

Article

Phosphorus Equilibrium Between Liquid Iron and CaO-SiO₂-MgO-Al₂O₃-FeO-P₂O₅ Slags: EAF Slags, the Effect of Alumina and New Correlation

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Abstract: The increased use of electric arc furnace (EAF) steelmaking using up to 100% direct reduced iron (DRI) has prompted an interest in better control of phosphorus since iron ore and, consequently, DRI have higher phosphorus and silica compared to scrap. There is limited work reported on slag chemistries corresponding to that in the EAF when DRI is used. In the current research, phosphorus equilibria between molten Fe–P alloys and CaO–SiO₂–Al₂O₃–P₂O₅–FeO–MgO_{saturated} slags were investigated. The results indicate that there is a significant decrease in the phosphorus partition coefficient (L_P) as alumina in the slag increases. The observed effect of alumina on the phosphorus partition is probably caused by the decrease in the activities of iron oxide and calcium oxide. Finally, an equilibrium correlation for phosphorus partition as a function of slag composition and temperature has been developed. It includes the effect of alumina and silica and is suitable for both oxygen and electric steelmaking-type slags.

Keywords: dephosphorization; EAF; BOF; phosphorus equilibrium

1. Introduction

Phosphorus is typically an undesirable residual element that has to be controlled. The development of new steel grades for next-generation applications result in ever tightening ranges for many residuals. Also, the steel industry is under constant pressure to keep costs down and maintain profitable margins. These opposing trends pressure the steelmakers to further optimize their processes to obtain maximum quality while use less “noble” iron sources.

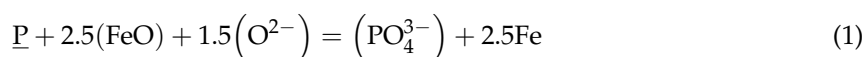
In EAF steelmaking, the use of DRI has been increasing with plants using charges of up to 100% DRI continuously. This source of iron has higher alumina and phosphorus contents than typical scrap and, thus, the impact of these elements must be evaluated with respect to dephosphorization.

The present work investigates the phosphorus equilibrium for slag chemistries relevant to EAF steelmaking, including the effect of alumina in the phosphorus partition. It is also a continuation of a previously published paper [1] that included the literature review on the topic, experimental setup, and Basic Oxygen Furnace (BOF) data.

1.1. The Dephosphorization Reaction

The equilibrium of phosphorus between liquid metal and slag has been extensively studied since the 1930s. Assis et al. [1] recently published an extensive literature review on many of the works that proposed correlations to predict the phosphorus equilibrium partition between metal and slag. In general, it is well documented that dephosphorization increases with increasing slag basicity and decreases with increasing temperatures. Basu and coworkers [2,3] also noted that dephosphorization initially increases with increasing FeO in the slag but then decreases after a certain point. They proposed that this behavior is a function of the slag basicity and temperature.

When slag species are considered, the phosphorus oxidation reaction (dephosphorization) can be expressed in an ionic form:



where the underlined species is dissolved in liquid iron. The capacity of the slag to hold the phosphorus, a term called apparent phosphorus equilibrium constant is defined as

$$K_P = \frac{(\%P)_{\text{slag}} / [\%P]_{\text{steel}}}{(\%T.\text{Fe})^{2.5}} \quad (2)$$

where $(\%P)_{\text{slag}}$ and $[\%P]_{\text{steel}}$ are the concentrations of phosphorus in the slag and the steel respectively and $(\%T.\text{Fe})$ is the total iron in the slag.

The phosphorus partition coefficient, L_P , can be defined as

$$L_P = \frac{(\%P)_{\text{slag}}}{[\%P]_{\text{steel}}} \quad (3)$$

In the 1980s, Suito et al. [4–8] studied phosphorus partitioning on various slag systems at temperatures between 1823 K and 1923 K. In 1984, Suito et al. [5] proposed a correlation for K_P :

$$\log\left(\frac{L_P}{T.\text{Fe}^{2.5}}\right) = 0.0720[(\% \text{CaO}) + 0.3(\% \text{MgO}) + 0.6(\% \text{P}_2\text{O}_5) + 0.144(\% \text{SiO}_2) + 0.6(\% \text{MnO})] + \frac{11570}{T} - 10.52 \quad (4)$$

Assis et al. [1] noted that the form of Suito's correlation describes how slag composition changes the activity coefficients of O^{2-} , PO_4^{3-} , and Fe^{2+} . The coefficients are the first interaction coefficients of a Taylor series.

In 2000, Ide et al. [9] revised the MgO coefficient from 0.30 to 0.15. They [9] used CaO crucibles to vary the MgO content in the slag.

1.2. The Effect of Alumina on Dephosphorization

Alumina is present in steelmaking slags and usually ranges between 3 and 7 wt.%. Alumina comes from gangue in DRI and Al in the scrap as well as from flux additions. It has not been extensively studied in primary steelmaking, and most of the literature work with respect to alumina was conducted for hot metal or ladle dephosphorization [10–15].

In 1946 Balajiva and coauthors [12] noticed a decrease of phosphorus partition for experiments containing high alumina levels. Ladle dephosphorization for highly basic slags saturated with MgO was studied by Ishii and Fruehan [13]. They found that increasing $(\text{Al}_2\text{O}_3/\text{FeO})$ ratio reduced the slag phosphorus capacity. Similarly, Li and coauthors [14] reported a negative influence of alumina on the phosphorus capacity of ladle dephosphorization, especially for slags where the $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$

ratio exceeded 0.66. The binary basicities were very high (above 5), the equilibration time was only 1 to 3 h and the slags contained Na_2O , which can improve phosphorus partition [8].

Miyata [15] reported the results of hot metal dephosphorization where 5 wt.% Al_2O_3 was added to the slag system $\text{CaO-SiO}_2\text{-FeO}_x$. This work recorded an improvement in dephosphorization, which claimed to be caused by the increase in slag fluidity. Mansour Al-Harbi [11] used the MTDATA thermodynamic package [10] and found that by increasing the alumina addition from 5 wt.% to 15 wt.%, the phosphorous content in the steel was reduced by almost 50% enhancing the phosphorus holding capacity of the slag.

2. Materials and Methods

A complete description of the experimental approach was described in detail by Assis et al. [1]. A brief description is provided below.

The current work concentrates on binary basicities (CaO/SiO_2) ranging from 1.0–2.7, FeO concentrations of up to 40 wt.%, and alumina of up to ~15 wt.% in the slag system $\text{CaO-SiO}_2\text{-MgO}_{\text{Saturated}}\text{-FeO-P}_2\text{O}_5\text{-Al}_2\text{O}_3$. Most of the experiments were performed at 1873 K (1600 °C); some experiments were performed at 1823 K (1550 °C) and 1923 K (1650 °C). Equilibrium was attained from both sides, i.e., phosphorus was transferred from slag to metal and from metal to slag. To do this, experiments were mostly run in pairs; one with initial phosphorus partition, L_P , above equilibrium and the other with L_P below equilibrium.

2.1. Equilibration Time

A wide range of holding times has been reported in previous works [2–5,12,16] for the phosphorus reaction. It was demonstrated by Assis et al. [1] that equilibrium could be achieved in ~10 h for the present conditions. Thus, 10 h of holding time was used in the present work.

2.2. Master Fe–P Alloy

A master Fe–P alloy was prepared by melting electrolytic iron containing 99.97 wt.% Fe and 0.0004 wt.% P with iron phosphide (Fe_3P) powder in an MgO crucible. The mixture was melted using a box furnace (CM 1712 GS FL, CM Furnaces Inc., Bloomfield, NJ, USA) heated at a rate of 2 K/min up to 1873 K (1600 °C) and held for 3 h. The furnace atmosphere was controlled by flowing high purity Argon gas. The furnace was cooled at a rate of 2 K/min to room temperature. The crucible was then crushed and the master alloy was polished to remove any traces of MgO from the surface. The composition of the master alloy was determined by inductively coupled plasma mass spectroscopy (ICP-MS). The final phosphorus content was 0.054 wt.%.

2.3. Iron Oxide

FeO was synthesized by mixing dried, reagent grade Fe_2O_3 with a slight excess of electrolytic iron power with a ratio of approximately 0.98. It was melted in an MgO crucible at 1273 K (1000 °C) under argon atmosphere. The temperature of 1273 K was chosen to not allow MgO dissolution to take place. The FeO-Fe mixture was then crushed and pulverized; any excess iron was removed by magnetic separation. The resulting powder was characterized with X-ray diffraction and confirmed that FeO had been produced.

2.4. Master Slag

A master slag was prepared with a targeted binary basicity of 1.0 and MgO content of 18 wt.%. CaO , SiO_2 , and MgO were dried in air at 1173 K (900 °C) for 8 h in a resistance box furnace. The products were mixed and melted for 4 h at 1873 K (1600 °C) under argon atmosphere in a graphite crucible. The liquid slag was then quenched in cold water by opening the furnace and pouring the contents of the crucible into the water. The solid slag was pulverized using a puck mill (Shatterbox 8530,

SPEX SamplePrep LLC, Metuchen, NJ, USA) and decarburized in an MgO crucible for 10 h at a temperature of 1473 K (1200 °C) in air atmosphere. The master slag was used to facilitate melting during the equilibrium experiments. The individual slag composition for each experiment was adjusted accordingly by adding other oxides to the master slag.

2.5. Experimental Procedure

For each experiment, approximately 12 g of Fe–P alloy and 6 g of premelted mixed slag were allowed to equilibrate for 10 h in high-density MgO crucibles. Ultra-high-purity argon was used for the atmosphere to prevent the oxidation of the melt. The oxygen partial pressure content was measured to be between 10^{-5} to 10^{-6} atm. The present work has studied only two-phase equilibrium between liquid metal and slag. Three-phase equilibrium takes much longer to be achieved due to poor contact between all three phases or due to the lower density of the gas phase limiting the amount of mass transferred per unit time. Phosphorus was added in the form of Fe_3P into the metal and $\text{Ca}_2\text{P}_2\text{O}_7$ in the slag. All experiments were carried out in a horizontal tube furnace (CM 1730-12 HTE, CM Furnaces Inc., Bloomfield, NJ, USA) with ten MoSi_2 heating elements. The furnace was calibrated by inserting a type B thermocouple through the alumina reaction tube and measuring the temperature at intervals of 2 cm. In order to achieve 1873 K (1600 °C) in the furnace hot zone, the controller of the furnace needed to be set to 1918 K (1654 °C). The furnace calibration was always rechecked upon replacement of the alumina reaction tube.

The furnace of heated at a rate of 2 K/min until the desired equilibrium temperature was achieved. The temperature was held for 10 h. The furnace was then cooled to 1573 K (1300 °C) at a rate of -21 K/min to promote rapid solidification of the samples and held for 10 min. The cooling would then continue at a rate of -2 K/min until room temperature was achieved.

The metal analysis for phosphorus was mostly carried out by ICP-MS at West Penn Testing Group (New Kensington, PA, USA) with a reported reproducible limit detection of 20 ppm; most of the experiments exceeded that level. A few metal samples were also analyzed for phosphorus by optical emission spectroscopy (OES) at Clark Testing (Jefferson Hills, PA, USA) and glow discharge mass spectrometry (GDMS) at EAG Laboratories (San Diego, CA, USA). Some metal samples were analyzed for total oxygen content using LECO combustion analysis. The slag samples were analyzed for CaO, SiO_2 , MgO, Al_2O_3 , FeO, and P_2O_5 using energy dispersive X-ray fluorescence (ED-XRF) at West Penn Testing (New Kensington, PA, USA).

3. Results

Initial and final compositions of the metal and slag for the current equilibrium experiments are listed in Tables 1 and 2, respectively. Sample coding consists of two capital letters followed by two numbers, e.g., MS05. The letters M and S stand for metal and slag respectively. The two digits refer to the order of the experiments. When it starts with M then S (MSXX), it means the experiment was designed to transfer phosphorus from metal to slag, i.e., dephosphorization, similarly, SMXX are experiments where rephosphorization occurred. As previously mentioned, a two-phase slag-metal equilibrium was established which is faster than a three-phase equilibrium with gaseous species. Randomly selected experiments were repeated to ascertain the reproducibility of the experimental results. The reproducibility in the estimation of phosphorus partition was within 6 per cent.

Table 1. Initial chemical compositions, temperature, and holding time for current equilibrium experiments; square brackets denote concentration in the metal.

Exp. ID	T K	Ht ¹ h	B2 ²	B3 ³	CaO wt. %	SiO ₂ wt. %	MgO wt. %	FeO wt. %	Al ₂ O ₃ wt. %	P ₂ O ₅ wt. %	[P] wt. %
MS01	1873	10	1.00	0.98	30.28	30.23	10.02	27.72	0.58	0.93	0.0456
SM01	1873	10	0.99	0.99	30.19	30.38	10.10	27.80	0.27	1.01	0.0008
MS02	1873	10	1.50	1.49	38.02	25.38	8.79	26.13	0.21	0.87	0.0426

Table 1. Cont.

Exp. ID	T K	Ht ¹ h	B2 ²	B3 ³	CaO wt. %	SiO ₂ wt. %	MgO wt. %	FeO wt. %	Al ₂ O ₃ wt. %	P ₂ O ₅ wt. %	[P] wt. %
SM02	1873	10	1.50	1.49	38.03	25.32	8.78	26.07	0.21	1.00	0.0018
MS03	1873	10	2.07	2.06	42.97	20.76	5.36	29.50	0.13	0.91	0.0425
SM03	1873	10	2.07	2.06	43.04	20.77	5.36	29.34	0.13	1.00	0.0011
MS04	1873	10	1.03	1.02	25.42	24.79	13.84	34.15	0.24	0.87	0.0426
SM04	1873	10	1.03	1.02	25.52	24.77	13.85	33.94	0.24	0.99	0.0043
MS05	1873	10	1.03	1.02	23.44	22.74	12.91	39.19	0.23	0.87	0.0426
SM05	1873	10	1.03	1.02	23.52	22.76	12.87	39.00	0.23	0.99	0.0047
MS06	1873	10	1.50	1.49	30.84	20.54	9.19	37.72	0.22	0.87	0.0426
SM06	1873	10	1.51	1.49	30.89	20.50	9.19	37.55	0.22	1.04	0.0032
MS07	1873	10	2.09	2.07	43.88	21.02	5.42	28.32	0.13	0.86	0.0426
MS08	1873	10	1.01	0.86	29.98	29.83	16.57	17.47	4.90	0.93	0.0523
SM08	1873	10	1.01	0.86	29.92	29.66	16.55	17.54	4.95	1.06	0.0019
MS09	1873	10	1.01	0.75	28.11	27.95	16.45	16.88	9.40	0.89	0.0523
SM09	1873	10	1.01	0.75	28.15	27.90	16.43	16.76	9.45	1.01	0.0019
MS10	1873	10	1.00	0.67	28.31	28.17	17.28	10.94	14.12	0.88	0.0523
SM10	1873	10	1.01	0.67	28.39	28.14	17.29	10.77	14.09	1.02	0.0035
MS11	1873	10	2.01	1.21	33.42	16.66	8.91	28.94	11.01	0.88	0.0523
SM11	1873	10	2.01	1.21	33.39	16.64	8.88	28.92	10.95	1.03	0.0023
MS12	1873	10	2.10	1.57	37.86	18.02	7.14	29.81	6.13	0.87	0.0523
SM12	1873	10	2.10	1.57	37.85	18.01	7.13	29.70	6.11	1.02	0.0015
MS14	1873	10	1.00	0.93	31.08	31.00	15.53	18.61	2.59	0.87	0.0523
SM14	1873	10	1.01	0.93	31.08	30.84	15.58	18.51	2.59	1.07	0.0020
MS15	1873	10	3.51	2.52	49.17	14.03	3.75	26.04	5.50	1.42	0.0523
SM15	1873	10	3.51	2.52	49.19	14.02	3.69	25.87	5.49	1.64	0.0009
MS16	1873	10	1.74	1.40	37.61	21.57	8.63	25.73	5.33	0.92	0.0523
SM16	1873	10	1.74	1.40	37.71	21.63	8.66	25.32	5.38	1.09	0.0010
MS17	1873	10	1.69	1.69	41.73	24.62	7.37	25.04	0.11	0.94	0.0523
SM17	1873	10	1.68	1.68	41.53	24.65	7.34	25.16	0.11	1.03	0.0015
MS20	1873	10	3.79	1.90	37.59	9.91	7.02	34.48	9.91	0.98	0.0551
MS21	1873	10	2.00	1.00	27.98	13.99	13.12	29.72	14.02	1.01	0.0542
MS22	1823	10	1.00	0.90	29.31	29.21	14.68	22.37	3.26	0.85	0.0521
SM22	1823	10	1.02	0.91	29.21	28.77	14.85	22.41	3.16	1.27	0.0018
MS23	1873	4	1.75	1.40	37.62	21.49	8.60	25.73	5.45	0.90	0.0550
SM23	1873	4	1.76	1.40	37.65	21.45	8.63	25.52	5.46	1.08	0.0012
MS24	1923	10	1.00	0.92	31.20	31.12	15.54	18.29	2.63	0.87	0.0546
SM24	1923	10	1.01	0.93	31.25	31.03	15.53	18.13	2.66	1.05	0.0019
MS25	1923	10	2.68	1.44	39.80	14.88	8.10	23.41	12.68	0.97	0.0541
MS26	1923	10	2.00	1.00	27.95	13.96	12.95	30.02	14.09	0.88	0.0537
MS27	1823	10	2.67	1.46	39.91	14.96	8.02	23.58	12.45	0.93	0.0538
MS28	1823	10	2.00	1.00	28.08	14.01	12.90	29.92	14.05	0.89	0.0538
MS29	1873	10	1.01	1.00	32.05	31.89	16.96	17.53	0.22	1.00	0.0541
SM29	1873	10	1.01	1.00	32.03	31.83	17.01	17.51	0.22	1.04	0.0015

¹ Ht = holding time; ² B2 = CaO / SiO₂; ³ B3 = CaO / (SiO₂ + Al₂O₃).**Table 2.** Equilibrium chemical compositions (final reported chemical analysis); square brackets denote concentration in the metal. Values were normalized to 100 pct.

Exp. ID	B2 ¹	B3 ²	CaO wt. %	SiO ₂ wt. %	MgO wt. %	FeO wt. %	Al ₂ O ₃ wt. %	P ₂ O ₅ wt. %	[P] wt. %	[O] wt. %
MS01	1.00	0.98	30.03*	29.98*	15.17	22.83	0.80	1.18	0.0141	NA ³
SM01	0.99	0.99	29.95*	30.13*	15.44	22.87	0.48	1.13	0.0131	NA ³
MS02	1.50	1.49	38.75*	25.87*	10.64	23.57	0.00*	1.17	0.0029	NA ³
SM02	1.50	1.49	38.52*	25.65*	10.20	24.58	0.00*	1.05	0.0030	NA ³
MS03	2.07	2.06	44.29*	21.40*	6.49	26.54	0.00*	1.29	0.0024	NA ³
SM03	2.07	2.06	43.70*	21.09*	7.03	27.06	0.00*	1.13	0.0024	NA ³

Table 2. Cont.

Exp. ID	B2 ¹	B3 ²	CaO wt. %	SiO ₂ wt. %	MgO wt. %	FeO wt. %	Al ₂ O ₃ wt. %	P ₂ O ₅ wt. %	[P] wt. %	[O] wt. %
MS04	1.03	1.02	26.69*	26.02*	16.35	29.73	0.00*	1.22	0.0100	NA ³
SM04	1.03	1.02	26.24*	25.48*	17.45	29.73	0.00*	1.09	0.0070	NA ³
MS05	1.03	1.02	25.40*	24.65*	15.56	33.09	0.00*	1.29	0.0090	NA ³
SM05	1.03	1.02	24.78*	23.98*	16.40	33.73	0.00*	1.11	0.0080	NA ³
MS06	1.50	1.49	33.14*	22.07*	10.37	33.08	0.00*	1.33	0.0024	NA ³
SM06	1.51	1.49	32.65*	21.67*	10.58	33.85	0.00*	1.25	0.0024	NA ³
MS07	2.09	2.07	43.72*	20.94*	7.69	26.45	0.00*	1.21	0.0024	NA ³
MS08	1.01	0.86	30.63*	30.47*	17.44	15.71	4.66	1.08	0.0309	NA ³
SM08	1.01	0.86	30.70*	30.43*	17.84	14.79	5.09	1.15	0.0262	NA ³
MS09	1.01	0.75	27.96*	27.80*	18.64	15.21	9.39	0.99	0.0343	NA ³
SM09	1.01	0.75	28.16*	27.91*	18.79	15.07	9.13	0.94	0.0315	NA ³
MS10	1.00	0.67	28.00*	27.86*	19.72	10.27	13.55	0.61	0.0855	NA ³
SM10	1.01	0.67	28.38*	28.12*	19.57	10.21	13.13	0.59	0.0764	NA ³
MS11	2.01	1.21	35.06*	17.48*	10.64	24.24	11.32	1.25	0.0060	NA ³
SM11	2.01	1.21	35.07*	17.48*	10.40	24.65	11.22	1.18	0.0061	NA ³
MS12	2.10	1.57	39.74*	18.91*	8.95	25.16	6.19	1.04	0.0033	NA ³
SM12	2.10	1.57	39.34*	18.72*	8.68	26.07	6.16	1.03	0.0032	NA ³
MS14	1.00	0.93	33.59	31.67	16.37	14.63	2.74	1.01	0.0240	NA ³
SM14	1.01	0.93	33.36	31.28	16.00	15.47	2.89	1.00	0.0200	NA ³
MS15	3.51	2.52	49.69*	14.17*	3.79	25.37	5.46	1.53	0.0008	0.035
SM15	3.51	2.52	49.54*	14.12*	3.78	25.55	5.44	1.57	0.0007	0.035
MS16	1.74	1.40	38.92*	22.32*	8.95	23.09	5.57	1.15	0.0027	0.072
SM16	1.74	1.40	38.82*	22.27*	8.90	23.34	5.54	1.13	0.0028	0.070
MS17	1.69	1.69	43.18*	25.47*	7.63	22.62	0.00*	1.10	0.0013	0.086
SM17	1.68	1.68	42.30*	25.11*	7.51	24.01	0.00*	1.07	0.0018	0.084
MS20	3.79	1.90	38.51*	10.15*	9.01	31.54	9.33	1.45	0.0012	NA ³
MS21	2.00	1.00	28.58*	14.29*	16.04	26.83	12.86	1.40	0.0100	NA ³
MS22	1.00	0.90	33.06	30.47	15.62	16.72	2.86	1.28	0.0106	NA ³
SM22	1.02	0.91	33.05	30.45	15.58	16.71	2.88	1.33	0.0103	NA ³
MS23	1.75	1.40	37.14*	21.21*	9.43	26.11	4.85	1.26	0.0036	NA ³
SM23	1.76	1.40	37.01*	21.09*	9.72	26.47	4.60	1.11	0.0026	NA ³
MS24	1.00	0.92	31.71*	31.63*	18.70	14.06	2.77	1.13	0.0290	NA ³
SM24	1.01	0.93	32.02*	31.80*	18.91	13.67	2.52	1.08	0.0275	NA ³
MS25	2.68	1.44	40.68*	15.20*	11.06	19.52	12.08	1.45	0.0035	NA ³
MS26	2.00	1.00	29.01*	14.49*	16.14	25.62	13.46	1.29	0.0092	NA ³
MS27	2.67	1.46	39.31*	14.73*	8.05	26.47	10.15	1.28	0.0023	NA ³
MS28	2.00	1.00	28.43*	14.19*	13.17	31.16	11.94	1.11	0.0086	NA ³
MS29	1.06	1.04	34.34	32.54	18.54	12.81	0.4	1.37	0.0248	NA ³
SM29	1.05	1.04	34.74	32.96	17.95	12.79	0.36	1.21	0.0193	NA ³

¹ B2 = CaO / SiO₂; ² B3 = CaO/(SiO₂ + Al₂O₃); ³ NA = Not Analyzed; * Estimated values.

The initial MgO saturation content in all slags used were estimated using FactSage. However, there was a consistent increase of the MgO concentration (MgO pick up) in all slag samples through the course of the experiments. The authors have recently published a paper about FactSage's tendency to slightly underestimate MgO saturation levels elsewhere [17].

As seen in Table 2, CaO and SiO₂ were estimated for most of the experiments. Ideally, the initial and final weights of CaO and SiO₂ in the slag should be equal and preserve a constant *CaO/SiO₂* ratio during the phosphorus reaction. Therefore, the expected change in their relative concentrations is small. To test this approach, several samples were analyzed for CaO and SiO₂ in order to evaluate the differences between the initial and final *CaO/SiO₂* ratios. The difference in the ratio was found to be less than ± 0.08 . This may have been due to hydration of the stored powders. The authors therefore have assumed that the initial and final *CaO/SiO₂* ratios to be equal and their contents were determined by mass balances.

4. Discussion

4.1. The Effect of Alumina on the Phosphorus Partition

There is limited amount of work describing the effect of alumina on the phosphorus partition. A series of equilibrium experiments were conducted to study the effect of alumina on the phosphorus partition. From the data in Figure 1, it is apparent that at constant CaO/SiO_2 ratio and FeO content, alumina decreases the phosphorus partition. At alumina concentration of 9–11 wt.% and CaO/SiO_2 ratio of 1.0 and 2.0, the phosphorus partition was lowered by more than half compared to slags with no alumina.

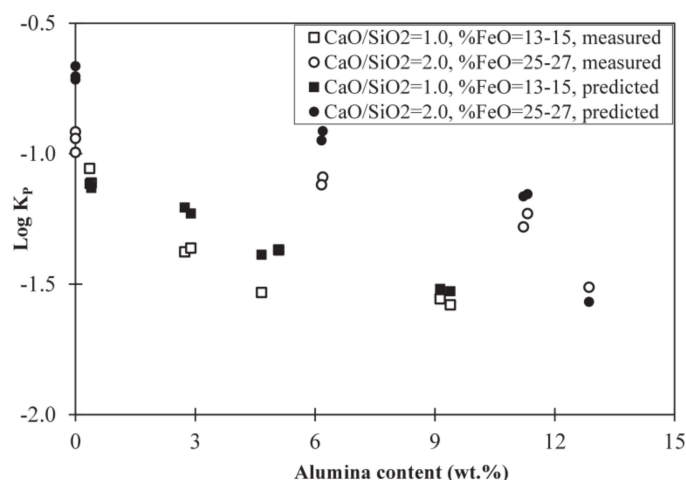


Figure 1. $\log K_p$ versus slag alumina content for binary basicities of 1.0 and 2.0 at FeO compositions of 13–15 and 25–27 wt.%, respectively, at 1873 K (1600 °C). Solid markers predicted by Equation (5).

Experiment 15 was carried out with a highly basic slag ($\text{CaO}/\text{SiO}_2 = 3.5$) and Al_2O_3 concentration of 5 wt.% in order to assess if the effect of alumina on dephosphorization persists at higher basicity. It was compared with one of the experiments from Assis et al. [1] that used similar slag and metal compositions. The result confirms the trend observed at lower basicity that as the alumina is added, the phosphorus partition is lowered.

The results discussed above are in agreement with some of the ones reported by Selin [18] and shown in Table 3. The experiments by Selin [18] labeled A21, E2, and C4 a binary basicity of about 1.6 with increasing alumina content. The effect of alumina on L_p is evident and L_p decreased from 129 to 38.5 when comparing experiments A21 and C4.

Table 3. Selected results from Selin and the present work.

Exp. ID	B2 ¹	B3 ²	CaO wt. %	SiO ₂ wt. %	MgO wt. %	FeO wt. %	Al ₂ O ₃ wt. %	P ₂ O ₅ wt. %	[P] wt. %	[O] ppm	L _p
C4 ³	1.60	1.15	35.3	22.0	11.5	20.2	8.78	0.93	0.0105	980	38.5
E2 ³	1.60	1.36	38.2	23.9	10.2	22.4	4.23	0.91	0.0065	1094	61
A21 ³	1.65	1.65	40.8	24.7	8.4	24.3	0.0	0.98	0.0033	1185	129
MS16	1.74	1.40	38.92*	22.32*	8.95	23.09	5.57	1.15	0.0027	720	186
SM16	1.74	1.40	38.82*	22.27*	8.90	23.34	5.54	1.13	0.0028	700	176
MS17	1.69	1.69	43.18*	25.47*	7.63	22.62	0.00*	1.10	0.0013	860	370
SM17	1.68	1.68	42.30*	25.11*	7.51	24.01	0.00*	1.07	0.0018	840	258

¹ B2 = $\text{CaO} / \text{SiO}_2$; ² B3 = $\text{CaO} / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$; ³ data from Selin [18]; * Estimated values.

From the above discussion, alumina levels expected in EAF and BOF steelmaking are detrimental to the dephosphorization ability of the slag. It is more significant in the slag chemistries prevalent in the EAF compared to those in the BOF. Further investigations must be made to clarify whether this

effect is due to changes in the activity of iron oxide (oxygen potential), oxygen anions (slag structure), the activity of phosphate ion in the slag, or a combination of two or more of these.

4.2. Comprehensive Equation for Phosphorus Equilibrium

The purpose of this section is to present the method that was used to develop a comprehensive equation for phosphorus partition for both EAF- and BOF-type slags. The adopted methodology is different from previous treatments but its final form is similar to the one proposed by Suito et al. [4,5]: it assumes that the $\log K_P$ is a linear function of the slag components and reciprocal temperature. The present data was combined with those from Assis et al. [1] and Suito et al. [4,5]. The experimental approach for the work of Assis et al. [1] and the current research was similar and thus it is reasonable to combine both data sets in the assessment of phosphorus partition. Literature data were also examined and evaluated considering two important aspects: the attainment of equilibrium (the equilibration time) and the presence of any solid phases in the slag.

It was demonstrated that holding times of four hours yielded compositions very close to equilibrium and 10 h ensured attainment of equilibrium. The holding time in the experiments conducted by Suito and coworkers [4,5] varied between three hours for non-SiO₂-containing slags and five h for slags with high SiO₂ and low FeO. The authors therefore assumed Suito's experiments were close or at equilibrium.

The second point to discuss is the presence of solid phases (undissolved oxides) in the slag which will affect the "apparent" slag composition making it either more or less demanding with respect to dephosphorization. The slags in the present experiments were assured to be completely liquid. Literature data was initially examined by FactSage [19] version 6.4 (ThermFact Inc., Montréal, Canada and GTT-Technologies, Herzogenrath, Germany) using the CON1 database, which was later integrated into the FToxid database and contains a more accurate description of slags containing P₂O₅ to predict the amount of solid phases in equilibrium with the liquid slag. This approach provided a better estimate of the actual liquid slag composition. The calculations made with FactSage 6.4 using CON1 were compared with FactSage 7.2 (ThermFact Inc., Montréal, Canada and GTT-Technologies, Herzogenrath, Germany) using FToxid and were found to be in close agreement. In FactSage 7.2 Equilib module, the same calculations can be carried by selecting the databases FToxid, FTmisc, and FactPS. The solution phases to be selected are FTmisc-FeLQ, FToxid-SLAGA, FToxid-MeO_A, FToxid-aC2Sa, FToxid-bC2Sa, FToxid-C2SP, FToxid-C3Pr, FToxid-C3Pa, FToxid-C3Pb, FToxid-M3Pa, FToxid-CMPc, and FToxid-M2Pa. A FactSage macro was used to expedite the calculations.

The fraction of liquid slag in the experiments conducted by Suito et al. [4,5] ranged between 81 and 99% according to the FactSage calculations. On the other hand, while evaluating some other literature data [2,3], significant concentrations of solids (C₂S and monoxide) were present in the slags with a calculated liquid fraction as low as 27%. The large amount of solids makes it difficult to evaluate the phosphorus partition in the remaining liquid.

An additional set of data, which was used in formulating the new equilibrium correlation, is that of Ide and Fruehan [9]. They used calcia crucibles and CaO saturated slags with a binary basicity of 2.9, and varied the concentration of MgO between 2.9 and 10.3 wt.%. The liquid fraction of the slags was above 80% according to the FactSage estimations. The use of calcia crucibles enables the MgO content to be varied without the constraints of maintaining a MgO saturated slag and provides a potentially better estimation of the MgO coefficient.

The steps to find the new correlation:

1. The MgO coefficient was fixed as reported by Ide and Fruehan [9]. The coefficient is $0.072 \times 0.15 = 0.0108$.
2. Evaluate $\log K_P - 0.0108(\% \text{MgO})$ as a function of $\text{wt.}\% \text{CaO}$, $\text{wt.}\% \text{SiO}_2$ and $\text{wt.}\% \text{P}_2\text{O}_5$ using the data from Suito et al. [4,5], Assis et al. [1], and the present data that did not contain Al₂O₃.

The resulting coefficients are 0.073 for CaO, 0.0105 for SiO₂, and 0.070 for P₂O₅. All *p*-values were below 0.05. The resulting equation is

$$\log K_P - 0.0108(\% \text{MgO}) = 0.073(\% \text{CaO}) + 0.0105(\% \text{SiO}_2) + 0.070(\% \text{P}_2\text{O}_5) - 4.3$$

3. Fix the CaO, MgO, SiO₂, and P₂O₅ coefficients as done above for MgO and evaluate the Al₂O₃ coefficient using the present alumina-containing data. The resulting coefficient is 0.0160 for Al₂O₃. The *p*-value was below 0.05. The resulting equation is

$$\begin{aligned} \log K_P - 0.0108(\% \text{MgO}) - 0.073(\% \text{CaO}) - 0.0105(\% \text{SiO}_2) - 0.070(\% \text{P}_2\text{O}_5) \\ = 0.160(\% \text{Al}_2\text{O}_3) - 4.34 \end{aligned}$$

The temperature dependence and intercept constant were then evaluated using the data from the present work and Suito et al. [4,5] for 1823–1923 K (1550–1650 °C). The new intercept is of −10.46 with a 95% confidence interval of 0.1. The temperature dependence is the same as reported by Suito et al. [4,5].

The final equation obtained is

$$\begin{aligned} \log \left(\frac{L_P}{T \cdot \text{Fe}^{2.5}} \right) = 0.073[(\% \text{CaO}) + 0.148(\% \text{MgO}) + 0.96(\% \text{P}_2\text{O}_5) + 0.144(\% \text{SiO}_2) \\ + 0.22(\% \text{Al}_2\text{O}_3)] + \frac{11570}{T} - 10.46 \pm 0.1 \end{aligned} \quad (5)$$

It is interesting to note that both CaO coefficient of 0.073 and the constant of −10.46 are in good agreement to the original correlation reported by Suito et al. [5] (0.072 and −10.52, respectively). Equation (5) is the same as reported by Assis et al. [1] but with the newly calculated Al₂O₃ coefficient included. Figure 2 compares the measured log *K_P* and newly calculated apparent phosphorus equilibrium constants by Equation (5). The new correlation represents well different sets of laboratory data including the current results and those of Assis et al. [1], Ide et al. [9], and Suito et al. [4,5]. The *R*² of 0.95 is high, and because the equation was fitted using multiple sets of data, it is capable of predicting the phosphorus partition over a wider range of slag compositions than previously developed correlations. Additionally, the mean absolute error is 0.152. A comparison of the measured *L_P* with the predicted *L_P* by Equation (5) is shown in Figure 3.

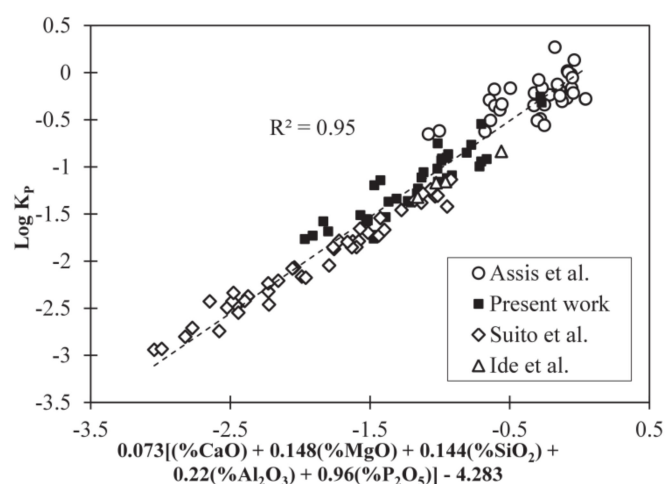


Figure 2. Apparent equilibrium constant versus Equation (5) at 1873 K (1600 °C). Data sets from Suito et al. [4,5], Ide et al. [9], Assis et al. [1], and the present work.

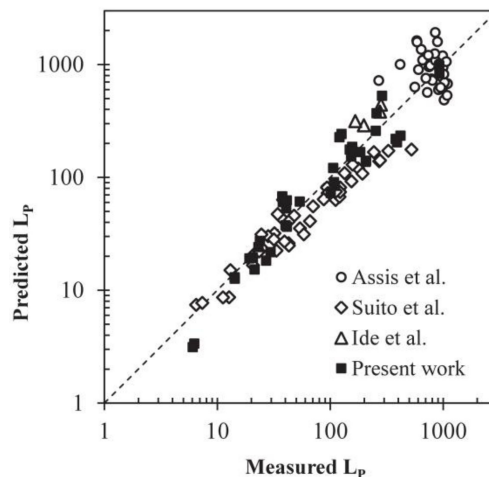


Figure 3. Measured phosphorus partition versus predicted phosphorus partition by Equation (5). Data sets from Suito et al. [4,5], Ide et al. [9], Assis et al. [1], and the present work.

In the new correlation, the coefficients of alumina and silica are small but positive. However, one must not confuse positive coefficients as enhancers of dephosphorization. Increasing silica and/or alumina would dilute CaO, which has the highest coefficient, thus decreasing K_P . Figure 4 demonstrates the change of $\log K_P$ when silica or alumina increases while the concentrations of the remaining components are adjusted proportionally. It can be seen that increasing either SiO_2 or Al_2O_3 decreases K_P .

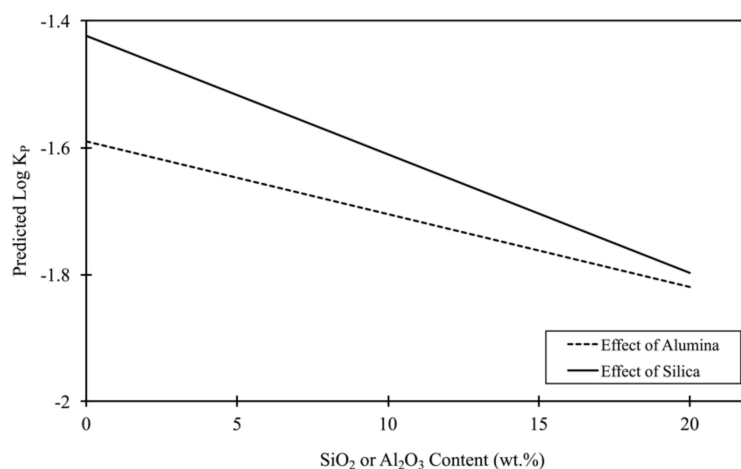


Figure 4. Calculated $\log K_P$ versus silica and alumina concentration as predicted by Equation (5).

The steelmaker can use Equation (5) to easily predict the equilibrium phosphorus partition in their operations by simply comparing the actual L_P measured using physical steel and slag samples with the equilibrium L_P predicted by Equation (5). The departure from equilibrium is related to the driving force for dephosphorization and can be a helpful indicator of the kinetics inside the furnace. As such, Equation (4) can be integrated into kinetic models and mass transfer equations to simulate furnace behavior. This however is not covered in this publication.

Equation (5) is a statistical correlation and is only valid within the range in which it was originally evaluated. This range is shown in Table 4.

Table 4. Range of slag compositions valid for Equation (5).

Variable	Min	Max
%CaO	54.01	10.94
%SiO ₂	33.75	0.48
%T.Fe	59.43	7.93
%MgO	21.94	3.78
%P ₂ O ₅	0.51	5.46
%Al ₂ O ₃	0	21.05
Temperature	1823	1923

5. Conclusions

This paper presented the continuation of the work described by Assis et al. [1]. It presented new sets of phosphorus equilibrium data using EAF-type slags with and without alumina, demonstrated the negative effect of alumina on L_P , and proposed a new improved correlation for predicting the phosphorus equilibrium partition. This new correlation includes the effect of alumina and can be used for both BOF and EAF-type slags to predict the equilibrium phosphorus partition. The negative effect of alumina in the correlation occurs due to the dilution of CaO in the slag. However, further investigations are needed to understand how alumina affects slag structure, the activity of iron oxide and the activity of the phosphate ion in the slag. Equation (5) is easy to use and enables the steelmaker to evaluate furnace performance with respect to dephosphorization. In a future publication, we will evaluate the departure from equilibrium in an extensive collection of plant data and discuss which types of furnaces operate closer to equilibrium.

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