### Production of low Phosphorous Steel in Basic Oxygen Steelmaking Process

### Sources of Phosphorous Input

• Hot Metal

Iron Ore Recycled BOF Slag Coke

All Phosphorous entering into blast furnace goes to hot metal due to reducing conditions .

- Retained Slag
- Poor Quality Scrap

### Need for Low Phosphorous Steels

- Causes hot shortness and temper embrittlement,
- Ductility and strength goes down if phosphorous is very high
- Essential when want to have excellent mechanical properties (Ductility, Toughness and Strength)
- For special applications (Automobiles EDD Applications [P] < 0.010)</li>
- Increasing proportion of continious cast heats where high temperature at end point is not favouable for dephosphorisation.
- High phosphorous heats causes more breakouts in continious casting due to formation of low melting point film.

### Major Factors affecting Dephosphorisation

- Total Phosphorous Input
- Initial charge balance (Scrap/Hot Metal Ratio)
- Basisity
- Oxidation level of slag (FeO content)
- Temperature (Entire trajectory)
- Blowing Regime (Lance Height vs Flow rate)
- Flux (Lime-size, Reactivity) and Iron ore addition scheme
- Slag Foaming Emulsification
- Droplet generation trajectory and residence time

#### Reaction mechanism inside the Oxygen Steelmaking Converter



The LD - converter process showing different reaction zones

#### Slag evolution during blow



Evolution of bath composition during blow



Influence on temperature trajectory of melt due to scrap mix



Thermodynamics of Phosphorous distribution between slag and metal

$$2[P] + 5(FeO) = (P_2O_5) + 5Fe$$

$$K_{eq} = \frac{a_{P_2O_5}}{a_{FeO}^5 [\%P]^2} = \frac{(\%P_2O_5)}{(\text{FeO})^5 [\%P]^2}$$

$$=\frac{N_{P_2O_5}}{[\% P]^2 N_{FeO}^5} \bullet \frac{\gamma_{P_2O_5}}{\gamma_{FeO}^5}$$

$$[P] + \frac{5}{2}[O] + \frac{3}{2}(O^{-2}) = (PO_4^{-3})$$

$$K_{p} = \frac{a_{PO_{4}^{-3}}}{a_{P} * a_{O}^{5/2} * a_{O^{-2}}^{3/2}} = \frac{N_{PO_{4}^{-3}} \bullet \gamma_{PO_{4}^{-3}}}{f_{P} \bullet [\%P] \bullet f_{O}^{5/2} \bullet [\%O]^{5/2} \bullet N_{O^{-2}}^{3/2} \bullet \gamma_{O^{-2}}^{3/2}}$$

## Proposed Models to predict the Phosphorous distribution between slag and metal

#### 2.1 Balajiva's model

Balajıva et al<sup>(1)</sup> proposed a model for prediction of phosphorous partition is as follows;

$$\log \frac{(P)}{[P]} = 5.9 \times \log(CaO) + 2.5 \times \log(FeO) + 0.5 \times \log(P_2O_5) + 10.6 \qquad \dots \dots \dots \dots (2.1)$$

In the above model turndown temperature is not taken as a parameter. According to this model phosphorus partition essentially depends upon mass percent CaO, mass percent FeO and mass percent  $P_2O_5$  in slag.

#### 2.2 Turkdogan's model

Turkdogan<sup>(2)</sup> developed a correlation from plant data is as follows;

Where, [O] is mass percent oxygen in metal.

(CaO) is mass percent CaO in slag.

(MgO) is mass percent MgO in slag.

 $(CaF_2)$  is mass percent  $(CaF_2)$  in slag.

In the above model effect of MgO and  $CaF_2$  on phosphorous distribution is included as a parameter.

#### 2.4 Healy's model<sup>(3)</sup> based on ionic theory of slag:

Healy's model is essentially based on ionic theory of slag. The following equation was developed from thermodynamic data on phosphorous activity and phosphate free energy.

$$\log \frac{(P)}{[P]} = \frac{22350}{T} + 0.08 \times (CaO) + 2.5 \times \log(Fe_t) - 16 \qquad \dots \dots (2.3)$$

Where (P) is mass % of phosphorus in slag

[P] Mass % of phosphorus in metal

Fe<sub>t</sub> is mass % of Fe in slag, calculated from total amount of different iron oxides present in the slag.

(CaO) is mass % of CaO in slag.

T is turndown temperature in Kelvin.



Fig-2.1 The effect of (FeO) and turn down temperature on phosphorous partition coefficient <sup>(4)</sup>

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Fig-2.2 Combined effect of basicity and (FeO) on dephosphorisation <sup>(4)</sup>

#### 2.5 Optical basicity model

According to optical basicity <sup>(5)</sup> model the phosphorus distribution is given by,

The optical basicity,  $\Lambda$ , for a complex slag is calculated as,

 $\Lambda = \Lambda_1 X_1 + \Lambda_2 X_2 + \dots$  (2.5)

Where,

 $X_1$  is equivalent fraction component oxides  $\Lambda_1$  is optical basicity of component oxides.

Optical basicity can be calculated from

$$\Lambda = \frac{\sum \frac{W_{i}O_{i}\Lambda_{i}}{M_{i}}}{\sum \frac{W_{i}O_{i}}{M_{i}}} \qquad \dots \qquad (2.6)$$

#### Where,

 $W_1$  is mass % of species.

 $O_1$  number of oxygen atoms in the molecule.

M refer to molecular mass

 $O_1/M_1$  is called oxidation number coefficient (known also as O/M ratio, for example O/M ratio for CaO is 2/56=0.375 where 2 is charge of cation Ca<sup>2+</sup> and 56 is the molecular mass of CaO).

An improvement of equation (2.6), has been suggested <sup>(6)</sup>

$$\log C_{p} = -18184 + 35.84 \times A - 22.35 \times A^{2} + 22930 \times \frac{A}{T} - 0.06257 \times FeO$$
$$-0.04256 \times MnO + 0.359 \times P_{2}O_{5}^{0.3} \qquad (2.7)$$

#### 2.6 Suito's model

Suito developed the following relationship for the phosphorous distribution;

$$\log \frac{(P)}{[P] \times (Fe_t)^{\frac{5}{2}}} = 0.720 \times [(CaO) + 0.3 \times (MgO) + ).6 \times P_2O_5 + 0.6 \times (MnO)]$$
  
+  $\frac{11570}{T} - 10.520$  .....(2.8)

Where,

(Fe<sub>t</sub>) total mass percent of Fe in slag

The above correlation includes the effect of MgO and MnO on phosphorous partition.

#### 2.7 Suito and Inoue's model

Suito and Inoue<sup>(7)</sup> reported that the phosphorous distribution data can be correlated by the expression;

According to equation (2.9) the phosphorous partition depends upon mass percent CaO, mass percent of MgO, pass percent of  $P_2O_5$ , mass percent of MnO in slag, and turndown temperature.

Where K<sub>P</sub> is 
$$K_{p} = \frac{a_{P_{2}O_{5}}}{[h_{p}]^{2}(h_{o})^{5}}$$

(CaO) is mass percent CaO in slag.
(MgO) is mass percent MgO in slag.
(MnO) is mass percent MnO in slag.
(P<sub>2</sub>O<sub>5</sub>) is mass percent P<sub>2</sub>O<sub>5</sub> in slag.

#### 2.8 Elliott's model

A correlation was proposed by Elliott et al <sup>(8)</sup>. Considering the phosphorous reaction:

The equilibrium constant for reaction (2.10) is given by the expression:

Where  $N_{PO_4^{3-}}$  and  $N_{O_{2-}}$  are the anionic mole fractions of phosphate and oxygen ions,  $N_{C_i}^{'}$ is an electrical equivalent cationic mole fraction,  $\gamma_i$  is activity coefficient, and  $K_i$  is the equilibrium constant for exchange reaction, e.g., for calcium:

#### 2.9 Molecular slag model

According to molecular slag model  $2P + 5FeO = P_2O_5 + 5Fe$ 

%Fe in slag is calculated from total amount of iron oxide present in the slag

$$\log \frac{(\% P2O5)}{[\% p]^2 \ (\% Fe)^5} = 7.04 \log(\% CaO) + \frac{9922}{T_c + 17.78} - 20.2 \quad \dots .$$

where T<sub>c</sub> is temperature in centigrade, [%p] is mass % of phosphorus in metal, (%P<sub>2</sub>O<sub>5</sub>) is mass % P<sub>2</sub>O<sub>5</sub> in slag, (%Fe) 1s mass % of Fe in slag, and (%CaO) is mass % of CaO in slag;

#### 2.10 Quadratic formalism model

Quadratic formalism model was proposed by Ban Ya et al <sup>(9)</sup>. It is based on regular solution model to calculate the interaction parameters between slag components. According to this model the basic reaction for oxidation of phosphorus is considered as  $2[P] + 5[O] = (P_2O_5)$ .

The activity of  $P_2O_5$  in a regular solution (expressed as  $aPO_{2.5}$ ) is given by

$$RT \ln \alpha_{P205}(l) = RT \ln \alpha_{P205(RS)} + 52720 - 230.706T$$

Where RS stands for regular solution.

$$RT \ln \gamma_{PO25(RS)} = -251040 X_{Ca0}^{2} + 83680 X_{Si02}^{2} - 37660 X_{Mg0}^{2} - 84940 X_{Mn0}^{2} - 31380 X_{Fe0}^{2} - 33470 X_{Ca0} X_{Si02} - 188280 X_{Ca0} X_{Mg0} - 243930 X_{Ca0} X_{Mn0} - 251040 X_{Ca0} X_{Fe0} + 112960 X_{Si02} X_{Mg0} + 74050 X_{Si02} X_{Mn0} + 94140 X_{Si02} X_{Fe0} - 184520 X_{Mg0} X_{Mn0} - 102510 X_{Mg0} X_{Fe0} - 123430 X_{Mn0} X_{Fe0} - (2.16)$$

Now, for the reaction  $2[P] + 5[O] = (P_2O_5)$ , the equilibrium constant is

And,

 $-RTlnK_{P} = -705420 + 556.472 \times T \qquad .....(2.18)$ RTln [%P] = RTlnaP <sub>2</sub>O<sub>5</sub> -5RTln [%O] -RTlnK<sub>P</sub> .....(2.19)

#### S N Chatterjee and P S Rao Model

a).  

$$\frac{(\% P)}{[\% P]} = 2.338 - 7.781(\frac{10^{4}}{T + 273}) - 0.00531 \ln(\% FeO) + 19.294 \ln\{\frac{(\% CaO)}{(\% SiO2)}\} + 0.038 \frac{10^{3}}{e^{Mn}} + 0.0075 * \frac{e^{MnO}}{100}$$
b).  

$$\frac{(\% P)}{[\% P]} = 13.37 + 8.627(\frac{10^{4}}{T + 273}) + 0.158 \ln[\% Mn] + 15.98 \ln(CaO / SiO2) + 0.0358(\frac{10^{3}}{e^{Mn}}) + 0.0089(\frac{e^{MnO}}{100})$$

### Kinetics of Phosphorous removal

 \* Mass transfer in slag phase as a rate controlling
 \* Mass transfer in metal and slag both phases in last part of blow

$$\frac{d (\text{pct P})}{dt} = \frac{k_s \rho_s A}{W_s} ((\text{pct P})_t - (\text{pct P})_b) \text{ wt pct s}^{-1}$$

where (pct P) denotes phosphorus in the slag,  $\rho$  is the density, A is the interfacial area, W is the weight of phase, and the subscripts S and i are the slag phase and interfacial, respectively.

$$Q \frac{d [\text{pct P}]}{dt} = \frac{k_s \rho_s A}{W_s} ((\text{pct } P)_i - (\text{pct } P)_b) \text{ wt pct } s^{-1}$$

where Q is the weight ratio of metal to slag.

# How to enhance the kinetics of Phosphorous transfer ?

- Create larger Interfacial area between Slag-metal interface (achieved by dispersing large number of metal droplets in slag phase and increasing their residence time by controlling the behaviour of slag formation)
- Increasing mass transfer coefficients (By increasing total mixing energy input to the system from CO evolution , combined effect of top and bottom blowing )
- Ensuring proper volume of slag (controlling the Kinetics of lime dissolution, Slag retention from last heats if required)

#### Mechanism of lime dissolution

### 4 CaOsolid + {2FeO.SiO2} = 2 (CaOFeO) solid solution + (2CaO.SiO2)solid



Figure 1.7: Lime dissolution in static slag proposed by Hachtel et al. and Oeters et al. [2,3]



Figure 1.8: Schematic diagram of slag component near the surface

#### Kinetics of lime dissolution

 $\frac{dn_{CaO}}{dt} = A.K_{CaO} \{C^b_{CaO} - C^i_{CaO}\}$ 

where the superscript 'i' of concentration C refers to the interface and 'b' refers to the bulk, A is the area of interface and kCaO is the mass transfer coefficient of CaO in bulk slag.

 $K_{CaO}$  given as a function of viscosity of slag-metal continuum at the solid-liquid interface .

### Expressions to estimate effective basisity of slag-metal continuum

$$\mu = A \mu_o \exp\left(\frac{E}{Bi^{(j)}}\right)$$

A =  $1.03-2.08 \times 10^{-3} \text{ T} + 1.05 \times 10^{-6} \text{ T}^2 = 0.53$  (at T=1702K) E =  $28.46-2.09 \times 10^{-2} \text{ T} + 4.0 \times 10^{-6} \text{ T}^2 = 4.50$  (at T=1702K)

$$\mu_{o} = \sum \mu_{oi} X_{i}$$

$$\mu_{o} = \mu_{oCaO} X_{CaO} + \mu_{oFeO} X_{FeO} + \mu_{oSiO_{2}} X_{SiO_{2}}$$

$$Bi^{(j)} = \frac{\alpha_{CaO} W_{CaO} + \alpha_{FeO} W_{FeO}}{\alpha_{SiO_{2}} W_{SiO_{2}}}$$



Simplified ternary diagram for CaO-SiO<sub>2</sub>-FeO slags showing a slag path within shaded region [1]

#### 2CaO·SiO2-3CaO·P2O5 system phase diagram



#### SEM images of slag after examination and results of EPMA Analysis (Courtesy : N Sasaki and Kitimura etall )





$$\begin{split} {[Si]}_i = tr. \\ nCaO \cdot P_2O_3 + f\text{-}CaO \end{split}$$





 $\Delta$ [Si] = 0.07mass%

Tah 3	Roculte	ofminaral	nhacas	analysis
140.0	Trepuno	of minerus	pricibes	unusyons.

Sam- ple	Mark	9	Quali anal	tative ysis	Phase	
		Ca	Si	Р	F e	1 1050
	Α	V	-	V	-	$nCaO \cdot P_2O_5$
Ι	В	V		-	-	CaO
	С		_	3 <u>4</u>	V	nCaO·FeO
	D	V	-	-		CaO
	E		V	V	Ι	$(C_2S-C_3P)_{ss}$
"	F	V	-	-	-	CaO
	G		-	-	V	m.Fe
	H	V	V	V	L	$(C_2S-C_3P)_{ss}$
iii	Ι		-	-	V	FeO
	J	( <b></b>	-		V	m.Fe
÷	K	V	V	V	-	$(C_2S-C_3P)ss$
īv	L	V	V	- 322	V	$3CaO \cdot 2SiO_2$

#### Micrographs to confirm higher solid solubility of Phosphorous in slag (courtesy :J. Halder , B. Snoeijer)

	N	Phase	<b>P</b> <sub>2</sub> <b>O</b> <sub>5</sub>
6.	1	C <sub>2</sub> S	5.00
12	2	C <sub>2</sub> S	4.52
7. 12. 14.	3	C <sub>2</sub> S	4.2
13	4	C <sub>2</sub> S	4,50
13.	5	C <sub>2</sub> S	4.51
	6	C <sub>2</sub> S	4.54
	7	C <sub>2</sub> S	4.32
	8	C <sub>2</sub> S	3.91
.11.	9	C <sub>2</sub> S	4.48
8. 5.	1	C <sub>2</sub> S	4.63
9. 9. 9. 9. 9. 9. 9. 9. 9. 9. 9. 9. 9. 9	1	Wustite	-
4.20	1	Residual	-
	1	Wustite	-
Topine C S S S	1	Wustite	-

Micrograph of high MgO, low Al2O3 slag, low phosphorus hot metal; P2O5 content of different phases



Point 1 dicalciumsilicate; Point 2 wustite solid solution; Point 3 calcium–aluminium–ferrite; Point 4 dicalcium silicate Optical micrograph of high phosphorus (0.2%) hot metal) low (0.9%) MgO slag. Basicity 3.9. Steel tapping temperature 1700 C (plant 2)



Point 1 dicalciumsilicate; Point 2 wustite solid solution; Point 3 calcium–aluminium–ferrite

Optical micrograph of (medium phosphorus (0.15%) hot metal) high MgO (7.5%) low Al2O3 (1%) slag. Basicity 3.4. Steel tapping temperature 1660 C



Point 1 dicalciumsilicate; Point 2 wustite solid solution; Point 3 calcium–aluminium–ferrite/calcium–ferrite Optical micrograph of (high phosphorus (0.15–0.2%) hot metal) high MgO (10%) and low Al2O3 (,2%) slag. Basicity 3. Steel tapping temperature 1680 C



Point 1 dicalciumsilicate; Point 2 wustite solid solution; Point 3 calcium–aluminium–ferrite/calcium–ferrite Optical micrograph of (high phosphorus (0.15–0.2%) hot metal) high MgO (10%) high Al2O3 (4%) slag. Basicity 3. Steel tapping temperature 1680 C

### Comparision of individual effects of different variables on Phosphorous distribution (J Halder et all)

S	Sign of the coefficient of selected variables for molecular theory model of three case study												
Data Set						V	ariables						
	T <sub>2</sub>	$\frac{1}{(T_2 - 255\ 22)}$	Log (CaO)	Log (Fe)	C <sub>2</sub>	SVO	Basicity	C <sub>2</sub> S	Ore	HTR	Hl <sub>2</sub>	Ore <sub>2</sub>	Rdolo2
1		+	+	1	0	At V	NA	8			+	+	
2		+	+	A	10	+	-4	EV					
3		+	+	18	10	+	11	5/0%		+	+		
1		+	+		2	+	+	5	+				
2		+	+	+	$\geq 1$	51		SI					
3		+			+	IAI V	7 I (A ( )	21	+				
1		+	+	7	41	40	OqT	21	2				
2		+	+	9	6	5	- 1.	SI	9				
3		+	+	E	+6	1	1	13					+
				1	ka	n	N	18					

#### Case Study - I

Pl	ant No	Operation-	Number	Composition of slag	Composi-	Turn down
		al	of data	(average)	tion of steel	tempera-
		restriction				ture ( <sup>0</sup> C)
1	Set-1	Ore20	60	%CaO 56, %SiO <sub>2</sub> 12	[P] 0.011,	1599-1705
		Rdolo2=0		%P <sub>2</sub> O <sub>5</sub> 1.2, %MnO 3,	[C] 0.05,	
				%MgO 3.5,	[Mn] 0.15	
				%FeO 22		
	Set-2	Ore2=0	110	%CaO 53, %SiO <sub>2</sub> 11.8	[P] 0.011,	1630-1708
		Rdolo2=0		%P <sub>2</sub> O <sub>5</sub> 1.2, %MnO 3.2,	[C] 0.05,	
				%MgO 3.3,	[Mn] 0.15	
				%FeO 23		
	Set-3	Ore2=0	112	%CaO 42.2-65, %SiO <sub>2</sub> 12	[P] 0.011,	1610-1699
		Rdolo20		%P <sub>2</sub> O <sub>5</sub> 1.2, %MnO 3.2,	[C] 0.05,	
				%MgO 3.3,	[Mn] 0.15	
				%FeO 23		

#### Case Study -- II

	Plant	No of	Composition of slag	Composition of	Turn down
		data		metal	temperature
					<sup>0</sup> C
2	Vessel-1	402	%CaO 45-60, %SiO <sub>2</sub> 11-17	[P] 0.014, [C],	1611-1750
			%P <sub>2</sub> O <sub>5</sub> 3.6, %MnO 0.6,	0.03,	
			%MgO 0.9,	[Mn] 0.028	
			%FeO 18-32		
	Vessel-2	380	%CaO 56, %SiO <sub>2</sub> 13	[P] 0.013, [C]	1591-1743
			%P <sub>2</sub> O <sub>5</sub> 3.6, %MnO 0.6,	0.029, [Mn]	
			%MgO 0.9,	0.027	
			%FeO 22		
	Vessel-3	270	%CaO 56, %SiO <sub>2</sub> 13	[P] 0.013, [C]	1601-1741
			%P <sub>2</sub> O <sub>5</sub> 3.5, %MnO 0.6,	0.03, [Mn] 0.027	
			%MgO 0.9,		
			%FeO 22		

#### Case Study -- III

P	ant No	Operational	Number	Composition of slag	Composi	Turn down
		restriction	of data		tion of	tempera-
					metal	ture ( <sup>0</sup> C)
1	Set-1	Ore20	331	%CaO 42, %SiO <sub>2</sub> 21.5	[P] 0.011,	1599-1705
		Rdolo2=0		%P <sub>2</sub> O <sub>5</sub> 1.4, %MnO 4,	[C] 0.05,	
				%MgO 8,	[Mn] 0.15	
				%FeO 13-30		
	Set-2	Ore2=0	140	%CaO 42.5, %SiO <sub>2</sub> 8-20	[P] 0011,	1600-1708
		Rdolo2=0		%P <sub>2</sub> O <sub>5</sub> 1.4, %MnO 5,	[C] 0.05,	
				%MgO 8,	[Mn] 0.15	
				%FeO13-30		
	Set-3	Ore2=0	246	%CaO 44, %SiO <sub>2</sub> 8-20	[P] 0.011,	1610-1699
		Rdolo20		%P <sub>2</sub> O <sub>5</sub> 0.1.4, %MnO 5,	[C] 0.05,	
				%MgO 8,	[Mn] 0 15	
				%FeO 13-30		

#### Results with case Study – I(Data Set –I)

	Operation	al constraint		Additional variable for tuning			
	Ore <sub>2</sub> 0,	Rdlo <sub>2</sub> =0		Ore <sub>2</sub> , H12, T <sub>2</sub> , S	VO, C <sub>2</sub>	, HTR	
Model	Dependent	Variables	selected	Variables	R	σ	
	variable			rejected			
		Variables	(t) value for				
			selected				
			variables				
Modified	$\log (P)$	1	5.7	HTR, log(Fe),	0.72	0.0024	
Healy's	P	$\overline{T_2}$		T <sub>2</sub>			
model		$Hl_2$	2.99				
		C <sub>2</sub>	-4.5				
		(CaO)	6.5				
		SVO	1.7				
		Ore <sub>2</sub>	1.47				
Modified	$(P)^{2}$	1	6.6	HTR, log(Fe),	0.74	0.0021	
molecular	$\log \frac{1}{[P]}$	$(T_2 - 255.22)$		T_2			
theory model		Hl <sub>2</sub>	2.75	1			
		Ore <sub>2</sub>	1.75				
		SVO	3.67				
		log(CaO)	4.65				
		C2	-4.42	1			
Modified	$\log \frac{(P)}{P}$	1	5.35	HTR, OB,	0.70	0.0021	
optical	[P]	$T_2$		SVO, T <sub>2</sub> ,			
basicity		Ore <sub>2</sub>	1.98	$\log(Fe), C_2$			
model		Hl <sub>2</sub>	2.68				
Modified	RTln[P]	Ore <sub>2</sub>	-2.6	HTR, Rtln[O]	0.74	0.0021	
quadratic		SVO	-5.04	, RTln[K <sub>P</sub> ]			
formalism		C <sub>2</sub>	3.28				
model		$RT \ln(a_{r_2o_5})$	2.5				
		HL <sub>2</sub>	-1.8				
		T2	4.8				

#### Results with case Study – I(Data Set –II)

	Operatio	onal constraint	Additional variable for tuning			
	Ore <sub>2</sub> =	0, Rdolo <sub>2</sub> =0	Dolo2, HI2,	T <sub>2</sub> , SVO	, C <sub>2</sub> , HTR	
Model	Dependent variable	Variables selected		Variables rejected	R	σ
		Variables	(t) value for selected variables			
Modified Healy's model	$\log \frac{(P)}{[P]}$	$ \frac{\frac{1}{T_2}}{\frac{\text{HL}_2}{C_2}} $ (CaO)	5.9 6.5 -5.4 2.66	HTR, (%CaO), T <sub>2</sub> , Hl <sub>2</sub> , SVO, dolo2	0.72	0.0023
Modified molecular theory model	$\log \frac{(P)^2}{[P]}$	$ \frac{1}{(T_2 - 255.22)} $ $ \frac{C_2}{\log(CaO)} $ SVO	6.06 -5.48 1.4 2.9	HTR, T <sub>2</sub> , dolo2, Hl <sub>2</sub> , log(Fe)	0.67	0.0023
Modified optical basicity model	$\log \frac{(P)}{[P]}$	$ \frac{1}{T_2} $ Hl2 C <sub>2</sub>	5.13 1.99 -3 4	HTR, OB, SVO, Hl <sub>2</sub> . dolo <sub>2</sub>	0.69	0.0022
Modified quadratic formalism model	RTln[P]	$\frac{RT\ln(a_{r_{1}o_{5}})}{SVO}$ $\frac{T_{2}}{C2}$	-3.85 5.27 2.48	HTR, Hl <sub>2</sub> , RTln[O], Dolo <sub>2</sub> , HTR, RTln(K <sub>P</sub> )	0.68	0.0018

#### Results with case Study – I(Data Set –III)

	Operation	al constraint		Additional variable for tuning		
	Ore <sub>2</sub> =0	, Rdolo <sub>2</sub> 0		$Hl_2, T_2, S$	SVO, C	2, HTR
Model	Dependent variable	Variables	sselected	Variables rejected	R	σ
		Variables	(t) value for selected variables			
Modified Healy's model	$\log \frac{(P)}{[P]}$	$     \frac{\frac{1}{T_2}}{\frac{Hl_2}{C_2}} $	3.34 -7.16	HTR, T <sub>2.</sub> , Log(Fe)	0.81	0.0033
		(%CaO) SVO	5.6 3.42			
Modified molecular theory model	$\log \frac{(P)^2}{[P]}$	$     \frac{1}{(T_2 - 255.22)}     HIL2     C_2     log(CaO)     SVO $	3.58 -4.95 3.47 4.33	T <sub>2</sub> , log(Fe), HTR	0.81	0.0036
Modified optical basicity model	$\log \frac{(P)}{[P]}$	$     \frac{\frac{1}{T_2}}{\frac{Hl_2}{C_2}}     OB   $	9.56 -4.48 -1.67	HTR, SVO, log(Fe)	0.76	0.0033
Modified quadratic formalism model	RTln[P]	$\frac{\text{SVO}}{\text{T2}}$ $\frac{\text{C2}}{R T \ln (a_{P_2O_3})}$	-5.5 9.4 4.7 3.5	HTR, RTln(K <sub>P</sub> ), RTln[O]	0.74	0.0027
		HI2	-2.2			

#### Results with case Study – II(Vessel –I)

High phosp	horous hot n	Additional variable for tuning				
				T <sub>2</sub> , SVO, C <sub>2</sub> , HTR, Ore,		
				Basicity	_	
Model Dependent Variables selected			ed	Variables	R	σ
	variable			rejected		
		Variables	(t) value for			
			selected			
			variables			
Modified	(P)	T <sub>2</sub>	-14 23	HTR, log(Fe)	0.8	0.0028
Healy's	$\log \frac{10}{[P]}$	(%CaO)	5 884	Basicity 1		
model		C2	-2.23	$T_2$		
		Ore	1.96	-		
Modified	$\log (P)$	1	-1.69 01 1	HTR,	0.79	0.0027
molecular	$[P]^{2}$	$(T_2 - 255.22)$	000	Basicity,		
theory		T2 19	-2.19	C <sub>2</sub>		
model		log(CaO)	4.7	151921		
		SVO	2.18	151		
		Ore	3.34			
		Log(Fe)	3.69	12181		
Modified	P	T <sub>2</sub>	-9.01	HTR, SVO,	0.5	0.0063
optical	[P]	Ore	3.43			
basicity		OB 📎	4.14	$T_2$		
model			TE OF TECH	NOC		
Modified	RTln[P]	SVO	-4.39	HTR, TDC,	0.66	0.0016
quadratic		$RT\ln(a_{P_2O_s})$	-1.65	RTIn[O],		
formalism		Ore	-2.26	HTR,		
model		T <sub>2</sub>	4.6	$RTIn(K_P)$		

#### Results with case Study – II(Vessel –II)

High	hot metal pho	osphorous. Low N	/IgO slag	Additional variable for tuning		
				T <sub>2</sub> , SVO, C <sub>2</sub> , H	TR, Ore,	Basicity
Model	Dependent	Variables selected		Variables	R	σ
	variable			rejected		
Modified	(P)	Variables	(t) value for			
Healy's	[P]		selected			
model			variables			
		C <sub>2</sub>	-1.5	HTR SVO $\frac{1}{2}$	0.61	0.00017
		(%CaO)	6 097	$\overline{T_2}$ ,		
		T <sub>2</sub>	-14.6	Basicity.		
		Ore	2.01	log(Fe).		
Modified	$(P)^{2}$	1	14.6	HTR, Basicity,	0.66	0.0016
molecular $\log \frac{1}{1}$	$log \frac{(-7)}{[P]}$ (T <sub>2</sub> - 255.22)		C <sub>2</sub> , Ore, T <sub>2</sub>			
theory		log(CaO)	3.6			
model		SVO	1.86	en		
		Log(Fe)	2.08	18		
Modified		$T_2 \ge$	-14.7	HTP SVO 1	0.63	.0017
optical	$\log \frac{(P)}{P}$	$C_2 \sim S$	-2.1	$T_2$ ,		
basicity	[P]	612	(ଇାଣ)ର	log(Fe),Ore		
Modified	RTln[P]	$RT \ln(a_{r})$	-165	HTR C	0.52	0.0063
quadratic	ici m[i ]			,RTln[O], HTR,	0.02	0.0005
formalism		Ore	4.6	RTln(K <sub>P</sub> ),		
model		T <sub>2</sub>	-2.26	01.00 540		
	1		OF TECH			

#### **Results with case Study – II(Vessel –III)**

High hot metal phosphorous. Low MgO slag				Additional variable for tuning			
				T <sub>2</sub> , SVO, C <sub>2</sub> , HTR, Ore,			
			Basicity				
Model	Dependent	Variables	selected	Variables	R	σ	
	variable			rejected			
Modifies	(P)	Variables	(t) value				
Healy's	$\log \frac{109}{[P]}$		for				
model	C- 1		selected				
			variables				
		TDC	2.3	(CaO), SVO,	0.66	0.0017	
		(CaO)	2.7	$\frac{1}{-}$ HTR			
		Ore	2.5	$T_2$ , $T_1$			
		T <sub>2</sub>	-12.3	Basicity,			
		100	000	log(Fe)			
Modified	$(P)^2$	10	9.12	HTR,	0.62	0.0015	
molecular	$\log \frac{(1)}{[D]}$	$(T_2 - 255\ 22)$	1	Basicity,			
theory model		12		T <sub>2</sub> , SVO,		1	
		Ore	2.86	log(Fe),			
		$C_2$	(1.910)	log(CaO)			
		TDC	2.06	HTR, SVO,	.6	0.016	
Modified	$_{100}(P)$	T <sub>2</sub>	-11.8	TDC			
optical	$\log \frac{10g}{[P]}$	OB	2.6	$T_2$ , IDC,			
basicity		in	TE	OB. log(Fe)			
model			- OF TECH			00010	
Modified	RTln[P]	$RT\ln(K_p)$	-4.23	HTR. $\frac{1}{-}$	.65	00013	
quadratic		Ore	-2.45	$] T_{2}'$			
formalism		SVO	-2.096	TDC,			
model				basicity,			
				$RT \ln(a_{P_2O_3})$			
				RTln[O]			

#### **Results - Case Study – III**

High MgO (7-11%) in slag and low phosphorous				Additional variable for tuning			
(<0.07%) hot metal				T2, SVO, C2, HTR, Ore, Basicity			
Data set	Dependent	Variables	selected	Variables	R	σ	
	variable			rejected			
		Variables (t) value for		1			
			selected				
			variables				
Set-1	$\log \frac{(P)}{P}$	1		HTR, Ore2,	0.69	0.0025	
	$\left[P\right]^{2}$	$(T_2 - 255.22)$	18 91	Hl2,			
		C <sub>2</sub>	1.93	log(CaO)			
		Basicity	2 10	10g(040)			
		SVO	1.55	1000			
Set-2	P	1	6.36	HTR,	0.59	0.0019	
	$\log \frac{10}{[P]^2}$	$(T_2 - 255.22)$	~~~~	Log(Fe),			
		Log(CaO)	24	Basicity,			
		205(040)		HTR, SVO			
Set-3	$\log (P)$		(200)	HTR, ,,	0.76	0.0017	
	$[P]^2$	$(T_2 - 255.22)$	15 01	Log(Fe),			
		c2	35	log(CaO),			
		rdlo2	25	basicity,			
		Log(CaO)	135	Val 1			
·····			TE OF TE	UNOL			

#### Key findings on Dephosphorisation (J Halder and Amitabh Shanker)

(1) Four thermodynamic models, namely the Healy's model, optical basicity model, molecular model and quadratic formalism model have been evaluated on operational data.
 (2) The models include lance height, carbon content, ore addition, dolomite addition and total slag mass as significant parameters, in addition to FeO and CaO content of slag and tapping temperature.

(3) The models show that phosphorus prediction is more accurate when no ore addition has been made but raw dolomite is added during the second blow period as a coolant and/or slag conditioner, and for this particular case the molecular model gives the best predictions.(4) Final carbon content in steel is found to be a significant parameter for prediction of phosphorus as most of models incorporate it as a significant parameter.

(5) Lance height becomes a significant parameter for prediction of phosphorus whenever raw dolomite or ore is added during the second blow.

(6) Regular solution model is more reliable for prediction of slag FeO than other approaches.

(7) The accuracy of phosphorus prediction models is better when ore or raw dolomite additions are made during the second blow.

(8)The performance of neural network for phosphorus prediction is slightly inferior to thermodynamic models.

#### Findings of Mark-Swinertton (University of Wollongong)

- The Phosphorous distribution increases by three times after mid of the blow.
- There is no significant difference in analysed Phosphorous in metal droplets and bulk till mid of the blow (As long as basisity <2.0 and FeO<10%).
- Increasing FeO at tap will not improve Dephosphorisation , however increased basisity will do it .
- There is significant difference in droplet phosphorous and bulk metal near end of the blow.
- About 30% of lime and 50% maganesia is not dissolved in tap slag .The MgO undissolved is 65% in mid of the blow .
- There is reversion of Phosphorous during 10-15 minutes of the blow .
- The minimum Dephosphorisation ratio is coinciding with the minimum FeO level in the slag.

# Control Parameters and suggested operating strategies

Control Parameter	Initial blow(first 30%)	Mid Blow (30- 80%)	Final Blow (last 20%)	Suggested Operating parameters
Temperature	Favourable	Not Favourable	Not Favourable	Proper charge ratio
FeO Level	Favourable	Not Favourable	Favourable	Lance height and Oxygen Flow rate
Basisity	Favourable	Favourable	Favourable	Flux Addition scheme of flux and fluidiser

Why good phos prediction and control control is critical?

•poor yield of steel due to reblows; iron loss,

• loss in the lining life of the converter,

loss due to poor recovery of ferroyalloys,
reduced life of ladles,
diversion of grades due to uncertain oxygen content of steel

### Requirement of Low Phosphorus Steels

- To have improved mechanical properties like temper embrittlement, low temperature ductility etc.
- To have better corrosion resistance and deep drawing properties
- To reduce hydrogen induced cracking and stress corrosion cracking

Continued...

- To prevent segregation during continuous casting
- To reduce chances of cracking during bending
- For the equipment in chemical industry
- For reprocessing equipment of the nuclear industry

### Measure of dephosphoriztaion

Dephosphoriztaion ratio is defined as ratio of P content in slag to that in metal and is equal to (%P)/[%P] or (%P)/[%P]<sup>2</sup>

### Models Developed in Present Work

- Healy's model
- Molecular theory model
- Optical basicity model
- Quadratic formalism model

### Conclusions

- Four thermodynamic models, namely the Healy's model, optical basicity model, molecular model and quadratic formalism model have been evaluated on operational data .
- The models include lance height, carbon content, ore addition, dolomite addition and total slag mass as significant parameters, in addition to FeO and CaO content of slag and tapping temperature.
- The models show that phosphorus prediction is more accurate when no ore addition has been made but raw dolomite is added during the second blow period as a coolant and/or slag conditioner, and for this particular case the molecular model gives the best predictions.

continued....

- Final carbon content in steel is found to be a significant parameter for prediction of phosphorus as most of models incorporate it as a significant parameter.
- Lance height becomes a significant parameter for prediction of phosphorus whenever raw dolomite or ore is added during the second blow.
- Regular solution model is more reliable for prediction of slag FeO than other approaches.
- The accuracy of phosphorus prediction models is better when ore or raw dolomite additions are made during the second blow.