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Effect of MgO Injection on Smelting in a Blast Furnace

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Abstract: The effects of the simultaneous injection of MgO and magnesite powder on the combustion of coals, properties of the primary slag, and softening-melting properties of the burden were investigated. There were four aspects to the results that we obtained. First, MgO showed catalytic activity for dehydrogenation and carboxyl group removal from coal; as a result, with increasing MgO, the combustion ratio and pyrolysis ratio of the coal investigated improved. Notably, when the content of MgO increased from 0% to 3.21%, the combustion ratio increased from 67.75% to 75.73%. Secondly, the MgO distribution in the slag sample was close to that in the standard slag after melting for 10 min. After 50 min, the difference in MgO content between the slag and standard slag samples was less than 1%. Thirdly, with an increase in the content of MgO, the short-slag feature of the slag was obvious, the viscosity fluctuated wildly, and the melting temperature increased significantly. It is proposed that the properties of the primary slag could be improved by decreasing the MgO content. Finally, with the increase in the MgO added to the burden, the softening-melting properties of the burden degraded. When the MgO content was 0.86%, $\Delta P_{\max}$ was only 2.04 kPa, and S 59 kPa·°C. However, when the MgO content was 2.61%, $\Delta P_{\max}$ was 20.00 kPa, and S 1349 kPa·°C. Therefore, the technology of MgO injection into tuyeres with pulverized coal was beneficial for blast furnace operation.

Keywords: MgO injection, coal combustion ratio, slag flowability, softening-melting properties of the burden

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Introduction

To date, it has been necessary to maintain a certain amount of MgO in the slag [1]. The method of adding MgO to the sinter or pellet is the one most broadly implemented. However, it also has some negative effects on smelting in the blast furnace (BF): the addition of MgO can decrease the strengths of the sinter and pellet [2–6], and the properties of the primary slag can also be affected. As we know, the resistance loss in the melting-dripping zone is 60% of the total loss in the BF [7]. The primary slag with high MgO becomes sticky, the flow of slag-iron is anomalous, and the softening-melting properties of the burden in the BF are deteriorated [8]. In order to avoid the negative effects mentioned above, MgO can be injected with pulverized coal through the tuyeres. This technology not only guarantees good quality of the sinter and pellet but also provides an effective method to completely solve the problem observed in the melting-dripping zone. In fact, many scholars and experts have researched this technology [9–11]. For example, some researchers [12] found that when the raw materials were changed from pellets with olivine addition to self-fluxing pellets, the basicity of the primary slag increased from 0.13 to 0.98, but the content of MgO decreased from 31.55% to 9.24%; the melting point, which was calculated based on the CaO-SiO₂-MgO ternary phase diagram, also decreased from 1600°C to 1400°C. The slag in the tuyeres was mainly composed of pulverized coal and coke ash. When the basicity of the slag was less than 0.1, the viscosity increased, and the melting point obtained by Yoagata was in the range 1650°C–1720°C [13]. Therefore, basic flux injected into the BF could decrease the viscosity of the slag in the tuyeres; as a result, the amount of slag in the bosh decreased, the softening-melting properties of the burden improved, the permeability in the BF developed, the coexistence zone of gas, liquid, and solid expanded, and the operation of the BF could be guaranteed [14]. Yamagata researched the process of pulverized coal injection into tuyeres with dolomite powder to decrease the content of silicon and sulfur in metal iron [13]. Notably, when the masses of the dolomite powder were 20 kg and 15 kg, the silicon and sulfur contents decreased 0.06% and 0.005% respectively, but the coke content increased 6.2 kg.

The injection of a converter slag into the BF by Jitan could achieve the objectives of reducing the slag in the bosh, controlling the basicity, and decreasing the silicon in the metal iron [15]. Okvist also researched the melting point of the slag in the tuyeres as flux was injected into the BF [16]; the results revealed that the flux injected could decrease the melting point of the slag in the tuyeres and also decrease the difference between the softening and melting temperatures. In order to further explore the flux injection process, an experiment using pellets as raw materials and converter slag as the flux was performed for two weeks [17]; the result indicated that the amounts of slag and silicon in the iron both decreased, and the ability of the slag to remove sulfur and alkali metals increased. Ichida et al. [18] investigated the effect of serpentine ore powder injected into the tuyeres on the burden structure in the lower part of the BF in the No.2 furnace of iKimitsu Iron & Steel plant; the results revealed that the melting point of the slag could be decreased, the permeability in the lower part of the furnace could be improved, and desulphurization could be accelerated. The effect of magnesium powder injection with pulverized coal from the tuyeres on the combustion ratio of coal was studied by some research scholars, which indicated that the addition of moderate light-burned magnesite contributed to the increase in the combustion ratio [19]. In addition, research on the grindability and conveyance performance of magnesite powder revealed that the injection of the powder into the tuyeres together with pulverized coal could meet the requirement of the PCI process [20].

Test method

In this test, grindability was obtained using the standard Hardgrove apparatus. According to the density of the sample that was determined by the pycnometer method, the transport velocity was calculated. The experimental apparatus for the combustion of coal is shown in Figure 1. The arc plasma installation is shown in Figure 2. The slag viscosity tester is shown in Figure 3. Finally, the apparatus for determining the softening-melting property is shown in Figure 4.

Measurement method for the combustion ratio of coal

It is acknowledged that combustion ratio represents the degree of combustion of pulverized coal and is defined as the ratio of the amounts of burned coal to combustible

1-hot-blast stove, 2-alundum tube, 3-combustion furnace, 4-cooling system, 5-ash chute, 6-coal injection bottle, 6-duster

Figure 1: Experimental apparatus for combustion of coal.

1-cathode, 2-insulating layer, 3-anode, 4-arc, 5-reactor, 6-sampling port, 7-plasma torch, 8-gas collecting pipe, 9--separator, 10-filter

Figure 2: Arc plasma installation.

1-stent, 2-torque sensor, 3-slag, 4-molybdenum transition head, 5-platinum-rhodium thermocouple, 6-corundum tube, 7-heating body, 8-platinum-rhodium thermocouple, 9-computer, 10-control cabinet

Figure 3: Slag viscosity tester.

1-gas valve, 2-O₂, 3-gas flow-meter, 4-air compressor, 5-gas-producing furnace, 6-gas washing bottle, 7-air leakage chamber, 8-H₂, 9-N₂, 10-pressure gauge, 11-platinum-rhodium thermocouple, 12-compression bar, 13-Iron-bearing feed 14-MoSi₂ high temperature furnace, 15-coke 16-receiving disc, 17-pressure device, 18-displacement sensor, 19-camera, 20-computer, 21-temperature controller

Figure 4: Softening-melting apparatus.

coal under a certain combustion condition. A lower combustion ratio suggests incomplete combustion of coal, as a result, the utilization ratio of pulverized coal in a BF decreases, and the permeability of the burden and high-temperature viscosity of the slag are both affected. Therefore, iron production in the BF is also affected. Using the experimental apparatus shown in Figure 1, the combustion ratio was determined. First, when the temperature of the furnace was 1300°C, dried pulverized coal of mass about 40 g was injected for 15 min, and the temperature of hot-blast air (2 L/min) was 900°C. Then, the residue was collected and analyzed. Finally, the combustion ratio was calculated by the following formula.

$$R = \left[1 - \frac{A_0 \times (100 - A_1)}{A_1 \times (100 - A_0)} \right] \times 100\% \quad (1)$$

where R is the combustion ratio of coal, A_0 the ash content of the coal before combustion, and A_1 the ash content of the residue.

Measurement method for pyrolysis ratio in arc plasma

The combustion of pulverized coal in the tuyeres includes three stages. The first is the emission of volatile matter, second is the decarbonizing-splitting decomposition, and the last step is the ignition and combustion of gaseous hydrocarbons. In fact, the emission of volatile matter and decarbonizing-splitting decomposition are both pyrolysis processes under high-temperature conditions. Therefore, the pyrolysis ratio determines the extent of combustion of the coal. Using the experimental apparatus shown in Figure 2, the pyrolysis ratio was determined. A plasma generator of power 50 kW, working current 150 A, and working voltage 280 V was used. Dried pulverized coal of mass about 100 g was injected at the rate of 1 g/s. During the process, argon as a protection gas was also injected at the rate of 4 L/min. In addition, the heating rate was controlled at 10⁵°C/s, and the testing temperature was

1500°C. Finally, the solid- and gas-phase products were collected after pyrolysis. The pyrolysis ratio was calculated by the following formulae.

$$M_r = \frac{M_c \times A_0}{A_1} \quad (2)$$

where M_r is the quality of the residue and M_c the quality of pulverized coal.

$$w = \frac{M_c - M_r}{M_c} \times 100\% \quad (3)$$

where w is the pyrolysis ratio.

Measurement of slag viscosity

First, pre-melting of the slag that was compounded using chemical reagents was performed. In a graphite crucible, 140 g of the slag were taken. Then, the crucible was placed in the furnace at room temperature, and argon (1.5 L/min) was injected from a bottle. The slag was maintained at the constant temperature of 1500°C and stirred with a molybdenum rod. After 20min, the measurement of the viscosity of the slag commenced. The next step involved cooling at the rate of 2°C/min. When the viscosity of the slag became 3 Pa s, the test ended.

Measurement of softening-melting properties

All the raw materials were dried. An ore of mass 170 g and size 6.3–10 mm and 44 g coke with sizes 10–16 mm were placed in the graphite crucible; the coke was first placed for 20 mm, then the ore was distributed over 50 mm, and finally, there was coke again for 20 mm. A mixture of N₂ and CO in 7:3 ratio was injected at the flow rate of 15 L/min. Using a certain heating rate, the burden was heated until it dripped.

The components of the coal and magnesite powder are listed in Tables 1 and 2, respectively.

Table 1: Industrial and elemental analysis of coal.

name	A/%	V/%	C/%	S/%	M/%	Calorific value/KJ/mol
Pingluo coal	9.7	9.0	81.8	0.19	8.7	28.7
Shenhua coal	7.4	36.0	57.8	0.31	17.9	23.4
Yangquan coal	11.15	8.14	81.45	1.14	5.9	28.22

Table 2: Main chemical components of magnesite (%).

name	CaO	MgO	SiO ₂	P	S
Magnesite	1.2	44.94	4.00	0.001	0.005

Effect of MgO on coal combustion

Effect on combustion ratio

The components of the coal and magnesite powder are listed in Tables 1 and 2, respectively. The particle size is 200 mesh. The effect of MgO on the combustion ratio of the pulverized coal is presented in Table 3.

Table 3: Combustion rates of mixed coals.

number	MgO/%	Pingluo coal/%	Shenhua coal/%	R/%
0#	0	40	60	67.75
1#	2.56	40	60	73.32
2#	3.21	40	60	75.73
3#	4.20	40	60	76.69
4#	4.91	40	60	77.48
5#	5.88	40	60	77.39
6#	7.81	40	60	78.41
7#	8.65	40	60	78.64

The effect of MgO on the combustion ratio of the coal (R) is shown in Figure 5.

Figure 5: Influence of MgO content on burning rate.

As can be seen from Figure 5, with an increase in the content of MgO, the R increased from 67.75% to 75.73%. It is noteworthy that the R increased slowly with the

increase in MgO from 4.20% to 8.65%. Notably, the R reached a maximum as the MgO content became 8.65%. Compared with the R of the coal without the addition of MgO, it increased about 11.32%. Based on the above analyses, it can be concluded that the addition of MgO to pulverized coal is favorable for increasing the combustion ratio of the coal.

Effect on pyrolysis ratio of pulverized coal

Since the pulverized coal is heated at a very high rate (10^3 – 10^6 K/s) in the tuyeres, it will decompose rapidly in this region and produce volatile matter and slag. As we know, pyrolysis of the coal affects its combustion ratio. The effect of MgO content on pyrolysis ratio is shown in Figure 6.

Figure 6: Influence of MgO content on the pyrolysis ratio of the coal.

As shown in Figure 6, the pyrolysis ratio increased linearly with the increase in MgO from 0% to 4.91%, followed by a slight change as the MgO content increased further. Therefore, when the amount of MgO added to the pulverized coal was 4.91%, the pyrolysis ratio could be increased by 11%; as a result, the combustion ratio of the coal had improved.

After pyrolysis in arc plasma, the arrangement of the carbon atoms in the slag will change. XRD can be used to analyze this change [21]. The results of the XRD analysis for 0# and 5# samples are presented in Figures 7 and 8, respectively.

From Figures 7 and 8, it can be seen that compared with the (002) peak of raw coal, that of 5# had increased in intensity. Apparently, the (002) peak reflected the lamellar

Figure 7: XRD analysis of 0# coal sample.

Figure 8: XRD analysis of 5# coal sample.

stacking height of the macromolecules in the pulverized coal. The higher the height, the stronger is the diffraction intensity. The rapid pyrolysis of coal at high temperatures produces a large number of free radical carbon atoms; because the time for this reaction is very short, a lot of the C^* that have not reacted would be incorporated into the slag, making the microcrystal size larger [22]. The addition of MgO into the coal of 5# contributed to the pyrolysis of the pulverized coal, therefore, the (002) peak intensity increased. In addition, the (001) peak intensity, which reflected the degree of condensation of the aromatic rings in the coal, also revealed an obvious change. The higher the

condensation degree, the stronger is the diffraction intensity. As we know, MgO is basic [23–25]. Under certain conditions, chemical adsorption between MgO and the acidic carboxyl groups in the coal occurred, which contributed to dehydrogenation and the removal of the carboxyl groups of the coal. Therefore, the (002) peak intensity of 5# coal was higher than that of the raw coal. Based on the above analysis, it can be concluded that an additive containing MgO in the pulverized coal could increase the combustion of the coal in the tuyeres to near completion.

Effect of MgO on slag properties

Formation of the slag

A mixture of slag and MgO was injected in the tuyeres for testing in the lab. First, two types of slags with different MgO contents were compounded using chemical reagents. Then, they were melted at 1500°C for 90 min in a high-temperature furnace. During the melting process, they were stirred with a molybdenum rod to form standard slag samples. The MgO contents in different standard slag samples are listed in Table 4. The sampling points are shown in Figure 9. The test results are presented in Table 5. The MgO content and its difference as a function of time are obtained, as shown in Figure 10.

Table 4: MgO contents in different standard slag samples.

	MgO/%	temperature/°C
1#standard slag sample	11.50	1500
2#standard slag sample	8.94	1500

In Table 5, Δ_{MgO} refers to the difference in the amount of MgO between the top of the sample and the standard sample, and Δ'_{MgO} is the difference in MgO content between the bottom of the sample and the standard sample.

It can be clearly seen from Table 5 and Figure 10 that after melting for 10 min, the distribution of MgO in 8# sample, with 2.56% MgO, was close to that in the 1# standard slag sample. After 50 min, Δ_{MgO} and Δ'_{MgO} both were less than 1%. The main reason for this phenomenon is that the addition of MgO forms Mg^{2+} and O^{2-} in the slag, then Mg^{2+} migrates at high temperatures and a balance is achieved in a very short time. In fact, owing to the constantly strong stirring of the air and high

Figure 9: Sampling points.

temperature in the tuyeres, the mixing speed and uniformity of the MgO injected and the slag are better than those obtained from the test. Therefore, the MgO injected into the furnace is beneficial for the formation of slag in the hearth.

Flowability of the slag

The main chemical components of the slags are listed in Table 6.

The η - t curves of the slags with different MgO contents are shown in Figure 11.

It can be seen in Figure 11(a) and 11(b) that with increasing MgO content, the η - t curves for the slags exhibited obvious short-slag features and the viscosity fluctuated wildly. In particular, the viscosity was minimum (0.25 Pa·s) when the MgO content was 8.88%, and the difference between the maximum and minimum in the test was 0.63 Pa·s. In addition, as shown in Figure 11(c), with an increase in the content of MgO, the melting temperature rose linearly. Notably, the melting temperature was 1314°C for the MgO content of 4.62%, while it was 1398°C for 12.58% MgO; the temperature difference is 84°C. As we know, an increase in the melting temperature results in the widening of the softening-melting zone and increasing of ΔP_{max} , which makes smelting in the BF difficult. Therefore, MgO injection into the tuyeres could improve the properties of the primary slag.

Table 5: Slagging results.

Sample name	MgO addition/g	Time/min	MgO at the top of the sample/%	$\Delta_{\text{MgO}}/\%$	MgO at the bottom of the sample/%	$\Delta'_{\text{MgO}}/\%$	Temperature/ $^{\circ}\text{C}$
Standard	0.00	90	11.43	0.00	11.93	0.00	1500
8#	2.56	10	10.50	0.93	10.40	1.53	1500
9#	2.56	30	9.94	1.49	10.08	1.85	1500
10#	2.56	50	11.17	0.26	11.40	0.53	1500
11#	2.56	70	10.90	0.53	11.19	0.74	1500
12#	2.56	90	10.88	0.55	11.04	0.89	1500

Figure 10: MgO content of the slag at different times.

Table 6: Major chemical composition of the slags (%).

Slag	CaO	SiO ₂	Al ₂ O ₃	V ₂ O ₅	TiO ₂	MgO	R _{CaO/SiO₂}
13#	47.48	28.72	8.74	1.18	9.27	4.62	1.60
14#	46.20	27.43	8.40	1.52	9.06	7.39	1.68
15#	45.56	27.00	8.23	1.45	8.88	8.88	1.69
16#	44.83	26.60	8.08	1.43	8.72	10.34	1.69
17#	44.30	26.29	7.94	1.41	8.57	11.49	1.69
18#	43.81	25.98	7.81	1.40	8.43	12.58	1.69

Softening-melting properties of the burden

The softening-melting properties are the most important for the burden. The resistance loss in the melting-dripping zone is about 60% of the total loss in the BF, and it is the restricted link of the operating stability of the lower part of the furnace. It is noteworthy that the MgO content that the BF needs has been confirmed. If MgO is injected into the furnace with pulverized coal, the MgO content of the burden

will decrease. Therefore, testing for different MgO contents of the burden in a high-temperature furnace will reveal the effect of MgO on the softening-melting properties of the burden. The main components of the burden and coke are listed in Tables 7 and 8, respectively.

The softening-melting properties are presented in Table 9. The relationship between MgO content and ΔP_{max} is shown in Figure 12. The relationship between MgO content and S is shown in Figure 13.

From Figures 12 and 13, it can be seen that with increasing amount of MgO, ΔP_{max} and S both increase linearly. As we know, ΔP_{max} depends on the amount and viscosity of the slag [26]. The change in akermanite content is the biggest distinction in the burden with different MgO contents. With an increase in the content of MgO, the akermanite content increases, and the temperature range over which akermanite exists is also widened; as a result, the properties of the slag deteriorate, which leads to an increase in the resistance loss [27]. From Table 9, it is easy to observe that when the MgO content is 0.86%, ΔP_{max} is only 2.04 kPa, and S is 59 kPa $^{\circ}\text{C}$. However, when the MgO content is 2.61%, ΔP_{max} becomes 20.00 kPa and S 1349 kPa $^{\circ}\text{C}$. The reason for this phenomenon is that the flowability of the slag showed an obvious deterioration with the addition of MgO, as a result, the permeability of the softening-melting zone in the BF became worse, which affected BF operation.

Conclusions

1. The addition of MgO to pulverized coal was favorable for increasing the R of the coal. Notably, with an increase in the content of MgO from 0% to 3.21%, the R increased from 67.75% to 75.73%.
2. MgO showed catalytic activity for dehydrogenation and carboxyl group removal from the coal; as a result, with increasing MgO content, the combustion and pyrolysis

Figure 11: Flowability of slags with different MgO contents.

Table 7: Major chemical components of burden.

Number	TFe/%	CaO/%	SiO ₂ /%	Al ₂ O ₃ /%	V ₂ O ₅ /%	TiO ₂ /%	MgO/%	R ₂
19#	55.62	8.86	5.36	1.63	0.22	1.73	0.86	1.65
20#	56.07	9.13	5.42	1.66	0.30	1.79	1.46	1.68
21#	55.82	9.13	5.41	1.65	0.29	1.78	1.78	1.69
22#	55.58	9.10	5.40	1.64	0.29	1.77	2.10	1.69
23#	55.38	9.10	5.40	1.63	0.29	1.76	2.36	1.69
24#	55.19	9.09	5.39	1.62	0.29	1.75	2.61	1.69

Table 8: Major chemical components of coke.

Industry analysis of coke/%								Ash composition of coke/%				
FC	V	A	H ₂ O	S	CaO	SiO ₂	MgO	Al ₂ O ₃	K ₂ O	Na ₂ O	Fe ₂ O ₃	TiO ₂
81.11	0.94	12.58	4.60	0.77	6.16	37.3	0.51	46.99	0.13	0.19	5.58	2.71

Table 9: Results of the softening-melting properties.

Number	T' ₁₀ /°C	T' ₄₀ /°C	ΔT' ₁ /°C	T _s /°C	T _d /°C	ΔT _{ds} /°C	ΔP _{max} /kPa	S/kPa·°C
19#	1174	1319	145	1320	1396	76	2.04	59
20#	1173	1330	157	1311	1452	141	8.06	497
21#	1216	1408	192	1330	1459	129	9.22	502
22#	1228	1396	168	1326	1441	115	12.89	794
23#	1227	1401	174	1326	1449	123	13.87	819
24#	1212	1384	172	1344	1470	126	20.00	1349

- ratios of the coal improved, which had a significant effect on increasing the utilization rate of the pulverized coal, decreasing the amount of coke, and improving BF operation.
3. The MgO distribution in the slag sample was close to that in the standard slag after melting for 10 min;
4. after 50 min, the difference in MgO content between the slag and standard slag samples was less than 1%. With an increase in MgO content, the short-slag feature was obvious, the viscosity fluctuated wildly, the melting temperature increased significantly, the melting-dripping zone broadened, and $\Delta P_{\max}$ increased; as a

Figure 12: Relationship between MgO content and $\Delta P_{\max}$.

Figure 13: Relationship between MgO content and S.

result, the softening-melting properties deteriorated and smelting in the BF was affected negatively. Consequently, MgO injection into the tuyeres could improve the properties of the primary slag.

- With increasing amount of MgO added to the burden, the softening-melting properties of the burden worsened. When the MgO content was 0.86%, $\Delta P_{\max}$ was only 2.04 kPa, and S was 59 kPa·°C. However, when the MgO content was 2.61%, $\Delta P_{\max}$ was 20.00 kPa, and S 1349 kPa·°C. Therefore, the technology of injecting MgO into the tuyeres with pulverized coal was beneficial for BF operation.

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