An Experimental Study of the Restriction on Flourine and Alkali Contents Containing in Baotou Blast Furnace Slag

Du Hegui  Ma Ximing
(Mailbox 313, Northeastern University, Shenyang Liaoning, 110006, P.R. China, Tel: 86-024-3893000-7718)

ABSTRACT

By experiments, it was found that the fluorine and alkali contents in Baotou B.F slag had serious influence on metallurgical properties of slag, in which the CaF_2 played a crucial role. When CaF_2 and K_2O+Na_2O were decreased to round 2.52% and 0.19% respectively, the viscosity and melting temperature (free running temperature) may be closed or obtained to the level of common B.F. slag. The good results will be obtained remarkably only for increasing the surface tension of the slag, when CaF_2 content contained in slag is decreased below 2.52%.

1. INTRODUCTION

An important breakthrough of fluorine-bearing ore smelting in Baotou B.F has been made in the past few years, and the productivity of 1.7-1.8 t/m^3.d or furthermore has been obtained in complex ore smelting.

However, Baotou iron ore contains much rare-earths except Fe, niobium, phosphorus, fluorine, postassium and sodium etc., therefore, a series of problems have been caused, such as relatively lower softening-melting temperature and its narrower zone, smaller size of sintering ore, stronger burden resistance to gas flow etc.

Besides, the circulation and accumulation of K, Na and F in B.F reduced the melting temperature and surface tension of slag, caused slag fusibility, easy solidifing but hard refusion, and further resulted in lining wear and breaking of coke strength, all of which leaded to frequent scaffolding, burning of tuyeres, shorter campaign life, operation unsmooth and hindering hard driving of B.F, and worsen its technical and economical indexes. It has been turned out that Na, K and F had harmful effects on Baotou B.F smelting operation together.

A good development has been made in the past several decades, F content in iron concentrate had been reduced to 1.2%-1.0% in 1990 from 1.8% in 1979 and K_2O+Na_2O content has retained 0.2%-0.3%, F content in sinter had also been decreased from 1.75% in 1993 to 0.5%-0.6% in 1995. At the same time, the addition of pellet without F in charge has made CaF_2 content reduced to 5.5%-6.5% from above 10%. The metallurgical properties of F-bearing slag has been improved so far.

It is clear that decreasing the content of F, K, and Na in slag will be beneficial for Baotou B.F smelting operation, but the thing most important is to determine the optimum content of F, K and Na in slag for acquiring better slag metallurgical properties (melting temperature and surface tension etc.) which will close to that of common B.F slags.

The viscosity, melting temperature and surface tension of bearing-F, K and Na slag were measured in laboratory to get the appropriate contents of F, K, Na in slag and optimum slag constituent, the purpose is to improve properties of Baotou B.F slag.

2. EXPERIMENTAL METHOD

2.1 Procedure

According to operation condition and slag compositions (listed in table1.) of Baotou B.F., the samples for experiment were synthesized and their compositions are listed in Table2.
Table 1 Compositions of Baotou B. F Slag (in wt.%)

<table>
<thead>
<tr>
<th>Date</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>FeO</th>
<th>CaF₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>MnO</th>
<th>FeO</th>
<th>S</th>
<th>P₂O₅</th>
<th>C</th>
<th>CaO/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1994</td>
<td>38.60</td>
<td>30.30</td>
<td>8.80</td>
<td>7.33</td>
<td>3.10</td>
<td>6.39</td>
<td>0.38</td>
<td>0.69</td>
<td>1.01</td>
<td>0.45</td>
<td>1.21</td>
<td>0.05</td>
<td>0.94</td>
<td>1.27</td>
</tr>
<tr>
<td>1995</td>
<td>32.66</td>
<td>27.66</td>
<td>10.88</td>
<td>9.22</td>
<td>3.10</td>
<td>6.39</td>
<td>0.38</td>
<td>0.69</td>
<td>1.22</td>
<td>1.17</td>
<td>1.12</td>
<td>0.05</td>
<td>1.18</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Compositions of Synthetic Slag (in wt.%)

<table>
<thead>
<tr>
<th>No.</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>FeO</th>
<th>CaF₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>MnO</th>
<th>FeO</th>
<th>S</th>
<th>P₂O₅</th>
<th>C</th>
<th>CaO/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>41.80</td>
<td>36.35</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>2.65(2.80)</td>
<td>0.09(0.15)</td>
<td>1.16</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>40.87</td>
<td>35.53</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>2.47(2.80)</td>
<td>0.72(0.75)</td>
<td>1.20</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>03</td>
<td>37.79</td>
<td>32.86</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>9.18(10.30)</td>
<td>0.08(0.15)</td>
<td>0.09(0.10)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>04</td>
<td>36.85</td>
<td>32.05</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>9.34(10.30)</td>
<td>0.74(0.90)</td>
<td>1.09(1.10)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>06</td>
<td>37.77</td>
<td>32.84</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>9.13(10.60)</td>
<td>0.00(0.00)</td>
<td>0.00(0.00)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>07</td>
<td>43.34</td>
<td>37.68</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>0.00(0.00)</td>
<td>0.09(0.15)</td>
<td>0.09(0.10)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>08</td>
<td>42.32</td>
<td>36.81</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>0.00(0.00)</td>
<td>0.73(0.93)</td>
<td>1.11(1.13)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>09</td>
<td>43.43</td>
<td>37.77</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>(0.00)</td>
<td>(0.00)</td>
<td>(0.00)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>43.43</td>
<td>37.77</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>(0.00)</td>
<td>(0.00)</td>
<td>(0.00)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*11</td>
<td>38.60</td>
<td>30.30</td>
<td>8.80</td>
<td>7.33</td>
<td>10.00</td>
<td>9.76(10.30)</td>
<td>0.73(0.90)</td>
<td>0.97(1.10)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>32.49</td>
<td>28.21</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>9.21(10.30)</td>
<td>0.00(0.00)</td>
<td>0.10(0.07)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>40.22</td>
<td>34.98</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>5.00(6.00)</td>
<td>0.08(0.090)</td>
<td>0.10(0.11)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>40.09</td>
<td>34.86</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>5.28(6.00)</td>
<td>0.86(0.90)</td>
<td>0.97(1.10)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>39.15</td>
<td>34.05</td>
<td>8.80</td>
<td>8.80</td>
<td>10.00</td>
<td>5.14(6.00)</td>
<td>0.86(0.90)</td>
<td>0.97(1.10)</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Baotou conventional slag

For the sake of the effects of fluorine and alkali metal oxide on slag properties, the Al₂O₃ (8.8%), MgO(10%) and R(CaO/SiO₂) were fixed in slag. With fluorine and alkali volatilization at higher temperature during the experiments, the contents of CaF₂, K₂O and Na₂O were a little lower in the final slag samples (beside parenthesis of table 2) than in the original one's (inside parenthesis of table 2) and their volatilization amounts were round 10-20% of original weight.

2.2 Method

Slag viscosity was measured by Rotating-type viscosimeter and its melting temperature was obtained from the curve between viscosity and temperature, with computer controlling furnace temperature and sampling, the twisting angle of the fine wire was converted into time and was recorded. The viscosity value was expressed as following:

\[ \eta = KV - c(V - V_0) \]

where, \( \tau_c \)-scanning time when cylinder in slag;

\( \tau_0 \)-scanning time when cylinder above slag.

Slag surface tension was determined by the Maximum Bubble Pressure Method.

3. RESULTS AND DISCUSSION

3.1. Influence of CaF₂ (K₂O+Na₂O) on slag viscosity

Based on experimental data, the curves between temperature and viscosity for different
samples were given in Fig. 1 and Fig. 2.

Fig. 1 it is obvious that the slag viscosity is decreased with CaF$_2$ varying from 0% to 9.24% and temperature fixed, the more CaF$_2$ contents, the lower viscosity. In the case of a little K$_2$O+Na$_2$O in slag (Fig. 1(a) and (b)), CaF$_2$ has a dominant effect on viscosity.

(2) CaF$_2$ in constant and K$_2$O+Na$_2$O in variation

Fig 2(a)-(d) show that the viscosity will be reduced with the increasing of (K$_2$O+Na$_2$O) while CaF$_2$ content in slag is constant of 0%, 2.52%, 5.14% and 9.24%, respectively. From Fig. 2(a) it can be seen that the sample No. 09 without CaF$_2$ and K$_2$O+Na$_2$O has almost the same T-η curve as the sample No. 07 with CaF$_2$ of 0% and K$_2$O+Na$_2$O of 0.19%, thus, it can be concluded that K$_2$O+Na$_2$O variation from 0 to 0.19% has a little effect on viscosity without CaF$_2$ in slag. From Fig 2(b) the same conclusion can be obtained while
(3) Influence of CaF₂ on slag viscosity at different temperatures

Fig.3(a) shows the influence of CaF₂ on slag viscosity at 1350°C. No bearing-CaF₂ slag has too higher viscosity (samples No.07-09), both the sample No.01 and No.05 bearing-2.52% CaF₂ have higher viscosity which is 4.0Pa.s and 8.1Pa.s, respectively. When CaF₂ content in slag is about 9.24% (samples No.03-06) and 5.14% (samples No13-15), there is a little difference of slag viscosity for the different K₂O+Na₂O content of 0.19% and 1.85%. It can be concluded that CaF₂ has a dominant effect on slag viscosity and when

\[ \text{CaF}_2 \text{ of 2.52\% in slag. However, as CaF}_2 \text{ is increased to 5.14\% (Fig.2(c)), K}_2\text{O+ Na}_2\text{O variation from 0.19\% to 1.85\% has a outstanding influence on slag viscosity. It is reasonable to consider the result from the action of both CaF}_2 \text{ and K}_2\text{O+Na}_2\text{O in slag. Fig.2(d) shows that there is a little difference of viscosity as K}_2\text{O+Na}_2\text{O varying from 0\% to 1.85\% when CaF}_2 \text{ being fixed at 9.24\%, it indicates that K}_2\text{O+ Na}_2\text{O has only a little effect on slag viscosity in this case and CaF}_2 \text{ is still the main influencing factor on slag viscosity.} \]
CaF₂ > 5.14% in slag, increasing CaF₂ will not decrease viscosity tremendously, in another words, as temperature over 1350°C, decreasing CaF₂ from 9.24 to 5.14% will not increase slag viscosity significantly. Fig3(b) shows the same result at 1450°C too.

3.2 Influence of CaF₂ (K₂O+N₂O) on slag melting temperature

The melting temperature being relevant to different content of CaF₂ (0-9.24%) and K₂O+N₂O (0-1.85%) is shown in Fig.4, from which it can be seen that as K₂O+N₂O content is 0%, 0.19% and 1.85%, respectively, slag melting temperature varied a little with CaF₂ variation between 5.14% and 9.24%, namely, when K₂O+N₂O content in slag is as low as 1.85%, decreasing CaF₂ from 9.24% to 5.14% couldn’t cause a increase by a wide margin, for instance, only about 11°C for both slag with K₂O+N₂O of both 0.19% and 1.85%, and round 18°C for the slag without K₂O+N₂O, the increase ratio of the former and the latter is 2.68°C/CaF₂ and 4.39°C/CaF₂ respectively. When reducing CaF₂ content from 5.14% to 4%, the melting temperature of the slag containing K₂O+N₂O of 0.19% without K₂O+N₂O will be increased about 20°C, its increase ratio is 17.54°C/CaF₂, by contrast, the melting temperature of the slag with K₂O+N₂O of 1.85% rarely increase, but for any of different (K₂O+N₂O) content, slag melting temperature will increase significantly if CaF₂ content is reduced to less than 4.0%. Therefore, in order to increase melting temperature of Baotou B.F slag, CaF₂ content must be controlled to less than 4.0%.

3.3 appropriate content of CaF₂ and (K₂O+N₂O) in slag

Fig4. shows that the melting temperature of the slag containing K₂O+N₂O of 1.85% is increased from 1305°C to 1329°C with decreasing CaF₂ from 9.24% to 2.52%, for the slags without and with K₂O+N₂O of 0.19%, their melting temperature are increased to 1382°C and 1369°C from 1329°C and 1321°C respectively. Obviously, under the condition of higher K₂O+N₂O content in slag, it is difficult to increase slag melting temperature by decreasing CaF₂ content in slag. when CaF₂ and K₂O+N₂O being reduced to 2.52% and 0.19% from 9.24% and 1.85% respectively, the slag melting temperature increases from 1305°C to 1369°C, which closes to that of common B.F slags. Therefore, 2.52% CaF₂ and 0.19% K₂O+N₂O in slag are appropriate for both the viscosity and melting temperature of Baotou B.F slag, which keeps operation smooth.
3.4 Influence of K, Na and F on slag surface tension

3.4.1 K$_2$O+Na$_2$O content

Slag density and surface tension measured by the Maximum Bubble Pressure Method are shown in Fig.5.

![Graph showing the relationship between density and temperature](image)

![Graph showing the relationship between surface tension and temperature](image)

Fig.5. The relationship between density of experimental slag (a), surface tension (b) and temperature.

Fig.5(a) indicates a linear relationship between density and temperature, and density is decreased with increasing temperature.

From Fig.5(b) sample No.10 containing no CaF$_2$ and K$_2$O+Na$_2$O has the maximum surface tension than others, sample No.08 containing Na$_2$O+K$_2$O of 1.84% has almost the same surface tension as sample No.10, for instance, 509.73 dyne/cm for the former and 496.98 dyne/cm for the latter at 1400°C, it is concluded that though alkali oxide is a surface active agent, its content in Baotou B.F. slag has a little effect on surface tension, namely, alkali oxide effects on slag surface tension independently is small. On the contrary, without alkali oxide in slag, the surface tension of sample No.6 containing 9.13% CaF$_2$ is very low, only 430.66 dyne/cm at 1400°C. Obviously, CaF$_2$ has a dominant effect on slag surface tension too.

The contents of CaF$_2$ and K$_2$O+Na$_2$O in sample No.04 are similar to those in Baotou B.F. slag, which surface tension closes to samples of No.06 only bearing-CaF$_2$. It indicates that effect of K$_2$O+Na$_2$O on surface tension is much less than CaF$_2$ if ignoring existence of K$_2$O+Na$_2$O or co-existing with CaF$_2$ in slag.

3.4.2 CaF$_2$ content

Fig.6 shows the influence of CaF$_2$ on slag surface tension. It can be seen that keeping K$_2$O+Na$_2$O of 1.80% in slag, decreasing CaF$_2$ from 9.24% to 5.14% results in a little increase in slag surface tension, for instance, 426.20dyne/cm for the former and 431.63dyne/cm for the latter at 1400°C. At the same temperature, the surface tension will increase to 446.590dyne/cm with CaF$_2$ decreasing to 2.52%. Hence, it can be concluded that a little amounts of CaF$_2$ (for example 2.52%) in slag, inspite of its existance alone or co-existing with Na$_2$O+K$_2$O, will cause a significant decrease in surface tension.

As shown in Fig.6(a)-(b), slag surface tension is reduced linearly with increasing temperature, but the decrease of surface tension for the slag only bearing-(K$_2$O+Na$_2$O) or without both K$_2$O+Na$_2$O and CaF$_2$ is less than that for the slag.
bearing-CaF$_2$. For example, the temperature coefficient of sample No.08 and sample No.04 is respectively as following:

\[
\frac{\partial \sigma}{\partial T} = -0.2136023 \text{ dyne/cm.}^\circ C \\
\frac{\partial \sigma}{\partial T} = -0.5257880 \text{ dyne/cm.}^\circ C
\]

![Graph](image)

Fig. 6. Effect of CaF$_2$ on surface tension of slag in 1400 °C (a) and 1500 °C.

4. conclusion

(1) The influence of CaF$_2$ on both viscosity and melting temperature of Baotou B.F. slag is much than that of K$_2$O+Na$_2$O.

(2) In order to improve metallurgical properties of Baotou B.F slag, CaF$_2$ content in slag must be reduced to below 4%, meanwhile, K$_2$O+Na$_2$O must be reduced too. When CaF$_2$ and K$_2$O+Na$_2$O is 2.52% and 0.19% respectively, slag viscosity and melting temperature closes to that of common salgs.

(3) CaF$_2$ has a dominant effect on slag surface tension in Baotou slag. The addition of a little amounts CaF$_2$ results in significant decreasing in surface tension, decreasing CaF$_2$ from 9.34% to 2.52% will not cause a big increase of surface tension, and CaF$_2$ content below 2.52% in slag is beneficial for increasing surface tension.