RESEARCH ARTICLE

THE EFFECT OF THERMODYNAMICS IN EFFECTIVE REMOVAL OF PHOSPHOROUS IN STEEL MAKING

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ABSTRACT

Numerous research works has been carried out for the removal of phosphorous from the steel since several decade because of its detrimental effect on mechanical properties of steel such as cold shortness temper embrittlement poor ductility and strength. In the present work, dephosphorization experiments have been carried out. Total fifteen heats were processed, experimenting on (0.017%C) low carbon steel. During each individual heat, the samples of slag and liquid metal have been collected. It is found that Rate of dephosphorization is mainly controlled by mass transfer in the slag. Addition of MgO may increase the melting point and viscosity of the slag which decreases the kinetic conditions of dephosphorization. It decreases the activity of CaO and FeO in slag and increase in Al_2O_3 decreases the viscosity of the melt which have a negative impact on phosphorous removal. The dephosphorization increases with increase in slag basicity and becomes maximum approximately 3, further increase in basicity beyond that has found to have negative impact on phosphorous removal.

INTRODUCTION

When phosphorous, manganese or silicon is added to steel, the tensile strength of steel increases and elongation decreases. Phosphorous has great influence towards the solid solution strengthening of ferrite. Modest quantity of phosphorous can increase the yield the ultimate strength of mild steel. It also increases the deep drawability and hardness of steel. It can also increase corrosion resistance and metal cutting characteristics. A balance between cold formability and hardness must be maintained to produce high strength formable steel. As phosphorous level increases, ductility of steel decreases severely due to the embrittlement. Phosphorous mainly comes from iron ore coke and recycled BOF slag. Due to depletion of good quality iron ore and increasing demand for low phosphorous steel, effective phosphorous control is an essential requirement. A highly basic slag is required to accept phosphorous from the metal into the slag. A high oxygen potential must exist to force phosphorous from the metal to the slag. Low temperature promotes the thermodynamics of phosphorous removal. While making steel charging of molten iron from the blast furnace is done the scrap metal and some fluxes are added oxygen is delivered at a supersonic velocity within few minutes lime and other fluxes are gradually added to the furnace. The fluxes the oxides formed by the oxidation of iron silicon and manganese The formed slag primarily consist of CaO, SiO2, MnO, FeO, P2O5 and MgO.

MgO is added to slag to reduce refractory wear. Within 16 minute blowing of Oxygen in furnace a slag metal emulsion forms in which the majority of refining occurs. In this work the phosphorous distribution ratios between xCaO.SiO2 particle and liquid CaO-SiO2-FeO slags have been measured as a function of slag composition and temperature. The aim of this research is to reduce phosphorous P2O5 which is rich in slag and also to fix it in combined form so that phosphorous reversible does not take place. Lime CaO and Dolo MgO is added as fluxing agent in the converter steel making process. It is very important to maintain FeO content of slag as it increases the oxidising power of slag. Whereas MgO minimize the chemical wear of refractory lining of the converter, but increases the melting point and viscosity of the slag. This study is carried out to evaluate the role or influence of oxides like CaO FeO, MgO, SiO2 and Al2O3 of slag and their kinetics on dephosphorisation of steel.

Literature survey: Balajiva and Turkdogan(1-3) used range of molecular representations to describe dephosphorization. It may also exist in molten slags as on ionic species. Slag can be treated as concentration solutions so that the activities of components of the slag are referred to in Roultian state. The roultian activity αi can be calculated using equation

$$\alpha i = \gamma i + Ni$$

γi is Resoultian activity coefficient of the species and
Ni is mole fraction of species in the solution

The henrarian activity hi is used in the calculation of free energy and can be calculated from Equation hi=fi(wt %). There are many theories (4,5) where researchers develop the empirical formulae showing behaviour of slag in the components.

Example Quotient of reaction $KI=\% P_2O_5/[P]^2[O]^2$

V ratio introduced by Herty(6,7) says that Measuring shifts the ultraviolet spectrum following the inclusion trace metal ions allows the experimental measurements of optical basicity values . Optical basicity (8-10) introduced by Duffy and Ingram They measured the energy shift of the ultraviolet absorption spectrum of Pb^{+2} spectrum reflected by the trend for an oxygen ion to release electrons toward Pb $^{+2}$ reflected and defined the value of shift relative to that of CaO as optical basicity. Turkdogan(10) found that CaF_2 does not affect the phosphorous distribution ratio. He showed the impact of CaF_2 in moderate Dicalcium silicate and magnesio-wusite. saturated with portions is equivalent to that of CaO for slag saturated with both dicalcium silicate and magnesio-wusite. In a study by Morales et al it was shown that increased additions of MnO do not adversely affect (8-9)dephosphorisation ability of slag. Concentration of Al_2O_3 greater than 3.5Weight % have a greater effect on dephosphorisation.
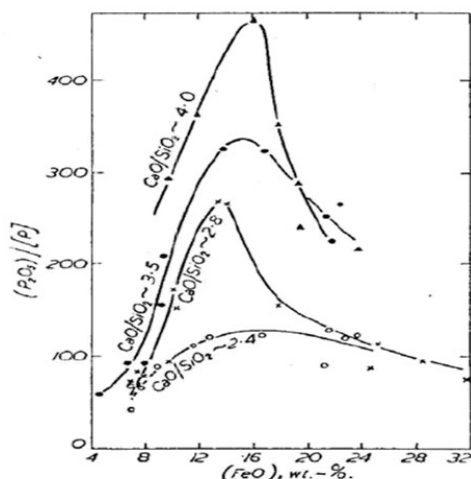

Figure 1. Showed the energy shift of ultraviolet spectrum of Pb+2 reflected by an oxygen ion to reflect and defined the value of shift relative to that of CaOas optical basicity.
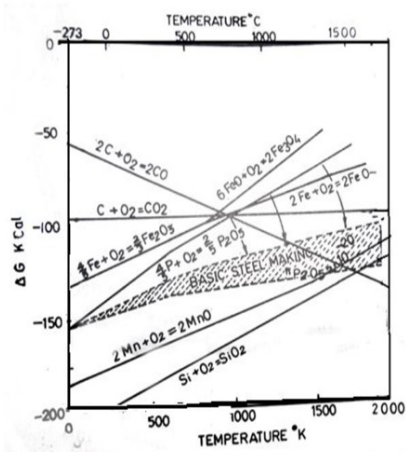

Figure 2 The solubility limit of MgO in MgO-SiO$_2$-CaO$_2$Fe$_2$O slag plotted as a function of slag V ratio 1600ºC.

Kinetics and Thermodynamics of dephosphorisation depends on the following factors

- The rate at which reactants and products move to and from the reaction sites
- The interfacial area of reaction

- The rate at which the reagents react at the reaction sites
- The rate of dephosphorization in the emulsion is dependent on the size of the metal droplets, small droplets are more extensively dephosphorised than larger droplets(11)

The bulk dephosphorization kinetics in the BOF are primarily controlled by the residence time of droplets in the emulsion and the emulsification rate which refers to the quantity of metal that is distributed as droplets in emulsion.
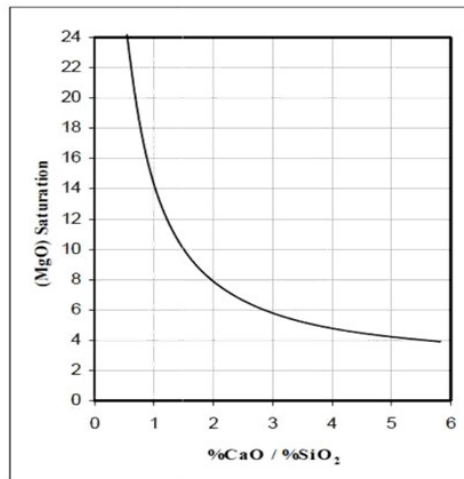

Figure 3. The affect of MgO on solubility isotherms at 1600ºC in the system (CaO+ MgO) SiO-FeO in equilibrium with liquid iron

Figure 3 show percentage phosphoros input into the converter absorbed in the slag phase as a function of the mass of O_2 blown into the furnace (3-4) Conditions during final stages of the blow are highly favourable for dephophorization.

These conditions include

- A low rate of decarburisation leading to high dissolved O_2 Concentration
- A highly basic slag which lowers γ P_2O_5 favours the oxidation of Phosphorous from the metal to the slag.
- Increased liquid slag mass
- High FeO concentration in the slag

Experimental: For this study Medium Carbon Steel is produced in 100Kg Air Induction furnace of 800V power supply, 50-100KW 2000KHz. frequency using a billet size of 40Kg low carbon steel Refractory lining is made up of MgO, Fluxes used were iron ore, calcium oxide (commercial grade) aluminium oxide and magnesium oxide. Amount of flux added was varied along with slag basicity during several experiments.

Table 1. Composition of steel formed

Element	C	Si	Mn	P	S	Al
Weight%	0.017	0.27	0.89	0.02	0.02	0.03

Table 2. Laboratory and commercial grade oxides like CaO, MgO, FeO, SiO2 are purchased from market and were mixed manually in the following combination

Heat No	CaO	SiO2	FeO	MgO	Al2O3	MnO	Basicity
1	57.8	19.3	15	5	2	1	3
2	46.5	15.5	25	10	2	1	3
3	48.75	16.25	20	10	4	1	3

Amount of slag is added to the melt as a thumb rule of 50Kg slag per ton of steel, During melting 2Kg of slag is used as the sample size was 40Kg. After manual mixing of the slag was heated at 1000ºC for 2 Hrs in muffle furnace shown in Figure 4.

Slag samples are collected by dipping as clean steel rod rotating it in the slag phase. Liquid steel tapped into permanent ingot mould of 25Kg section which was preheated upto 400-500ºC in a Muffle furnace.

Figure4 Muffle Furnace: Both the collected metal and slag samples were analyzed. Optical emission spectrometer (ARL 3460) was used for analyzing metal samples whereas slag samples were analyzed using (XRF PW 2400) . The metal samples were taken out from metal mould and the surface on which the sparks were to be made was machined. Metal samples were polished using aluminium oxide paper 60 grade To ensure homogenity sparking were carried out at four different points in Ar atmosphere. and then the average result was taken.

Calculations

Slag system used here for dephosphorization consist of the following ingredients CaO-Al2O3-FeO-MgO

Slag basicity=%CaO/.%SiO$_2$

Degree of dephophorization in the melt before solidification=[(Pi-Pf)/Pi]x100

Pi=initial phophorous

Pf=final phosphorous

From the results it can be observed that degree of dephosphorization varies from 10% to high as 60% for various heat. FeO content in the slag is needed to be 15-35% for effective dephosphorization at the lowest possible temperature.

To study the effect of FeO on Dephosphorization the amount of FeO was varied in input slag chemistry by keeping other oxides constant like MgO, Al$_2$O$_3$ and Basicity as shown in table No.5 given below

The relation between FeO content in slag and dephosphorisation (%) can be plotted in Figure 5

RESULTS AND DISCUSION

The results show chemical analysis of metal samples. From the data it can be observed that degree of dephosphorization varies from 10% to as high as 60 % for various heats. FeO content in the slag is needed to be 15–35 % for effective dephosphorization. Another very important condition for dephosphorization is lowest possible temperature. In primary steel making, oxygen is used as an agent for oxidation of dissolved impurities like C, Si, Mn and P. The process is also known as oxygen steelmaking. On the other hand, in induction furnace steel making, no direct oxygen is introduced in the bath. The impurities are oxidized by introducing FeO in the bath. Thus, presence of FeO is important as it corresponds to oxygen potential of the slag. Removal of phosphorous takes place by oxidation. The product, phosphorous pentoxide is being held by basic constituents, like CaO, present in the slag. In steel making processes basicity of the slag is maintained by addition of calcined lime. The reaction may be given by,

$$[P] + \frac{5}{2}[O] + \frac{3}{2}(O^{2-}) \rightarrow (PO_4^{3-})$$
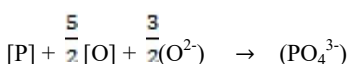
The results for metal samples are given in Table 5 respectively. To study the effect of FeO on Dephosphorization, the amount of FeO was varied in input slag chemistry by keeping other oxides constant like MgO, Al$_2$O$_3$ and Basicity as shown in table no 5 below:

By using table no 6 a relation between FeO content in slag and dephosphorization (%) can be ploted in terms of a histogram as shown in figure 5 Below:

By using table no 7 a relation between FeO content in slag and dephosphorization (%) can be ploted in terms of a histogram as shown in figure 6 Below:
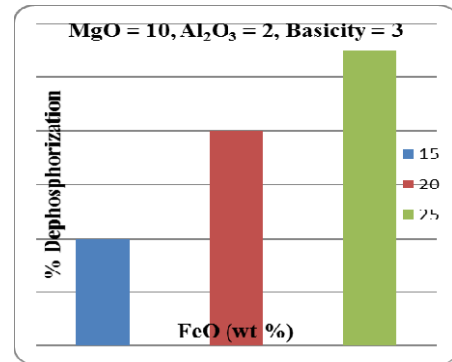

Figure 5. Showing effect of FeO variation by keeping MgO at 15(wt %) on degree or percentage of dephosphorization

By using table no 8 a relation between FeO content in slag and dephosphorization (%) can be ploted in terms of a histogram as shown in figure 8 Below:
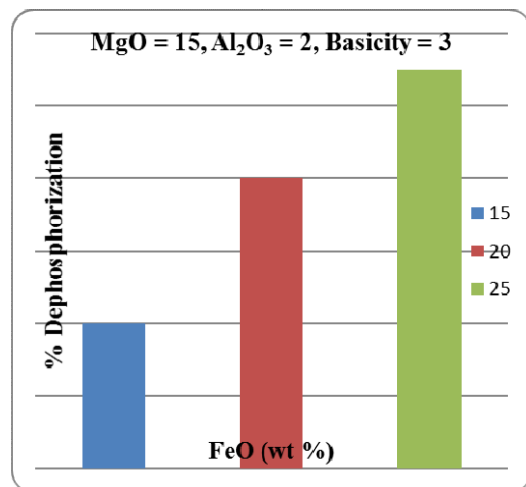

Figure 6. Showing effect of FeO variation by keeping MgO at 10(wt %) on degree or percentage

The dephosphorization ratio increases with increase in FeO content of slag upto an optimum value of FeO at all basicities further increase in FeO beyond that the dephosphorization decreases. For a given basicity of slag as FeO content of slag increases oxidizing power of slag increases and phosphorous oxidation will be favored because CaO of slag decreases the activity of P$_2$O$_5$ by forming a stable compound. Beyond the optimum value in slag FeO replaces CaO and may either combine with CaO or with P$_2$O$_5$. FeO is a weak base compared with CaO as a result of which the dephosphorization ratio decreases. With addition of FeO beyond an optimum value the maximum dephosphorization ratio increases with increase in the basicity of slag. Higher basicity requires high amount of CaO dissolved in slag, any undissolved CaO will not be effective for dephosphorization. Optimum value of FeO is more or less independent of the basicity of slag.

Table 3. Shows the metal sample composition after analysis and also shows the percentage or degree of dephosphorization

Heat No	C	Si	Mn	P	S	Al	% Dephosphorization
1	0.13	Traces	0.25	0.016	0.01	0.113	20
2	0.018	Traces	0.1	0.009	0.011	0.748	55
3	0.031	Traces	0.17	0.16	0.018	0.33	20

Table 4. Showing variation in degree of dephosphorization on varying FeO by keeping MgO at 5(wt%)

Heat No	FeO	MgO	Al2O3	Basicity	De-P(%)
1	15	5	2	3	20
2	20	5	2	3	60
3	25	5	2	3	55

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Table 5. Shows the metal samples composition after analysis and also shows the percentage or degree of dephosphorization.

Heat no	C	Si	Mn	P	S	Al	De-P (%)
1	0.13	Traces	0.35	0.016	0.01	0.113	20
2	0.12	0.017	0.27	0.02	0.016	0.035	10
3	0.11	Traces	0.069	0.008	0.012	0.017	60
4	0.032	Traces	0.1	0.009	0.012	0.043	55
5	0.021	Traces	0.2	0.016	0.02	0.178	20
6	0.056	Traces	0.183	0.012	0.016	0.192	40
7	0.018	Traces	0.1	0.009	0.011	0.748	55
8	0.037	0.003	0.32	0.018	0.013	0.58	10
9	0.047	traces	0.2	0.013	0.01	0.43	35
10	0.024	0.01	0.21	0.016	0.016	1.32	20
11	0.051	0.001	0.14	0.01	0.012	0.19	50
12	0.046	0.001	0.1	0.01	0.01	0.24	50
13	0.054	traces	0.12	0.011	0.01	0.04	45
14	0.04	0.0014	0.17	0.009	0.009	0.5	50
15	0.031	0.001	0.17	0.16	0.018	0.33	20

Table 6. Showing variation in degree of dephosphorization on varying FeO by keeping MgO at 5(wt %).

Heat no	FeO	MgO	Al_2O_3	Basicity	De-P (%)
1	15	5	2	3	20
3	20	5	2	3	60
4	25	5	2	3	55

Heat no	FeO	MgO	Al_2O_3	Basicity	De-P (%)
5	15	10	2	3	20
6	20	10	2	3	40
7	25	10	2	3	55

Table 7. Showing variation in degree of dephosphorization on varying FeO by keeping MgO at 15(wt %).

Heat no	FeO	MgO	Al_2O_3	Basicity	De-P (%)
8	15	15	2	3	10
9	20	15	2	3	35
10	25	15	2	3	20

Table 8. Showing variation in degree of dephosphorization on varying MgO.

Heat No	MgO	FeO	Al_2O_3	Basicity	De-P(%)
1	5	15	2	3	20
5	10	15	2	3	20
8	15	15	2	3	10

Table 9. Showing variation in degree of dephosphorization on varying Al_2O_3

Heat no	MgO	FeO	Al_2O_3	Basicity	De-P (%)
14	10	20	0	3	50
6	10	20	2	3	40
15	10	20	4	3	20

The effect of MgO on dephosphorization, the amount of MgO was varied in input slag chemistry by keeping other oxides constant like FeO, Al$_2$O$_3$ and Basicity as shown in table no 9 below:

By using table no 9 a relation between MgO content in slag and % dephosphorization can be ploted in terms of a histogram as shown in figure 8 Below:
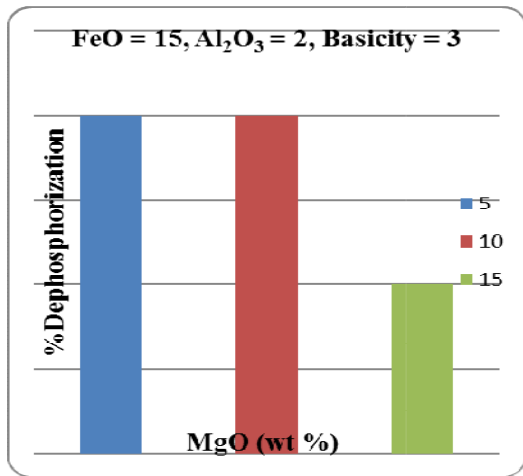

Figure 7. Showing effect of MgO variation on degree or percentage of dephosphorization

Increase in MgO has negative impact on phosphorous removal similarly as studied during literature survey. Rate of dephosphorization is mainly controlled by mass transfer in the slag. Addition of MgO may increase the melting point and viscosity of the slag which decreases the kinetic conditions of dephosphorization. Also decrease the activity of CaO and FeO in slag, leading to lowering the phosphorous distribution

ratio Lp = $\dfrac{(wt\% P2O5)}{(wt\% P)}$, between slag and molten steel.

The effect of Al$_2$O$_3$ on Dephosphorization, the amount Al$_2$O$_3$ of was varied in input slag chemistry by keeping other oxides constant like FeO, MgO and Basicity as shown in table no 10 below:
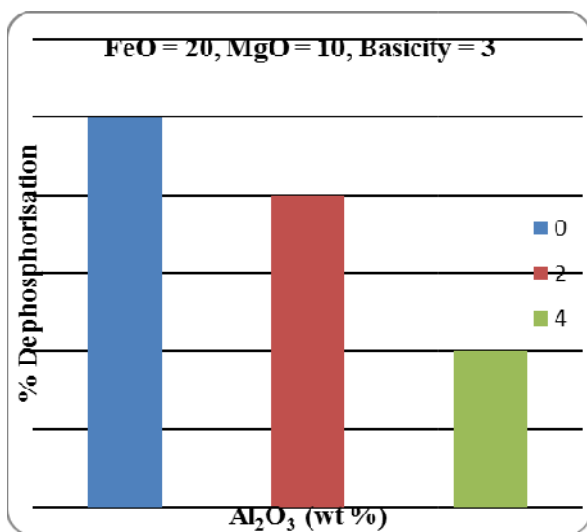

Figure 8. Showing effect of Al$_2$O$_3$ variation on degree or percentage of dephosphorization

By using table no 10 a relation between Al$_2$O$_3$ content in slag and % dephosphorization can be ploted in terms of a histogram as shown in figure 10 Below:

Increase in Al$_2$O$_3$ has negative impact on phosphorous removal similarly as studied during literature survey. This is because SiO$_2$ in the melt was replaced by an equivalent amount of Al$_2$O$_3$. This resulted in a decrease in the solubility of MgO. Increase in Al$_2$O$_3$ decreases the viscosity of the melt which has negative impact on phosphorous removal. The effect of basicity on Dephosphorization, the basicity was varied in input slag chemistry by keeping other oxides constant like FeO, MgO and Al$_2$O$_3$ as shown in table no 9 below:

By using table no 11 a relation between slag basicity and % dephosphorization can be ploted in terms of a histogram as shown in figure 9 Below:
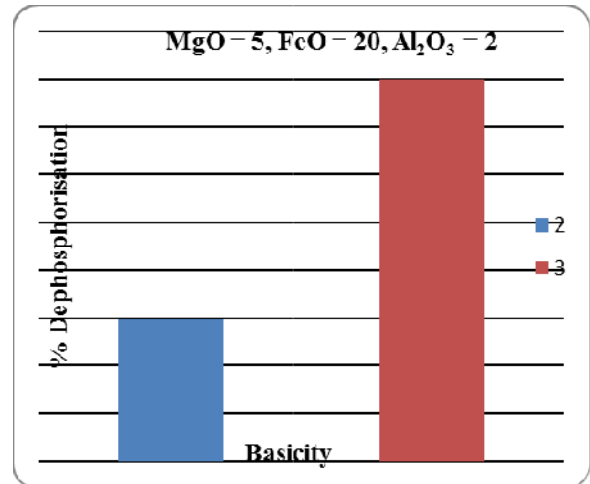

Figure 9. Showing effect of slag basicity on degree or percentage of dephosphorization

The dephosphorization increases with increase in slag basicity and becomes maximum approximately 3 further increase in basicity basicity beyond that has negative impact on phosphorous removal thats why basicity of slag was kept upto 3. Increase in basicity beyond 3 decreases the further increase in basicity viscosity of the melt which have has negative impact on phosphorous removal.

CONCLUSION

For a given basicity of slag as FeO content of slag increases oxidizing power of slag increases and phosphorous oxidation will be favored because CaO of slag decreases the activity of P$_2$O$_5$ by forming a stable compound. Beyond the optimum value in slag FeO replaces CaO and may either combine with CaO or with P$_2$O$_5$. FeO is a weak base compared with CaO as a result of which the dephosphorization ratio decreases. Rate of dephosphorization is mainly controlled by mass transfer in the slag. Addition of MgO may increase the melting point and viscosity of the slag which decreases the kinetic conditions of dephosphorization. Also decrease the activity of CaO and FeO in slag. Increase in Al$_2$O$_3$ decreases the viscosity of the melt which have has negative impact on phosphorous removal. The dephosphorization increases with increase in slag basicity and becomes maximum approximately 3 further increase in basicity beyond that has negative impact on phosphorous removal. The best conditions for phosphorous removal from liquid steel can be summarized as A high basic, lime rich slag. A satisfactory high level of oxidation of iron (FeO content). The lowest possible temperature. The lowest possible amount of undissolved free lime in slag.

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