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Effect of MgO and Al_2O_3 variations in oxygen steelmaking (BOF) slag on slag morphology and phosphorus distribution

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Operational data of BOF and the slag samples for different starting conditions of phosphorus (0.06–0.26 per cent P) and silicon content (0.3–1.2 per cent Si) of hot metal have been analysed. The contribution of parameters that are well known to affect phosphorus distribution at tap, like basicity, temperature, FeO content of slag, slag mass etc., is investigated through the models of ionic theory of slag, optical basicity, regular solution approach and molecular theory of slag. The best overall results are obtained by the model based on molecular theory of slag in which several operational parameters are also incorporated. The investigations of different slag samples, based on optical, SEM, EPMA and X-ray studies, reveal the effect of MgO and Al_2O_3 on slag morphology and phosphorus distribution in different phases. It is important to consider phosphorus distribution ratio in the solid and liquid part of slag. The solid part of slag, which is mostly dicalciumsilicate, can contain up to 5 per cent phosphorus. The phosphorus content of the liquid part of slag may depend upon the phosphorus content of hot metal or phosphorus load of slag. It is found that incorporation of effect of dicalciumsilicate in the model improves the accuracy of prediction. For better process control, the addition of iron ore towards the end of blow must be avoided while treating high phosphorus hot metal or during the production of ultra low phosphorus steels.

Keywords: steelmaking, BOF, phosphorus distribution, slag morphology, MgO, Al_2O_3, dicalciumsilicate, process control, models

Introduction

Production of low phosphorus steel (0.06–0.015 per cent phosphorus at tap) in a single blow in the BOF, especially when the phosphorus content in hot metal is high (above 0.2 per cent) and silicon content is also variable (0.6–1.2 per cent Si) is a challenging problem. To improve the control of phosphorus it is necessary to employ a prediction model. Some typical models[1-9] are summarized in Table I.

In (BOF) oxygen steelmaking it is difficult to predict the distribution of phosphorus between slag and metal by direct application of models (listed in Table I), even though a pseudo-steady state is usually attained between slag and metal towards the end of the blow. This is because under practical (shop-floor) conditions, besides the slag composition and temperature, the phosphorus distribution is found to depend also upon other parameters, such as slag mass, turndown carbon, initial phosphorus content of metal, intensity of bottom stirring, lance height, oxygen flow rate, addition scheme and timing of addition of fluxes and iron ore. Therefore, each plant usually develops its own blowing practice and, on the basis of analysis of plant data, adapts a suitable model for control and prediction of phosphorus at tap. The selection of a control model is not a simple task.

It is now well established that dicalciumsilicate (C_2S) has greater solubility for phosphorus than the liquid part of slag. While taking a decision, cost considerations of various kinds also step in, depending upon the quality of steel to be made. For example, the phosphorus distribution can be improved by increasing the basicity of slag but, then, lime is expensive and it also changes the morphology of the slag, including the percentage of dicalciumsilicate (C_2S) in the final slag, which affects the physical properties of the slag.

It is to be noted that the models listed in Table I do not explicitly take into account the effect of precipitation and/or dissolution of C_2S on phosphorus distribution. In the present work the objective is to study different models of prediction of phosphorus distribution and understand the effect of MgO and Al_2O_3 on phosphorus distribution and slag morphology for a wide range of operating practices at different steel plants. Morphological investigations (optical, SEM, EPMA and XRD) of the slag samples collected from different plants have been carried out, both for low and high MgO slag practice (0.2–11 per cent MgO) and low and high phosphorus (0.06–0.26 per cent P) hot metal. Methodologies of producing low phosphorus steel, especially from high phosphorus hot metal, can be evolved on the basis of this study.

Table I Some model equations for prediction of phosphorus distribution

Turkdogan's model[2]	$\log\frac{(P)}{[P]} = 5.9x\log(CaO) + 2.5x\log(FeO) + 0.5x\log(P_2O_5) + 10.6$
Healy's model[3]	$\log\frac{(P)}{[P]} = \frac{22350}{T} + 0.08\times(CaO) + 2.5\times\log(Fe_t) - 16$
Optical basicity model[5,6]	$\log C_P = -18184 + 435.84\Lambda - 22.35\Lambda^2 + 22390(\Lambda/T) - 0.06257 \times FeO - 0.04256 \times MnO + 0.359 \times (P_2O_5)^{0..3}$
Suito's model[7]	$\log\frac{(P)}{[P]x(Fe_t)^{\frac{5}{2}}} = 0.720x[(CaO) + 0.3(MgO) + 0.6(P_2O_5 + MnO)] + \frac{11570}{T} - 10.520$
Suito and Inoue's model[7]	$\text{Log}(K_P) = 0.145 \times [(CaO) + 0.3(MgO) + 0.6(MnO)] + (22810/T) - 20.56$
Molecular slag model[1]	$\log\frac{(\%P_2O_5)}{[\%P]^2(\%Fe)^5} = 7.04\log(\%CaO) + \frac{9922}{T_c + 17.8} - 20.2$
Quadratic formalism model[9]	$RT\ln a_{P2O5}(l) = RT\ln a_{P2O5(RS)} + 52720 - 230.706T$

Case studies chosen for phosphorus prediction

Four different case studies, covering a wide range of metal and slag composition, are briefly described here. The plant data for case study-1 pertains to low phosphorus (<0.07 per cent P) hot metal and low MgO (<2 per cent MgO) slag practice. The plant data for case study-2 is for high initial phosphorus (0.2–0.26 per cent P) hot metal and low MgO (<2 per cent MgO) slag practice. The plant data for case study-3 is for low initial phosphorus (<0.07 per cent) hot metal and high MgO slag (7–11per cent MgO) practice. In the case study-4, data from 4 steel plants is analysed to study the effect of MgO and Al_2O_3 on slag morphology at tap and the distribution of phosphorus in different phases, including the precipitation and dissolution of dicalciumsilicate.

Plant data for case study-1: low initial phosphorus and low MgO in slag

In case study-1, for a 300 ton BOF with bottom stirring, a sublance is used for in-blow measurements. The data collected is regrouped on the basis of additions of ore during the second part of the blow (Ore_2) and raw dolomite during the second part of the blow ($Rdolo_2$). The data set-1 (60 heats) contains those heats in which no raw dolomite is added during the second part of the blow but ore has been added during the second part of the blow. The data set-2 (110 heats) contains those heats in which neither ore nor raw dolomite has been added during the second part of the blow. Data set-3 (112 heats) contains those heats in which raw dolomite has been added but ore has not been added during the second part of the blow. Average analysis of slag is: 56 per cent CaO, 17 per cent SiO_2, 1.2 per cent P_2O_5, 3 per cent MnO, 3.5 per cent (max) MgO and 20 per cent FeO. Average analysis of metal is 0.011 per cent P, 0.05 per cent C, and 0.15 per cent Mn in the temperature range of 1873–1973 K. The hot metal contains approximately 0.06 per cent P.

Plant data for case study-2: high initial phosphorus and low MgO in slag

In case study-2, for a 140 ton BOF with bottom stirring, data of three separate converters, vessel 1 (402 heats), vessel 2 (380 heats) and vessel 3 (270 heats), have been analysed. Filtering is done to eliminate bad/abnormal data, or data which violate the usual process operational restrictions. Average slag analysis is 56 per cent CaO, 17 per cent SiO_2, 3.6 per cent P_2O_5, 0.6 per cent MnO, 0.9 per cent MgO, and 22 per cent FeO. Liquid steel contains 0.013–0.023 per cent P, approximately 0.04 per cent C and 0.028 per cent Mn in the temperature range 1883–2023 K. The hot metal contains 0.2–0.26 per cent P and 0.5–1.2 per cent Si.

Plant data for case study-3: low initial phosphorus and high MgO in slag

In case study-3, for a 300 ton BOF with bottom stirring, a sublance is used for in blow measurements. This data set is classified into three separate groups, as already explained, on the basis of additions of ore during second blow (Ore_2) and raw dolomite during second blow ($Rdolo_2$). The only difference between case study 1 and case study 3 is that in the latter the slag contains 8–10.5 per cent MgO.

Case study-4: slag morphology and distribution of phosphorus in different phases

Slag samples from four steel plants have been collected and analysed. Two of these plants (both 140 ton BOF) have a high MgO slag practice, one with bottom stirring facility and the other without. The third plant (300 ton BOF) has bottom stirring but experiments were conducted with two different operating practices (with and without bauxite additions). The fourth plant has 300 ton BOF vessels with a high MgO slag practice but with low phosphorus hot metal. The purpose was to see the combined effect of MgO and Al_2O_3 on the slag morphology and phosphorus distribution between steel and slag, as well as the effect of C_2S precipitation in slags on this phosphorus distribution.

Testing and tuning of 'conventional' phosphorus prediction models

For the data pertaining to the case studies-1,-2, and -3, four different models (listed in Table I) were tested: Healy's model, the optical basicity model, the regular solution model, and the molecular theory model. The term 'conventional' simply means that no separate role is assigned in the model to the existence of C_2S as a separate phase and, irrespective of its composition and temperature, the slag is assumed to be a single homogenous liquid phase.

The various parameters incorporated into the stepwise multiple linear regression analysis for tuning the four models were: steel tapping temperature (T_2), lime content of the slag (log CaO), iron content of the slag (log Fe), steel carbon content at tap (C_2), slag mass (SVO), basicity, ore added in the first part of the blow, mass ratio of hot metal to scrap (HTR), lance height in the last part of the blow (Hl_2), ore added in the second part of the blow (Ore_2), and raw dolomite added in the second part of the blow ($Rdolo_2$). It was found that out of the four models, when compared on

Table II: Results of application of molecular theory model to case study-1,2,3; R is product moment correlation coefficient and σ is standard error of estimate ($\sigma_{y,x}$) for actual versus predicted phosphorus in steel.

Data set	Equation	R	σ
Set-1 for case study-1	$\log\frac{(P)}{[P]^2}=\frac{29641.7}{(T_2-255.22)}+0.0043\times HL_2-18.37\times C_2$ $+4.75\times\log(CaO)+1.9\times10^{-5}\times SVO+0.00017\times Ore_2-22.9$	0.74 0.8*	0.0021
Set-2 for case study-1	$\log\frac{(P)}{[P]^2}=\frac{22986.1}{(T_2-255.22)}-20.37\times C_2+2.6\times\log(CaO)$ $+9.29\times10^{-6}\times SVO-13.79$	0.67	0.0023
Set-3 for case study-1	$\log\frac{(P)}{[P]^2}=\frac{30914.95}{(T_2-255.22)}+0.033\times HL_2-14.96\times C_2$ $+1.61\times\log(CaO)+1.38\times10^{-5}\times SVO+0.029\times HTR-18.03$	0.81	0.0035
Vessel-1 for case study-2	$\log\frac{(P)}{[P]^2}=\frac{11953.49}{(T_2-255.22)}+0.0082\times\log(CaO)$ $+0.041\times SVO+1.57\times\log(Fe)-6.09$	0.79	0.0027
Vessel-2 for case study-2	$\log\frac{(P)}{[P]^2}=\frac{11009.93}{(T_2-255.22)}+2.95\times\log(CaO)$ $+0.0041\times SVO+0.74\times\log(Fe)-8.6$	0.66	0.0016
Vessel-3 for case study-2	$\log\frac{(P)}{[P]^2}=\frac{9210.33}{(T_2-255.22)}+1.8\times C_2+0.01\times ORE-1.5$	0.62	0.0015
Set-1 for case study-3	$\log\frac{(P)}{[P]^2}=\frac{25610.1}{(T_2-255.22)}+1.74\times C_2+.0036\times SVO$ $+0.074\times Basicity-11.89$	0.69 0.75*	0.0025
Set-2 for case study-3	$\log\frac{(P)}{[P]^2}=\frac{20178.01}{(T_2-255.22)}+1.097\times\log(CaO)-10.04$	0.59	0.0019
Set-3 for case study-3	$\log\frac{(P)}{[P]^2}=\frac{27718.3}{(T_2-255.22)_2}+4.35\times C_2+0.58\times\log(CaO)$ $+5.07\times10^{-5}\times Rdolo_2-13.96$	0.76	0.0017

Note: The R values marked with '*' correspond to the case when C_2S is incorporated in the regression model Ore_2 and $Rdolo_2$ are, respectively, ore and raw dolomite added after sublance measurement; SVO is slag mass; HTR is the mass ratio of hot metal to scrap in charge; C_2 is carbon content at tapping; HL_2 is the lance height in the blowing period after sublance measurement; T_2 is temperature at tapping in K; ORE is total ore added in a blow; log (Fe): the Fe is % total iron in slag; (P) and [P], are, respectively, per cent phosphorus in slag and metal.

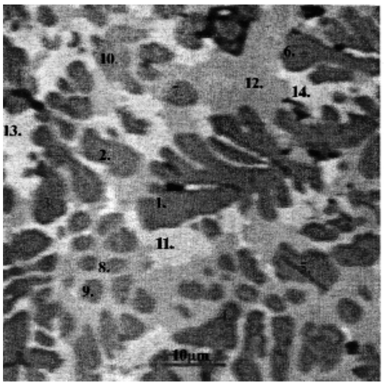
the basis of correlation coefficient and standard error of prediction of actual versus predicted phosphorus, the molecular slag model gave the best overall results (details given elsewhere[10]).

As anticipated from thermodynamic considerations, the signs of the coefficients of all variables, except for the case of carbon, are positive. The coefficient of steel carbon content at tap (C_2) shows both positive and negative values (Table II). For the case of low MgO slags, the coefficient of C_2 is negative (expected from thermodynamic considerations), but for the case of high MgO slags it is positive. The positive coefficient can be partly attributed to the viscosity of high MgO slags. A higher viscosity of the slag would hinder the reversion of phosphorus from slag to metal, perhaps due to a lower mass transfer rate in the slag. Also, a higher carbon content of steel at tap implies shorter oxygen blowing times and therefore less time available for reversion of phosphorus from slag to metal. Thus the effect of steel carbon content may change from positive to negative due to kinetic reasons. This is why the phosphorus distribution at tap is so sensitive to the slag condition (fluidity and foaminess of slag).

The results (Table II) show that the tapping temperature has the largest influence on phosphorus distribution and that the selection of parameters (statistically significant ones, based on ‘t’ test) varies from one case to another.

Effect of MgO and Al_2O_3 on slag morphology and phosphorus distribution (case study-4)

The MgO and Al_2O_3 contents of slag affect the slag morphology, the proportion of solid and liquid slag, and the distribution of phosphorus in different phases, specially the phosphorus content of dicalciumsilicate under different operating conditions. Slag samples from different plants (Table III) were investigated as follows.



N	Phase	P_2O_5
1	C_2S	5.00
2	C_2S	4.52
3	C_2S	4.2
4	C_2S	4.50
5	C_2S	4.51
6	C_2S	4.54
7	C_2S	4.32
8	C_2S	3.91
9	C_2S	4.48
1	C_2S	4.63
1	Wustite	-
1	Residual	-
1	Wustite	-
1	Wustite	-

Figure 1. Micrograph of high MgO, low Al_2O_3 slag, low phosphorus hot metal; P_2O_2 content of different phases

High MgO, low Al_2O_3 slag and low phosphorus hot metal

The micrograph in Figure 1 pertains to the slag containing CaO (42 per cent), MgO (8 per cent), FeO (22 per cent), Al_2O_3 (1.4 per cent), with a basicity of 3.4 and steel tapping temperature is ~1670°C. The hot metal contains low phosphorus (<0.07 per cent P). The X-Ray diffraction analysis shows that the mineral phases present in the sample are $2CaO.Fe_2O_3$, $2CaO.SiO_2$ and Ca-Fe-Al ferrite and wustite solid solution. EPMA shows that the phosphorus content of the C_2S grains may vary from 4.2–5 per cent, depending upon the size of the grains. The large C_2S grains contain 5 per cent phosphorus and the smaller grains contain 4.2 per cent phosphorus. Whether this phosphorus is present as dissolved phosphorus or as fractions of $Ca_5(PO_4)_2(SiO_4)_6$ is yet to be determined.

Table III Details of slag composition collected from different steel plants

Plant	Converter specification and type of slag	Average bulk slag composition	Microstructure
1	High MgO (8 %), low Al_2O_3 slag and low phosphorus (<0.07 %), 0.4 % Si in hot metal Bottom stirring, 300 ton converter	CaO (42 %), MgO (8 %), FeO (22 %), Al_2O_3 (1.4 %), Basicity 3.4, 1670 °C	Figure 1
2	Low MgO (0.9 %), low Al_2O_3 slag and high phosphorus (0.2-0.26), 0.8 % Si in hot metal Bottom stirring, 140 ton converter	CaO (53 %), MgO (0.9 %), FeO (24 %), Al_2O_3 (0.9 %), Basicity 3.9, 1700 °C	Figure 2
3	High MgO (7.5%), low Al_2O_3 (1 %) slag, medium phosphorus (0.12 %), 0.5 % Si in hot metal. No bottom stirring, 140 ton converter	FeO (20 %), MgO (7.%), Al_2O_3 (1%), Basicity 3.4, 1660 °C	Figure 3
4	Case-A High MgO (10 %), low Al_2O_3 (<2%) slag and medium phosphorus (0.12%), 0.6 % Si in hot metal. Bottom stirring, 300 ton converter	CaO (47 %), FeO (18 %), MgO (10 %), Al_2O_3 (2%), Basicity 3, 1680 °C	Figure 4
	Case-B High MgO (10 %), high Al_2O_3 (4 %) slag and medium phosphorus (0.12%), 0.6 % Si in hot metal. Bottom stirring, 300 ton converter	CaO (47 %), FeO (18 %), MgO (10 %), Al_2O_3 (4 %), Basicity 3.2, 1680 °C	Figure 5

Almost no phosphorus is observed in wustite solid solution. No evidence of tricalciumsilicate (C_3S) is seen in the sample (Figure 1).

Low MgO, low Al_2O_3 slag and high phosphorus hot metal

Micrograph in Figure 2 is obtained for slag containing CaO (53 per cent), FeO (24 per cent), Al_2O_3 (0.9 per cent), and low MgO (~0.9 per cent) for a 140 ton BOF. The hot metal contains high phosphorus (0.2 per cent), and the slag basicity is ~ 3.9 at a tapping temperature of ~1700ºC. The SEM/EPMA analysis of the slag sample shows that the grey grains (marked as 1) have only an approximate composition of C_2S because the molar ratio of CaO to SiO_2 varies from one grain to another and is generally higher than the stoichiometric ratio of 2. The white grains (marked as 2) are wustite solid solution and small dark (black) grains (marked as 3 in the micrograph) are $2CaO.Fe_2O_3/CaO.Fe_2O_3$/calcium-aluminium-ferrite. A typical spot analysis (mass per cent) of different phases in the sample is as follows:

Phase	Mg	Al	Si	P	S	Ca	Ti	Mn	Fe
Ca-Fe-Al	0.00	1.74	0.78	0.20	0.31	42.01	5.28	0.55	49.12
Wustite solid solution	3.04	0.09	0.28	0.32	0.58	5.55	0.00	4.90	85.24
C_2S	0.00	0.17	15.69	4.76	0.52	70.21	1.03	.030	7.33
C_2S	0.00	0.21	17.47	4.55	0.47	71.73	1.18	0.21	4.17

It can be seen from the spot analyses that the C_2S contains 4.5–4.75 per cent phosphorus, whereas wustite solid solution contains 0.32 per cent P. Actually, the phosphorus content varies from one location to another and the ratio of phosphorus in the C_2S to phosphorus in the wustite solid solution varies in the range of 15:1 to 25:1. The content of MgO also varies from one location to another; at some locations the MgO content is as much as 3 per cent, while at others it is absent. No tricalciumsilicate (C_3S) is seen in the sample (Figure 2).

High MgO, low Al_2O_3 slag and medium phosphorus hot metal, 140 ton vessel, no bottom stirring

The micrograph in Figure 3 is obtained for FeO (20 per cent), MgO (7.5 per cent), Al_2O_3 (1 per cent), and basicity 3.4 when the phosphorus content of hot metal is (0.12 per cent P) and slag basicity is 3.5 at 1660ºC. The EPMA analysis of the slag sample shows that the grains (marked as 1) are C_2S and the white grains (marked as 2) are wustite solid solution. The ratio of MgO in the wustite solid solution to the MgO in C_2S is approximately 2:1. The ratio of phosphorus in the C_2S to the phosphorus in the wustite solid solution is of the order of 17:1.

High MgO, low Al_2O_3 slag and medium phosphorus hot metal, 300 ton vessel with bottom stirring

The micrograph in Figure 4 is obtained for CaO (47 per cent), FeO (18 per cent), MgO (10 per cent), basicity 3, Al_2O_3 (~2 per cent) and slag basicity is ~3.2 at ~1680ºC. The phosphorus content of the hot metal is 0.12 per cent.

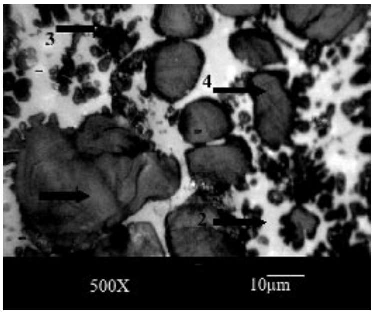


Figure 2. Optical micrograph of (high phoshorus (0.2%) hot metal) low (0.9%) MgO slag. Basicity 3.9. Steel tapping temperature 1700ºC (Plant-2)
Point-1 Dicalciumsilicate, Point-2 Wustite solid solution
Point-3 Calcium-aluminium-ferrite, Point-4 Dicalciumsilicate

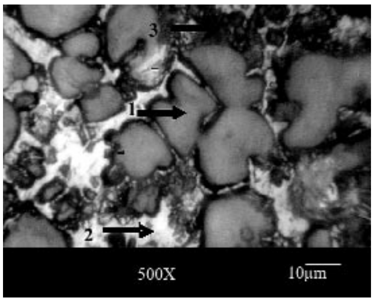


Figure 3. Optical micrograph of (medium phoshorus (0.15%) hot metal) high MgO (7.5%) low Al_2O_3 (1%) slag. Basicity 3.4. Steel tapping temperature 1660ºC (Plant-3)
Point-1 Dicalciumsilicate, Point-2 Wustite solid solution
Point-3 Calcium-aluminium-ferrite

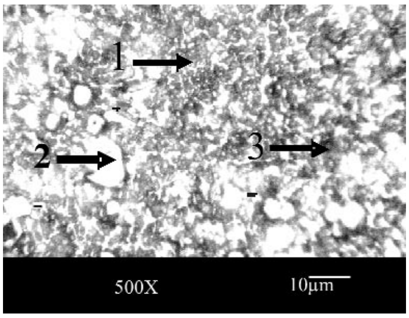


Figure 4. Optical micrograph of (high phosphorus (0.15–0.2%) hot metal) high MgO (10%) and low Al_2O_3 (<2%) slag. Basicity 3. Steel tapping temperature 1680ºC (Plant-4 case-B)
Point-1 Dicalciumsilicate, Point-2 Wustite solid solution
Point-3 Calcium-aluminium-ferrite/Calcium-ferrite

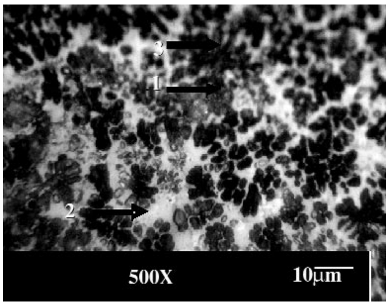


Figure 5. Optical micrograph of (high phoshorus (0.15–0.2%) hot metal) high MgO (10%) low Al_2O_3 (4%) slag. Basicity 3. Steel tapping temperature 1680ºC (Plant-4 case-A)
Point-1 Dicalciumsilicate, Point-2 Wustite solid solution
Point-3 Calcium-aluminium-ferrite/Calcium-ferrite

High MgO, high Al_2O_3 slag and medium phosphorus hot metal

The micrograph in Figure 5 is obtained for CaO (47 per cent), FeO (18 per cent), MgO (10 per cent), Al_2O_3 (4 per cent), when the phosphorus content of hot metal is (0.15 per cent P) and the slag basicity is ~3.2 at ~1680ºC.

The optical micrograph of the low Al_2O_3 (Figure 4) slag sample shows a higher volume fraction C_2S and a smaller amount of calcium-aluminium-ferrite, as compared to the high Al_2O_3 slag (Figure 5).

Discussion

The following general observations can be made on the basis of optical, SEM, EPMA and X-Ray diffraction investigations regarding the effects of MgO and Al_2O_3, size of the C_2S grains and phosphorus content of hot metal on phosphorus distribution:

(i) C_2S is stabilized by higher slag basicity, lower steel tap temperature and higher phosphorus content of hot metal.
(ii) The presence of MgO in the slag reduces the size of the C_2S grains as well as the phosphorus content of C_2S.
(iii) The presence of Al_2O_3 stabilizes calcium-aluminium-ferrite and reduces both the amount and the crystal size of C_2S and also its phosphorus content.

According to the ionic theory of slags, in a slag containing more than 7 per cent MgO, primarily the MgO containing wustite tends to become solid at steelmaking temperatures. Wustite is first precipitated and the fluid slag becomes depleted in mobile cations before the PO_4^{3-} binding dicalciumsilicate is formed. Due to this, both the amount of C_2S and the phosphorus content of C_2S are reduced. Thus, dephosphorization is hindered.

In converter slags with high alumina contents (say 4 per cent Al_2O_3), the aluminium-binding anion complexes, together with $Fe_2O_5^{4-}$ and Ca^{2+}, initially form calcium-aluminium-ferrite on solidification and the PO_4^{3-} anion complexes are not incorporated in its crystallites. The formation of dicalciumsilicate is also hindered because in the presence of Al_2O_3 the calcium-aluminium-ferrite forms in preference to C_2S. If aluminium is present as AlO_4^{5-} anion complex in the fluid converter slag, the tetrahedrons SiO_4^{4-}, AlO_4^{5-} and PO_4^{3-}, form simple chains by polymerization. A partial substitution of SiO_4^{4-} by AlO_4^{5-} or PO_4^{3-} may occur as a result of ion isomorphism. On solidification, the tetrahedrons of AlO_4^{5-} and PO_4^{3-} are incorporated in the crystallites of dicalciumsilicate by partial substitution of SiO_4^{4-} ions. Addition of bauxite to converter slags causes a surplus of AlO_4^{5-} anion complexes. If neutralization is taken into consideration, the incorporation of PO_4^{3-} anion complexes in dicalciumsilicate crystallites is suppressed due to the surplus of AlO_4^{5-} anion complexes. Thus, in the presence of Al_2O_3 in the slag dephosphorization is hindered.

The results of EPMA analysis for the case of low phosphorus hot metal show that the percentage of P_2O_5 in the wustite solid solution is negligible but in the case of high phosphorus hot metal the ratio of P_2O_5 dissolved in dicalciumsilicate and wustite solid solution may vary. In fact it is possible to manipulate or control the phosphorus content of steel at end point simply by modifying the addition patterns of lime stone/raw dolomite and also by adjusting the bottom stirring rate[11]. The formation and dissolution of dicalciumsilicate is, therefore, an important parameter for the control of dephosphorization in the case of high phosphorus hot metal.

The percentage of C_2S in the slag can be calculated (with some approximations, viz. constant MgO and Al_2O_3 content of slag, complete mixing, pseudo-equilibrium, etc.) for an overall slag composition by reducing the bulk slag composition to a pseudo-ternary CaO'-FeO'-SiO_2' slag system. At a given tapping temperature, the slag may be either liquid or, alternatively, consist of two parts, namely C_2S and liquid slag. The calculated basicity of this liquid slag will be different from the bulk slag (because part of the SiO_2 will be locked up in the solid C_2S). The solid part of slag can be further assumed to contain a different (but fixed) percentage of P_2O_5. The P_2O_5 content of the liquid part of the slag can be calculated by mass balance. In principle, the molecular theory of slag can be applied to the liquid part of slag to predict the phosphorus distribution. The procedure adopted to do regression analysis and then to calculate the phosphorus content of steel is explained in detail elsewhere[10].

Based on this approach, when C_2S is incorporated as a parameter in the regression analysis, the best correlation coefficient (for actual versus predicted phosphorus in steel) is obtained, as shown in Figure 6, when the ratio of P_2O_5 (in C_2S and liquid slag) is assumed to be 5 or higher. The improvement obtained in the R-value, with respect to the results presented in Table II, is about 7–10 per cent. This indirectly confirms the role of precipitation and dissolution of C_2S in the case of high phosphorus hot metal.

Further, it is found with this procedure that (log Fe) is not selected as parameter in the regression equation. Shop-floor experience has also shown the poor efficacy of the addition of iron ore (in the late stages of blow) or high FeO content of slag on dephosphorization, particularly in the case of high phosphorus hot metal. Practical results[11] do confirm that iron ore additions must be avoided after 75 per cent of the blow is over, if the phosphorus content of hot metal is high or ultra low phosphorus steel is to be produced.

Conclusions

(1) Healy's model, the molecular slag model, the optical basicity model and the quadratic formalism model have been tested for 3 different case studies with different hot metal and slag compositions. It has been found that the molecular slag model, when adapted to a particular plant situation by incorporating operational parameters with the help of multiple linear regression, gives the best results in all the cases.

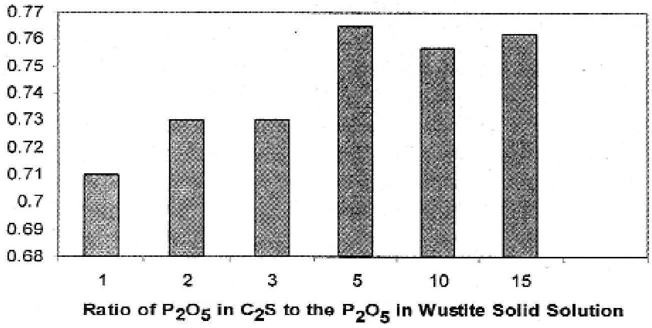


Figure 6. Improvement in correlation coefficient with various assumed ratios of P_2O_5 in C_2S and liquid slag

(2) The coefficient of the carbon content of steel at tapping is negative in the case of low phosphorus hot metal and low MgO slag practice but positive for a high MgO slag.

(3) Incorporation of C_2S as an additional parameter in the prediction model improves the correlation coefficient for the prediction of the phosphorus content of steel at tapping.

(4) Increase of the FeO content of the slag by iron ore addition towards the end of the blow may not be helpful and should be avoided.

(5) The solubility of phosphorus is much more in C_2S (4.2–5 %) than in wustite solid solution (0.32 per cent max). It may, however, vary depending on the phosphorus load of the slag or, alternatively, on the phosphorus content of hot metal.

(6) Both MgO and Al_2O_3 as slag components decrease the phosphorus distribution ratio between steel and slag. The slag morphology is also significantly altered by the presence of MgO and Al_2O_3 in the slag. The size of dicalciumsilicate grains as well as the dissolution of phosphorus in C_2S decrease if a slag contains higher levels of MgO. The presence of Al_2O_3 stabilizes calcium-aluminium-ferrite and reduces the amount of C_2S and also the phosphorus content of C_2S.

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