The Effect of Flux type and Oxygen Blowing on Simultaneous Removal of Phosphorus and Sulfur from Molten Iron

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Abstract

This research was conducted to study the effect of lime based Flux with the composition of $CaO-20\%CaF_2-8\%FeO$ on simultaneous removal of phosphorus and Sulfur from hot metal. The effects of Na_2O and oxygen blowing were also studied. The experiments were performed using an induction furnace and hot metal produced in Isfahan Steel Company in the temperature range 1350-1450 ºC. The results showed that simultaneous removal of these elements was possible. It was also indicated that addition of Na_2CO_3 as the supplier of Na_2O caused a considerable improvement in the removal process. This was mainly because of an increase in slag basicity and CO_2 gas evolution. Oxygen blowing into the melt improved the phosphorus removal slightly. However, an increase in melt temperature resulted in some sulfur return from slag to hot metal. On the other hand, increase in melt oxygen potential due to oxygen blowing decreased desulfurization to some extent. According to the results obtained, 35% and 75% decrease in phosphorus and sulfur content of the melt was achieved respectively. The initial silicon content of hot metal was found to be an important parameter. The results showed that the hot metal silicon content should be reduced to less than 0.15% before phosphorus removal starts.

Keywords: desulfurization, dephosphorization, lime based flux, Na_2O.

1. Introduction

One of the necessities of new steelmaking processes is pretreatment of molten iron before delivering the melt to convertor shop [1]. Decreasing elements such as phosphorous and sulfur is a part of pretreatment of molten iron which is done by adding fluxes with a specific chemical composition to the melt [1-2]. Using the suitable thermodynamic conditions, it is possible to remove phosphorus and sulfur simultaneously from the iron melt. Some researchers explained that the Na_2CO_3 is a high performance reagent for the simultaneous removal of phosphorus and sulfur [3-5]. However from environmental point of view and effect of the usage of Na_2CO_3 on the refractory lining, it has a limited use. In recent years there has been a wide spread replacement of fluxes with a chemical composition based on lime and containing low amounts of CaF_2 [6-7]. Therefore, this research has been undertaken to study the effect of using basic flux based on lime with low oxygen potential on the simultaneous removal of phosphorus and sulfur. Furthermore the effects of using a reduced Na_2O flux and the blowing of oxygen into melt on the removal processes were investigated.

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2. Methodology

Three types of experiments were designed and performed to study the simultaneous removal of phosphorous and sulfur from molten iron supplied by Isfahan steel company. These experiments were carried out using an induction furnace with magnesite refractory in the temperature range 1350-1450 ºC. At the beginning of each experiment, two samples with designation A were taken from the melt to identify its chemical composition. Raw materials used to produce lime based flux were calcium fluoride, oxide scale of iron and sodium carbonate with proper composition and size distribution. The prepared flux which was 10% of the melt (weight basis), was then divided into four equal parts and each part was added to the melt during 5 minutes. Samples were taken from the hot metal and slag at the end of flux addition and they were designated B, C, D and E. After deslaging at the end of each 5 min. stage of flux addition, the other parts of flux were added to the melt. The lime based fluxes used for three types of experiments were as follows:

Type 1. Flux with low oxygen potential and composition of $CaO-20\%CaF_2-8\%FeO$

Type 2. Flux with low oxygen potential containing a low percentage of Na_2CO_3 with the composition of $CaO-20\%CaF_2-8\%FeO-6\%Na_2O$.

Type 3. Flux containing Na_2O and Oxygen blowing into the melt.

Each type of experiment was carried out twice to confirm the consistency of the results.

In the third type of experiment, a steel lance with zirconia isolated covering was used for the oxygen blowing into the melt.

It should also be mentioned that at different stages of each type experiment two samples from each hot metal and slag were taken to confirm the reliability of the results. The average of the chemical composition of the taken samples was used to demonstrate the amount of element removal.

3. Results and discussion
3.1. First type of experiments
The results of the analysis of hot metal and slag samples are shown in tables 1 and 2 respectively. The results show that 11% removal of phosphorus and 35% removal of sulfur are achieved (from samples A to E). There was also a 94% decrease in the melt silicon content. Fig. 1 indicates the changes of these elements versus time.

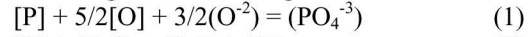The phosphorus and sulfur have been removed according to the following reactions [1-2].

$$[P] + 5/2[O] + 3/2(O^{-2}) = (PO_4^{-3}) \qquad (1)$$
$$[S] + (O-2) = (S-2) + [O] \qquad (2)$$

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

Element \ Sample	%P	%S	%Si	%C
A1	0.300	0.048	0.350	3.890
A2	0.302	0.049	0.350	3.910
A$_{ave}$	**0.301**	**0.049**	**0.350**	**3.900**
B1	0.305	0.042	0.221	3.850
B2	0.303	0.043	0.218	3.835
B$_{ave}$	**0.304**	**0.043**	**0.220**	**3.843**
C1	0.284	0.039	0.130	3.830
C2	0.281	0.039	0.140	3.800
C$_{ave}$	**0.283**	**0.039**	**0.135**	**3.815**
D1	0.283	0.035	0.090	3.770
D2	0.277	0.036	0.100	3.735
D$_{ave}$	**0.280**	**0.036**	**0.095**	**3.753**
E1	0.277	0.031	0.020	3.680
E2	0.275	0.032	0.030	3.630
Eave	**0.276**	**0.032**	**0.025**	**3.655**

Table 2. chemical composition of slag samples in the first type of experiments.

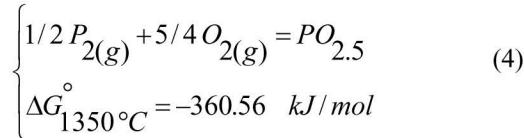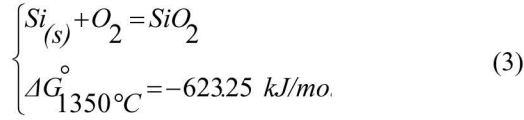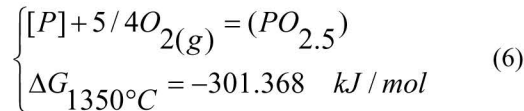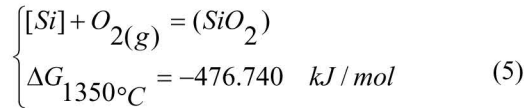| Element or component \ Sample	%P	%S	%CaO	%SiO$_2$	%MgO	%FeO	%MnO
B$_S$	0.003	0.024	29.11	25.14	15.11	5.55	3.69
C$_S$	0.004	0.059	27.82	39.43	18.13	5.51	4.45
D$_S$	0.124	0.051	28.37	34.99	21.32	4.84	4.60
E$_S$	0.210	0.058	25.81	35.06	25.93	3.64	5.02
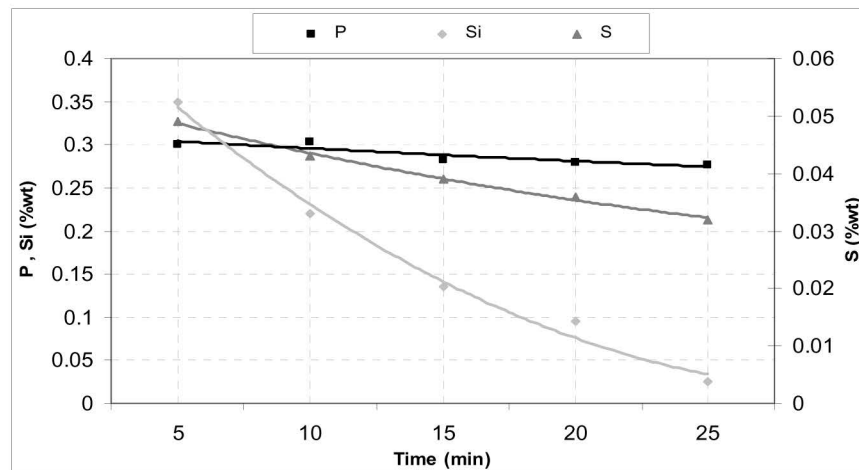
Fig. 1. the phosphorus, sulfur and silicon change against time in first type of experiments.

CaO content of the flux is considered as the supplying source of oxygen ion in slag while FeO is the supplying source for oxygen dissolved in the melt. The results of the first type of experiments showed that the amount of silicon content of heat should be reduced to a certain extent to make the phosphorus removal possible. The standard Gibbs free energy changes in 1350 ℃ for the oxidation reactions of phosphorus and silicon can be calculated as:

$$\begin{cases} Si_{(s)} + O_2 = SiO_2 \\ \Delta G^{\circ}_{1350\,℃} = -623.25 \ kJ/mol \end{cases} \quad (3)$$

$$\begin{cases} 1/2\,P_{2(g)} + 5/4\,O_{2(g)} = PO_{2.5} \\ \Delta G^{\circ}_{1350\,℃} = -360.56 \ kJ/mol \end{cases} \quad (4)$$

The phosphorus and silicon activities in hot metal with composition 3%C, 0.6%Si, 0.3%P, 0.5%Mn and 0.06%S using raoultian standard state are calculated as $a_{Si} = 1.663 \times 10^{-5}$ and $a_p = 1.24 \times 10^{-5}$ [8].

Assuming the phosphorus and silicon oxides are pure and the partial pressure of oxygen is one atmosphere, the oxidation reactions are as follows.

$$\begin{cases} [Si] + O_{2(g)} = (SiO_2) \\ \Delta G_{1350\,℃} = -476.740 \ kJ/mol \end{cases} \quad (5)$$

$$\begin{cases} [P] + 5/4\,O_{2(g)} = (PO_{2.5}) \\ \Delta G_{1350\,℃} = -301.368 \ kJ/mol \end{cases} \quad (6)$$
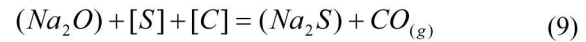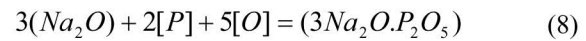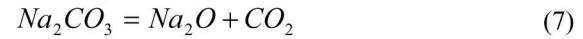
It is clear that in these conditions the silicon oxide is more stable than phosphorus oxide. Therefore, it is necessary for the removal of phosphorus from hot metal that silicon content is reduced to a certain extent. This can be the reason that in the first 10 minutes of this experiment phosphorus was not eliminated whereas sulfur began to eliminate from the beginning of the experiment.

3.2. Second type of experiment

The effect of adding 6% Na_2O to lime based flux was studied in the second type of experiments. The chemical composition of analyzed hot metal and slag samples in this series of experiments are shown in tables 3 and 4 respectively. Fig 2 shows the alteration of phosphorus, sulfur and silicon in hot metal against the time. In this method there were 35% removal of phosphorus, 75% removal of sulfur and the highest amount decrease in melt silicon content, which in nearly the total amount of silicon content.

Na_2CO_3 is recognized as an effective compound in the simultaneous removal of phosphorus and sulfur. Adding Na_2CO_3 to the flux caused its dissociation according to reaction 7 and the removal of phosphorus and sulfur according to reactions 8, 9 [5].

$$Na_2CO_3 = Na_2O + CO_2 \quad (7)$$
$$3(Na_2O) + 2[P] + 5[O] = (3Na_2O.P_2O_5) \quad (8)$$
$$(Na_2O) + [S] + [C] = (Na_2S) + CO_{(g)} \quad (9)$$

On the other hand, as Iwai and Kunisada [9] have emphasized, in the presence of Na_2O in slag the removal of silicon increases according to the following reaction.

$$3(Na_2O) + 2[S] + [Si] = 2(Na_2S) + (Na_2O.SiO_2) \quad (10)$$
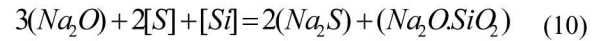
However the effect of the presence of Na_2O in the flux composition and its improvement influence on the removal process can be explained as follows. Na_2CO_3 with 850 ℃ melting point was in the molten state in the temperature of the experiments thus the melt phase volume in slag increased. On the other hand, Na_2CO_3 decreased the melting point of the lime based flux and increased mass transfer in the slag phase [5].

Table 3. chemical composition of hot metal samples in the second type of experiments.

Element / Sample	%P	%S	%Si	%C
A₁	0.271	0.067	0.210	3.82
A₂	0.270	0.067	0.140	3.690
A_ave	**0.271**	**0.067**	**0.175**	**3.755**
B₁	0.268	0.060	0.152	3.661
B₂	2.269	0.057	0.125	3.620
B_ave	**0.269**	**0.059**	**0.139**	**3.641**
C₁	0.267	0.043	0.020	3.510
C₂	0.258	0.039	0.010	3.520
C_ave	**0.263**	**0.041**	**0.015**	**3.515**
D1	0.220	0.035	0.008	3.330
D2	0.232	0.034	0.009	3.321
D_ave	**0.226**	**0.034**	**0.009**	**3.226**
E1	0.185	0.018	0.002	3.240
E2	0.166	0.015	0.002	3.260
Eave	**0.176**	**0.017**	**0.002**	**3.250**

Table 4. chemical composition of slag samples in the second type of experiments.

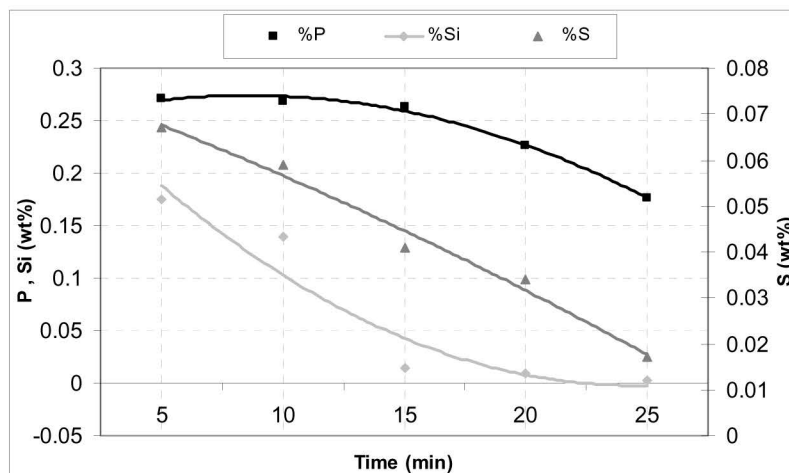| Element or component / Sample	%P	%S	%CaO	%SiO$_2$	%MgO	%FeO	%MnO
B$_{S-Na}$	0.051	0.065	35.65	23.15	5.33	6.25	4.01
C$_{S-Na}$	0.090	0.079	39.07	22.90	8.50	7.16	4.59
D$_{S-Na}$	0.250	0.0750	39.36	20.27	11.14	7.20	2.99
E$_{S-Na}$	0.644	0.077	47.26	17.32	12.73	5.24	2.55

Fig. 2. the phosphorus, sulfurous and silicon change against time in second type of experiments.

Considering the fact that Na_2CO_3 has been the source of Na_2O, the role of CO_2 produced by the dissociation of Na_2CO_3 can be viewed in two ways. Firstly, the production of CO_2 by the continuous adding of flux containing Na_2CO_3 causes a kind of stirring effect in the melt and improves the mass transfer which will have a useful effect on removal of both elements. Secondly, the production of this gas causes melt oxygen potential to increase and improves the removal of phosphorus and silicon. Some researches believe that adding Na_2O to the flux composition increases the basic power of slag and in this way has a suitable effect on the results of the removal processes.

3.3. Third type of experiments

The third type of experiments in this research was conducted using flux similar to the second type and accompanied by the blowing of oxygen into melt. The results of the chemical analysis of melt and slag samples in these experiments can be seen in tables 5 and 6 respectively. As shown in figure 3 the removal of phosphorus is increased a small amount and is reached 40% in comparison to type 2 experiment. However desulfurization is decreased considerably and is reached 45%. The following points are worth mentioning.

Temperature effects: Oxygen blowing increases the melt temperature which thermodynamically decreases the removal of phosphorus.

Phosphorus Return: The return of phosphorus to the melt occurs because of increase in the activity of P_2O_5 in slag. At the same time because of increase in temperature, which is caused by the blowing of oxygen into melt, compounds such as $CaO.P_2O_5$ lose their stability and thus phosphorus returns to the melt. However, the considerable decrease in desulfurization is caused by high oxygen potential.

Considering the reactions mentioned earlier, it can be noticed that in the first 10 minutes of the type one experiments, phosphorus was not removed but the amount of silicon decreased to 0.14 percent. Therefore in this part it is tried to find the relation between phosphorus removal and the silicon content by using the results of the analysis of slag samples. To study the effect of silicon content of the melt on phosphorus reaction, first, the amount of equilibrium oxygen content with carbon in the melt was calculated. This was done using the equilibrium between carbon, oxygen and CO and considering the melt to be saturated with carbon. The amount of equilibrium dissolved oxygen was 1.60×10^{-2} percent. Then the experimental equations 11 and 12 [10]. were used to calculated the equilibrium constant of phosphorus oxidation reaction and activity coefficient of P_2O_5 in lime based slag. The equilibrium oxygen for the removal of phosphorus in this slag was calculated as 4.69×10^{-4} percent.

The amount of oxygen in equilibrium with carbon is sufficient to begin the removal reaction of phosphorus. However, lack of removal of phosphorus

in the first 10 minutes of type 1 experiments is associated with the amount of primary silicon of hot metal. Moreover, by using the silicon oxidation reaction and gaining the activity of SiO_2 from the ternary diagram [1] (fig. 4) and by substituting oxygen amount in equilibrium with phosphorus on silicon reaction, the amount of melt silicon content was calculated as 0.14 percent. Therefore it can be concluded that according to the results of this research for phosphorus removal it is necessary that the amount of silicon content in melt is reduced to lower than 0.15 percent.

$$LogK_{po} = 7.93Log(\%CaO + 0.3\%MgO - 0.05\%FeO) + (21660/T) - 26.929 \qquad (11)$$

$$Log\gamma_{P205} = -0.985(23X_{CaO} + 17X_{MgO} + 8X_{FeO}) - (22270/T) + 8.818 \qquad (12)$$

Table 5. chemical composition of hot metal samples in the third type of experiments.

Element / Sample	%P	%S	%Si	%C
A_1	0.268	0.060	0.280	4.070
A_2	0.264	0.056	0.250	4.040
A_{ave}	**0.266**	**0.058**	**0.265**	**4.055**
B_1	0.252	0.056	0.160	3.950
B_2	0.252	0.055	0.155	3.855
B_{ave}	**0.252**	**0.056**	**0.158**	**3.903**
C_1	0.215	0.051	0.040	3.850
C_2	0.200	0.050	0.050	3.720
C_{ave}	**0.208**	**0.051**	**0.045**	**3.785**
D_1	0.195	0.048	0.012	3.600
D_2	0.185	0.044	0.009	3.652
D_{ave}	**0.190**	**0.046**	**0.011**	**3.626**
E_1	0.163	0.033	0.002	3.440
E_2	0.157	0.030	0.001	3.420
E_{ave}	**0.160**	**0.032**	**0.002**	**3.430**

Table 6. Chemical composition of slag samples in the third type of experiments.

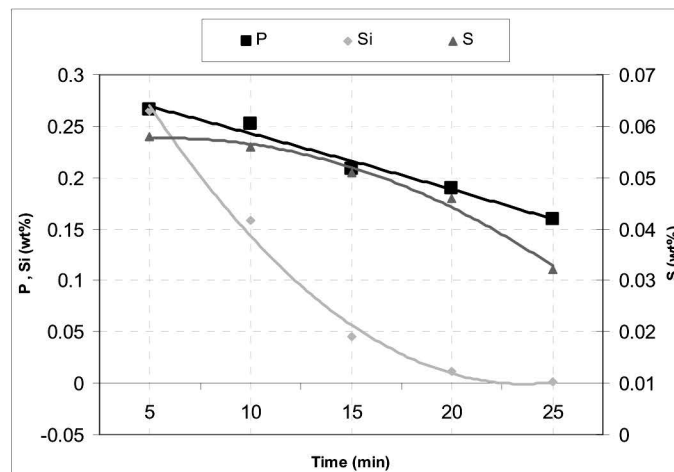| Element or component / Sample	%P	%S	%CaO	%SiO_2	%MgO	%FeO	%MnO
B_S	0.157	0.048	36.01	25.57	12.47	5.64	2.26
C_S	0.427	0.070	36.04	21.53	12.00	7.37	3.58
D_S	0.352	0.064	37.32	20.25	19.94	5.26	3.11
E_S	0.270	0.070	39.61	16.82	21.49	5.00	1.19

Fig. 3. The phosphorus, sulfurous and silicon change against time in third type of experiments.
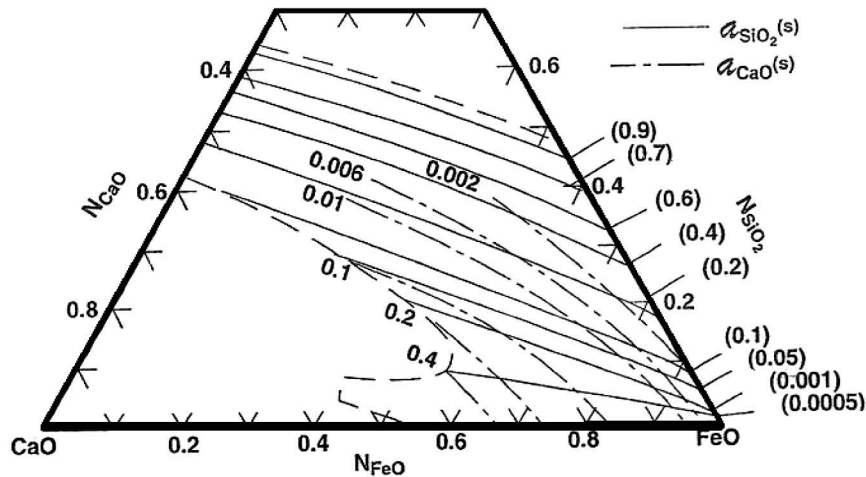
Fig. 4. Activities of CaO and SiO₂ (by Gibbs-Duhem integration) in CaO-FeO-SiO₂ melts in equilibrium with liquid iron [1].

4. Conclusions

• Generally, the simultaneous removal of phosphorus and sulfur from molten iron using basic flux based on lime is possible with a low oxygen potential and without sodium carbonate.

• Adding a small amount of Na_2O to the flux increases the simultaneous removal of phosphorus and sulfur considerably.

• The blowing of oxygen into melt increases the removal of phosphorus slightly but decreases desulfurization considerably.

• Using lime based flux containing 6 percent Na_2O, the best condition for simultaneous removal of phosphorus and sulfur was achieved in this research where 35% removal of phosphorus and 75% removal of sulfur were obtained.

It was recognized that the amount of silicon content of the melt should be decreased to less than 0.15% to make the removal of phosphorus possible.

Nomenclature

$A_{(ave)}$ The average analysis of hot metal samples before the beginning of process in the first state

$B_{(ave)}$ The average analysis of hot metal samples in the middle of process in the first state

$C_{(ave)}$ The average analysis of hot metal samples at the end of process in the first state

$A_{Na(ave)}$ The average analysis of hot metal samples before the beginning of process in the second state

$B_{Na\ (ave)}$ The average analysis of hot metal samples in the middle of process in the second state

$C_{Na\ (ave)}$ The average analysis of hot metal samples at the end of process in the second state

$A_{Na+O\ (ave)}$ The average analysis of hot metal samples before the beginning of process in the third state

$B_{Na+O\ (ave)}$ The average analysis of hot metal samples in the middle of process in the third state

$C_{Na+O\ (ave)}$ The average analysis of hot metal samples at the end of process in the third state

B_S The average analysis of slag samples in the middle of process in the first state

C_S The average analysis of slag samples in the middle of process in the second state

C_{S-Na} The average analysis of slag samples at the end of process in the second state

B_{S-Na+O} The average analysis of slag samples in the middle of process in the third state

C_{S-Na+O} The average analysis of slag samples at the end of process in the third state

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