

NEW TRENDS IN BASIC OXYGEN FURNACE DEPHOSPHORIZATION

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Abstract

Except for special grades of steel where it is used as an alloying element, phosphorus is regarded as an impurity that must be removed. Considering the conventional integrated iron and steelmaking, there are primarily two processes for phosphorus removal. The first is a hot metal dephosphorization (DeP) process that is applied to a blast furnace for hot metal before the steelmaking process. The second is the basic oxygen furnace steelmaking (BOS), a unique method primarily used for steelmaking, with the exception of stainless steels. Hot metal phosphorus content has a direct impact on BOS. An increase of phosphorus in hot metal is mainly related to the use of high P_2O_5 containing iron ores. In the current literature review, new trends of phosphorus removal in converter steelmaking are outlined. The double-slag practice was reported to be successful when hot metal P content was larger than 0.100%. It was indicated that the tapping temperature was critical for the production of low-phosphorus grades for which maximum allowable P content was 0.007% and that high tapping temperatures should be avoided. The tap-to-tap time for the double-slag process was slightly longer than the conventional converter steelmaking. It was further reported that the double-slag practice would be more economical than an establishment of a separate hot metal dephosphorization unit, if low-phosphorus grades did not have a significant share in the product mix of a steelmaking company. End-point phosphorus prediction was one of the important recent trends of converter steelmaking. A mixed injection of CO_2-O_2 to a basic oxygen furnace was applied to enhance dephosphorization, and promising results were reported. Unfortunately, a successful process for recycling of BOS dephosphorization slag has not been reported yet.

Keywords: Phosphorus; Iron and steelmaking; Hot metal; Steel; Double-slag

1. Introduction

Except for special grades of steel where it is used as an alloying element, phosphorus is regarded as an impurity that must be removed. The iron-phosphorus system has been well studied in previous literature [1,2]. Iron and phosphorus form compounds with the following crystal structures: Fe_3P (body centered tetragonal), Fe_2P (hexagonal), and FeP (orthorhombic) [1]. The Fe-P phase diagram is illustrated in Figure 1.

It has been reported that the solubility of phosphorus in α -iron at 1050°C is 2.8 wt%, whereas it is slightly lower when in γ -iron [4]. At hot metal and steelmaking temperatures, phosphorus dissolves in liquid metal. The diffusion mobility of phosphorus in iron is below that of carbon. The phosphorus diffusion coefficient in α -iron at 700°C was reported as 2.7×10^{-12} cm²/s, whereas the diffusion coefficient in γ -iron at 1100°C was determined as 1.2×10^{-9} cm²/s [5]. Due to its low mobility, homogeneous distribution of

phosphorus in steel is very difficult and, therefore, it tends to segregate along the grain boundaries. Spitzig studied the effects of phosphorus on the mechanical properties of low-carbon irons. It was found that the addition of 0.05 and 0.1 wt% P to low-carbon irons increased the yield strength at 295 K by 40 to 50% [6]. Phosphorus also increases the hardness of steel and improves the machinability of free-machining steels. Phosphorus promotes temper embrittlement [7]. An increase in the amount of phosphorus has a negative effect on the toughness of steel. In an effort to examine the effect of sulfur and phosphorus on the impact behavior of 18B steel, it was found that steel toughness was reduced 20 to 35% when sulfur content was raised from 0.030 to 0.055%, and phosphorus content was increased from 0.025 to 0.050%, lowering the percentage of ductile fractures and increasing the ductile to a brittle transition temperature of 20–30°C [8]. With improvements in steelmaking technologies and increased customer expectations, such sulfur and phosphorus

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compositions are no longer viable. For example, in the production of interstitial-free (IF) grades, the negative effect of phosphorus on deep-drawing and extra deep-drawing properties restricts the allowable phosphorus content to a maximum of 0.010 or 0.015% in grades produced for the automotive and whiteware industries [9]. The significance of dephosphorization should also be expressed for advanced high strength steels (AHSS) [10,11], which are currently very popular in modern steelmaking. It was reported that, with increased customer demands, a further reduction of phosphorus (e.g. 0.007%max.) might not be conducted with the conventional BOS process [10].

Phosphorus in hot metal comes from the charged materials of the blast furnace, namely iron ore, coke, and fluxes. Phosphorus in the charge is in the form of P_2O_5 , $3CaO.P_2O_5$, and $3FeO.P_2O_5.SiO_2$ in the ore reacts with $3CaO.P_2O_5$ and $3FeO.P_2O_5$, and forms free P_2O_5 vapor as a result. P_2O_5 is then reduced by solid carbon, and P eventually dissolves in the hot metal. Since dephosphorization necessitates oxidizing conditions, it cannot be performed in blast furnaces where reducing conditions prevail [12]. Considering

the conventional integrated path of iron and steelmaking, there are two possible processes for phosphorus removal. The first process is the hot metal dephosphorization (DeP) method that is applied to a blast furnace for hot metal (i.e. between the blast furnace and a basic oxygen furnace). It originated in Japan in 1982 at Kimitsu works, Nippon steel [13] and then spread into the steelmaking world. Hot metal dephosphorization can be applied in either the hot metal ladle [14] or in the torpedo car [15,16]. The process is simply the injection of a dephosphorization agent together with a carrier gas, namely N_2 and most of the time O_2 . When O_2 is used, a typical dephosphorization agent could contain 38% sinter dust, 35% mill scale, 25% CaO, and 2% CaF_2 [15]. Most of the time, more than 90% of the phosphorus is eliminated from the hot metal [16]. In a book dealing with metallurgical processes, phosphorus removal methods were compared, and it was reported that hot metal dephosphorization using the torpedo car took more than 40 minutes: the longest duration of all the documented methods [17]. Since the major target of the present manuscript is not to describe hot metal

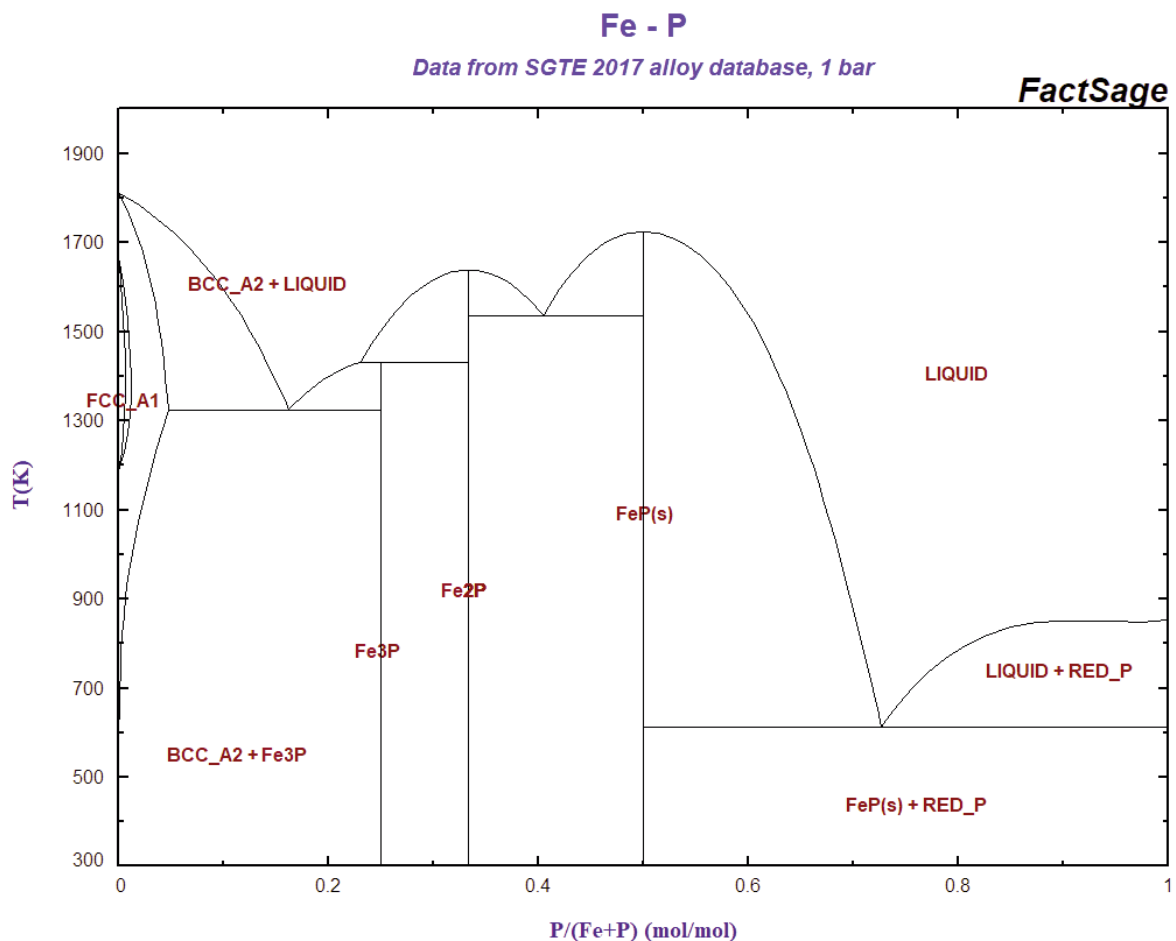


Figure 1. Fe-P phase diagram, Source: Thermochemical data of FactSage 7.2 [3]



dephosphorization, readers may refer to related literature for further details.

The second phosphorus removal process is the basic oxygen furnace steelmaking (BOS), a unique method primarily used for steelmaking, with the exception of stainless steels. In this case, the phosphorus content of the hot metal has a direct impact on BOS. The phosphorus increase in a hot metal is mainly related to the use of iron ores containing high P_2O_5 . In the current study, new trends in basic oxygen furnace dephosphorization are outlined.

2. Phosphorus Removal in Basic Oxygen Steelmaking

According to the studies conducted concerning the phosphate capacities of slags (an example of which would be Y. Sun et al.'s published paper [18]), an estimate for the standard free energy of formation (ΔG°) of pure liquid P_2O_5 was presented as (1) and (2), where the square brackets are indicating the dissolved species and T is the temperature in K [19].



$$\Delta G^\circ = -832384 + 632.65T \text{ (J/mol)} \quad (2)$$

In converter steelmaking, four primary requirements must be fulfilled to remove phosphorus from a metal: low temperature, high basicity of slag, high oxygen potential, and low slag viscosity. Considering the impurities coming from the hot metal oxidized during O_2 -blowing in a converter, phosphorus pentoxide is the least stable and requires the highest oxygen potential for oxidation. Variations of ΔG° with temperature for some pure element-pure

oxide systems are shown in Figure 2. As it can be seen from Figure 2, the P_2 - P_2O_5 line appears at the top among the provided pure element-pure oxide systems, meaning that oxidation of phosphorus is the most difficult one. Therefore, the high oxygen potential of a system must be maintained throughout the oxygen blowing process to remove the phosphorus to the slag phase of P_2O_5 . Moreover, a highly oxidizing converter slag should be kept in the converter during the tapping process; therefore, slag carry-over to the ladle should not be allowed. Otherwise, phosphorus reverts back to the steel when reducing conditions prevail in the ladle slag, which is desired for further metallurgical operations in secondary steelmaking.

The phosphorus slag-metal distribution ratio was clearly established many years ago. An explanation of the factors affecting Healy's formula [20] regarding dephosphorization can easily be calculated using equation (3):

$$\log \frac{(\%P)}{\%P} = \frac{22350}{T} - 16.0 + 0.08(\%CaO) + 2.50 \log(\%Fe_{total}) \quad (3)$$

where the species shown in parenthesis are illustrating the ones in slag, $\%P$ is representing the phosphorus dissolved in liquid steel, all in weight per cents, and T is the temperature in K. The term $(\%P)/\%P$, appearing at the left-hand side of the equation (3), serves as the phosphorus distribution ratio (e.g. [21]) or phosphorus partition ratio (e.g. [22]) and is sometimes shown as L_p [21]. Therefore, one can easily deduce that more phosphorus is eliminated from the metal when the partition ratio is higher. As it can be inferred from expression (3), a great extent of oxidation of phosphorus takes place at the very beginning of the oxygen blowing process when the temperature of the converter is at the lowest. $(\%CaO)$ in equation (3) illustrates the basicity of the slag. One

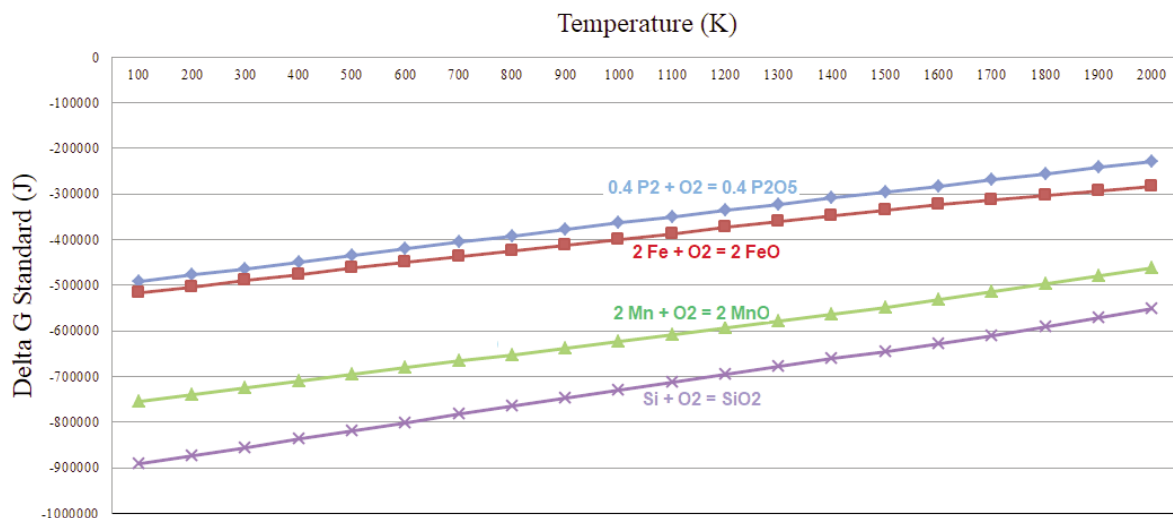


Figure 2. Variations of standard free energy changes of some oxidation reactions with temperature (constructed using the thermochemical data of FactSage 7.2 [3])



of the most important reasons of high basicity practice in converters is to remove phosphorus from the metal during the oxygen blowing process. For this reason, an addition of around 5-6 tons of lime is conducted just before the start of oxygen blowing for a 120-ton converter, and the simplified basicity of the converter slag (%CaO/%SiO₂) is, therefore, kept above 5 [9]. In expression (3), the (%Fe_{total}) shows the iron oxide in the slag, and it is mostly in the form of wustite [23]; it is mostly, therefore, shown as Fe₁O. It was reported that the iron oxide content of the slag increases as more phosphorus is eliminated from the metal [24]. Although a mathematical quantification of the effect of viscosity of slag is not encountered in Healy's formula, or in formulas found in other available literature, it should be indicated that high slag viscosities should be prevented in order to avoid slowing down the kinetics of converter dephosphorization. As an example, please see the paper published by Chen and He which demonstrated that the kinetics of dephosphorization were negatively affected when the slag viscosity was larger than 0.2 Pa·s [25].

% Dephosphorization, which is alternatively identified as the dephosphorization ratio in related literature, can be calculated as:

$$\%Dephosphorization = \frac{P_0 - P_f}{P_0} \times 100 \quad (4)$$

where P₀ and P_f denote the phosphorus content of the steel before and after the dephosphorization period, respectively.

In integrated steelmaking plants, to oxidize phosphorus to the slag phase and eliminate P reversion to steel, the BOS process conditions must be strictly controlled. Slag carry-over should also be minimized as much as possible. Bulk use of some ferroalloys and especially ferromanganese may cause an increase in the phosphorus composition of steels due to their phosphorus content. The main source of phosphorus in integrated iron and steelmaking is the phosphorus present within the iron ore. Therefore, high phosphorus-containing iron ores yield high phosphorus hot metals. Charging a high phosphorus hot metal to a basic oxygen furnace causes certain problems in BOS, therefore, most of the time, the use of high phosphorus ores is avoided by steelmaking companies. Moreover, the phosphorus content of a hot metal increases when the basic oxygen furnace slag is used in sinter making. The problems created due to high phosphorus hot metal usage in conventional BOS are outlined as follows:

As one of the charged materials (i.e. hot metal) contains more phosphorus, it is difficult to produce low P containing grades [24]. Therefore, the number of grade change events in the converter and the number of heat downgrades due to phosphorus rise

[9]. In addition, a converter slag contains more P₂O₅, so more phosphorus returns to the steel when the slag carry-over takes place [26]. This impacts the number of grade changes and heat downgrades. Correspondingly, those events cause delays in production planning [9].

When hot metal phosphorus content is high, the oxygen blowing practices of the converter should be changed. The changes cause an increase in the oxidation of iron and, therefore, the amount of iron oxide in slag will increase. Additionally, higher FeO content in the converter slag means a higher rate of refractory erosion [27], decreasing the campaign life of the converter and causing a greater number of interruptions to reline the converter vessel. All these events decrease the production rate and increase the cost of steelmaking [9]. Moreover, for the case of slag carry-over, higher FeO content in the slag decreases the efficiency of deoxidizing agents and ferroalloys in ladle metallurgy. As a result, more deoxidation materials and ferroalloy will be used, increasing the costs [28].

When hot metal phosphorus content is high in order to achieve grade specification, the number of re-blowing events will increase. A natural consequence of re-blowing is an increase in the nitrogen content of liquid steel [29], causing difficulties in the production of grades containing low N. This is more pronounced and problematic if there is no suitable degasser for N removal. The refractory life of the vessel will be shortened due to re-blowing [30]. Moreover, each re-blowing event necessitates the addition of more lime to keep the slag basicity at required levels. Additionally, each re-blowing event causes a delay in tapping time by approximately 10 minutes, decreasing the productivity of the steel plant [9]. In conventional oxygen steelmaking, all of these main problems caused by a high hot metal phosphorus content are summarized in Table 1.

Table 1. Main problems in conventional oxygen steelmaking due to high-phosphorus hot metal usage

Grade changes	<ul style="list-style-type: none"> • Regrading of heat (Delays in production planning) • Downgrading of heat (Delays in production planning) • Increase in severity of slag carry-over
Changes in O ₂ -blowing practice	<ul style="list-style-type: none"> • Increase in FeO content of slag • Higher deterioration rate of refractories
Increase in # of reblowing events	<ul style="list-style-type: none"> • Delays in tapping of steel (Delays in production planning) • Increase in N content of steel (Difficulty in production of low-N steels if a suitable degasser is not available, causing delays in production planning) • More lime usage to adjust basicity of slag



3. New Trends of Phosphorus Removal in Converter Steelmaking

Together with customer demands, the production of low-P steels has gained importance, especially in the last decade. Correspondingly, in the integrated route of steelmaking process, efforts have also been concentrated on converters to remove more phosphorus through different practices. Among those, the most recent method for phosphorus removal is generally called the “double-slag practice”. The double-slag practice simply adds a slag tapping operation before the middle of conventional oxygen blowing period. Therefore, phosphorus oxidized in the first blowing process is simply eliminated from the system with this slag tapping operation. Phosphorus that is removed in the first blowing period represents the majority of the phosphorus present in hot metal. Afterwards, in the second blowing period, the so-called “semi-steel” is decarburized further and some additional phosphorus removal takes place. The efforts are repeated to prevent phosphorus reversion to the steel. This requires an extreme care during the steel’s tapping process in order to minimize “slag carry-over,” just like the conventional basic oxygen furnace (BOF) process. Compared to the conventional BOF process, deslagging periods in the double-slag practice surely cause a certain extension in tap-to-tap time. On the other hand, the double-slag process is economically more advantageous than the establishment of a separate dephosphorization plant when a steelmaking company has a limited number of low phosphorus steels in its product mix. The first applications in double-slag practice were reported in Japan in 1970s [31,32], where external hot metal treatment operations like desiliconization and dephosphorization were generated. A great majority of those studies were in Japanese.

In a paper published in the millennium, Kitamura et al. outlined the three-type hot metal refining processes established in Nippon Steel: i.e. conducted within a torpedo car, hot metal ladle, or LD converter. Those processes are actually beneficial to reduce the slag volume in the primary steelmaking. The authors introduced “the multi-refining converter,” abbreviated as MURC, which combines dephosphorization and decarburization in the same converter. The MURC process also makes use of recycling the second (i.e. decarburization) slag to the converter [33]. Ogawa et al. gave the details of the MURC process in another

paper. The trials were performed in an 8-ton converter. The typical hot metal composition treated in that small capacity furnace was reported as 4.0-4.8%C, 0.21-0.39%Si, and 0.08-0.15%P. The flowsheet of the MURC process is shown in Figure 3. The dephosphorization ratio was reported to increase with the application of separate steps for dephosphorization and decarburization. Total lime usage was found to decrease due to the dephosphorization process with a low basicity slag and a recycling of the decarburization slag. Numerical findings of the study in relation to productivity, lime usage, etc. were all given in Japanese and, therefore, could not be outlined [34].

Naito et al. studied certain operational items in relation to the intermediate deslagging in the MURC process. The authors, in conjunction with Nippon Steel & Sumitomo Metal Corporation, investigated the tilting pattern of the converter, properties of the metal-slag system, and the shape of the converter mouth. With the application of the water model, the authors concluded that a metal’s spilling tendency increased as the viscosity of the slag increased and as the density difference between the steel and slag became smaller. It was further outlined that the installation of a weir to the mouth of the vessel was found to be beneficial for eliminating metal spill, which is one of the most important difficulties of slag dumping in the double-slag practice [35]. In another paper about the double-slag process, it indicated that 55% of the Nippon Steel’s production was based on the MURC process and that lime usage in BOF was reduced by more than 40% [36]. This one, and other similar BOF practices, originated in Japan, which have mostly dealt with hot metal phosphorus values much higher than 0.09-0.12%. Later, these practices spread into Chinese steelmaking companies [37]. It was discovered that an increase in phosphorus content of the iron ores (Phosphorus \geq 0.1% is something difficult to treat economically) necessitates more aggressive oxygen steelmaking technologies to achieve mass production of low phosphorus steels [38].

Tian et al. investigated the double-slag operation in a basic oxygen furnace for the production of low phosphorus steels. The typical chemical composition of the hot metal of the Chinese steel company was reported to be 4.30-4.50%C, 0.18-0.60%Si, 0.13-0.19%Mn, 0.07-0.10%P, and 0.005%S. In the steelmaking plant having three 210 t converters, the

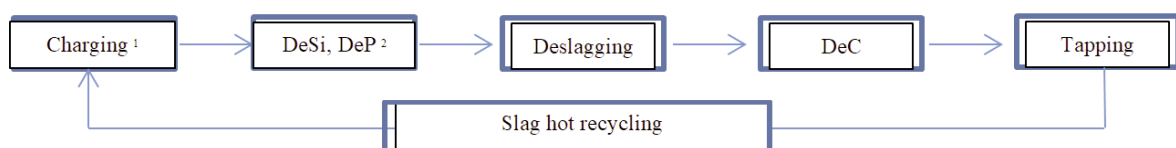


Figure 3. The flowsheet of the MURC process (¹Hot metal and scrap are charged to BOF; ²Flux addition is conducted)

number of heats was subjected to the double-slag practice. Plant trials were conducted in such a way that 5 minutes of initial blowing was followed by tilting of the converter for slag tapping, which enabled the removal of the P_2O_5 -rich slag. The phosphorus removed in the first blowing period was reported to be around 80% of the hot metal's phosphorus content. Then, the converter was returned back to the blowing position and 8-9 minutes of second O_2 -blowing was applied to obtain the desired carbon content. According to the results, during the first blowing period, three "state-of-the-art" factors for phosphorus removal were of great importance: A high Fe^{3+} content of the slag, oxygen potential, high basicity of the slag, and a low temperature. In the second blowing period, the effect of oxygen potential on phosphorus removal was not very pronounced. A similar finding was outlined for slag basicity such that basicity values greater than 6 were not advised. One of the most important conclusions of the paper was related to the steel tapping temperature; it was concluded that it was impossible to reach phosphorus content of less than 0.005% for crude steel when the tapping temperature was greater than 1943 K [39].

Yang et al. studied to optimize some process parameters for the BOS that contained a maximum allowable phosphorus content of 0.007% while also implementing the double-slag practice. A number of trials was conducted in a Chinese steelmaking company having six converters, each being with 180 t capacity. Hot metals charged to the converters had typical compositions of 4.2-4.7%C, 0.23-0.54%Si, 0.16-0.24%Mn, and 0.07-0.09%P. Deslagging was performed two times, both at the end of the first blowing (i.e. dephosphorization) and at the end of the second blowing (i.e. the decarburization period). The authors reported that phosphorus content of 0.0042% was attained before the tapping of steel. The average time of the first and second blowing was calculated as 4.4 and 9.3 minutes, respectively. According to the kinetic studies, dephosphorization that occurred before the intermediate deslagging was controlled by a mass transfer of phosphorus from the metal/slag interface to the bulk slag, whereas dephosphorization after intermediate deslagging was controlled by equilibrium thermodynamic conditions like slag composition and temperature. The optimum time for the first deslagging was determined when 14 m³ O_2 /t of hot metal was blown onto the hot metal [40].

Wu et al. investigated the application of the double-slag practice for hot metals obtained from usage of high phosphorus iron ores. Double-slag trials were conducted in a 120 t converter and the average chemical composition of the hot metals charged to the converter was outlined as 4.0-5.8%C, 0.4-0.8%Si, 0.15-0.37%Mn, and 0.102-0.203%P. In an effort to enhance the slagging, the authors tried using calcium

ferrite pellets. Among different stoichiometry, pellets having "iron oxides to CaO wt. ratio" of 3:1 were determined to be charged to the converter as an additional fluxing agent to the lime, light-burned dolomite, and sinter mixture. With the use of calcium ferrite pellets, the researchers aimed to adjust the slag composition and viscosity so as to decrease the deslagging temperature by 30-50°C and also prevent phosphorus reversion to the molten steel. Together with the incorporation of petrographic analysis of the slag samples, it was concluded that average dephosphorization efficiency was found to increase to 91% with calcium ferrite fluxing. Moreover, calcium ferrite addition was reported to be beneficial for lowering the melting temperature of the converter slag and for decreasing the amount of free calcium oxide and metallic iron present in the final slag [41].

In a technical report, Inoue et al. outlined certain improvements in JFE Steel Co. in relation to production capacity. One of the improvements was a new process named the Double-slag Refining Process (DRPTM) for phosphorus removal. In DRPTM, two converters are used successively. In the first converter, desiliconization and removal of the SiO_2 -rich slag is followed by dephosphorization. Afterwards, the metal, which can be called as semi-steel, is tapped into a ladle and is then charged into the second converter for final O_2 -blowing decarburization. The steel is then tapped into a ladle and sent to the secondary steelmaking plant. The authors concluded that the application of DRPTM resulted in a 44% reduction in total CaO consumption compared to the conventional blowing [42].

Wang et al. analyzed the double-slag process with industrial tests that used a 150-ton converter from the Tangsteel Company. The average hot metal composition was reported as 4.25-4.67%C, 0.16-0.58%Si, 0.16-0.25%Mn, and 0.11-0.12%P. To obtain sufficient fluidity for efficient deslagging, a slag having a basicity in the range of 1.5-2.0 was intended to be formed in the first blowing period. It was reported that the % dephosphorization value of 71% was achieved when the basicity was adjusted to 1.7. The authors underlined the increased production efficiency with efficient dephosphorization and quick iron-slag separation, and those benefits only required an additional four minutes when compared to the conventional process time [36].

Liu et al. studied the dephosphorization behavior in an early stage of the converting process. A double-slag practice, called the return-slag and double-slag operation (RDO), was applied using an 80-ton converter. The RDO process was explained as follows: First, around 2/3 of the final slag having a basicity of 3-4 is to remain in the converter. Second, the cooling and solidification of the slag is conducted by means of splashing together with dolomite

addition. Third, scraps and hot metal are charged into the converter as in the single stage operation. Fourth, oxygen blowing is conducted for dephosphorization. Fifth, dephosphorization slag is quickly dumped. Sixth, oxygen blowing for decarburization and the tapping of steel is performed, then the slag is returned (Figure 4). The authors concluded that the highest dephosphorization ratio in the early stage was obtained when the slag basicity and slag tapping temperature were in the range of 1.2-2 and 1600-1700 K, respectively. It was found that dicalcium silicate precipitation occurred simultaneously with phosphorus enrichment in the slag. X-ray photoelectron spectroscopy observations revealed that the slag contained both dicalcium silicate and calcium phosphate, which were probable implications of a reaction between Ca^{2+} with SiO_4^{4-} and PO_4^{3-} in the first blowing period. It was further suggested that dicalcium silicate and calcium phosphate could make a solid solution [43].

According to statistical data shared by the Worldsteel Association in 2016, 12% of oxygen used within steelmaking was conducted with double-slag process. At the same time, a share of the single slag process was reported as being 81%. The extent of the double-slag process is expected to increase in the future. According to the same source, it was indicated that reduction of total slag quantity with the double-slag operation was around 6 kg/ton of crude steel, although a negligible rise in dephosphorization efficiency was noted from 89.5-89.7%. Another study related to 300 t converters operating in China, and the average lime usage in a single slag process and double-slag operation were given as 37.6 kg and 28.3 kg per ton of crude steel, respectively. Therefore, the lime consumption in oxygen steelmaking was found to be reduced to around 25% with the double-slag practice. Together with those benefits, the author commented on the possibility of recycling the dephosphorization slag obtained from the double-slag operation, and that it was not easy due to high phosphorus and Fe_xO_y content of the slag as well as its skeleton structure [44].

In this section, up to now, the double-slag processes applied in BOS were outlined. For an easy

comparison, those processes and the conventional single-slag practice are tabulated together with their main factors and are illustrated in Table 2.

Other than the aforementioned studies related to double-slag practice, the end point phosphorus prediction in converter steelmaking has been a hot topic for a decade or more. Since TSC (Temperature Sampling Carbon) and TSO (Temperature Sampling Oxygen) measurements do not account for phosphorus, whether the desired phosphorus content is achieved or not can only be analyzed from the chemical analysis results of the steel sample. This is a time consuming business, even if the laboratory is established next to the converter. Amount of fluxes to be added can also be optimized if the steelmaker has a prediction about the end point phosphorus content so that excessive usage of fluxes can be avoided. Therefore, numerous studies have been conducted to predict the final phosphorus composition of the crude steel at the end of the oxygen blowing process. Those studies were generally based on certain mathematical models and so-called “intelligent models” that aim to improve the predictions’ precision. As an example, in one of them, Wang et al. utilized Weighted K-Means and a group method of data handling (GMDH) for predicting the endpoint of a phosphorus composition in BOF [45]. In another example, he and Zhang benefited from the principal component analysis (PCA) and back propagation (BP) neural network to predict the final phosphorus content at the end of the oxygen blowing process. In the latter case, steelmaking plant studies including 60 heat levels resulted in an end-point phosphorus content rate of 96.67%, 93.33%, and 86.67% when the prediction errors were within $\pm 0.007\%$, $\pm 0.005\%$, and $\pm 0.004\%$ [46]. Such results were a good reference when considering the so-called “quick direct tapping” of a converter. However, the details of those models are not included in the scope of this paper. Similarly, some modifications in the conventional single stage blowing, such as alterations in O_2 -blowing practices, design changes in traditional lances (e.g. use of nozzle-twisted oxygen lances), etc., are not categorized in the extent of the present work.

One of the recent proposals for dephosphorization

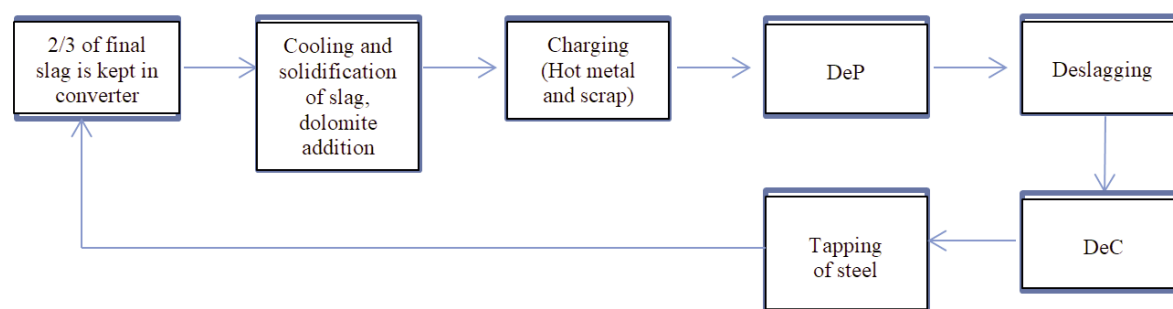


Figure 4. The flowsheet of the return-slag and double-slag operation (RDO)

in steelmaking converters was related to the use of CO₂-O₂ mixed blowing instead of the conventional O₂

Table 2. Dephosphorization practices in BOS*

Single-slag process	Conventional Basic BOF Process	<ul style="list-style-type: none"> • Charging • O₂-blowing • Tapping of steel • Deslagging (Slag splashing may be applied)
Double-slag processes	Double-slag practice (in general)	<ul style="list-style-type: none"> • Charging • O₂-blowing for deP • Tapping of slag before the middle of conventional BOF O₂-blowing, deP slag is discarded • O₂-blowing for deC of so-called "semi-steel" • Tapping of steel • Deslagging of the second (deC) slag
	The Multi-Refining Converter (MURC) Process	<ul style="list-style-type: none"> • Charging • O₂-blowing for deSi, deP (flux addition is conducted) • Deslagging, deP slag is discarded • O₂-blowing for deC of so-called "semi-steel" • Tapping of steel • Hot deC slag is recycled
	The Double-slag Refining (DRP TM) Process	<p>Two converters are utilized. In the first converter;</p> <ul style="list-style-type: none"> • O₂-blowing for deSi • Removal of SiO₂-rich slag • O₂-blowing for deP • Tapping of steel to a ladle • deP slag is discarded <p>In the second converter;</p> <ul style="list-style-type: none"> • Semi-steel is charged to the converter • O₂-blowing for deC • Tapping of steel • Deslagging of the second (deC) slag
	The Return-slag and Double-slag Operation (RDO)	<ul style="list-style-type: none"> • 2/3 of final converter slag having basicity of 3-4 is remained in the converter • Cooling and solidification of slag by means of splashing, dolomite addition • Charging • O₂-blowing for deP • Deslagging, deP slag is discarded • O₂-blowing for deC of so-called "semi-steel" • Tapping of steel • Slag is returned

*Abbreviations: deP: Dephosphorization, deSi: Desiliconization, deC: Decarburization

blowing practice. CO₂ usage in iron and steelmaking was outlined deeply in a review paper, and its utilization in basic oxygen furnaces, especially for stirring purposes, has been well known [47]. Lv et al. suggested a mixed injection of CO₂-O₂ to increase the dephosphorization ratio. Plant trials were conducted in a 30 t steelmaking converter, and a 300 t special dephosphorization converter was used for the duplex steelmaking. The authors outlined the heat effects of the reactions taking place during oxygen blowing. Even though they knew that the reactions between CO₂ and C or Fe are endothermic, they proposed the usage of a CO₂-O₂ mixture instead of a pure O₂ so that lower molten bath temperatures, which are metallurgically more suitable for dephosphorization, could be obtained. For the trials in the 30 t converter, the furnace design was changed in such a way that a mixed blowing was conducted through the top lance together with a usual practice of N₂+Ar bottom blowing. For the trials in the 300 t vessel, the final design of the converter had a mixed blowing top lance together with CO₂ injection from the bottom nozzles. From the former converter, the application of the mixed injection was reported to decrease the average end-point phosphorus content from 0.051 to 0.037%. Likewise, from the latter vessel a decrease from 0.051 to 0.044% was noted. It was concluded that all plant trials resulted in higher dephosphorization and phosphorus partition ratio (i.e. (%P)/%P) values while iron losses decreased [48]. Those results may be regarded as promising and even challenging, especially for the future works. However, the end-point phosphorus compositions within the aforementioned study were all greater than 0.035%, which is a decently high phosphorus value; furthermore, the customer demands of the current steelmaking era were also quite high.

4. Conclusions

The new trends in phosphorus removal in BOS were outlined. In the last two decades, the new technologies that might differ slightly from one another can be summarized under the generic heading of the "double-slag process" that originated in Japan and then spread into China. The double-slag process was found to be successful especially for the treatment of high phosphorus hot metals (P > 0.100%). In some practices, the decarburization slag is recycled and, therefore, is charged to the converter. The process was reported to be effective to reduce the flux consumption and the amount of the slag produced in converters. In some studies, the optimum time for the first deslagging was also determined in terms of the volume of oxygen sent per ton of hot metal. Dephosphorization slag (i.e. the first slag) must be dumped as quickly as possible. The steel tapping



temperature was found to be very critical to achieve low phosphorus compositions less than 0.007%; so, high tapping temperatures must be avoided. The use of some fluxes like calcium ferrite was reported to be successful to increase the dephosphorization ratio. Metal spills during dephosphorization slag dumping were discussed as one of the most important problems of the double-slag practice, so weir designs for the converter mouth were found to be beneficial for eliminating metal spills. The total tap-to-tap time in the double-slag operation was reported to be slightly extended when compared to the single slag (i.e. conventional) process. However, the double-slag operation was reported to be more economical than trying to establish a separate dephosphorization plant, especially if the share of low phosphorus qualities in the product mix of a company was not very large. Unfortunately, a successful recycling of dephosphorization slag has not been reported yet. Another important new trend related to converter dephosphorization is “end-point phosphorus prediction” in BOS. Numerous studies have been conducted about this issue, especially in the last decade. One of the recent proposals related to dephosphorization in BOF was the mixed injection of $\text{CO}_2\text{-O}_2$ instead of the conventional oxygen blowing, and promising results were obtained.

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NOVI TREND OVI U POSTUPKU UKLANJANJA FOSFORA U KISEONIČNOM KONVERTORU

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Apstrakt

Osim za specijalne vrste čelika kod kojih se koristi kao legirajući element, fosfor se posmatra kao nečistoća koja mora da se ukloni. Ako se posmatra konvencionalna integrisana proizvodnja gvožđa i čelika, postoje dva osnovna postupka za uklanjanje fosfora. Prvi postupak je smanjivanje sadržaja fosfora u tečnom sirovom gvožđu (defosforizacija tečnog sirovog gvožđa) koji se primenjuje na tečni metal u visokim pećima pre postupka proizvodnje čelika. Drugi postupak je proizvodnja čelika u kiseoničnom konvertoru, koji predstavlja jedinstveni metod koji se koristi za proizvodnju čelika, sa izuzetkom nerđajućih čelika. Sadržaj fosfora u tečnom sirovom gvožđu direktno utiče na postupak proizvodnje čelika u kiseoničnom konvertoru. Povećanje sadržaja fosfora u tečnom sirovom gvožđu je uglavnom povezano sa upotrebom rude železa sa visokim sadržajem P_2O_5 . U ovom pregledu literature su navedeni novi trendovi u uklanjanju fosfora u proizvodnji čelika u konvertoru. Utvrđeno je da je postupak dvostruke šljake uspešan kada je sadržaj fosfora u tečnom metalu veći od 0,100%. Ustanovljeno je i da je temperatura ispuštanja tečnog metala iz peći presudna za proizvodnju čelika sa niskim sadržajem fosfora kod kojih je maksimalni dozvoljen sadržaj P 0,007%, i da se visoke temperature ispuštanja moraju izbegavati. Vreme između dva ispuštanja je tokom rada sa dvostrukom šljakom nešto duže nego prilikom konvencionalne proizvodnje čelika u konvertoru. Takođe je utvrđeno i da je postupak rada sa dvostrukom šljakom ekonomičniji od formiranja odvojenog postrojenja za defosforizaciju tečnog metala, ako vrste čelika sa niskim sadržajem P nemaju značajan udeo u integrisanoj proizvodnji gvožđa i čelika u kompaniji. Predviđanje konačnog sadržaja fosfora predstavlja jedan od važnijih novih trendova u proizvodnji čelika u konvertoru. Primenjeno je injektiranje mešavine CO_2-O_2 u kiseonični konvertor da bi se povećala defosforizacija i rezultati su se pokazali kao obećavajući. Nažalost, još uvek nije utvrđen uspešan postupak za recikliranje šljake nastale tokom defosforizacije u kiseoničnom konvertoru.

Ključne reči: Fosfor; Proizvodnja gvožđa i čelika; Tečni metal; Čelik; Rad sa dvostrukom šljakom.

