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Research on the foaming property of blast furnace slag bearing TiO_2

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PZH (Pan Zhi Hua) Iron and Steel (Group) Corporation, the biggest steel company in southwest China, has been using titanium-vanadium-magnetite as the main raw materials for blast furnace ironmaking processing for over 30 years. One of the problems that has a negative affect on the blast furnace operation is slag foaming. Based on the chemical components of the blast furnace slag-bearing higher TiO_2, the foaming properties were studied. The TiO_2 content, which is calculated according to the total titanium content in all the forms of titanium compound in the slag, in this research is 30% weight per cent. Different forms of titanium compounds have different actions on the slag foaming behaviour that depends on the reduction condition in the blast furnace. The relationships among slag foaming performance and the binary alkalinity of the slag, the content of CaF_2, MnO in slag, and the amount of gas injected in slag are investigated. The results show CaF_2 and MnO have a stronger anti-foaming affect on the slag, even in the lower percentage. The way to measure high TiO_2 slag foaming performance and how to eliminate foamy slag are also discussed.

Keywords: blast furnace slag bearing TiO_2, foamy slag, foaming performance

Introduction

It has been proved in production and in practice at home and abroad that TiO_2 has no bad effect on the smelting process when the TiO_2 content in the slag is less than 20%. TiO_2 can even improve the technical and economical index and the quality of hot metal if its content is less than 5% during smelting magnetite in the blast furnace[1,2]. When the content of TiO_2 in slag exceeds 25% there are some special problems, for example slag becoming ropy, iron contained in slag, and slag becoming foamy. Laboratory experiments were carried out to measure the performance of slag samples with rising foam, to observe the factors that affect the performance of slag with rising foam and the degree of the effect. Then we can clarify the mechanism for producing foamy slag and search for the feasible ways to eliminate foamy slag in theory.

The chemical component of the samples and experimental means

The chemical component of experimental samples

The chemical component of experimental samples are listed in Table I. The chemical component of the slag taken from PZH's blast furnace on site is listed in the last line of the table for comparison. The low titanic compound of slag on site was not analysed because of difficulties. The compounds containing titanium in slag were divided into a four-part –TiO_2, Ti_2O_3, TiC, TiN—mix on account of the real conditions of the blast furnace and the result of a former investigation[3] when we mixed the sample. In addition, the Ti is converted into TiO_2 in order to ensure that the amount of TiO_2 is 30%.

Sample no. 103 is a base sample blended with CaF_2 and MnO. All samples were blended by reagent.

Discussion on the methods of measuring the performance of slag with raising foam.

The degree for slag to raise foam is decided by the performance of slag with raising foam. There is no uniform means to measure the slag performance in raising foam. It is well known that there are two reasons for slag to raise foam. One is the speed of gas production in slag. The other is whether slag performance is available for gas to discharge. What is called slag performance in raising foam is the latter. The author suggests that the speed of producing gas in slag must be determined when researching slag performance in raising foam.

Former experimental gas was provided by reaction, that is, the reaction between the graphite crucible' wall and furnace slag or between slag and iron provided with gas. Adopting this experimental method has two problems. Firstly, controlling the speed of producing gas is difficult. Secondly, the gas produced by reaction and the slag component vary with the process of the chemical reaction, which leads to the slag property changing too, which then affects the analysis of the experimental result. Considering these two problems, the following method was used in the experiment. The slag was separated from the graphite crucible by lining the graphite crucible wall, with an Mo sheet to prevent a reaction between the slag and wall. Foam was produced by injecting neutral gas into the slag through an outside transport gas pipe. Slag foam raising or the index for slag raising foam is the difference between the height of the slag surface and its height when gas injection is stopped at a certain speed of gas production. This method for measuring the slag property for foam raising is reliable and easy.

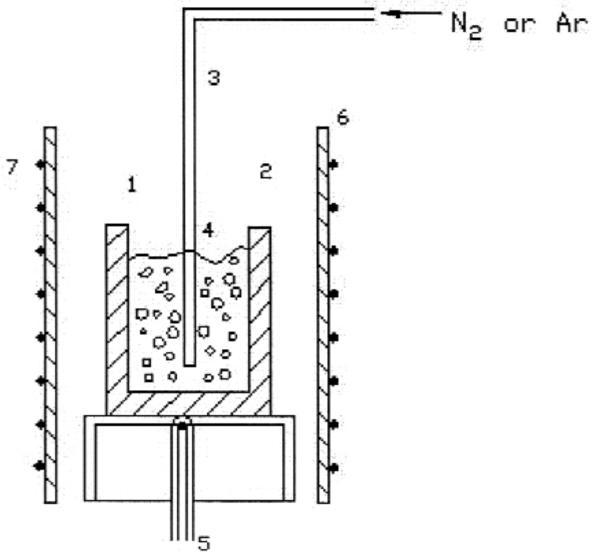

Figure 1. Experimental equipment for foaming performance measuring 1—molybdenum sheet; 2—graphite crucible; 3—blowing tube; 4—slag; 5—thermocouple; 6—furnace tube; 7—molybdenum wires

Experimental method

The equipment to measure the slag property of foam raising is shown in Figure 1. The slag sample was placed in a graphite crucible and it was placed in a constant high temperature strap of Mo thread furnace. The temperature was raised to a determined value (1450°C). It was heated for 20 minutes until the slag sample was homogeneous. An Mo thread, whose diameter was 0.1 mm was inserted into the slag to measure the initial height of the slag surface. Then an Mo gas blowing pipe was placed in the slag. Its inner diameter was 2 mm, the distance between it and the bottom of crucible was 4 mm. The slag height was measured every 5 minutes for 20 minutes. Using the average value of 4 times the height measured as the height of the slag surface and subtracting the initial slag height, the slag foam raising performance was obtained. It is worth noting especially that the inner diameter of the gas pipe, the amount of gas blown and the slag sample will affect the slag's raising foam performance. Therefore, the result must be based on the condition of maintaining these conditions, or it has no significance.

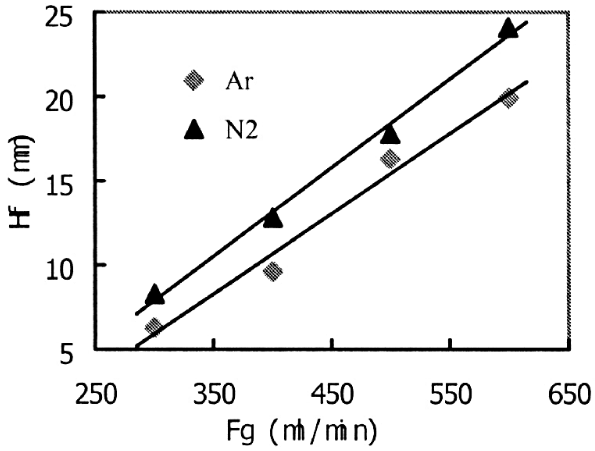

Figure 2. Relationship between foaming performance (Hf) and gas blowing flux (Fg).

Experimental result

Experiments were done in 3 groups, and the effect of binary alkalinity and the content of CaF_2 and MnO in the slag on the slag performance of raising foam was observed. What followed is the experimental result.

Relationship between slag foam raising performance and gas type or blowing amount

Foam raising performance is measured separately for different blowing amounts using refined N_2 gas (99.9%) and Ar gas (Figure 2). The result illustrates that slag foam raising performance will be more serious as the gas amount rises whether it is N_2 or Ar. The relationships were obtained between the amount of gas and the foam raising performance using linear regression on experimental data:

N2 $Hf = -7.54 + 0.0517F_g$
Ar $Hf = -8.60 + 0.048F_g$
In the formula H_f —slag foam raising performance
F_g —the amount of gas

The correlation coefficient of the first formula is 0.9935. That of second is 0.9880.

Table I
Components of slag samples

Sample Number	CaO	SiO_2	Al_2O_3	MgO	TiO_2	Ti_2O_3	MnO	FeO	K_2O	Na_2O	TiN	TiC	Total TiO_2 converted by Ti	CaF_2		R
101	18.77	26.81	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00		100.00	0.70
102	21.59	23.99	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00		100.00	0.90
103	23.88	21.70	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.10
104	25.76	19.82	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.30
105	27.35	18.23	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.50
201	23.35	21.23	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00	1.00	100.00	1.10
202	22.83	20.75	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00	2.00	100.00	1.10
203	22.30	20.28	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00	3.00	100.00	1.10
204	21.26	19.32	14.00	9.00	22.92	4.00		1.50	0.50	0.50	0.67	1.33	30.00	5.00	100.00	1.10
301	23.61	21.47	14.00	9.00	22.92	4.00	0.50	1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.10
302	23.30	21.18	14.00	9.00	22.92	4.00	1.10	1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.10
303	22.30	20.27	14.00	9.00	22.92	4.00	3.00	1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.10
304	21.26	19.32	14.00	9.00	22.92	4.00	5.00	1.50	0.50	0.50	0.67	1.33	30.00		100.00	1.10
PX	24.67	22.41	13.84	9.12	24.82		0.88	2.74	0.51	0.52					100.00	1.10

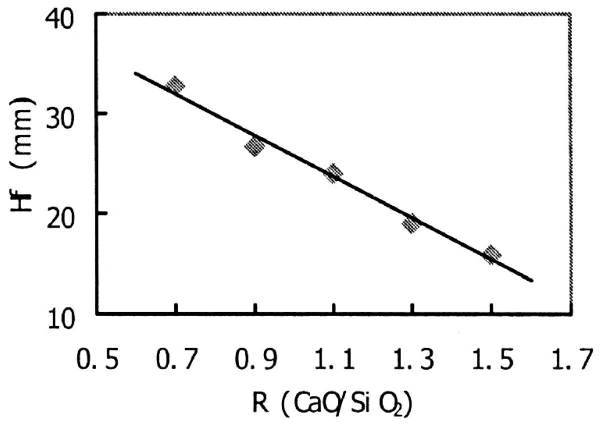

Figure 3. Relationships between foaming performance (Hf) and binary alkalinity (CaO/SiO_2)

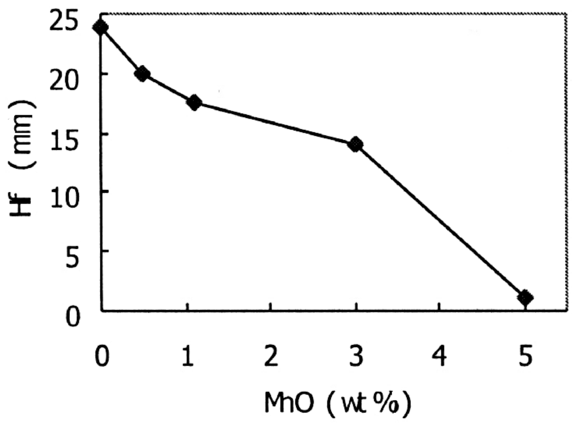

Figure 5. Relationship between foaming performance (Hf) and MnO content

The experimental conditions were: base slag, temperature 1450°C, a 100g slag sample, the inner diameter of the graphite crucible 45 mm and its height 80 mm. It was discovered that it is difficult to blow gas into slag when the amount of gas blown is less than 300 mm/minute in the process of the experiment. The other conditions of the 3 groups were the same; in addition, the amount of gas was 600 mm/minute.

The effect of binary alkalinity (CaO/SiO_2) on the slag's foam raising performance

Binary alkalinity is one of the very important properties of slag. By changing binary alkalinity, one can observe the effect of it on the foam raising performance and on maintaining the other components of the slag. The result is shown in Figure 3. The slag foam raising performance becomes weaker as the alkalinity varies from low to high. Their relation is shown in the following formula:

$$H_f = 46.0 - 20.35R \quad [1]$$

The correlation coefficient of the formula is 0.9764.

The relationship between the amount of CaF_2 and the slag foam raising performance

The ionization degree of CaF_2 is very high. F^- has a great effect on the structure and property of slag when CaF_2 is added into the slag. Therefore, the relations between the CaF_2 content and the slag foam raising performance were observed in the experimental research. The slag foam raising performance worsened rapidly when the content of CaF_2 in the slag rose. The performance of foam raising does not apparently change when the CaF_2 content is more than 3%. CaF_2 can be considered good material to erase foamy slag.

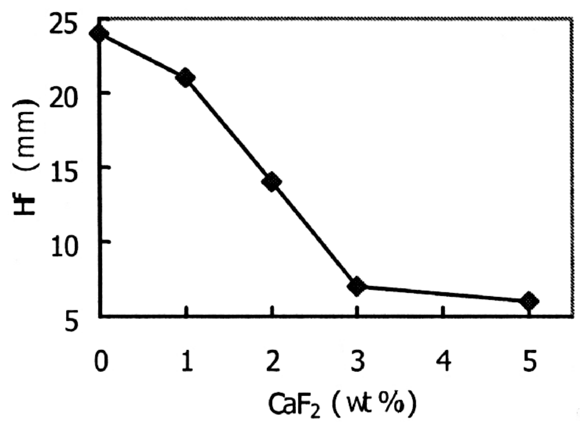

Figure 4. Relationships between foaming performance (Hf) and CaF_2 content

The relation between the amount of MnO and the foam raising performance

The experimental result (Figure 5) illustrates that the effect of MnO on the slag performance of raising foam is similar to CaF_2. The foam raising performance can worsen as the amount of MnO rises. However, the effect of MnO is weaker than that of CaF_2 when the amount of MnO is less than 3% and, the effect of MnO on erasing foam is obvious when its amount is high. Therefore, MnO is a good material to erase foam.

Discussion

According to the above experimental result, we discuss the foam raising performance of slag that is high in Ti.

The mechanism by which slag raises foam is similar to the cryogenic solution. Usually the surface viscosity of a solution plays a large role according to research about the life-span of foam and foam raising performance. Surface tension, however, does not have an absolute relation with foam raising performance. Relevant literature[5-11] has described this in full. In fact, it has been proved in our research work[3]. There is a close relation between the foamy performance of furnace slag containing high Ti and the forming of Si-O composite anions absorbed at the surface[12].

Therefore, we have known the content of CaO to rise and that of SiO_2 in slag to decrease when the binary alkalinity of slag rises. That makes the content of SiO_2 absorbed at the surface decrease and the Si-O anion disintegrate, which worsens to the slag foam raising performance. But in practice, it is difficult to erase foam by raising alkalinity. We only can try our best to raise alkalinity under permissible conditions.

CaF_2 and MnO may both worsen the slag foam raising performance. Its reason is similar to raising slag alkalinity. The F^- of CaF_2 and the O^{2-} of MnO may both make Si-O complex anion radicals disintegrate, and make the structure of SiO_2 surface film simply absorbed at the slag surface.

As illustrated before, the effect of destroying foam is very obvious when the content of CaF_2 is less than 3%. But when its content exceeds 3%, the effect is almost the same. This illustrates that the complex anion radical in slag has been disintegrated to the simplest form. Therefore the effect is not obvious if we raise the content on the basis of this. Inversely, the effect of erasing foam is weak when the content of MnO is less than 3%, and when its content exceeds 3% its effect is very obvious. This illustrates that the O^{2-} dissociated by MnO has a weak effect on the disintegrating effect of the Si-O complex anion when the content of MnO is low.

The reason may be that the dissociating balance of MnO is controlled by the slag components, and that the O^{2-} dissociated is less when the content of MnO is low. It is feasible to inhibit the foamy tendency of slag by adding fluorite and poor manganese minerals in practice. Adding CaF_2 it may improve the slag performance and reduce the amount of Fe contained in the slag and improve the desulphurizing capacity of slag in addition to erasing foam. The process is also not complex.

There are two causes that are due to the foaming phenomenon. On the one hand, titanium oxide and high smelting point particles, such as titanium carbide and titanium nitride in the reductive atmosphere, will change the surface characteristics of slag, which is convenient for stabilizing foam in the slag. On the other hand, a large amount of gas will be immixed in the process of tapping. Moreover, if titanium oxide cannot be adequately reduced with the operation of a low temperature and high oxygen potential in the blast furnace, titanium oxide can still be further reduced with the generation of monoxide carbon to provide enough gas for foaming.

As for the surface characteristics of slag, surface tension and surface viscosity play an important part in the process of foaming. Surface tension is the main factor in the process of foam generation, while the surface viscosity is the main factor in the stabilization of foam. The active material of the surface of slag can reduce the surface tension, which is convenient for the generation of foam but not necessary for the increase of the surface viscosity. It was also found that the contribution to the foaming of slag is determined by the strength of both.

Conclusion

Raising slag binary alkalinity can worsen the slag foam raising performance, and inhibit foamy slag. But it is difficult to apply in practice.

CaF_2 and MnO are both good materials to erase foam. But they have a strong effect on erasing foam when the content of CaF_2 is low or the content of MnO is high (3–5%). These two materials have great practical value.

In this experimental research, a method was used to measure the foam height of slag in conditions of constant temperature and a constant amount of blowing gas. This is a better way to measure the foam raising performance of slag containing high Ti.

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