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

Du Hegui Ma Ximing
(Mailbox 313, Northeastern University ,
Shengyang 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.INTRODUCATION

An important breakthrough of fluorine-bearing ore smelting in Baotou B.F. has been made in the past few years, and the productivity of 1.7-1.8t/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, burnning 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 temperture 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, Na, K 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.%)

Date	CaO	SiO_2	Al_2O_3	MgO	R_xO_y	CaF_2	K_2O	NaO_2	MnO	FeO	S	P_2O_5	C	CaO/SiO_2
1994	38.60	30.30	8.80	7.33	3.07	10.76	1.11	0.93	1.01	0.45	1.21	0.05	0.94	1.27
1995	32.66	27.66	10.88	9.22	3.10	6.39	0.38	0.69	1.22	1.17	1.12	0.05		1.18

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

No.	CaO	SiO_2	Al_2O_3	MgO	CaF_2	K_2O	Na_2O	CaO/SiO_2
01	41.80	36.35	8.80	10.00	2.65(2.80)	0.09(0.15)	1.16	1.15
02	40.87	35.53	8.80	10.00	2.47(2.80)	0.72(0.75)	1.20	1.15
03	37.79	32.86	8.80	10.00	9.18(10.30)	0.08(0.15)	0.09(0.10)	1.15
04	36.85	32.05	8.80	10.00	9.34(10.30)	0.74(0.90)	1.09(1.10)	1.15
06	37.77	32.84	8.80	10.00	9.13(10.60)	0.00(0.00)	0.00(0.00)	1.15
07	43.34	37.68	8.80	10.00	0.00(0.00)	0.09(0.15)	0.09(0.10)	1.15
08	42.32	36.81	8.80	10.00	0.00(0.00)	0.73(0.93)	1.11(1.13)	1.15
09	43.43	37.77	8.80	10.00	(0.00)	(0.00)	(0.00)	1.15
10	43.43	37.77	8.80	10.00	(0.00)	(0.00)	(0.00)	1.15
*11	38.60	30.30	8.80	7.33	10.76	1.11	0.93	1.27
12	32.49	28.21	8.80	10.00	9.21(10.30)	0.73(0.90)	0.97(1.10)	1.15
13	40.22	34.98	8.80	10.00	5.00(6.00)	0.00(0.00)	0.00(0.00)	1.15
14	40.09	34.86	8.80	10.00	5.28(6.00)	0.086(0.090)	0.105(0.11)	1.15
15	39.15	34.05	8.80	10.00	5.14(6.00)	0.86(0.90)	0.97(1.10)	1.15

*Baotou conventional slag

For the sake of the effects of fluorine and alkali metal oxide on slag properties, the Al_2O_3 (8.8%), MgO(10%) and R(CaO/SiO_2) were fixed in slag. With fluorine and alkali volatilization at higher temperature during the experiments, the contents of CaF_2, K_2O and Na_2O were a little lower in the final slag samples (beside parenthese of table 2) than in the orignal one's (inside parenthese of table2) and their volatilization amounts were round 10-20% of original weigth.

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:

$$\eta = K\nabla\tau (\nabla\tau = \tau_i - \tau_0)$$

where, τ_i-scanning time when cylinder in slag;

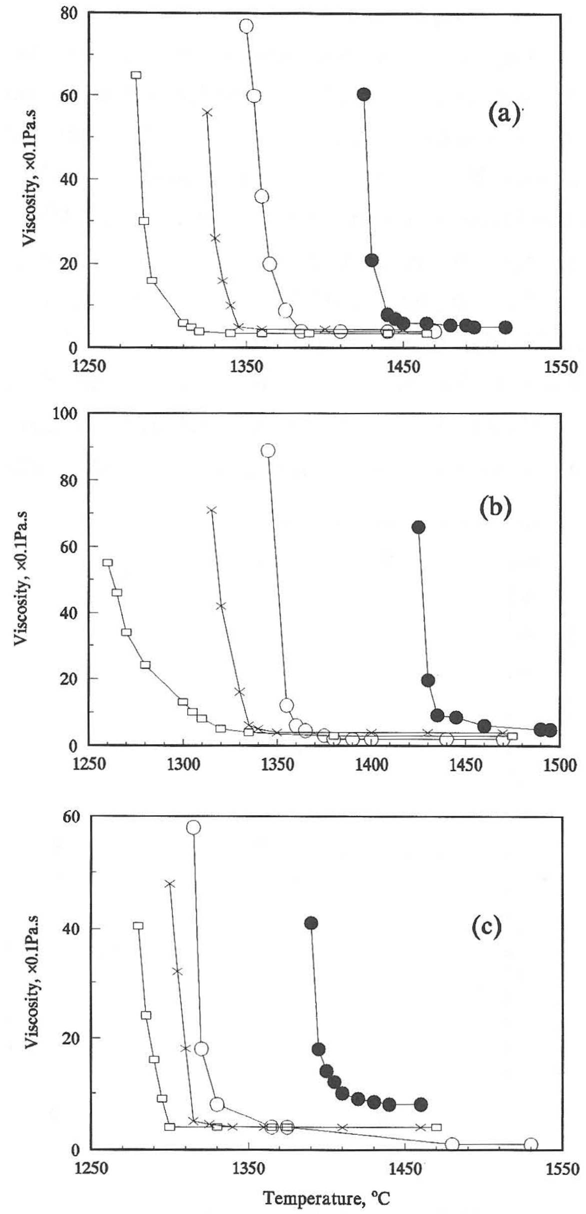
τ_0-scanning time when cylinder above slag.

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

3. RESULTS AND DISCUSSION

3.1. Influence of CaF_2 (K_2O+Na_2O) on slag viscosity

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



○–05; □–06; ●–09; ×–13.

○–01; □–03; ●–07; ×–14.

○–02; □–04; ●–06; ×–15.

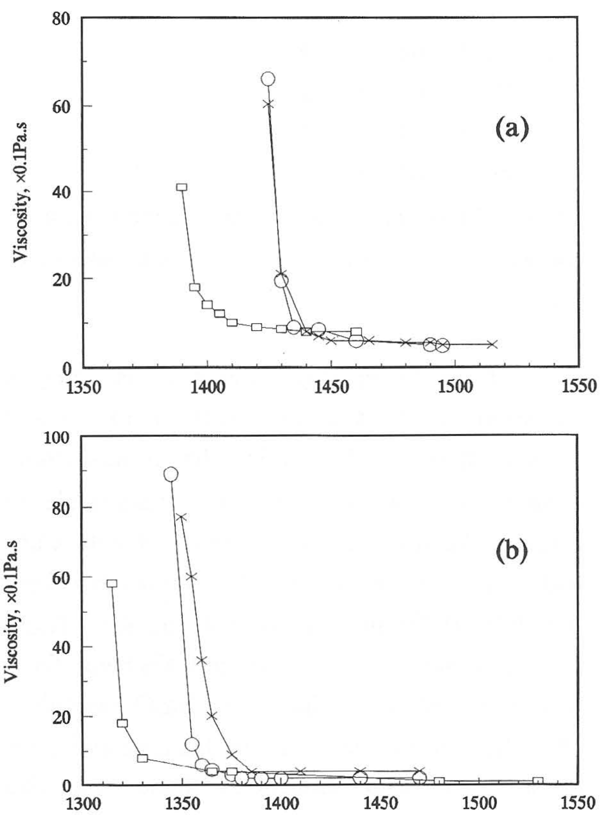
Fig.1. Influence of CaF_2 contents on slag viscosity (keep certain amount of K_2O+Na_2O)

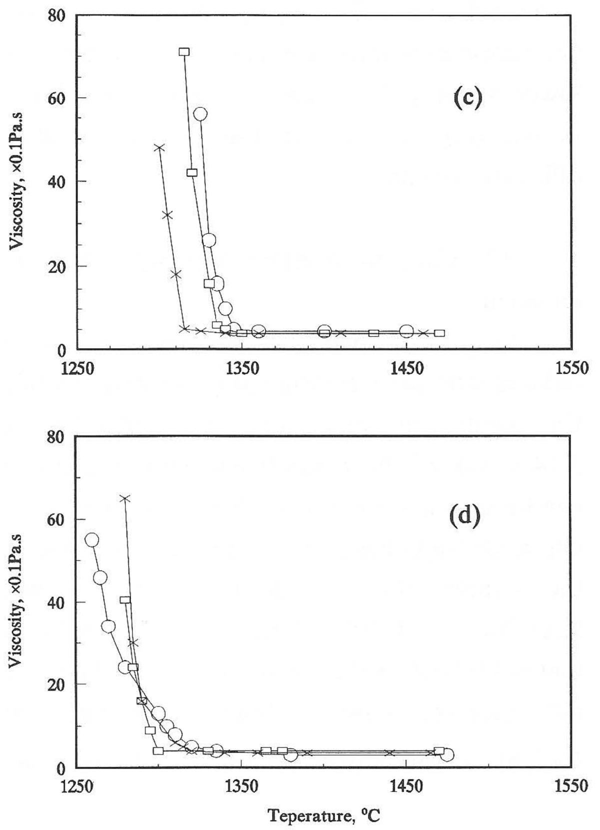
(1) K_2O+Na_2O in constant and CaF_2 in variation

K_2O+Na_2O content was 0%, 0.19% and 1.8% in Fig.1(a), (b) and (c), respectively. From 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_2O+ Na_2O in slag (Fig.1(a)and (b)), CaF_2 has a dominant effect on viscoity.

(2) CaF_2 in constant and K_2O+Na_2O in variation

Fig2(a)-(d) show that the viscosity will be reduced with the increasing of (K_2O+Na_2O) 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_2O+Na_2O has almost the same T-η curve as the sample No.07 with CaF_2 of 0% and K_2O+Na_2O of 0.19%, thus, it can be concluded that K_2O+Na_2O variation from 0 to 0.19% has a little effect on viscosity without CaF_2 in slag. From Fig2(b) the same conclusion can be obtained while





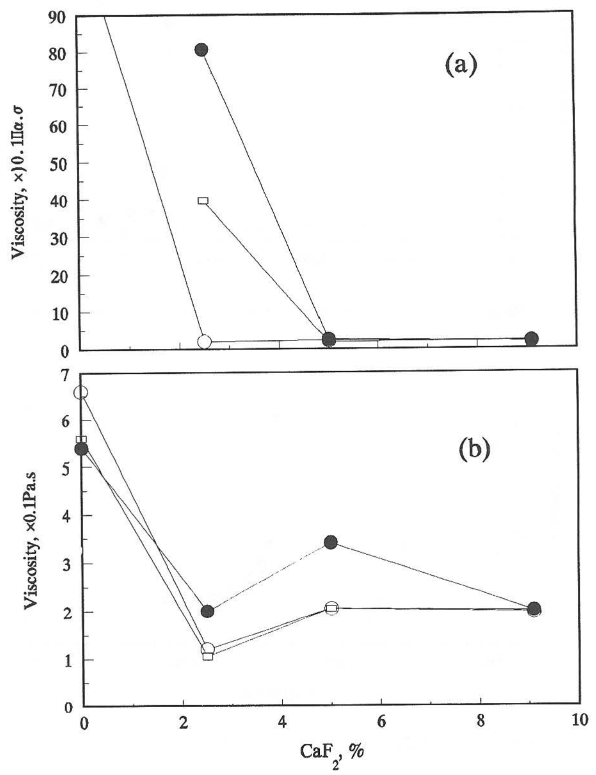
○–07; □–08; ×–09.
○–01; □–02; ×–05.
○–13; □–14; ×–15.
○–03; □–04; ×–06.

Fig.2. Influence of K_2O+Na_2O contents on F-containing slag viscosity (keep certain amount of CaF_2)

CaF_2 of 2.52% in slag. However, as CaF_2 is increased to 5.14% (Fig.2(c)), K_2O+ Na_2O 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 and K_2O+Na_2O in slag. Fig.2(d) shows that there is a little difference of viscosity as K_2O+Na_2O varying from 0% to 1.85% when CaF_2 being fixed at 9.24%, it indicates that K_2O+ Na_2O has only a little effect on slag viscosity in this case and CaF_2 is still the main influencing factor on slag viscosity.

(3) Influence of CaF_2 on slag viscosity at different temperatures

Fig3.(a) shows the influence of CaF_2 on slag viscosity at 1350°C. No bearing-CaF_2 slag has too higher viscosity (samples No.07-09), both the sample No.01 and No.05 bearing-2.52% CaF_2 have higher viscosity which is 4.0Pa.s and 8.1Pa.s, respectively. When CaF_2 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 K_2O+Na_2O content of 0.19% and 1.85%. It can be concluded that CaF_2 has a dominant effect on slag viscosity and when



(a) 1350 °C (b) 1450 °C

● – (K, Na)=0.0%.
○ – (K, Na)=1.85%; □ – (K, Na)=0.19%;
● –(K, Na)=0.0%.

Fig.3. Influence of CaF_2 contents on slag viscosity

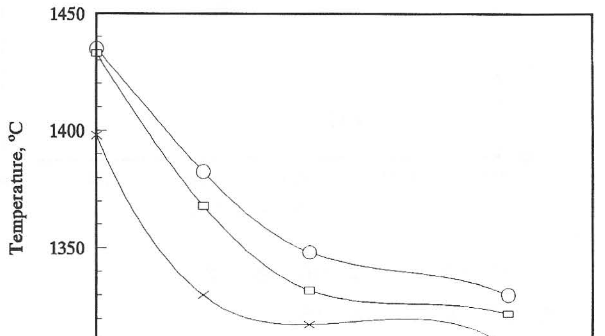
CaF_2>5.14% in slag, increasing CaF_2 will not decrease viscosity tremendously, in another words, as temperature over 1350°C, decreasing CaF_2 from 9.24 to 5.14% will not increase slag viscosity significantly. Fig3(b) shows the same result at 1450°C too.

3.2 Influence of CaF_2 (K_2O+Na_2O) on slag melting temperature

The melting temperature being relevant to different content of CaF_2 (0-9.24%) and K_2O+ Na_2O (0-1.85%) is shown in Fig.4, from which it can be seen that as K_2O+Na_2O content is 0%, 0.19% and 1.85%, respectively, slag melting temperature varied a little with CaF_2 variation between 5.14% and 9.24%, namely, when K_2O+ Na_2O content in slag is as low as 1.85%, decreasing CaF_2 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 K_2O+Na_2O of both 0.19% and 1.85%, and round 18°C for the slag without K_2O+Na_2O, the increase ratio of the former and the latter is 2.68°C/CaF_2 and 4.39°C/CaF_2 respectively. When reducing CaF_2 content from 5.14% to 4%, the melting temperature of the slag containing K_2O+Na_2O of 0.19% without K_2O+Na_2O will be increased about 20°C, its increase ratio is 17.54°C/CaF_2, by contrast, the melting temperature of the slag with K_2O+Na_2O of 1.85% rarely increase, but for any of different (K_2O+Na_2O) content, slag melting temperature will increase signficantly if CaF_2 content is reduced to less than 4.0%. Therefore, in order to increase melting temperature of Baotou B.F. slag, CaF_2 content must be controlled to less than 4.0%.

3.3 appropriate content of CaF_2 and (K_2O+Na_2O) in slag

Fig4. shows that the melting temperature of the slag containing K_2O+Na_2O of 1.85% is increased from 1305°C to 1329°C with decreasing CaF_2 from 9.24% to 2.52%, for the slags without and with K_2O+Na_2O 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 K_2O+Na_2O content in slag, it is difficult to increase slag melting temperature by decreasing CaF_2 content in slag. when CaF_2 and K_2O+Na_2O 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% CaF_2 and 0.19% K_2O+Na_2O in slag are appropriate for both the viscosity and melting temperature of Baotou B.F slag, which keeps operation smooth.



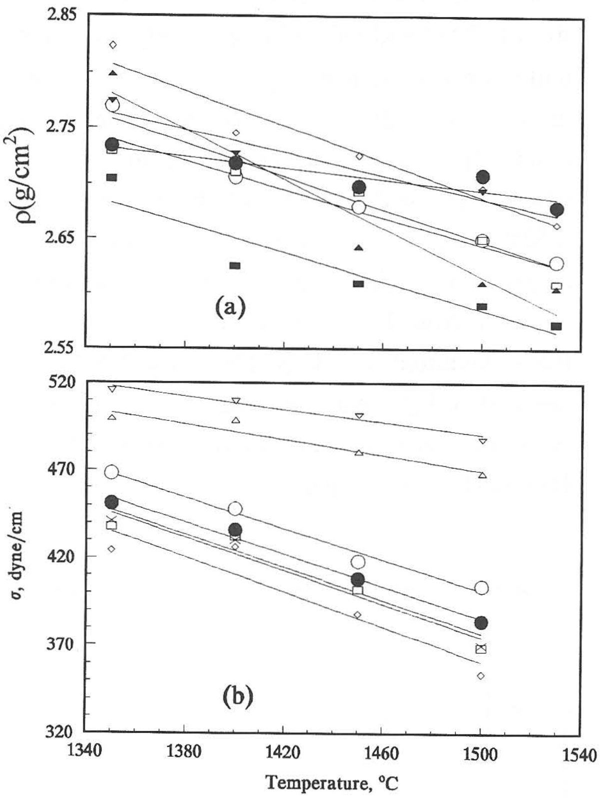
○ – (Na_2O+K_2O)=0.0%;
□ – (Na_2O+K_2O)=0.19%
× – (Na_2O+K_2O)=1.85%.

Fig.4. The relationship between melting temperature and the content of CaF_2 and (Na_2O+K_2O) .

3.4 Influence of K, Na and F on slag surface tension

3.4.1 K_2O+Na_2O content

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



○–02; □–04; ●–06; ◆–08;
■–10; ▲–13; ▲–15.

Fig.5. The relationship between density of experimental slag (a), surface tention (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_2O+Na_2O has the maximum surface tension than others, sample No.08 containing Na_2O+K_2O 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.

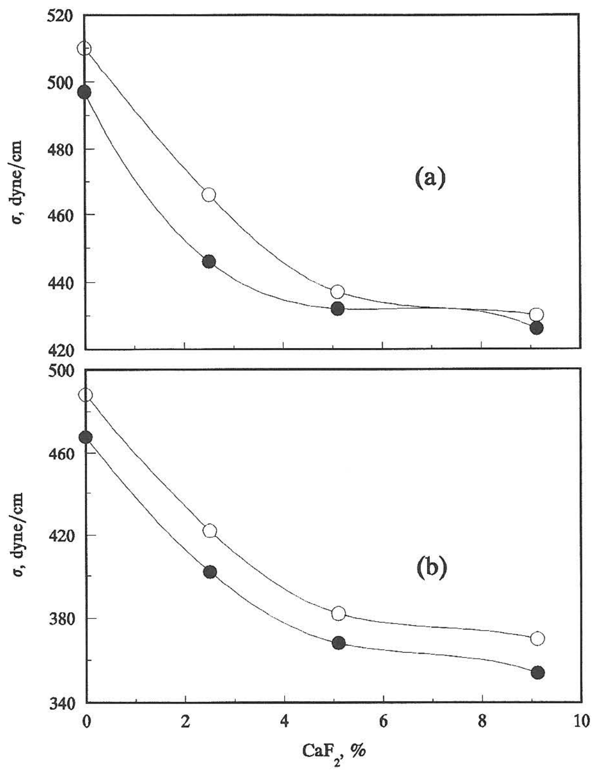
The contents of CaF_2 and K_2O+Na_2O in sample No.04 are similar to those in Baotou B.F. slag, which surface tension closes to samples of No.06 only bearing-CaF_2. It indicates that effect of K_2O+Na_2O on surface tension is much less than CaF_2 if ignoring existance of K_2O+Na_2O or co-existing with 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_2O+ Na_2O 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_2O+K_2O, 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_2O+Na_2O) or without both K_2O+Na_2O 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:

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



○ – $(Na_2O+K_2O)=1.80\%$;
● – $(Na_2O+K_2O)=0.0\%$

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_2O+Na_2O.

(2) In order to improve metallurgical properities of Baotou B.F slag, CaF_2 content in slag must be reduced to below 4%, meanwhile, K_2O+Na_2O must be reduced too. When CaF_2 and K_2O+Na_2O 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.