

Phosphorus Partition Between Liquid Crude Steel and High-Basicity Basic Oxygen Furnace Slags

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The phosphorus partition between the unkilld liquid crude steel and the high basicity ($\text{CaO}/\text{SiO}_2 = 4.2$), basic oxygen furnace (BOF) slags with varying compositions of Al_2O_3 , TiO_2 , and MnO is studied at temperatures 1600 and 1650 °C. The tests are conducted in both “slag-to-metal” and “metal-to-slag” directions and for durations of 30 and 60 min. The measured results are compared with the values reported in literature and found to be in good agreement with some of them. It is found in the investigation of high-basicity BOF slags, that Al_2O_3 , MnO , and TiO_2 lower the phosphorus partition. The phosphorus partition increases with increasing optical basicity. The phosphorus partition shows a maximum when the FeO content is in range of 25–30 mass%. The MgO content slightly increases the phosphorus partition.

grades, sulfur or phosphorus and other elements can also serve as the alloying elements. The reported examples for phosphorus alloying are, the hot-rolled high-strength sheet steel with 0.04 mass% of phosphorus^[1] and phosphorus-alloyed IF steel.^[2] However, in most of the cases, P is considered as a nondesirable element and maximum dephosphorization is required during the primary steelmaking operation.

The efficiency of the phosphorus removal process during the primary steel making is usually evaluated using the following parameters.

Phosphorus partition L_P

$$L_P = (P)/[P] \quad (1)$$

where (P) is phosphorus content (in mass [%]) in the slag, and [P] is phosphorus content (in mass [%]) in the steel,

Phosphate capacity^[3–5]

$$\frac{1}{2} \{P_2\} + \frac{5}{4} \cdot \{O_2\} + \frac{3}{2} \cdot (O^{2-}) = (PO_4^{3-}) \quad (2)$$

$$C_{PO_4^{3-}} = \frac{(PO_4^{3-})}{p_{P_2}^{1/2} \cdot p_{O_2}^{5/4}} \quad (3)$$

where { } denotes gas, (PO_4^{3-}) is the content (in mass%) of phosphate ion in the slag, and p_{P_2} and p_{O_2} are the partial pressures of phosphorus and oxygen, respectively.

Degree of dephosphorization^[6]

$$\eta_{[P]} = \frac{[\%P]_a - [\%P]_e}{[\%P]_a} \times 100\% \quad (4)$$

where [% P]_a—is the initial phosphorus content in hot metal, [% P]_e—is the final phosphorus content in steel after dephosphorization.

The first model for the prediction of phosphorus partition between the metal and the slag was established by Balajiva and Vajragupta^[7] and Winkler and Chipman^[8] in 1946–1947

$$\log \frac{(\%P)}{[\%P]} = 2.5 \times \log(\%FeO) + 0.08 \times (\%CaO) + \frac{22350}{T} - 16 \quad (5)$$

$$\log \frac{(\%P)}{[\%P]} = 2.5 \times \log(\%FeO) + 7 \times \log(\%CaO) + \frac{22350}{T} - 24 \quad (6)$$


Since 1946, many researchers^[4,9–19] have investigated the phosphorus partition experimentally. Thereby, many models

1. Introduction

High-quality steels require a higher degree of cleanliness, which is necessary for the quality and durability of the product. When it comes to the cleanliness of steel, the removal of undesirable constituents such as the nonmetallic inclusions, the tramp elements namely copper, tin, or the impurity elements namely oxygen, nitrogen, carbon, sulfur, and phosphorus are always implied. Selection of elements to be considered as an impurity element or as trace element depends on the desired steel grade and the subsequent production route. For example, some electrical steels are sensitive to manganese or titanium; interstitial-free (IF) steel needs low carbon levels. In few cases of other steel

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Table 1. Overview of experimental investigation of phosphorus partition.

Authors	Slag system	Temperature/ crucible	Samples mass	Hold time [h]	Results
Morales and Fruehan ^[9]	CaO–SiO ₂ –MnO–FeO–P ₂ O ₅ –MgO, Fe _t <20%, B = 1–4, B = (%CaO + MgO)/SiO ₂	1600 °C, MgO	10 g steel, 20 g slag	8	L _{Mn} , C _{PO4} ³⁻
Kobayashi et al. ^[10]	MnO–SiO ₂ –Fe _t O, MnO–SiO ₂ –Fe _t O–MgO FeO–MAX = 12.4 mass%	1400–1650 °C, fused MgO	1 g iron/10 g slag 2 g iron/3.5 g slag	3–12	L _p , new equation for logC _{PO4} ³⁻
Lee and Fruehan ^[11]	CaO–SiO ₂ –MgO–FeO–P ₂ O ₅ FeO–MAX = 10.3%, CaO/SiO ₂ < 2	1550–1580 °C, MgO	5 g iron, 5 g slag	4	New equation for log L _p
Li et al. ^[12]	MgO–CaO–FeO _x –Al ₂ O ₃ –SiO ₂ Fe _t –MAX = 58 mass%	1550–1600 °C, densely sintered pure MgO	8 g iron, 6 g slag	1–3	L _p , C _{PO4} ³⁻
Basu et al. ^[13]	CaO–SiO ₂ –P ₂ O ₅ –MgO–FeO FeO–MAX = 15%, CaO/SiO ₂ = 1.5–3.5	1600–1650 °C, dense-sintered MgO	–	4–10	L _p
Basu et al. ^[14]	CaO–SiO ₂ –FeO _x –P ₂ O ₅ –MgO FeO–MAX = 25%, CaO/SiO ₂ = 1.5–3.5	1600–1650 °C, dense-sintered MgO	–	8	L _p
Basu et al. ^[15]	CaO–SiO ₂ –FeO _x –MgO–P ₂ O ₅ – (S) CaO/SiO ₂ = 1.5–3.5	1600–1650 °C, dense-sintered MgO	–	8	L _p
Maruoka et al. ^[3]	Al ₂ O ₃ –CaO–FeO–MgO–SiO ₂ Fe _t –MAX = 31 mass%, CaO/SiO ₂ = 0.5–1.34	1350 °C, densely sintered MgO	1 g iron foil, 10 g slag	20	L _p , new equation for logC _{PO4} ³⁻
Ek et al. ^[16]	CaO–SiO ₂ –FeO–MnO–MgO	1650 °C, Mo	10 g Cu, 7 g slag	24	C _{PO4} ³⁻
Zhou et al. ^[17]	CaO–FeO–SiO ₂ –P ₂ O ₅ – (15%)–CaF ₂	1300 °C, Fe	Equilibrium between iron crucible/iron flakes and slag.	12	L _p
Assis et al. ^[18]	CaO–SiO ₂ –MgO–FeO–P ₂ O ₅ FeO–MAX = 34.6 %, B < 3, B = (%CaO + MgO)/SiO ₂	1600 °C, MgO	12–18 g metal, 6–8 g slag	10	L _p
Drain et al. ^[4]	CaO–SiO ₂ –MgO–Fe _t O– (TiO ₂ –MnO–Al ₂ O ₃ –P ₂ O ₅) Fe _t O–MAX = 59.2 mass%, CaO/SiO ₂ < 3	1650 °C, dense MgO	30 g Fe–P–Ti alloy, 4 g slag	12	New equation for L _p and logC _{PO4} ³⁻

for the phosphorus partition were established theoretically or experimentally. These are published as a function of temperature and chemical composition of the slag constituents. **Table 1** shows an overview of some of the crucial existing experimental investigations of phosphorus partition reported in the presently available literature. The reported investigations of the phosphorus partition in the literature are conducted under several typical conditions. Experiments were usually executed with long test durations of up to 24 h, small metal and slag samples, and various metal/slag ratios. Most of the experiments were carried out in the high density MgO crucibles, often with a low CaO/SiO₂ ratio below 3 under an inert gas atmosphere. Studies of the phosphorus partition with short times and a high CaO/SiO₂ ratio were also previously investigated. Balajiva and Vajragupta^[7] conducted his experiments in less than 40 min. Winkler and Chipman^[8] and Schuermann and Fischer^[19] carried out the experiments for a duration of 30 min. The slags used in the investigations of Schuermann and Fischer^[19] had the CaO/SiO₂ ratio between 3 and 9.8.

Dephosphorization is often carried out today in basic oxygen furnace (BOF) using the high basic slags. BOF slag in European industries is characterized today by their low MnO, Al₂O₃, and TiO₂ contents. This will change over time due to the scrapping of the high manganese and high aluminum Transformation-Induced Plasticity and Twinning-Induced Plasticity (TRIP/TWIP) steels, scrapping of titanium alloyed iron

alloys or use of directly reduced iron, hot bricketed iron. Other modern steels such as heat resistant steel (EN1.4767) or nitriding steel (EN1.4742) also contain aluminum. Scrapping of these steels in BOF or electric arc furnace, will increase the Al₂O₃ content in the slag, due to the oxidation of aluminum. Increasing the MnO, Al₂O₃, and TiO₂ contents in the slag will not only change its thermophysical properties,^[20] but will also affect the reactions occurring during the process.

The aim of this work is to investigate the phosphorus partition between the crude steel and high basicity slag as a function of MnO, Al₂O₃, and TiO₂ contents. The industrial slag from one of the European integrated steel plant with the ratio CaO/SiO₂ = 4.2 is taken as the initial slag, into which pure oxides are mixed. The test durations carried out in this work are shorter, and the sample size is larger in comparison with the similar studies reported previously. Relatively bigger samples of slag and steel weighing 25 and 50 g, respectively, are selected to obtain a large amount of slag for a quality chemical analysis. The test time is limited to 30 min to assure the minimum infiltration of slag and minimum damage of the MgO crucible. The duration of this experiment is also close to the actual time required to produce crude steel in the BOF. To check the possible achievability of a state close to equilibrium in this work, some experiments are also carried out for 60 min in both directions, i.e., “from metal to slag” and “from slag to metal.”

2. Experimental Section

The experiments presented in this work are carried out in three series. An industrial grade BOF-slag collected from a European integrated steel plant was used in the first series of experiments, the composition is shown in **Table 2**. The slag was ground up to the fraction <100 μm, mixed, and premelted with the aim of homogenization of chemical composition. The CaO/SiO₂ ratio of the slag was 4.2. To be able to investigate the influence of MnO, Al₂O₃, and TiO₂ on the phosphorus and manganese removal in the first series of experiments, the pure oxides (3.0 and 8.0 mass% of Al₂O₃; 1.0, 3.5, and 6.0 mass% of TiO₂; and 1.9 and 6.8 mass% of MnO) were added to slag E1. According to the FactSage calculation (FactSage7.2, FactPS, FTOxid, all “Base-Phase,” Thermfact/CRCT Montreal, Canada, and GTT-Technologies, Aachen, Germany), all the examined slags in the first series of experiments were saturated with both CaO and MgO, except for the slag with an addition of 8.0 mass% of Al₂O₃, which was saturated only with MgO at the investigated temperatures range of 1600–1650 °C.^[20]

Pure, high density 99.8 mass% MgO, ceramic crucibles (Final Advanced Materials, Bad Bergzabern, Germany) of 60 mm height, and inner and outer diameters of 32 and 38 mm, respectively, with very low porosity, was used for the present equilibrium experiments.

The initial chemical composition of the steel used in this work is shown in **Table 3**. Before the experiment, the initial steel was melted and alloyed with FeP25 (17.45 mass% P, 0.618 mass% Si, 0.508 mass% Cr, 0.314 mass% Al, 0.312 mass% Ca, 0.055 mass% Mn, and 0.031 mass% S). The measured phosphorus content of the initial samples in the first series of experiments was 770–990 ppm.

As, it will be shown later in Section 3, during Series 1 of the experiments, slag diffusion into the crucible wall and dissolution of crucible material in the slag was observed. The second series of experiments were carried out only at a temperature of 1600 °C. To reduce the interaction with the crucible ceramic, the MgO content in the slags of the second series was increased to 10 and 15 mass%. In the second series of experiments, only the effect of Al₂O₃ on the phosphorus removal was investigated. The additions of Al₂O₃ in the second series were between 5 and 15 mass%. The steel of series 2 was alloyed with FeP25 before the experiments to achieve 790 ppm of P, **Table 3**.

Table 2. Chemical analysis of investigated industrial slag [mass%].

Slag	CaO	SiO ₂	FeO	MgO	Al ₂ O ₃	MnO	Cr ₂ O ₃	P ₂ O ₅	TiO ₂
E1	48.91	11.62	23.17	8.12	1.97	3.02	0.34	2.07	0.78

Table 3. Initial chemical composition of investigated steel [mass%].

	C	Si	Mn	P	S	Cr	Al	Ti	O _{total}
Series 1: Delivered and after alloying with FeP25	0.004–0.009	0.005–0.009	0.129–0.369	0.005–0.006 0.077–0.099	0.005–0.0090	0.003	0.001–0.06	0.0010–0.0650	10–20 ppm
Series 2: after alloying with FeP25	0.005	0.005	0.021	0.003 0.079	0.007	0.003	0.001	0.001	69–81 ppm
Series 3	0.005	0.005	0.021	0.003	0.007	0.003	0.001	0.001	69–81 ppm

To check the possible achievability of a state close to equilibrium in short experiment time, the experiments of third series were also carried out. In this case, the transfer of phosphorus occurred from the slag to the steel. In series 3, slags from series 2 were used with ≈2 and 10 mass% Al₂O₃. Of course, it would have been ideal to conduct experiments in series 3 with exact the same phosphorus content in the steel/slag system as in series 2. For example, in the case of a slag with 2 mass% Al₂O₃ and 790 ppm [P] in a steel sample, this would correspond to an increase in the (P₂O₅) to 2.41 mass% for experiments with steel containing only 30 ppm [P]. This would lead to raising the initial (P)/[P] only from 11 to 352. As, it will be shown later in Section 3, the final (P)/[P] of series 2 with ≈2 mass% of Al₂O₃ is in range between 200 and 400. Thermodynamic calculations with FactSage7.2 for slag with 2.41 mass% of (P₂O₅) showed final (P)/[P] of 302, which was not much different from the initial value 352. The initial value of (P)/[P] increases to 728, and the final (P)/[P] calculated with FactSage 7.2 was declining to 314, with an increase in the P₂O₅ content to 5 mass%. Based on these observations, it was decided to carry out experiments of series 3 with 5 mass% of P₂O₅. The phosphorus content of steel used in series 3 was 30 ppm, **Table 3**.

The experiments were carried out in a middle frequency (MF) 40 induction heating furnace which is schematically shown in **Figure 1**. Steel samples weighing 50 g with initial total oxygen content between 10 and 81 ppm were used for each experiment. The 0.1 g iron ore with 88.83 mass% of Fe₂O₃ was added to the steel melt with the purpose of increasing the oxygen content of the steel melt in series 1 and 2. After the addition of iron ore, the

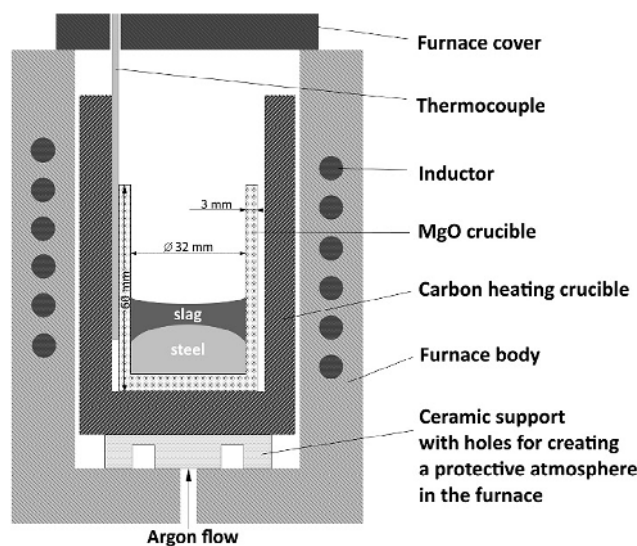


Figure 1. Furnace MFG-40 with MgO crucible inside, schematically.

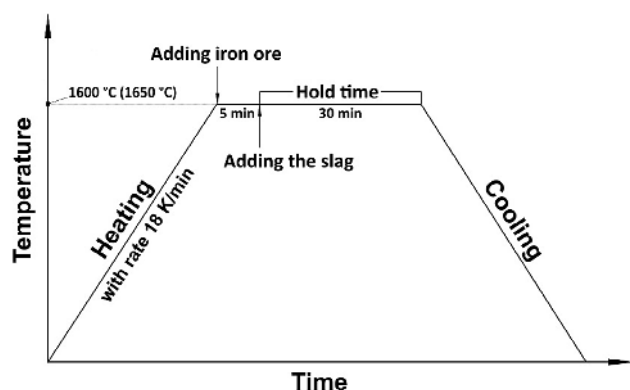


Figure 2. Experiment progress schematically.

slag (25 g) was added after the melting of steel in the crucible to provide slag to metal ratio of 1:2. This sample was kept at a constant temperature for 30 min in all the series and for 60 min only in series 2–3, after complete melting. Later, these samples were cooled at a cooling rate of about 20 K min⁻¹ in series 1 and 60 K min⁻¹ in series 2 and 3.

The experiments were carried out at the temperatures of 1600 in all series and 1650 °C in series 1 under argon gas atmosphere. Argon flow rate is maintained at 4 L min⁻¹. Thermocouple of type B Pt/Pt-Rh was used in the present experiments with an error of ±5 °C.

After the experiments, the chemical analyses of steel and slag samples were carried out using inductively coupled plasma optical emission spectrometer 5100 VDV Dual View (supplied by Agilent, Santa Clara, CA 95051, USA) and a Bruker AXS S8 Tiger (XRF). The time-temperature cycle of the experiment is schematically shown in **Figure 2**.

3. Results and Discussion

Table 4 and **5** shows the chemical composition of the steel and slag samples after the experiments. According to the FactSage 7.2 calculations, all the examined slags of series 1 must be MgO saturated.^[20] But MgO-pick-up can be observed from the chemical analysis of the slags of series 1. During the experiment, a fraction of the slag diffuses into the crucible wall and dissolves the MgO. Thereby, the MgO-pick-up at the temperature of 1650 °C is higher than at 1600 °C. One example of the diffused slag in the crucible wall is shown in **Figure 3**. MgO-pick-up during the phosphorus partition experiments is also reported in various literatures.^[13,21] The researchers suggested, that the dissolution of MgO from the crucible refractory is inevitable during holding of liquid slag at the reported temperature.^[21] Deo et al.^[22] analyzed the phosphorus partition of industrial crude steel and high basic slag samples and reported that, MgO decreases the phosphorus partition ratio between the steel and the slag. According to Ek et al.,^[16] the addition of MgO between 4 and 13 mass% does not show any strong impact on the phosphate capacity.

Diffusion of the slag in the crucible wall can have a strong influence on the equilibrium results, especially for the small slag samples. In the case of investigations with the small steel samples with the mass of a few grams, the convex interface of the molten steel will be formed due to the surface tension. This is a typical situation was observed and utilized in sessile or constrained drop experiments for the measurement of surface tension and density of the liquid metal.^[23] The slag can slide into the gap between the steel curve and the crucible. The contact surface between steel and slag can decrease with the simultaneous dramatic growth of the slag/crucible interface. This not only enhances the reaction and the diffusion of the slag into the crucible but upon cooling will also result in the poor slag sampling for the chemical analysis. The larger slag samples allow better homogenization after the test and result in better analysis. The devices for chemical analysis also have their own limitations on minimum geometry and mass of sample, which hinders the accuracy of analysis results in the case of small samples.

To check the correct selection of the holding time for these experiments, the tests are carried out in “two mass transfer” direction. In series 1 and 2, the phosphorus was transferred “from steel to slag.” Using steel samples with a high [P] content, the experiments of the series 1 and 2 are started with (P)/[P] between 9 and 12. The experiments of series 3, where the phosphorus is transferred from slag to steel, the (P)/[P] on the start of the experiments is more than 700. The experimental conditions in S3/34 are equal to the conditions in S2/20, which led to approximately similar values of (P)/[P] 213.59 and 225.34, respectively. The results of other similar experiments are shown in **Table 5**. Experiment S3/33 with the ratio (P)/[P] = 696 overlaps with experiments S2/18, S2/22 and S2/26, with the ratios (P)/[P] from 207 to 643. In addition, the holding time in series 2 is increased from 30 to 60 min, as shown in **Figure 4**. The optical basicity is calculated using the coefficients for individual oxides reported by Mills and Sridhar.^[24] It can be seen that the measured (P)/[P] at an optical basicity of less than 0.7 gives a better agreement between them, than at a higher optical basicity. Also, the (P)/[P] increases with the increasing optical basicity (**Table 6**).

3.1. Phosphorus Partition

3.1.1. Comparison with Literature Data

To compare the measured values of (P)/[P] with the literature data of the phosphorus partition, the Equation (7)–(12) from literature are used:

Suito and Inoue^[25] proposed, in 1984, the following equation for the phosphorus partition. This equation was obtained experimentally from the results of the equilibrium tests with CaO–FeO–SiO₂–P₂O₅–MnO magnesia-saturated slags with a CaO/SiO₂ ratio between 1 and 2.5 and a temperature range between 1550 and 1650 °C.

$$\log \frac{(\%P)}{[\%P] \cdot (Fe_t)^{2.5}} = 0.072 \times [(\%CaO) + 0.3 \times (\%MgO) + 0.6 \times (\%MnO) + 0.6 \times (\%P_2O_5)] + \frac{11570}{T} - 10.52 \quad (7)$$

Table 4. Chemical analysis of the slag samples after experiments [mass%]. Bold values denotes variable of composition in the test.

Series/slag	Time [min]	°C	CaO	SiO ₂	FeO	MgO	Al ₂ O ₃	MnO	Cr ₂ O ₃	P ₂ O ₅	TiO ₂	(P)/[P] measured
S1/E1	30	1600	43.00	10.93	27.10	10.77	2.14	2.77	0.34	2.18	0.76	433.20
S1/2	30	1600	42.5	10.34	24.31	11.58	5.25	2.64	0.31	2.26	0.82	615.71
S1/3	30	1600	42.7	10.48	23.83	8.61	8.40	2.73	0.33	2.11	0.82	920.49
S1/4	30	1600	42.46	9.78	28.89	10.28	1.77	2.72	0.30	2.03	1.77	443.76
S1/5	30	1600	40.33	9.77	29.41	9.23	2.05	2.57	0.32	2.0	4.32	459.27
S1/6	30	1600	38.55	9.33	30.45	8.53	1.92	2.50	0.31	1.90	6.51	376.27
S1/7	30	1600	45.06	10.96	22.86	8.46	2.34	4.64	0.31	4.59	0.76	334.11
S1/8	30	1600	43.41	10.83	21.86	7.96	3.22	7.06	0.31	4.63	0.72	376.12
S1/9	30	1650	39.74	9.66	27.27	15.68	1.92	2.69	0.32	2.01	0.72	381.05
S1/10	30	1650	39.09	9.50	23.85	17.26	4.84	2.39	0.29	2.02	0.75	631.23
S1/11	30	1650	41.12	10.15	23.02	11.37	8.58	2.63	0.32	1.99	0.82	789.85
S1/12	30	1650	42.52	9.59	27.84	11.71	1.59	2.74	0.29	2.01	1.72	487.88
S1/13	30	1650	46.66	11.28	20.98	8.04	2.18	5.02	0.33	4.74	0.76	252.79
S1/14	30	1650	43.27	10.34	23.96	8.52	2.04	6.98	0.31	3.86	0.72	210.90
S2/15	30	1600	41.84	9.98	32.35	8.31	2.22	2.49	0.28	1.85	0.68	366.23
S2/16	60	1600	39.97	9.75	33.65	8.83	2.51	2.98	0.27	2.08	0.66	313.62
S2/17	30	1600	42.11	10.26	28.82	8.41	4.85	2.43	0.26	2.18	0.68	260.82
S2/18	30	1600	42.35	9.98	25.15	14.72	2.13	2.55	0.29	2.18	0.65	206.74
S2/19	30	1600	42.76	10.36	23.39	12.43	5.41	2.41	0.26	2.29	0.68	339.25
S2/20	30	1600	39.72	9.83	21.66	13.33	10.16	2.34	0.25	2.09	0.63	225.34
S2/21	30	1600	38.31	9.54	21.76	11.24	14.06	2.16	0.22	2.11	0.61	98.44
S2/22	60	1600	41.72	10.59	25.23	14.27	2.66	2.34	0.26	2.30	0.63	426.93
S2/23	60	1600	43.41	11.07	23.45	11.05	5.45	2.30	0.24	2.36	0.66	458.13
S2/24	60	1600	40.59	10.32	23.16	10.66	10.09	2.16	0.22	2.16	0.65	182.83
S2/25	60	1600	37.33	9.29	21.77	12.31	14.38	2.09	0.21	2.02	0.59	79.88
S2/26	60	1600	43.16	14.79	25.42	8.86	1.99	3.07	0.57	1.69	0.45	642.88
S2/27	60	1600	43.48	14.69	24.82	6.46	4.93	2.88	0.49	1.77	0.47	368.25
S2/28	60	1600	40.46	13.30	23.51	7.38	10.03	2.82	0.51	1.53	0.45	188.12
S2/29	60	1600	36.68	12.04	24.16	9.09	13.21	2.60	0.45	1.38	0.40	104.63
S2/30	60	1600	36.89	11.87	22.86	10.07	13.39	2.66	0.46	1.39	0.40	129.16
S2/31	60	1600	36.92	11.75	22.45	9.28	14.78	2.62	0.43	1.38	0.40	117.75
S3/32	30	1600	40.00	9.86	25.96	13.92	2.27	2.41	0.27	4.66	0.64	359.94
S3/33	60	1600	39.61	10.14	26.93	12.85	2.58	2.27	0.25	4.74	0.62	608.90
S3/34	30	1600	28.87	9.27	24.65	9.90	9.12	2.22	0.22	5.11	0.63	213.59
S3/35	60	1600	40.62	9.88	23.13	8.77	9.51	2.12	0.21	5.12	0.65	181.69

Suito and Inoue^[26] reported, in 1995, the modified formula, using the same slag as reported in the study by Suito and Inoue^[25] but with additions of CaF₂ and MnO, for the phosphorus partition as

$$\log \frac{(\%P)}{[\%P] \cdot (Fe_t)^{2.5}} = 0.072 \times [(\%CaO) + 0.3 \times (\%MgO) + 0.6 \times (\%P_2O_5) + 0.2 \times (\%MnO) + 1.2 \times (\%CaF_2) - 0.5 \times (\%Al_2O_3)] + \frac{11570}{T} - 10.52 \quad (8)$$

Assis et al.^[21] presented, in 2019, the following equation. Assis used the slags with a CaO/SiO₂ ratio between 2 and 3.5. The FeO content was between 10.77 and 39.19 mass%, Al₂O₃ between 0.13 and 14.12, and MgO between 7.02 and 17.29.

$$\log \frac{(\%P)}{[\%P] \cdot (Fe_t)^{2.5}} = 0.073 \times [(\%CaO) + 0.148 \times (\%MgO) + 0.144 \times (\%SiO_2) + 0.96 \times (\%P_2O_5) + 0.22 \times (\%Al_2O_3)] + \frac{11570}{T} - 10.46 \pm 0.1 \quad (9)$$

Table 5. Chemical analysis of the steel samples after experiments [mass%].

Series/slag	Time [min]	°C	C	Si	Mn	P	S	Cr	Al	Ti	O _{total} [ppm]
S1/E1	30	1600	0.009	0.005	0.045	0.0022	0.008	0.003	<0.001	<0.001	461
S1/2	30	1600	0.002	0.005	0.047	0.0016	0.008	0.015	<0.001	0.003	380
S1/3	30	1600	0.008	0.005	0.033	0.001	0.010	0.01	<0.001	<0.001	305
S1/4	30	1600	0.004	0.005	0.038	0.002	0.007	0.003	<0.001	<0.001	216
S1/5	30	1600	0.0049	0.005	0.025	0.0019	0.0099	0.003	<0.001	0.0016	572
S1/6	30	1600	0.0045	0.005	0.028	0.0022	0.0108	0.003	<0.001	0.0011	1047
S1/7	30	1600	0.003	0.005	0.108	0.006	0.010	0.003	<0.001	<0.001	478
S1/8	30	1600	0.003	0.005	0.08	0.008	0.009	0.003	<0.001	<0.001	362
S1/9	30	1650	0.004	0.005	0.051	0.0023	0.006	0.003	<0.001	<0.001	465
S1/10	30	1650	0.003	0.005	0.048	0.0014	0.009	0.015	<0.001	0.002	370
S1/11	30	1650	0.008	0.005	0.032	0.0011	0.011	0.011	<0.001	0.003	309
S1/12	30	1650	0.005	0.005	0.039	0.0018	0.007	0.003	<0.001	0.0019	379
S1/13	30	1650	0.005	0.005	0.068	0.0056	0.010	0.002	<0.001	<0.001	396
S1/14	30	1650	0.005	0.005	0.095	0.008	0.008	0.003	<0.001	<0.001	394
S2/15	30	1600	0.0079	0.0064	0.0302	0.0022	0.0084	0.003	0.001	0.0035	611
S2/16	60	1600	0.0062	0.0071	0.0298	0.0029	0.0096	0.003	0.001	0.0029	61
S2/17	30	1600	0.0051	0.005	0.0324	0.0036	0.0093	0.003	0.001	0.0036	549
S2/18	30	1600	0.0044	0.005	0.0245	0.0046	0.0097	0.003	0.001	0.0018	630
S2/19	30	1600	0.0043	0.005	0.0289	0.0030	0.0094	0.003	0.001	0.0016	563
S2/20	30	1600	0.0045	0.005	0.0209	0.0041	0.0117	0.003	0.001	0.0013	515
S2/21	30	1600	0.0053	0.005	0.023	0.0094	0.0175	0.003	0.001	0.001	697
S2/22	60	1600	0.0046	0.005	0.0298	0.0024	0.0093	0.003	0.001	0.0035	515
S2/23	60	1600	0.0051	0.0081	0.0303	0.0023	0.01	0.003	0.001	0.005	537
S2/24	60	1600	0.0054	0.005	0.026	0.0052	0.0133	0.003	0.001	0.0023	571
S2/25	60	1600	0.006	0.0063	0.0237	0.0111	0.0182	0.003	0.001	0.003	639
S2/26	60	1600	0.0054	0.005	0.0377	0.0012	0.0163	0.0188	0.001	0.0016	677
S2/27	60	1600	0.0061	0.005	0.0285	0.0021	0.0182	0.0156	0.001	0.0025	622
S2/28	60	1600	0.0059	0.005	0.0294	0.0036	0.0228	0.0233	0.001	0.0019	682
S2/29	60	1600	0.0048	0.005	0.0234	0.0058	0.0240	0.0196	0.001	0.0015	776
S2/30	60	1600	0.0049	0.005	0.0264	0.0047	0.0256	0.0177	0.001	0.0023	690
S2/31	60	1600	0.0047	0.005	0.0235	0.0051	0.0266	0.0157	0.001	0.0025	692
S3/32	30	1600	0.0056	0.0055	0.0254	0.0057	0.0097	0.003	0.001	0.0034	663
S3/33	60	1600	0.0051	0.0128	0.0272	0.0034	0.0105	0.003	0.001	0.0041	696
S3/34	30	1600	0.0046	0.005	0.0165	0.0105	0.0149	0.0066	0.001	0.0028	666
S3/35	60	1600	0.0060	0.005	0.0215	0.0123	0.0146	0.0074	0.001	0.0015	708

Assis et al.^[27] proposed, in 2012, the following formula. This equation was derived from the revision of the Suito correlation^[25] using experimental data from previous studies^[14,15]

$$\log \frac{(\%P)}{[\%P] \cdot (Fe_t)^{2.5}} = 0.068 \times [(\%CaO) + 0.42 \times (\%MgO) + 1.16 \times (\%P_2O_5) + 0.2 \times (\%MnO)] + \frac{11570}{T} - 10.52 \quad (10)$$

Drain et al.^[4] also considered TiO₂ in a similar equation

$$\log \frac{(\%P)}{[\%P] \cdot (Fe_t)^{2.5}} = 0.068 \times [(\%CaO) + 0.42 \times (\%MgO) + 1.16 \times (\%P_2O_5) + 0.2 \times (\%MnO) + 0.087 \times (\%TiO_2)] + \frac{11570}{T} - 10.52 \quad (11)$$

This equation was obtained from the equilibrium experiments between Fe–P master alloy (0.181 mass% [P]) and synthetic CaO–SiO₂–MgO–FeO–TiO₂ slags with a CaO/SiO₂ ratio between 1 and 3.

Ide and Fruehan^[28] reported the following equation, which was obtained from experimental results of high FeO-containing

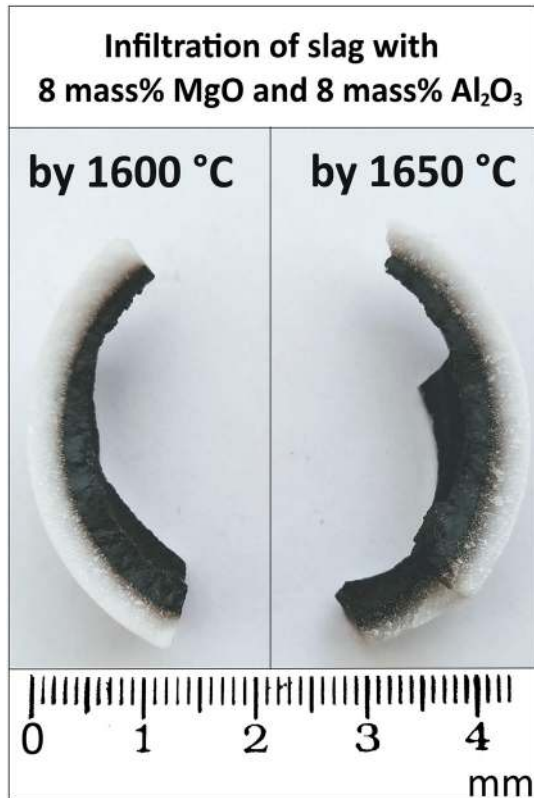


Figure 3. Crucible wall with diffused slag.

slag (23.2–35.9 mass%) with a CaO/SiO₂ ratio between 2.42 and 3.29

$$\log \frac{(\%P)}{[\%P] \cdot (Fe_t)^{2.5}} = 0.072 \times [(\%CaO) + 0.15 \times (\%MgO) + 0.6 \times (\%MnO) + 0.6 \times (\%P_2O_5)] + \frac{11570}{T} - 10.52 \quad (12)$$

The values measured in this work (P)/[P] are compared with the calculated phosphorus partition and plotted with respect to the optical basicity, in **Figure 5**.

It must also be emphasized that the equations obtained from the literatures used for the calculation and comparison with this work were actually derived for the slags with CaO/SiO₂ ratio lower than 3.5, whereas the slags investigated in this article have basicity about 4.2. Influence of basicity on phosphorus partition and phosphorus capacity has also been studied in the past. There is no consensus observed in this issue. Lee and Fruehan^[11] reported that the phosphate capacity increases with increasing [(%CaO) + (%MgO)]/(%SiO₂). On the contrary, the investigations from other works^[14] show that increasing the basicity [(%CaO)]/(%SiO₂) from ≈2.5 to 2.6 has practically no effect on the phosphorus distribution. Moreover, Zhou et al.^[17] reported that the phosphorus distribution decreased as the basicity [(%CaO)]/(%SiO₂) increased from 3.76 to 7.2. However, in that particular case of study, the experimental conditions and

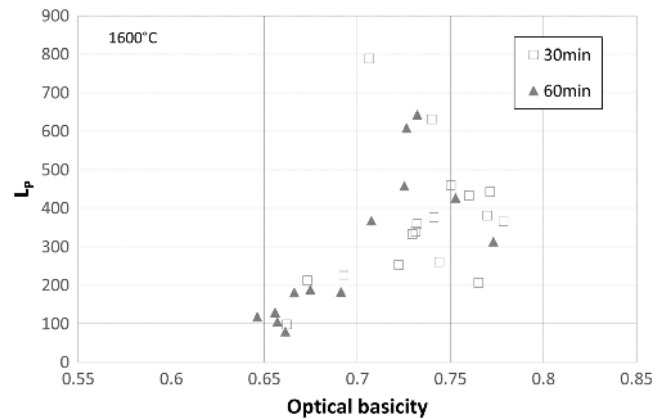


Figure 4. Comparison of experiments results at different holding times.

Table 6. Comparison of the experiment results of series 2 and 3.

Similar experiments of the series 2 and 3	(P)/[P]
S3/34 = S2/20	213.59 ≈ 225.34
S3/35 = S2/28	181.69 ≈ 188.12
S3/35 = S2/24	181.69 ≈ 182.83
S3/32 = S2/15	359.94 ≈ 366.23

the presence of a substantial amount of CaF₂ (13–16 mass%) in the slag make the results hardly comparable with the present experimental conditions. All the aforementioned studies indicate that the area of high-basicity slags is only marginally studied till now.

The measured (P)/[P] values of this work are compared with values from literature with respect to the optical basicity and the logarithm of activity coefficient of P₂O₅ in the slag, as shown in **Figure 6**. The following equation is used for the calculation of the logarithm of activity coefficient of P₂O₅^[26]

$$\log \gamma_{P_2O_5} = -1.02(23 \times X_{CaO} + 17 \times X_{MgO} + 8 \times X_{FeO} - 26 \times X_{P_2O_5} + 14 \times X_{MnO} + 20 \times X_{CaF_2} - 3 \times X_{Al_2O_3}) - \frac{23000}{T} + 9.49 \quad (13)$$

To compare the experimental data obtained at a temperature of 1600 °C, phosphorus partitions measured in previous studies^[13,14,18,19] are chosen. Whereas, to compare the data for the temperature of 1650 °C, measured phosphorus partitions from the study by Drain et al.^[5] are chosen. **Table 7** shows a comparison of the experimental conditions in present and previous works.

As shown in **Figure 5**, the best matching of experimental results is with the model of Assis et al.^[21] It has to be emphasized that the values calculated using the literature equations also differ from each other.

A comparison of the measured (P)/[P] values in this work with the measured values from the literature, is shown in **Figure 6**. It shows that the values from this work are in agreement with the

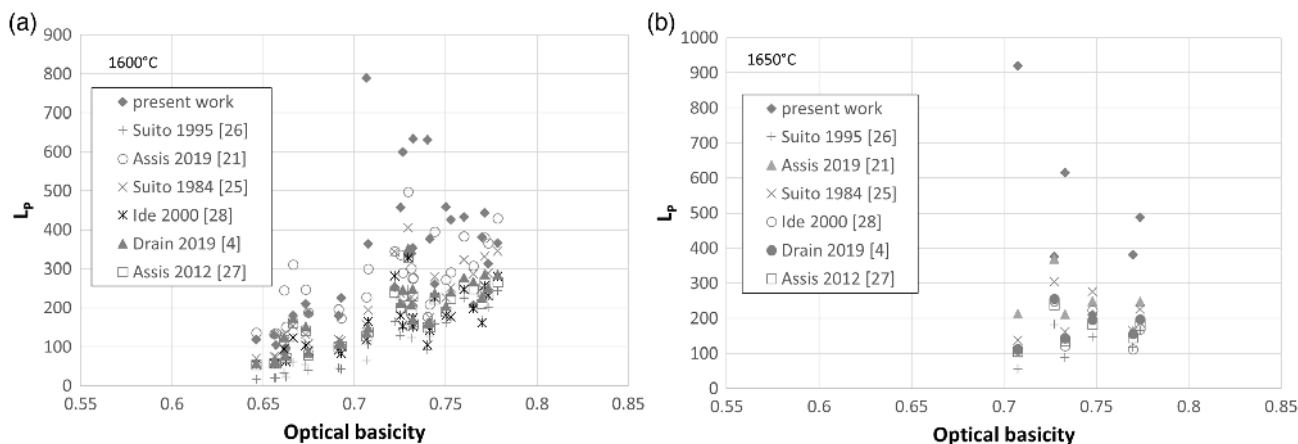


Figure 5. Phosphorus partition as a function of optical basicity measured in this work and calculated with Equation (7)–(11) at temperatures a) 1600 °C and b) 1650 °C.

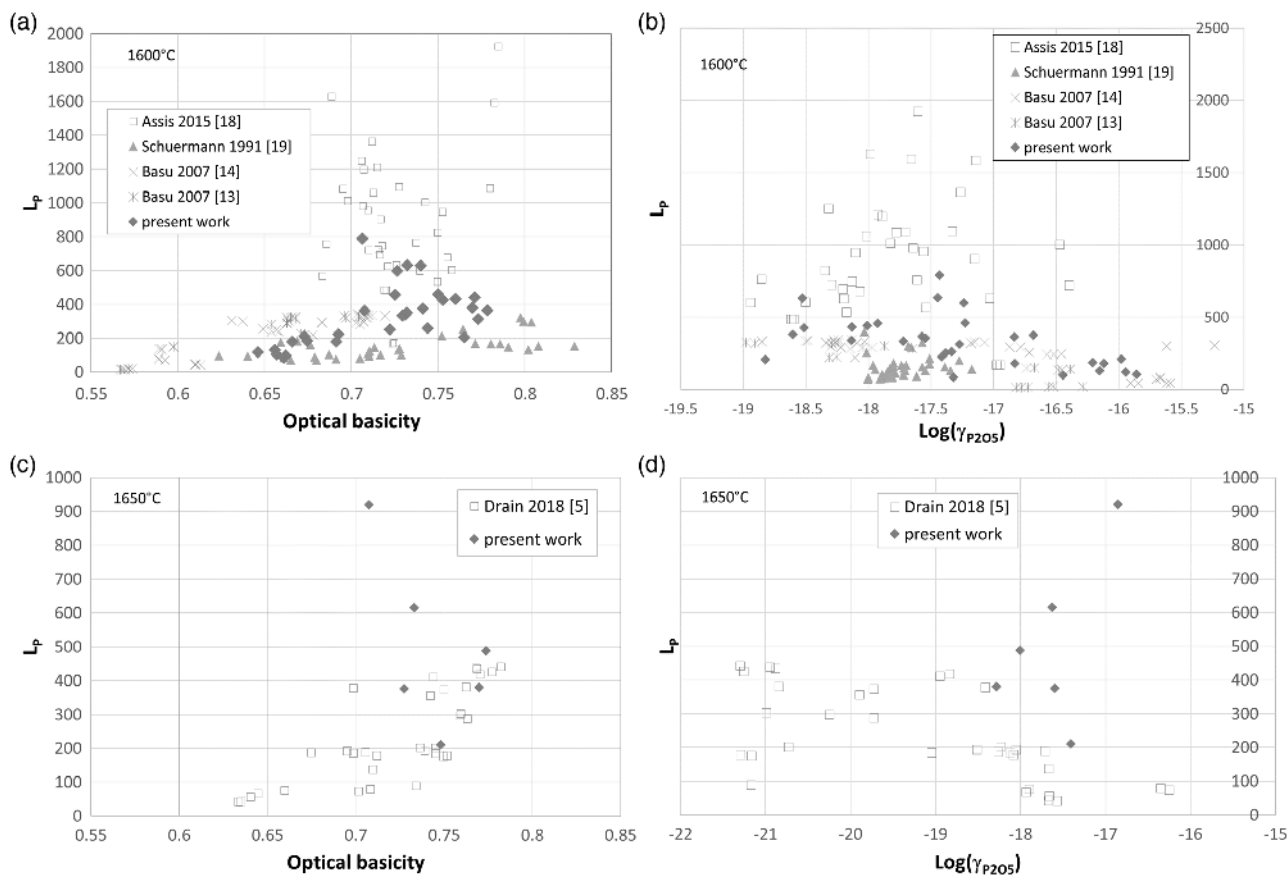


Figure 6. Phosphorus partition as a function of optical basicity and $\log_{p_2O_5}$ measured in this work and from literature at temperatures between 1600 °C and 1650 °C.

values of experiments with high CaO/SiO₂ ratio slags reported in the studies by Basu et al.^[13,14] and Assis et al.^[18] obtained higher values in almost all the optical basicity range. However, the chemical compositions of slags given in that work did not contain Al₂O₃. As it will be shown further in this work, that Al₂O₃ reduces (P)/[P].

3.1.2. Influence of Al₂O₃

The measured (P)/[P] for temperature of 1600 and 1650 °C and CaO/SiO₂ between 3.9 and 4.2, and as a function of Al₂O₃ content, is shown in **Figure 7**. The measured (P)/[P] for investigated slags decreases with the Al₂O₃ content. The literature sources

Table 7. Comparison of the experiment conditions in present and previous works.

	Slag	CaO/SiO ₂	FeO [mass%]	Al ₂ O ₃ [mass%]	Temperature [°C]	Time
Assis et al. ^[18]	CaO–SiO ₂ –MgO–Al ₂ O ₃ –FeO–P ₂ O ₅	2–3.5	19.34–36.12	–	1600	10 h
Basu et al. ^[13,14]	CaO–SiO ₂ –MgO–FeO–P ₂ O ₅	1–3	6.44–29.25	–	1600	4–10 h
Schuermann and Fischer ^[19]	CaO–SiO ₂ –MgO–Al ₂ O ₃ –FeO–P ₂ O ₅ –MnO	2.56–9.8	7.25–42.75	0.1–10.37	1600	30 min
Drain et al. ^[5]	CaO–SiO ₂ –MgO–Al ₂ O ₃ –FeO–P ₂ O ₅ –TiO ₂ –MnO	1.8–5.6	5.3–31.2	0.1–0.6	1650	10 h
Present work	CaO–SiO ₂ –MgO–Al ₂ O ₃ –FeO–P ₂ O ₅ –TiO ₂ –MnO	4.2	12.27–38.03	1.59–18.6	1600, 1650	30 min

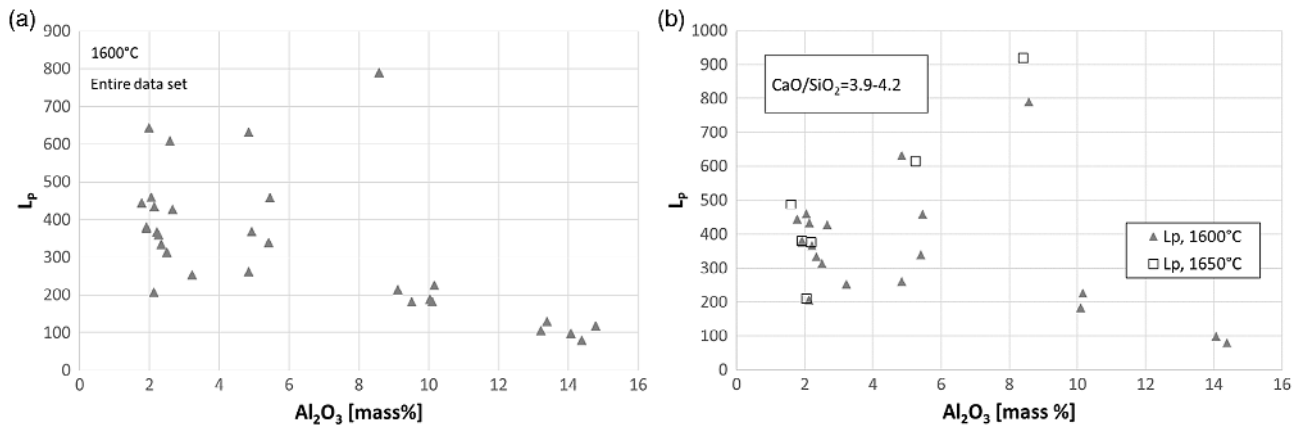


Figure 7. a) Phosphorus partition as a function of Al₂O₃, b) temperature and Al₂O₃.

have also reported the decrease in phosphorus partition with Al₂O₃. Deo et al.^[22] reported, that Al₂O₃ between 1 and 4 mass% decreases the phosphorus distribution ratio between steel and slag. In their work,^[26] the morphology of the investigated slag was significantly altered by the presence of Al₂O₃. The presence of Al₂O₃-stabilized calcium–aluminum–ferrite and reduced the amount of 2CaSiO₄ and also the phosphorus content of 2CaSiO₄. Li et al.^[12] investigated the slag with Al₂O₃ upto 24 mass% and found, that Al₂O₃ in the MgO-saturated CaO–FeO_x–SiO₂ system decreases the phosphate capacity of the slags and increases the MgO solubility in the slags. Maruoka et al.^[3] also reported about decrease in the phosphate capacity with Al₂O₃ addition. Li et al.^[29] have found that Al₂O₃ can successfully work as a CaF₂ replacements and improves dephosphorization.

3.1.3. Influence of TiO₂

The measured (P)/[P] for temperatures 1600 and 1650 °C, a CaO/SiO₂ between 3.9 and 4.2 and an Al₂O₃ content less than 5 mass % as the function of TiO₂ content, is shown in **Figure 8**. The scattering of data for TiO₂ less than 1 wt% can be explained by the different contents of MgO and FeO in the slags. For a clear assessment of the effect of TiO₂ on (P)/[P] of the slags studied in this work, further researches are needed. Increase in TiO₂ in the examined slag deteriorates the phosphorus distribution, which is concomitant with the literature findings. From the literature, it is known that increase in TiO₂ deteriorates the L_p. For example

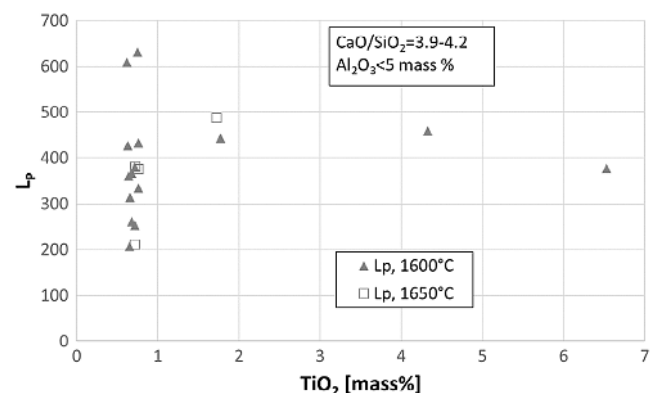


Figure 8. Phosphorus distribution as function of temperature and TiO₂.

Drain et al.^[4] found that increase in TiO₂ lowers the L_p in CaO–SiO₂–MgO–Fe_tO–TiO₂ slag. In this case, the experiments were conducted with 4 g of the slag.

3.1.4. Influence of MnO

The measured (P)/[P] for CaO/SiO₂ between 3.9 and 4.2 and an Al₂O₃ content less than 5 mass% with respect to temperature and MnO content is shown in **Figure 9**. The measured (P)/[P] values decrease with the MnO addition. Other studies of the influence of MnO on the phosphorus distribution from

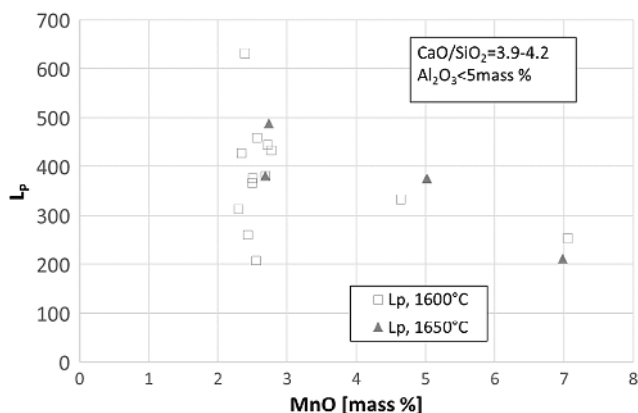


Figure 9. Phosphorus distribution as function of temperature and MnO.

literature are known, but they do not allow to draw a consensus view on this issue. For example, the investigation^[9] showed, that the additions of MnO to the slags did not affect the ability of the slag to remove phosphorus. The phosphate capacity in work^[10] increases with the molar ratio of MnO to SiO₂ in MnO–SiO₂–Fe₂O slag and slightly decreases beyond the composition of $X_{MnO}/X_{SiO_2} = 2$. It is estimated that the addition of MnO leads to the rise in the solid fraction of the present slags, from the FactSage 7.2 calculations reported in the previously published work of authors.^[20] Decrease in temperature from 1650 to 1600 °C has resulted in increase in the solid fraction on around 3–4 mass% depending on the slags.^[20] Solid fraction growth reduces the amount of CaO available for the reaction with phosphorus in the liquid phase. The calculation method of lime saturation proposed in work^[30] does not include MnO, and, therefore could not be compared with this study.

It is quite common to consider MnO behavior in the slag to be similar to FeO. In the publication of Urban et al.,^[31] the operating data for the slags with the basicity 3.4–3.6 were reported as a function of FeO. In that work, maximum for L_p of FeO is around 23–24 mass%. Over that amount, L_p decreases with FeO. In the

present slag for MnO series, we have between 21 and 23 mass% of FeO. This means that with the addition of MnO, the compositions of this work, move to the right of optimum, and L_p decreases. It paves the way for another further dedicated research.

3.1.5. Influence of FeO and MgO

Experiments in this work also allows us to gain some useful information on the effect of FeO on (P)/[P]. The dataset shown in **Figure 10a** shows that FeO content tends to have an optimum value between 25% and 30% and a basicity of 3.9–4.2 at 1600 °C. Also, the activity coefficient of P₂O₅, shown in **Figure 10b**, decreases with rising FeO content and appears to decrease when FeO content is increased beyond 25–30 mass%.

A similar dataset for the MgO shown in **Figure 11** shows positive effect of MgO on the (P)/[P] at 1600 °C under the conditions of basicity around 3.9–4.2 and less than 5% of Al₂O₃. In both FeO and MgO datasets, some data points are out from the general trend and should be attributed to the outliers.

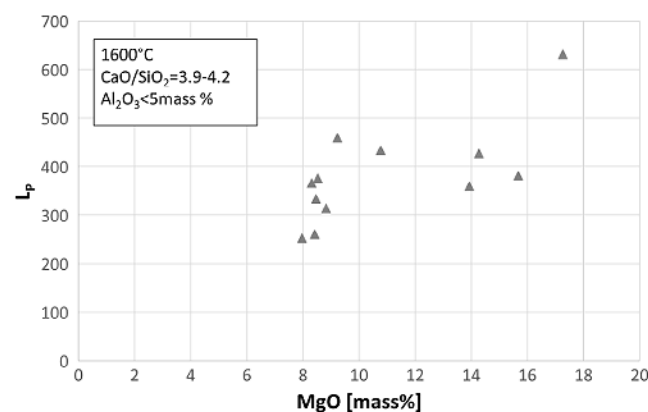


Figure 11. Effect of MgO on the (P)/[P] at 1600 °C.

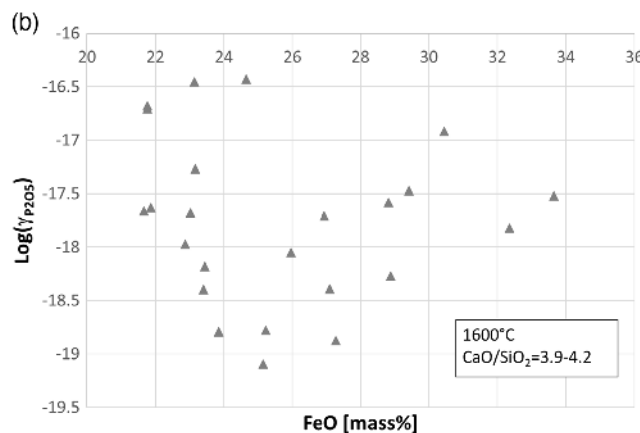
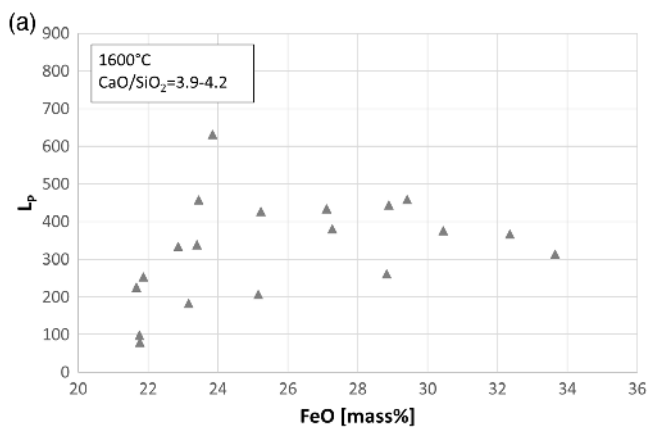


Figure 10. Effect of FeO on the (P)/[P] and $\log_{p_2O_5}$ at 1600 °C.

4. Conclusions

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The phosphorus partition between the unkilld crude steel and the high basicity BOF slags ($\text{CaO}/\text{SiO}_2 = 4.2$) with the varying additions of Al_2O_3 , TiO_2 , and MnO are experimentally investigated at the temperature range of 1600–1650 °C and for 30 and 60 min. The temperature during experiments is controlled with type B Pt/Pt-Rh thermocouple with an error of ± 5 °C. The experiments are conducted in the directions of “slag to metal” and “metal to slag.” The results of phosphorus partition for both directions, and for 30 and 60 min tend to be similar. The measured values are compared with those calculated using literature correlations as well as with the measured values known in literature for similar slags compositions. The results are summarized as following: 1) the measured values of phosphorus partition are very close to the values predicted by correlations reported in the literature. The best agreement of the measured L_p is found with the model equations from Assis et al.^[21] 2) The measured values of the phosphorus partition in this work have the best agreement with the measured values reported by Basu et al.^[13,14] 3) Phosphorus partition increase with the increase in optical basicity. 4) Phosphorus partition decreases with the increase of Al_2O_3 content in slags with a CaO/SiO_2 ratio between 3.9 and 4.2. 5) Phosphorus partition is hindered by an increase in the MnO contents of the slag. 6) An optimum for phosphorus partition depending on FeO content exists between 25% and 30%, for the given CaO/SiO_2 ratio between 3.9 and 4.2. 7) The MgO content in studied slags slightly favors P partition.

In this work, 35 phosphorus partition experiments are carried out. However, for more clear dependencies much higher number of tests is needed.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Al_2O_3 , basic oxygen furnaces, FeO , MnO , phosphorus partitions, slags, TiO_2

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