperature at MgO = 5.4 mass%, Al₂O₃ = 15 mass% and TiO₂ = 0.5 mass%.

Fig. 11 The effect of Al₂O₃ content on the viscosities of SiO₂-CaO-Al₂O₃-MgO-TiO₂ semi-synthetic slag as a function of temperature at C/S = 1.2, MgO = 5.4 mass% and TiO₂ = 0.5 mass%.

3.2.2 Multiple regression

The data for viscosity (2.6–75 poise), composition of the slags (the same ranges as liquidus temperature cases), and slag temperature were multiple-regression to get an equation with $R^2 = 0.97$ as eq. (2):

$$\begin{aligned} \mu = & a'\text{SiO}_2^2 + b'\text{CaO}^2 + c'\text{MgO}^2 + d'\text{Al}_2\text{O}_3^2 \\ & + e'\text{TiO}_2^2 + f'\text{SiO}_2 + g'\text{CaO} + h'\text{MgO} \\ & + i'\text{Al}_2\text{O}_3 + j'\text{TiO}_2 + k'T^2 + l'T \end{aligned} \quad (2)$$

The iso-viscosity distribution diagram can be obtained in the diagram (Al₂O₃ = 15 mass%, slag temperature = 1500°C) by using the same calculation method as above the isotherms diagram, as shown in Fig. 12. Each curve in Fig. 12 describes the distribution of viscosity related to the slag composition, with that also two distinct regions can be specified. The first region (as blue-colored) is specified for

Fig. 12 The iso-viscosity diagram for SiO₂-CaO-Al₂O₃-MgO-TiO₂ semi-synthetic slag at 1500°C, Al₂O₃ = 15 mass% and TiO₂ = 0.5 mass%.

the slag where viscosity is not affected by MgO contents (when C/S = 1.0–1.2, MgO = 5–13 mass%). The second region (as red-colored) is specified for the slag where the viscosity increases with decreasing MgO content (when C/S > 1.2, MgO < 9%). Therefore, there is no influence on the final viscosity by reducing MgO when C/S = 1.0–1.2. In terms of the BF operation range for CSC, the slag viscosity ranges from 5 to 6 poise and the slag composition approaches to the first region. However, the dominant factor for avoiding high viscosity is C/S, and good slag viscosity can be still obtained as long as C/S is precisely controlled to about 1.20.

The iso-viscosity distribution diagrams (for 15 mass% Al₂O₃ at 1450 and 1400°C, respectively) could be also developed in this study, as shown in Fig. 13. It was found that the distribution tendency of slag viscosity was similar to the distribution tendency for 1500°C, the only difference being the lower slag temperature, the higher slag viscosity at the same composition. The slag viscosities are respectively 8–9 poise at 1450°C and 16–17 poise at 1400°C for the BF operation range in CSC. In addition, Fig. 14 shows the diagram for slag isotherms as a function of compositions at a fixed viscosity (= 8 poise) by using the same calculation method as the iso-viscosity diagram, and the directions of the two arrowheads in this plot indicates that the slag temperature goes from low to high temperature. It is observed that slag temperature should be higher than 1450°C to keep the slag viscosity in 8 poise; however, it needs a much higher slag temperature while maintaining the better slag fluidity.

3.3 Comparison of liquidus isotherms with slag isotherms

Comparing the results of Fig. 8 with Fig. 14, it is shown that the liquidus temperature will decrease as reducing the MgO content from the CSC's BF operation range (6.4–6.7 mass%) to 5 mass%, and there is only minor effect on the slag temperature (<5°C). It follows from above-mentioned that the MgO content could be lowered from current 6.5

Fig. 13 The iso-viscosity diagram for SiO_2 - CaO - Al_2O_3 - MgO - TiO_2 semi-synthetic slag at 1450 and 1400°C ($\text{Al}_2\text{O}_3 = 15 \text{ mass\%}$ and $\text{TiO}_2 = 0.5 \text{ mass\%}$).

Fig. 14 The slag isotherms diagram for SiO_2 - CaO - Al_2O_3 - MgO - TiO_2 semi-synthetic slag at fixed viscosity ($= 8 \text{ poise}$), $\text{Al}_2\text{O}_3 = 15 \text{ mass\%}$ and $\text{TiO}_2 = 0.5 \text{ mass\%}$.

to 5.4 mass% in the conditions of $\text{Al}_2\text{O}_3 = 15 \text{ mass\%}$, $\text{TiO}_2 = 0.5 \text{ mass\%}$ and $\text{C/S} = 1.2$ under the stable blast furnace operation with the high thermal level.

	MgO (%)	Slag Volume (kg/tHM)
2006(avg.)	6.5	266
2007.09	5.5	259

Fig. 15 The practical results of lower MgO content in CSC's BF.

Fig. 16 Degree of BF slag discharge for each hot metal tapping in CSC's BF.

3.4 Applications

3.4.1 Lower slag volume rate inside BF

S. H. Yi and J. R. Kim showed that the permeability was not changed at the bosh zone when the MgO content was decreased from 6.2 to 4.1%, and good slag fluidity was obtained under the conditions of slag basicity ($\text{C/S} = 1.18$ and $\text{MgO} = 5\%$).^{2,3)} K. Higuchi also indicated that when the MgO content decreased to 5.4%, the blast furnace operation cost and slag volume were reduced.⁴⁾ In this study, it was suggested the suitable lower MgO content was at 5.4%, and it had been adopted in CSC's BFs. One example was shown in Fig. 15, and the practical results indicated slag volume was actually reduced by using 5.5% MgO of final slag.

3.4.2 Real-time system for BF slag fluidity

The interruption of slag flow often occurs with the bad permeability for hot metal flow inside BF hearth, and seriously affect the stability of furnace practice. The bad permeability for liquid flow is usually caused by the bad slag fluidity, which can be expressed by using the index such as slag liquidus temperature and viscosity. The developed formula of slag liquidus temperature and viscosity had been installed in the process computer of all CSC's BFs to present slag fluidity in real time. This system can immediately provide BF staffs some information to control the variation of slag fluidity by making the effective operating adjustment. After installing this system, the degree of BF slag discharge for each hot metal tapping was increased in CSC's BFs (as Fig. 16), and a more stable BF operation was achieved.

4. Conclusion

From above investigation, the following conclusions are drawn:

- (1) Experimental results indicate that the lower liquidus temperature and the better viscosity stability of slags lay in the conditions of $\text{MgO} = 5.4\%$, $\text{Al}_2\text{O}_3 = 15\%$, $\text{TiO}_2 = 0.55\%$ and $\text{C/S} = 1.2$ for the variation of MgO contents (0–15%). And slag fluidity became worse with the increase of Al_2O_3 content for the range of composition studied.
- (2) The observations in the liquidus isotherms and iso-viscosity diagrams of blast furnace final slag show that liquidus temperature decreases with decreasing MgO content and the viscosity of slag could be regarded as being independent of MgO content in the range of

$\text{MgO} = 5\text{--}9\text{ mass}\%$, $\text{Al}_2\text{O}_3 = 15\text{ mass}\%$, $\text{C/S} = 1.0\text{--}1.2$.

- (3) The lower MgO content (5.4%) had been implemented to reduce the slag volume, and the real-time system for BF slag fluidity had been installed in all CSC's BFs as useful tool for daily operation.

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