

ESTIMATION OF PHOSPHORUS DISTRIBUTION RATIO AT THE END OF BLOWING IN BOF

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Abstract

In integrated steel plants, the removal of phosphorous normally takes place during the primary basic oxygen furnace (BOF) steelmaking process. Phosphorous is usually introduced to the integrated steelmaking process through blast furnace additions, such as iron ore, coke, sinter, and fluxes. Among the others parameters such as optimizing the charging system, oxygen supply system, oxygen lance parameters of the converter, the flux quality in combination with temperature process control can improve the BOF efficiency of Dephosphorization. Phosphorus partition ratio (L_P) is usually used to evaluate the thermodynamic efficiency of the dephosphorization of slags with different compositions in steelmaking processes. However, this parameter is only useful in equilibrium conditions, and it is not accurate when used to evaluate slag efficiency in industrial processes. Because of this, the aim of this work was to study the phosphorus partition ratio estimated from the experimental results in real plant conditions of two different BOF steel plants and compare them with well-known published models. In the present study, data from two steel plants (further Plant A and Plant B) were evaluated applying Healy's, Suito and Inoui's, Zhang's as well as Assis's equations. The calculated values were compared against measured values.

Keywords: BOF; phosphorus distribution ratio; dephosphorization; activity coefficient of P_2O_5 .

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Introduction

A long time ago, phosphorus was recognized as a deleterious trace element in steel, which must be strictly controlled. Reducing phosphorus content in the steel is one of the critical factors to enhance the steel properties. In recent times, lowering phosphorus content has become a critical requirement for steels used in thin sheets for deep drawn applications, automobile exteriors, pipelines for transporting natural gas and petroleum products, or heavy plates for shipbuilding.

Phosphorous is primarily introduced to the integrated steelmaking process through blast furnace additions, such as iron ore, coke, sinter, and fluxes [1-3]. Therefore, raw material selection is crucial in maintaining the desired phosphorous level in the final product [4].

Effect of phosphorus on the properties of steels

Steels containing phosphorous can have good and bad properties. Phosphorous has a significant influence on the solid solution strengthening of the ferrite. The addition of a modest quantity of phosphorous can increase the yield and ultimate strength of the mild steel. It also increases the deep drawability and hardness of steel. Referable to the above advantages, such steels are used for cold forming operations. Phosphorous in steel can also improve corrosion resistance and metal cutting characteristics [5]. Table 1 summarizes the impact of phosphorous on the various steel properties.

Table 1. Effects of phosphorus on properties of steels [6].

Property	Effect of phosphorus
1 Strength	Strong positive (strengthens ferrite)
2 Bake hardenability	Positive
3 Ductility	Strong negative
4 Galvannealing	Can improve resistance to powdering
5 Phosphatability	Positive
6 Enameling	
a. Fish scaling	Negative
b. Pickling	Positive
7 Weldability	Not harmful for [%P]<0.1
8 Core loss in motor lamination	Strong negative
9 Fracture toughness	Strong negative

The most common form widely used as a measure of slag's ability to remove phosphorus from the melt is phosphorus partition ratio between slag and metal, mathematically expressed [4], applying Equation (1):

$$L_P = \frac{(\%P_2O_5)}{[\%P]} \quad 1$$

In the available literature, many correlations have been developed to predict the phosphorus partition ratio as a function of metal and slag composition as well as temperature. However, there are still disagreements between the laboratory and calculated data on the equilibrium phosphorus partition ratio [6].

Although the quantification of phosphorus equilibrium is extremely important, many steelmaking furnaces do not operate at equilibrium, usually due to liquid slag

formation, kinetics and time constraints. Thus, it is important to know how close to equilibrium steelmaking furnaces operate to suggest optimal slag compositions to promote dephosphorization [6].

A number of studies in the past have been carried out to develop predictive models for the equilibrium partition ratio of phosphorus (L_p) as a function of slag chemistry and temperature [4, 7-18]. Such models use empirical regression equations of the measured equilibrium data to estimate the L_p . Recently *Drain et al.* carried out a critical assessment of more than 90 different phosphorus partition models with the industrial converter data and proposed a new relationship that can be applied for a wide range of slag constituents [19]. Several phosphorus distribution ratio models are illustrated in Table 2. *Healy* [13] proposed an empirical correlation for phosphorus distribution as a function of slag composition and temperature. This correlation was suggested for CaO-SiO₂-Fe₂O type of slag with high content of CaO and Fe₂O. *Turkdogan* [10] critically assessed the slag-metal equilibrium for simple and complex slags based on the previous laboratory scale experiments and derived a new partition ratio for phosphorus. In the 1980s, *Suito et al.* [8] derived a correlation for phosphorus distribution in MgO-saturated slags of CaO-FeO-SiO₂-P₂O₅-MnO system. The correlation is based on the ionic concept developed by *Healy*. Additionally, *Ide and Fruehan* [12] varied the MgO concentration in their experiments and proposed a revised version of *Suito's* correlation for equilibrium phosphorus distribution [4].

It is well known that, the calculation of theoretical phosphorus distribution ratios L_p is difficult due to the fact that dephosphorization reaction in the BOF at EOB is under non-equilibrium condition. According to results published in the earlier mentioned studies [4, 7-13, 20-24], the empirical formulas for calculating L_p are summarized in Table 2.

In this work, some models from Table 2 and 3 have been used to determine the phosphorus partition coefficient and activity coefficient of P₂O₅ (log $Y_{P_2O_5}$) [25, 26], based on classic thermodynamic approach.

Table 2. Various formulas to describe the phosphorus partition ratio.

L_p models	Formulas of the L_p models	Ref.
<i>Healy</i>	$\text{Log}(\%P)/[\%P] = 22350/T + 0.08(\%CaO) + 2.5\text{log}(\%Fet) - 16 \pm 0.4$	[1,13]
<i>Suito-Inoue</i>	$\text{Log}(\%P)/[\%P] = 0.0720[(\%CaO) + 0.022(\%MgO) + 0.043(\%P_2O_5) + 0.014(\%MnO) + 2.5*\text{log}(\%Fet) + 11570/T - 10.520$	[1, 20]
<i>Zhang</i>	$\text{Log}(\%P)/[\%P] = 11000/T + (1/T) * (162*\%CaO + 127.5*\%MgO + 28.5 * \%MnO) + 2.5*\text{log}(\%FeO) - 0.000628*SiO_2 - 10.76$	[21]
<i>Assis</i>	$\text{Log}(\%P)/[\%P] = 0.073[(\%CaO) + 0.148(\%MgO) + 0.8(\%P_2O_5) + 0.113(\%SiO_2)] + 2.5\text{log}(Fe_T) + 11570/T - 10.403$	[22]

Formulas for calculation of activity coefficient of P₂O₅ (log $Y_{P_2O_5}$) used in this work are shown in Table 3.

Table 3. Equations for prediction of activity coefficient of P_2O_5 ($\log Y_{P_2O_5}$).

	Formulas	Ref.
Mori	$9.4-38.09*\Lambda$	[24]
Turkdogan	$-34850/T-3.85-0.058(\%CaO)$ for $P_2O_5 < 10\text{wt.}\%$	[10, 23]

Experimental procedure

The present investigations were conducted at two different steelmaking plants using blast furnace-basic oxygen steelmaking (BF-BOF) to produce liquid steel. External Dephosphorization through hot metal pre-treatment was not used. The target for the production of low phosphorus steel was achieved by single-stage blowing of hot metal in the BOF. The production was tested with a 100t Top-Blowing BOF of 25 heats (Steel-Plant A) [25] and 180t Combined blowing BOF of 14 heats (Steel-Plant B) [26] in the further marked as Plant A and Plant B. The composition and temperature of steel and slag are shown in Tables 4 and 5.

Table 4. Chemical composition of analyzed steel in Plant A and Plant B.

Heat	Plant A						Plant B					
	P_{HM}	C	Mn	P	η_P	T, [°C]	P_{HM}	C	Mn	P	η_P	T, [°C]
1	0.07	0.031	0.100	0.012	83	1680	0.114	0.0182	0.0760	0.0065	94	1710
2	0.07	0.032	0.050	0.007	90	1666	0.104	0.0248	0.1110	0.0076	93	1704
3	0.05	0.040	0.080	0.006	88	1653	0.089	0.0195	0.1210	0.0089	90	1722
4	0.05	0.029	0.085	0.006	88	1648	0.098	0.0208	0.1640	0.0109	89	1707
5	0.07	0.041	0.091	0.006	91	1662	0.094	0.0203	0.0760	0.0060	94	1696
6	0.07	0.082	0.090	0.005	93	1657	0.090	0.0247	0.1360	0.0095	89	1695
7	0.06	0.048	0.070	0.007	88	1644	0.095	0.0331	0.1850	0.0112	88	1720
8	0.06	0.030	0.110	0.011	82	1656	0.098	0.0270	0.1140	0.0078	92	1720
9	0.06	0.026	0.133	0.011	82	1664	0.106	0.0500	0.1670	0.0104	90	1718
10	0.06	0.023	0.121	0.011	82	1680	0.099	0.0264	0.1190	0.0104	89	1713
11	0.06	0.032	0.103	0.009	85	1658	0.098	0.0179	0.1050	0.0089	91	1696
12	0.06	0.028	0.110	0.013	78	1666	0.089	0.0391	0.1180	0.0083	91	1681
13	0.06	0.021	0.070	0.010	83	1670	0.094	0.0267	0.1440	0.0197	79	1688
14	0.07	0.039	0.122	0.009	87	1659	0.106	0.0377	0.2070	0.0201	81	1716
15	0.07	0.043	0.092	0.008	89	1658	0.096	0.0244	0.1540	0.0253	74	1719
16	0.07	0.035	0.090	0.010	86	1677	0.099	0.0505	0.2260	0.0265	73	1715
17	0.06	0.030	0.105	0.011	82	1658						
18	0.07	0.018	0.120	0.016	77	1660						
19	0.07	0.020	0.290	0.024	66	1647						
20	0.07	0.028	0.132	0.020	71	1659						
21	0.07	0.031	0.089	0.006	91	1649						
22	0.07	0.034	0.077	0.007	90	1656						
23	0.06	0.043	0.078	0.007	88	1657						
24	0.05	0.028	0.120	0.018	64	1678						
25	0.06	0.029	0.099	0.008	87	1641						

Table 5. Slag chemical composition of analyzed heats, wt. %.

Heat	Plant A						Plant B					
	CaO	SiO ₂	Fe tot.	MnO	MgO	P ₂ O ₅	CaO	SiO ₂	Fe tot.	MnO	MgO	P ₂ O ₅
1	49.34	13.91	26.21	5.02	4.08	1.21	46.24	7.02	26.0	2.10	1.47	1.68
2	36.40	9.59	30.68	4.81	3.98	0.71	47.93	10.12	22.9	2.93	1.33	1.59
3	42.79	12.39	20.40	5.07	3.73	0.87	43.07	10.47	25.5	3.40	2.20	1.65
4	45.83	12.34	19.66	4.58	5.24	0.80	51.18	11.35	18.7	3.40	1.65	1.79
5	51.91	15.28	14.10	4.48	4.87	0.98	37.85	6.12	34.7	2.88	2.69	1.21
6	49.52	15.29	15.02	4.54	4.15	0.88	48.12	11.12	20.5	3.61	3.32	1.67
7	47.13	12.90	19.93	4.21	3.62	0.94	50.29	10.82	19.6	3.96	1.85	1.66
8	40.62	20.87	15.48	4.75	4.43	0.69	50.13	9.06	21.5	2.93	3.36	1.07
9	45.58	19.30	13.04	5.76	3.05	0.92	61.67	14.76	10.8	2.18	1.44	1.14
10	50.92	16.29	12.40	5.44	2.92	0.93	45.87	10.55	24.2	3.27	1.45	2.01
11	49.06	14.33	15.39	5.04	3.21	0.93	40.96	8.34	29.1	3.40	1.66	2.02
12	46.59	14.76	14.34	5.18	3.55	0.90	55.27	6.78	22.8	2.54	1.55	1.42
13	49.08	17.43	13.16	5.70	3.22	0.84	54.67	6.54	21.2	2.45	1.51	1.56
14	48.85	15.31	13.10	5.15	3.49	0.99	56.06	13.58	13.9	3.06	1.70	2.31
15	50.91	14.38	15.47	5.01	2.69	0.95	49.59	12.69	19.4	3.60	1.25	2.73
16	48.78	12.34	19.37	4.96	2.81	0.92	56.49	14.55	13.7	2.90	1.58	2.34
17	50.34	14.87	12.47	5.22	3.40	1.03						
18	50.08	15.26	11.61	5.41	2.71	1.11						
19	51.67	15.28	11.42	5.31	2.74	1.09						
20	52.52	15.74	11.64	5.51	2.78	1.12						
21	46.38	11.53	19.04	5.08	3.42	1.07						
22	44.35	10.22	19.82	5.53	3.9	0.31						
23	40.74	8.41	24.21	4.98	3.54	0.86						
24	46.27	14.71	14.85	6.29	3.7	1.3						
25	47.33	13.9	15.46	5.3	4.53	1.09						

Results and discussion

The removal of phosphorus from the furnace charge is a well understood process. It can be described by the DePhos coefficient $L_P = (\%P_2O_5)/[P]$, which represents the distribution between slag – $(\%P_2O_5)$, and metal – $[P]$. It is well known that the L_P depends on many process parameters such as temperature of the melt, slag ferrous content $(\%Fe_{tot.})$, slag V-ratio $(\%CaO)/(\%SiO_2)$, $(\%MgO)$, refractory wear, campaign life, top or combined blowing BOF process, flux quality, slag volume, etc.

The obtained results of our study are listed in Tables 6 and 7.

Table 6. The log L_p measure vs. log L_p calculated applying various models.

Heat	Plant A				Plant B				Assis	
	Lp m.	Healy	Zhang	Suito-Inoue	Lp m.	Healy	Zhan g	Suito-Inoue		
1	2.00	2.94	2.84	2.68	2.90	2.41	2.51	2.22	2.17	2.52
2	2.01	2.16	2.00	1.85	2.10	2.32	2.54	2.25	2.02	2.54
3	2.16	2.30	2.14	1.88	2.20	2.27	2.16	1.95	1.93	2.26
4	2.12	2.53	2.47	2.18	2.40	2.22	2.56	2.31	1.94	2.57
5	2.21	2.58	2.52	2.23	2.47	2.30	2.23	2.00	1.93	2.24
6	2.25	2.48	2.37	2.03	2.37	2.24	2.49	2.33	1.91	2.49
7	2.13	2.68	2.50	2.24	2.52	2.17	2.47	2.25	1.86	2.51
8	1.80	1.81	1.68	1.48	1.79	2.14	2.56	2.42	1.90	2.57
9	1.92	1.97	1.79	1.63	1.93	2.04	2.74	2.48	1.53	2.70
10	1.93	2.25	2.09	1.87	2.19	2.29	2.38	2.11	1.99	2.45
11	2.01	2.47	2.30	2.06	2.35	2.36	3.09	2.81	2.17	2.97
12	1.84	2.15	2.00	1.71	2.07	2.06	2.58	2.34	1.79	2.63
13	1.92	2.23	2.08	1.83	2.16	2.03	2.41	2.14	1.92	2.52
14	2.04	2.27	2.12	1.80	2.17	1.95	2.60	2.35	1.77	2.66
15	2.07	2.62	2.42	2.19	2.48					
16	1.96	2.58	2.40	2.20	2.49					
17	1.97	2.34	2.19	1.89	2.22					
18	1.84	2.23	2.04	1.82	2.12					
19	1.66	2.42	2.22	1.96	2.26					
20	1.75	2.43	2.26	2.00	2.31					
21	2.25	2.54	2.37	2.16	2.40					
22	1.65	2.38	2.24	1.85	2.22					
23	2.09	2.30	2.12	1.83	2.18					
24	1.86	2.09	1.97	1.82	2.07					
25	2.13	2.44	2.34	2.04	2.30					

Table 7. Calculated values of the activity coefficient of P_2O_5 ($\log Y_{P_2O_5}$), (see Table 3, and reference [25])

Heat	Plant A		Plant B	
	Turkdogan, for % $P_2O_5 < 10$	Mori	Turkdogan, for % $P_2O_5 < 10$	Mori
1	24.56	19.30	24.11	18.84
2	23.93	18.00	24.26	18.86
3	24.43	18.60	23.82	18.36
4	24.65	19.30	24.42	19.53
5	24.87	19.70	23.74	17.85
6	24.78	19.10	24.35	19.75
7	24.76	19.30	24.25	19.63
8	24.27	17.60	24.24	20.27
9	24.49	18.30	24.93	20.75
10	24.65	19.40	24.06	18.44
11	24.74	19.40	24.79	17.92
12	24.53	18.90	24.62	20.07
13	24.63	18.80	24.22	20.36
14	24.72	19.30	24.66	19.98
15	24.85	19.50		18.77
16	24.55	19.40		19.87
17	24.82	19.50		
18	24.78	19.40		
19	25.00	19.70		
20	24.93	19.80		
21	24.67	19.40		
22	24.49	19.10		
23	24.27	18.90		
24	24.40	19.10		

Figures 1 and 2 show the comparison between measured and calculated phosphorus partition ratio (L_p) for Plant A and Plant B, applying Healy's, Suito, and Inoui's, Zhang's as well as Assis's equations. For Plant A, the predicted L_p values using Healy's equation are very close to the measured values. However, for Plant B, Healy's equation over predicts the L_p values by a factor of 2 to 3. The over prediction by Healy's equation is a common observation and has been reported by others. The fact that Healy's equation predicts the phosphorus partition in Plant A very close to actual measured values can be attributed to the fact that Healy's equation may have been developed for low phosphorus hot metal based on the ionic theory of slags.

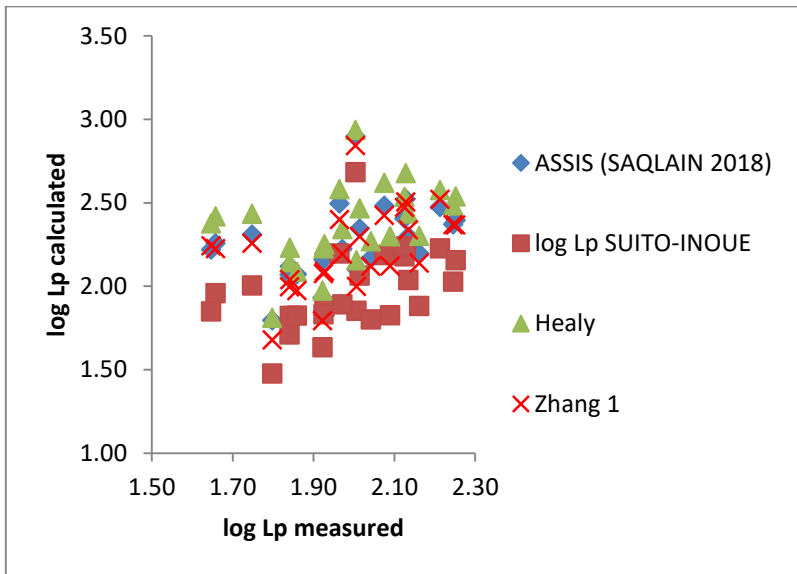


Fig. 1. Comparison of $\log L_p$ values estimated using predicted $\log L_p$ equations with measured values at Plant A.

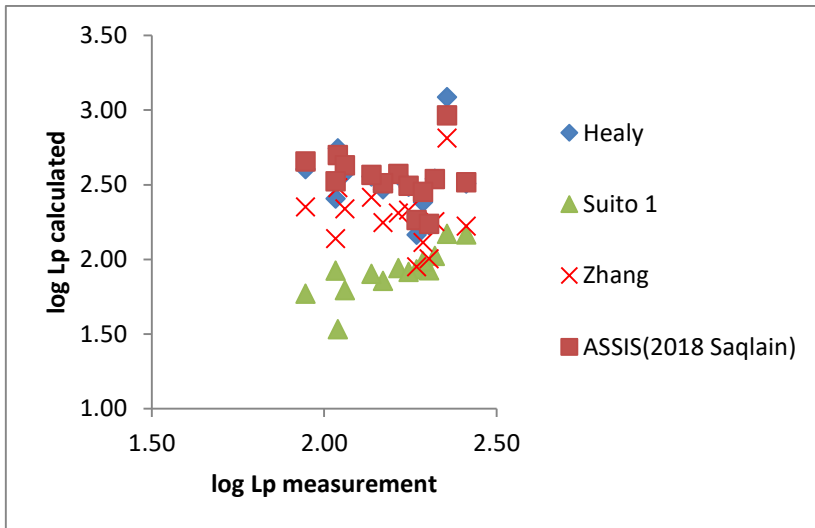


Fig. 2. Comparison of $\log L_p$ values estimated using predicted $\log L_p$ equations with measured values at Plant B.

On the other hand, the dephosphorization rate (De-P rate) can be used as a key indicator, which can be calculated by Equation (2):

$$De-P\ rate = 100\% \left(1 - \frac{m_1 P_1}{m_2 P_2} \right) \tag{2}$$

where,

De-Prate is the dephosphorization rate, %; m_1 and m_2 are the mass of steel before and after the treatment, respectively, kg; P_1 and P_2 are the phosphorus content before and after the treatment, respectively, mass%.

Therefore, the correlations between calculated log Lp of literature models with DeP-rate, [%] for Plant A and Plant B are given in Figures 3 and 4.

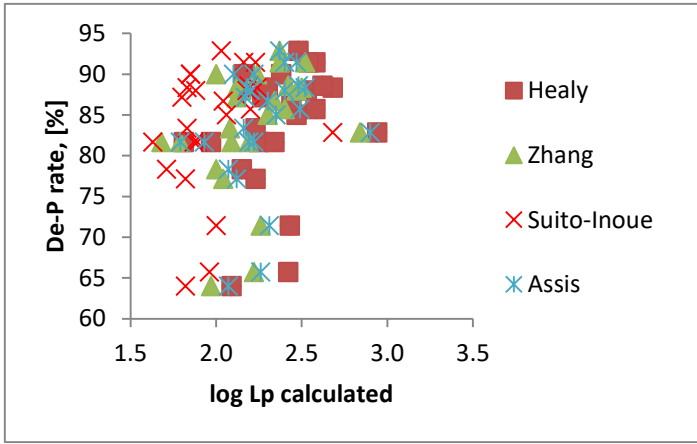


Fig. 3. Plant A: Correlation between calculated log Lp of literature models with DeP-rate, [%].

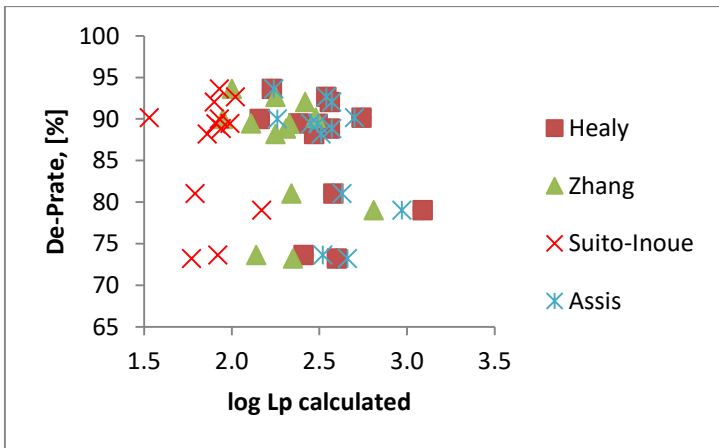


Fig. 4. Plant B: Correlation between calculated log Lp of literature models with DeP-rate, [%].

Figures 5 and 6 have compared the activity coefficient of the P₂O₅ calculated using Turkdogan and Mori model for both Plants. It is evident that there is a stronger correlation in the activity coefficient of the P₂O₅ calculated from Plant B log Y_{P₂O₅}-Turkdogan-log Y_{P₂O₅} Mori compared with correlation in Plant A.

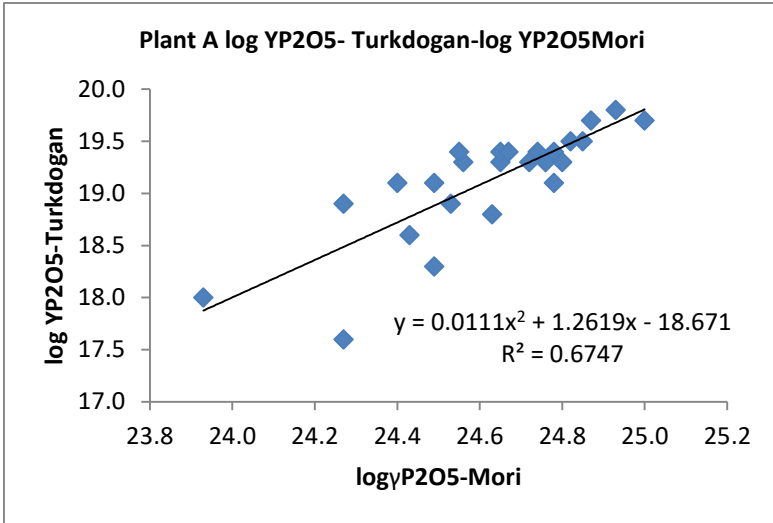


Fig.5. Plant A log Y_{P₂O₅}-Turkdogan-log Y_{P₂O₅}Mori.

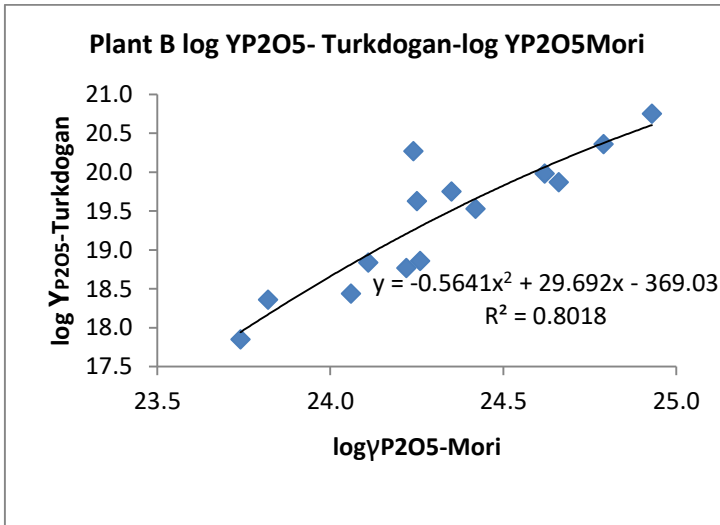


Fig. 6. Plant B log Y_{P₂O₅}-Turkdogan-log Y_{P₂O₅}Mori.

Conclusions

This study investigated the dephosphorization behavior of two different steel plants for a single slag practice by analyzing phosphorus distribution ratio LP and the activity coefficient of P_2O_5 . According to the data of the two steel mills, one uses top blowing and the other uses top and bottom combined blowing. From the data in Table 4 and Table 5, there is little difference between the two. Consequently, these two types of blowing were taken to test the overall performance of the proposed procedure.

Based on industrial results, the conclusions are given as follows:

1. To achieve low phosphorus content in steel at the EOB in BOF, one needs low P input and high Lp is needed among the other parameters;
2. Analyzed models for calculation of Lp give a scattered value which confirms that the results are far from reaching equilibrium;
3. There is a stronger correlation in the activity coefficient of P_2O_5 ($\log Y_{P_2O_5}$ -Turkdogan- $\log Y_{P_2O_5}$ Mori) calculated from Plant B compared with the correlation in Plant A.
4. There is a need to develop in further work and on much more analyzed heats, an equation that could be used as a predictive tool for estimating the phosphorus partition in steel plants.

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