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PHASE DIAGRAM CALCULATION OF HIGH ALUMINA BLAST FURNACE SLAG SYSTEMS AND EXPERIMENTAL STUDY OF THEIR FLUIDITY[1]

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Abstract

Firstly, the commercial thermodynamic software package FactSage was applied in the calculation of phase diagram from the view point of melting point for the definition of slag composition range at different Al_2O_3 content levels; secondly, the KTH melt viscosity model was used in viscosity at 1,450°C calculation for slag compositions proposed by FactSage; thirdly, slag specimen were prepared with Al_2O_3 content of 18 wt.%, 20 wt.%, 25 wt.%, 30 wt.%, 35 wt.% for viscosity experiments based on analysis of the above theoretical calculation results; and finally optimization schemes were proposed of blast furnace slag composition at different Al_2O_3 content levels. This kind of research method with the combination of theory and experiment accelerated remarkably working process, reduced test cost and improved reliability and accuracy of the results. Taking the highest Al_2O_3 content 20 wt.% that is possibly attained in China at the present as an example, it is revealed by this work that CaO/SiO_2 ratio should be regulated between 1.20 and 1.30 and MgO content should be controlled at about 8 wt.%. Control of lower MgO content is favorable for the decrease of slag volume and coke rate. This concept has already been applied into the practical production of blast furnaces in Wuhan Iron and Steel Corporation (Group).
Key words: Phase diagram calculation; Viscosity calculation; High alumina blast furnace slag; Properties optimization.

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1 INTRODUCTION

It is commonly believed that too high alumina contents in slag, say over 16 wt.%, is harmful to blast furnace operation. Due to soaring prices and insufficient supply of iron ores, a great number of Chinese steel makers are importing and using Australian ores and Indian ores. These two kinds of ore fines are generally characterized by higher alumina contents, about 2 wt.% for Australian ores, 1.88 wt.% for Indian ores, in contrast to less than 1 wt.% in domestic ores. As a result, in addition to many other factors such as higher raw materials qualities, remarkably lowered slag volumes etc, the alumina contents in blast furnace slag are constantly getting higher and higher and even exceeded this 16 weight percent limit in many blast furnace plants [1]. The melting point and viscosity of high alumina blast furnace slag are both high and very high level of heat reservation in the hearth must then be maintained for maintaining sufficient slag fluidity. As a consequence, hot metal silicon content will get higher, coke rate will be increased, throughput will go down and furnace campaign life will be shortened. In order to keep or even improve all sorts of economic-technical indices of the blast furnace, one of the most important measures is the optimization of blast furnace slag properties including melting point and fluidity. Sufficient desulphurization and de-alkalization capacities, of course, must be ensured at the same time.
By means of the phase diagram calculation and viscosity-temperature curve measurement, the issue of improving the fluidity of blast furnace slag with a variety of alumina content was investigated in this paper.

2 BASIC DEMANDS FOR SLAG PROPERTIES OF REGULAR BLAST FURNACE OPERATION

The following demands for slag properties must be met for smooth operation of any blast furnaces: 1) Least slag volumes under the prerequisite for the requirement on desulphurization and de-alkalization capacities, 2) Relative stable concentrate of the main components, 3) The formation of primary slag takes place in a stable region of the furnace, 4) Comparatively good fluidity so as to absorb adequate heat from gas and ensure good stack permeability in the primary slag formation region, 5) Neither too high nor too low melting point.
The slag temperature at the tuyear level is determined by its melting point. If the melting point is too low, i.e. an acid slag, it begins melting at higher positions of the furnace and would not be able to absorb adequate heat for elevating its temperature due to its too high descending speed. On the other hand, however, if the melting point is too high, i.e. a basic slag, it begins melting at lower positions of the furnace and its temperature would be very high on arriving at the tuyear level. Therefore, a basic slag (high melting point slag) can heat up the hearth while an acid slag behaves in an opposite way and will cool down the hearth. The cooling effect of a lower basicity slag is not only due to the lower temperatures on its melting, but also due to a large amount of heat consumption for the reduction of a plenty of iron and manganese oxides, which are not reduced in time within the upper furnace parts because of its quicker descending speeds into the hearth. Therefore, the fluidity and melting properties of slag play a most important role in the control of hearth heat. In this sense, it can be understood that too high fluid capacity and too sticky slag are the two extremes and both should be avoided in practical blast furnace operation.

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3 STUDY ON MELTING PROPERTIES OF HIGH ALUMINA CONTENT BLAST FURNACE SLAG BY MEANS OF THE FACTSAGE

3.1 Brief Introduction Into the FactSage

The FactSage is a commercial thermodynamic software package and developed by the GTT-Technologie company of Germany and the Thermfact/CRCT company of Canada. It has been widely applied in many metallurgical processes such as non-metallic inclusion removal from molten steel [2], gas solubility estimation in molten slag [3], flux composition selection of dephosphorization pretreatment process of high phosphorus hot metal [4] and so forth. The version of 6.1 was used in this paper and its two databases of oxides were tested in study.

3.2 Patterns in Variation of Melting Point of Quarternary Slag Systems Shown in Computed Phase Diagrams

The computed phase diagram for the slag system SiO_2-CaO-MgO-Al_2O_3 with 20 wt.% alumina content by using database FToxid was shown in Figure 1a while the one by using database Fact was shown in Figure 1b. The regions encompassed by the isotherms depicted liquid phase areas within a temperature range from 1,300°C to 1,500°C. By making a comparison between Figure 1 and Figure 2[5], it is demonstrated that the basic patterns in variation of melting point of high alumina blast furnace slag systems that are presented in the computed phase diagrams are essentially the same as experimentally measured phase diagram (refer to the 1,400°C isotherms in Figure1 and Figure 2).

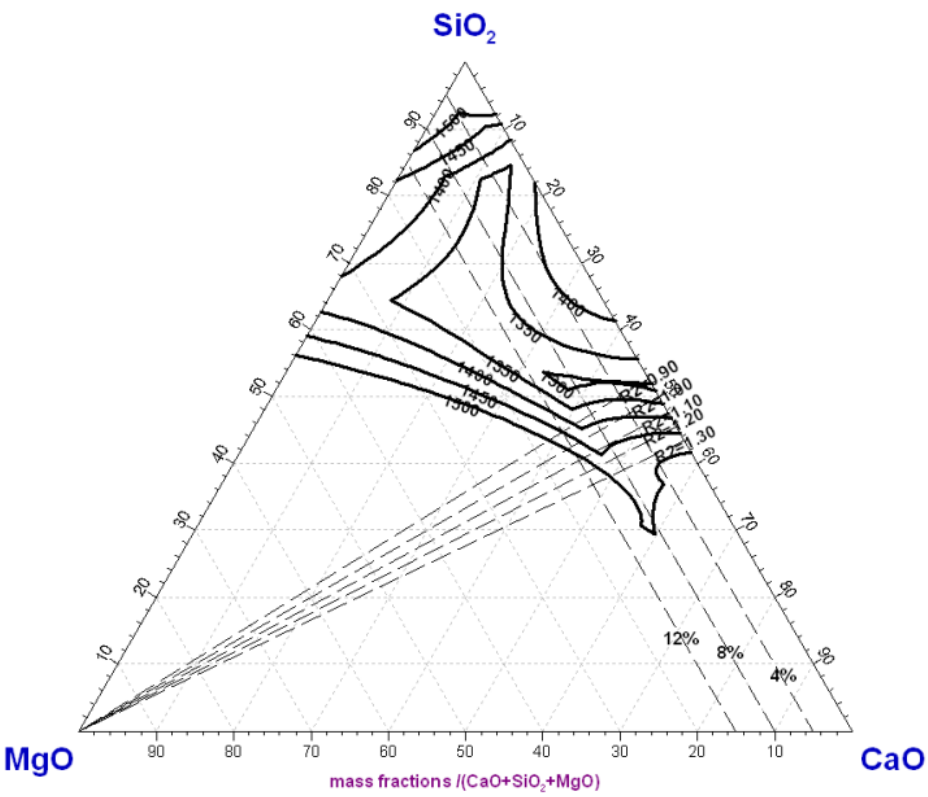

Figure 1. (a) Isotherms of the quarternary slag system with 20 wt.% Al_2O_3 (by using database FToxid).

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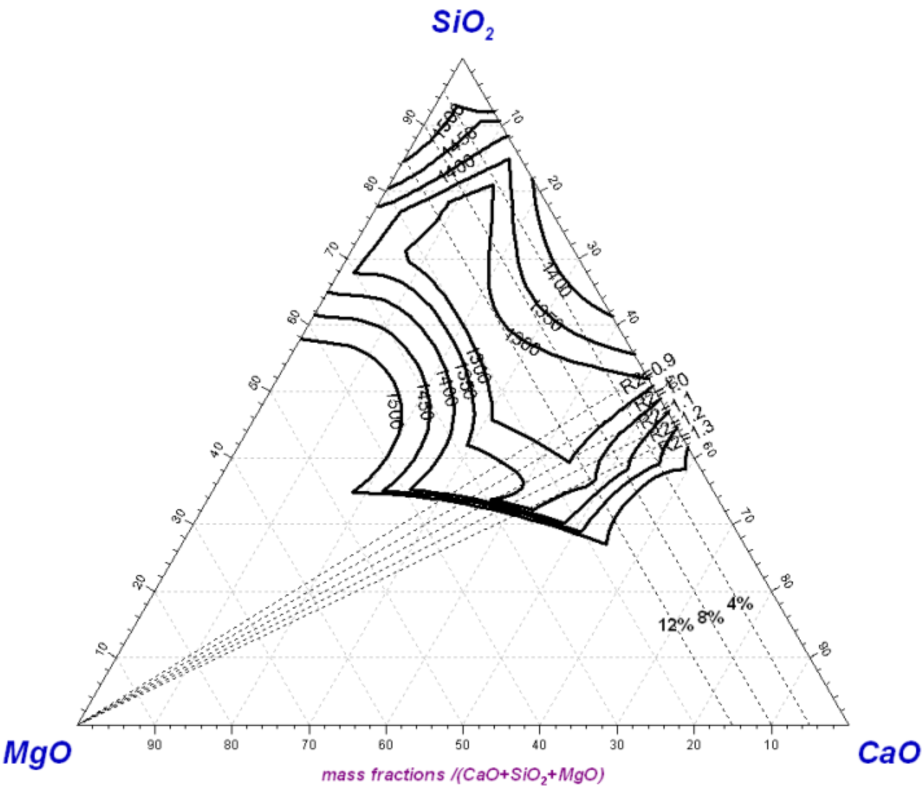

Figure 1. (b) Isotherms of the quarternary slag system with 20 wt.% Al_2O_3 (by using database Fact).

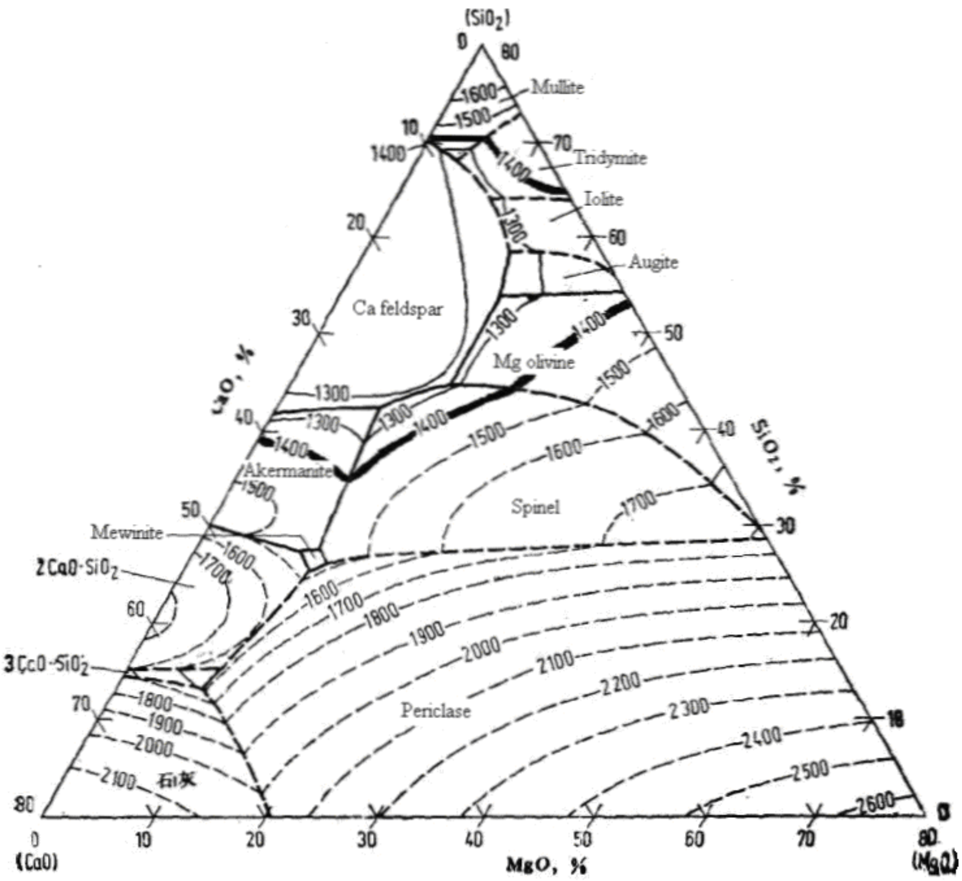

Figure 2. Measured Phase diagram of CaO-MgO-SiO_2 system with 20 wt.% Al_2O_3.

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In Figures 1a and 1b, the three straight lines that are parallel to the SiO_2-MgO side are iso-MgO lines and those radials from top point "MgO" to its opposite side are iso-CaO/SiO_2 ratio lines, i.e. iso-basicity lines referring to numeric data near the radials. Generally speaking, at a constant binary basicity, the melting point of this quarternary slag system with 20 wt.% alumina content is increasing with the increase in MgO content. And similarly, at a constant MgO content, the melting point of this slag system is increasing with the increase in the binary basicity. The distinction between Figure 1(a) and 1(b) is the difference of liquid phase areas at a constant slag composition. This distinction comes from these two different databases used for phase diagram calculation. In practical applications, it is recommended to analyze variation patterns of melting point of this quarternary slag system by combining the phase diagrams of the two different databases.

4 STUDY ON FLUIDITY OF HIGH ALUMINA CONTENT BLAST FURNACE SLAG BY MEANS OF THE KTH MODEL

4.1 Brief Introduction Into the KTH Model

In recognition of much time consuming and great costs for viscosity measurements, the development of mathematical models capable of making viscosity estimation for melts comprising of all kinds of oxides are continuously conducted. The world-wide well-known models include KTH model[6] of the Royal Institute of Technology, Sweden, Urbain model[7] of the Queensland University, Australia and Iida model[8] of the Osaka University, Japan. In this paper, the KTH model was applied for making prediction of slag viscosity values.
In the KTH model, slag viscosity is expressed in the Arrennius form. The Gibbs activation free energy ΔG^* of an oxides mixture in the viscosity expression is calculated by taking the interactive effects between different cations in the presence of O^{2-} into account.

4.2 Patterns in variation of slag viscosity calculated by the KTH model

The predicted viscosity of the quarternary slag system with 20 wt.% alumina content was shown in Figures 3, 4 and 5. The slag compositions for viscosity calculation were selected within the liquid phase areas of 1,450°C of the computed phase diagrams. In these three figures, the left and right vertical straight lines represent respectively the lower and upper limits of CaO content in slag for calculation.

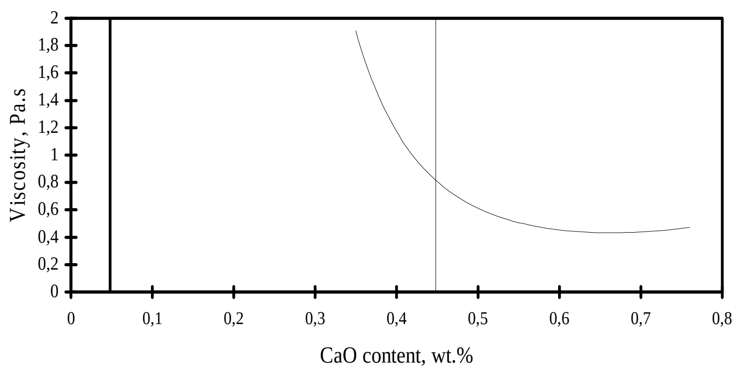

Figure 3. Viscosity at 1450 °C as a function of CaO content for the slag with 4 wt.% MgO and 20 wt.% Al_2O_3.

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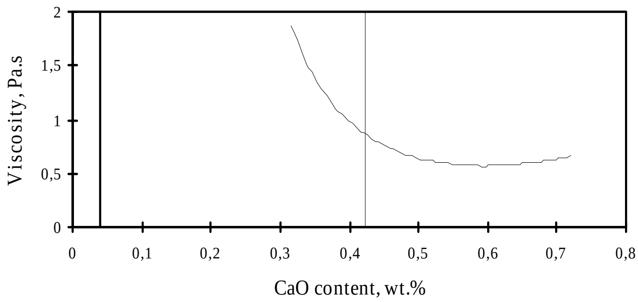

Figure 4. Viscosity at 1,450°C as a function of CaO content for the slag with 8 wt.% MgO and 20 wt.% Al_2O_3.

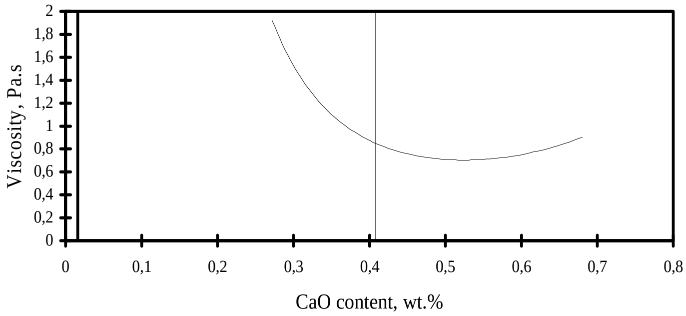

Figure 5. Viscosity at 1,450°C as a function of CaO content for the slag with 12 wt.% MgO and 20 wt.% Al_2O_3.

5 EXPERIMENTAL STUDY ON FLUIDITY OF HIGH ALUMINA CONTENT BLAST FURNACE SLAG

5.1 Experimental Materials and Schemes

Five levels of alumina content in slag specimen, i.e. 18, 20, 25, 30 and 35 wt.%, were selected for viscosity measurement. The slag compositions for alumina content level 20 wt.%, in which Chinese blast furnace operators are mostly interested at the present, are given in Table 1.

Table 1. Slag compositions for viscosity experiment

Slag no.	Content of main components, wt.%				CaO/SiO_2	**Erro!**
	Al_2O_3	MgO	CaO	SiO_2		
1	20	4	43	33	1.3	0.89
2	20	8	40	32	1.25	0.92
3	20	12	37	31	1.19	0.96
4	20	12	38	30	1.27	1.00
5*	17.21	10.66	37.05	35	1.06	0.91
6	20	9.8	34.2	36	0.95	0.786

** No.5 is the industrial slag of BF No.8, Wuhan Iron and Steel Company Limited, in 2010 and used as a reference of the synthesized laboratory slag.*

5.2 Results and Summary

Figure 6 shows the experimental results for the quarternary slag system with 20 wt.% alumina content.

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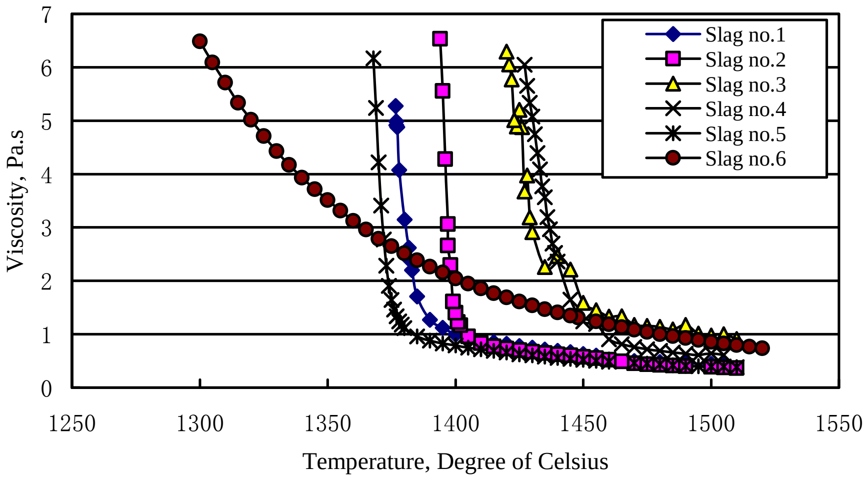

Figure 6. Viscosity as a function of temperature of the quarternary slag system with 20 wt.% Al_2O_3.

Some interesting findings that are deduced from the experimental results are listed as below:

- In general, the viscosity value at temperatures above the free-running temperature of Slag no.1, 2 and 5 were all relatively small, being all below 1.0 Pa.s at temperatures higher than 1400 ^{o}C and below 0.5 Pa.s at temperatures higher than 1,500°C.
- The free-running temperature of Slag No.1 with 4 wt.% MgO content and 1.30 binary basicity is 1,385°C, only 10°C higher than the industrial slag. And above the free running temperature, the two viscosity–temperature curves almost matched together. This implies that Slag No.1 is suitable for blast furnace production.
- The free-running temperature of Slag No.2 with 8 wt.% MgO content and 1.25 binary basicity is 1,400°C, only 25°C higher than the industrial slag. Similarly, at temperatures above the free running temperature the both viscosity–temperature curves also almost matched together. This implies that if Slag No.2 is chosen, the slag temperature must be controlled above 1,400°C to protect from slag fluidity becoming worse in a great deal.
- For Slag no.3 and no.4 with 12 wt.% MgO content, whose binary basicity was respectively 1.19 and 1.27, their free-running temperatures were all high (1,435°C and 1,445°C, respectively) and viscosities at temperatures higher than 1,460°C were close to or exceeded 1.0 Pa.s. This means that these two kinds of slag were not desirable for blast furnace operation due to poor fluidity, thermal stability and chemical stability.
- Slag no.6 was a kind of acid slag and its composition was determined by referring to practical blast furnace slag of India. Its viscosity–temperature diagram is slick and no obvious inflection points could be found in it. However, its viscosities were big and exceeded 1.0 Pa.s at temperatures even beyond 1,500°C. This means the higher furnace heat practice has to be taken for ensuring fine fluidity of this kind of slag.

In summary, for the quarternary blast furnace slag system with 20 wt.% alumina content, it is recommended that the MgO content is between 4 wt.% and 8 wt.% while the CaO/SiO_2 ratio is 1.20 or slightly higher under the condition of steady furnace heat. Never select too high MgO contents exceeding 12 wt.%.

Control of relatively lower MgO contents and lower $(CaO+MgO)/(SiO_2+Al_2O_3)$ ratios is

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favorable for decrease in slag volume and coke rate, and also in production cost. This concept has already been applied into the practical production of blast furnaces in Wuhan Iron and Steel Corporation (Group), abbreviated by WISCO. In the industrial blast furnace slag of WISCO, the MgO contents are within the range of 8.85~9.15%, CaO/SiO_2 ratios are ranging from 1.09 to 1.14 and $(CaO+MgO)/(SiO_2+Al_2O_3)$ ratios are about 0.925 to 0.945 at the alumina content level of 15.82 to 16.25% [9-10].

6 CONCLUSIONS

The following conclusions can be reached by this work:

- The FactSage® thermodynamic software package has been successfully employed for making preliminary selection of high alumina content blast furnace slag system from the view point of good fluidity. The KTH model has been successfully used for making forecast of viscosity of the above selected slag systems. The combination of the FactSage® software and the KTH model contributes greatly to the design of experimental scheme and the reduction of laboratory test works and costs.
- For the blast furnace slag system with 20 wt.% alumina content, the most possibly highest level under the present raw materials condition in China, a magnesium oxide content range of 4 to 8 wt.% and a binary basicity range of 1.20 to 1.30 are proposed for practical blast furnace operation.
- According to the authors' previous investigations[11-12], the furnace smooth running is more likely affected by the primary slag properties than the final slag properties. Composition optimization of the blast furnace primary slag with high alumina contents will be our future task.

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