

The Effect of CaF₂ Content in Hot Metal Pretreatment Flux Based on Lime

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Abstract

This research was conducted for the purpose of studying the effect of CaF₂ content in the composition of hot metal pretreatment flux, based on lime. It was followed in regards to the importance of fluorine amount decrease in hot metal pretreatment and steel making processes. For this purpose, lime based fluxes including 40, 30, 20 and 10 percent calcium fluoride were prepared and hot metal pretreatment experiments were done in an induction furnace at the temperature range of 1350-1450°C. The obtained results indicated that by using the flux containing 30 percent calcium fluoride, simultaneous removal of phosphorous and sulfurous are in the highest level which is known as a result of slag making with suitable liquid phase volume and adequate basicity. On the other hand, a flux with 20 percent CaF₂ caused a small fall in the refining process results. In regards to the harmful effects of fluorine on refractory walls and considering environmental issues, a flux including 20 percent fluorine was introduced as a providing optimum condition. The results have been studied with respect to CaO-CaF₂ equilibrium phase diagram, as well as the effect of CaF₂ amount on phosphate capacity and lime efficiency of slag.

Keywords: CaF₂, hot metal pretreatment, lime based flux.

1. Introduction

Calcium fluoride with the melting point of 1386°C is known as a powerful reagent in hot metal pretreatment and steel making slag, which is based on lime. CaF₂ decreases slag melting point and increases lime solubility and slag fluidity as well and improves hot metal refining process. Previous studies have illustrated CaF₂ is the most effective composition to increase lime solubility in the slag¹. In most previous studies performed on hot metal pretreatment fluxes, CaF₂/CaO was in the high levels. Some researches², by using 40 percent CaF₂ in lime basis flux, have made slags with suitable fluidity. In recent years, steelmakers were advised to limit the fluorine consumption because of its harmful effects on refractory walls and environmental issues^{3,4}. On the other hand, increase in calcium fluoride ratio to lime decreases the basic capacity of slag¹. So, today, it is essential to make slags with optimum content of fluorine. The experiments of simultaneous removal of phosphorous and sulfurous from hot metal carried out by using lime based fluxes have included different amounts of CaF₂ to obtain an optimum content of calcium fluoride in the flux composition.

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2. Methodology

In order to study the effect of different amounts of CaF₂ on simultaneous removal of phosphorous and sulfurous from molten iron, primary materials needed to the experiments include of hot metal, lime, fluorine and oxide scale of iron were used in special chemical compositions and particle size distribution. The produced fluxes were dried at 100°C for 2 hours. The experiments were carried out in an induction furnace with magnesite refractory at the temperature range of 1350-1450°C in four stages by using fluxes including 40, 30, 20 and 10 percent CaF₂, respectively. The temperature of experiment was controlled at 1400°C by using a laser pyrometer. In each stage of experiments, the first sample was taken before flux addition to identify the exact chemical composition of molten iron. Dried fluxes were added to the surface of the melt during 20 minutes and further samples were taken after 5, 10, 15 and 20 minutes; then they were analyzed.

3. Results and Discussion

The results of different stages of simultaneous removal of phosphorous and sulfurous from molten iron, using 40, 30, 20 and 10 percent of CaF₂ in the flux composition are shown in Tables 1 to 4 respectively. Also, phosphorous and sulfurous changes against time in different stages are plotted in Figures 1 to 4.

Table 1. chemical composition of hot metal samples in the first stage

Time (min) \ Element	Si	P	S	C
0	0.370	0.261	0.065	4.155
5	0.240	0.262	0.055	3.957
10	0.160	0.254	0.043	3.337
15	0.080	0.221	0.033	3.229
20	0.004	0.173	0.021	3.251

Table 2. chemical composition of hot metal samples in the second stage

Time (min) \ Element	Si	P	S	C
0	0.390	0.267	0.062	4.055
5	0.208	0.265	0.050	3.875
10	0.190	0.252	0.038	3.420
15	0.080	0.215	0.025	3.347
20	0.005	0.166	0.017	3.212

Table 3. chemical composition of hot metal samples in the third stage

Time (min) \ Element	Si	P	S	C
0	0.330	0.268	0.066	4.351
5	0.210	0.264	0.057	4.012
10	0.140	0.256	0.046	3.597
15	0.050	0.229	0.037	3.313
20	0.004	0.171	0.020	3.155

Table 4. chemical composition of hot metal samples in the fourth stage

Time (min) \ Element	Si	P	S	C
0	0.400	0.259	0.059	4.110
5	0.340	0.261	0.050	3.912
10	0.270	0.251	0.041	3.784
15	0.190	0.231	0.033	3.420
20	0.110	0.210	0.030	3.227

The results showed that in the first stage, 40 percent CaF_2 in flux composition, 34 percent dephosphorization and 68 percent desulfurization occurred. In the second stage, 30 percent CaF_2 in flux composition, 38 percent removal of phosphorous and 73 percent removal of sulfurous were obtained. The corresponding figures for third stage were 36 percent and 70 percent, respectively. Finally, in the last stage with 10 percent fluorine in the composition of flux, 19 percent removal of phosphorous and 49 percent of sulfurous was occurred. The study of results showed that when the amount of CaF_2 decreased from 40 percent to 30 percent, phosphorous and sulfurous removal increased. On the other hand, in the third stage with 20 percent fluorine, desulfurization degree and dephosphorization degree went down slightly. Finally in the last stage, removal process decreased dramatically for both P and S which indicates a decrease in slag fluidity.

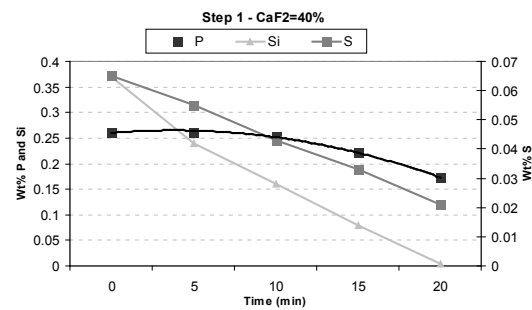


Fig. 1. Phosphorus, sulfurous and silicon change vs. time in the first stage.

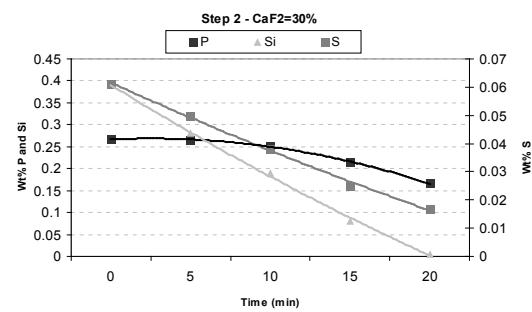


Fig. 2. Phosphorus, sulfurous and silicon change vs. time in the second stage.

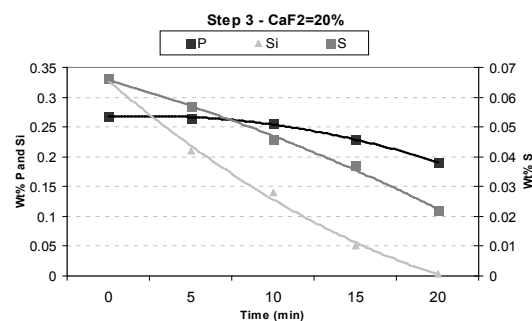


Fig. 3. Phosphorus, sulfurous and silicon change vs. time in the third stage.

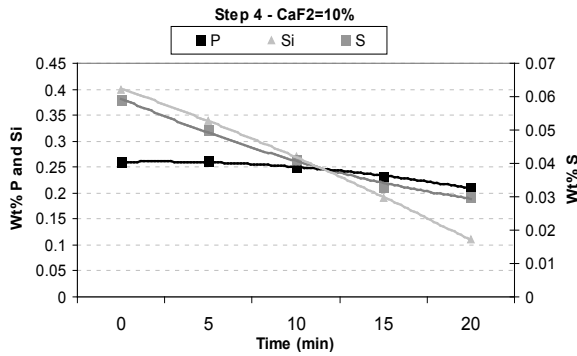


Fig. 4. Phosphorus, sulfur and silicon change vs. time in the fourth stage.

CaO-CaF₂ equilibrium phase diagram is shown in Figure 5. According to this diagram, if the amount of CaF₂ increases from 1 to 80 percent at 1400°C, CaO and liquid phase will be the stable phases. Liquid phase volume in the slag depends on CaF₂ amount; the decrease in CaF₂ amount reduces liquid phase volume. As a direct result of that, lime dissolution decreases steadily. The study of the first stage indicates that despite using 40 percent CaF₂ in flux composition, refining process is less effective than the second stage.

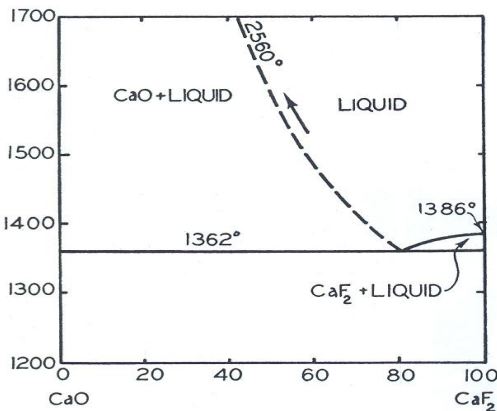


Fig. 5. CaO-CaF₂ equilibrium phase diagram.

In order to deal with this matter, it is essential to consider Figure 6. This figure shows the effect of CaF₂ amount on phosphate capacity of slag. It is clear that increasing CaF₂ amount in lime basis flux decreases phosphate capacity because of low basic capacity of CaF₂ in comparison with CaO. So, hot metal pretreatment reaches its maximum degree by using 30 percent CaF₂ in the flux composition. But with respect to this important fact the increase of CaF₂ to 30 percent in the second stage has no particular effect on the refining results compared with third stage, and considering the environmental issues and refractory walls problems, the use of flux containing 20 percent CaF₂ is identified as the optimum condition.

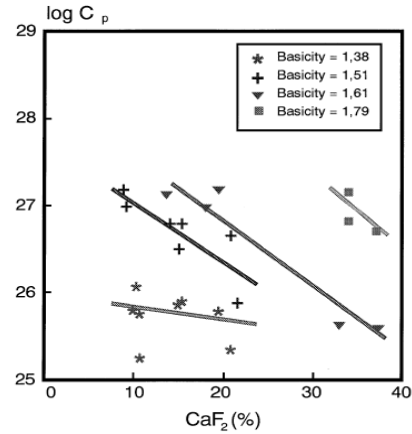


Fig. 6. Effect of CaF₂ on phosphate capacity.

Additional studies on lime efficiency in different stages using practical relations, illustrated by Kitamura⁴⁾, has been done.

$$E_{CaO} = (27.1 \times \Delta [\%P]) \times 100 / W_{CaO} \quad (1)$$

E_{CaO}: lime efficiency (%)

W_{CaO}: lime weight (Kg/ton)

Figure 7 indicates lime efficiency in different stages. It is clear that the increase in CaF₂ amount to more than 30 percent has no significant effect on lime efficiency because of decrease in the basic capacity of slag.

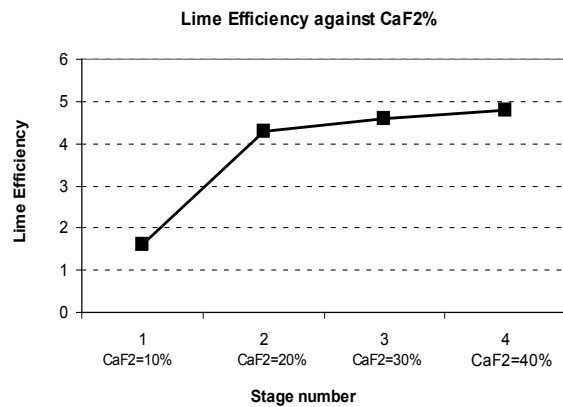


Fig. 7. Lime efficiency in different stages.

4. Conclusions

- Hot metal pretreatment results in the second stage, 30 percent CaF₂ in the flux composition, are in the maximum level, resulted by making the slag with suitable fluidity and basicity.
- Refining process in the third stage, using a flux containing 20 percent of CaF₂, is identified as the optimum condition.

3. The increase in the amount of fluorine to more than 30 percent due to decrease of slag basicity, has no any positive effect on lime efficiency.

References

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