

De-Phosphorization Strategies and Modelling in Oxygen Steelmaking

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ABSTRACT

Today the task and aim of the Basic Oxygen Steelmaking (BOS) Technology is to supply molten steel produced from Hot Metal, Scrap, Flux and other Coolant/Fuel Charge just in time to meet the logistic requirements of a modern Steel Melt and Continuous Casting Shop. Most of the metallurgical Work has been moved into Secondary Metallurgy Aggregates, which are especially designed to fulfill the analytic requirements raised from the product specifications. At least the adjustment of the melt temperature required for further processing and the removal of Phosphorus are the main metallurgical tasks of BOF operations beside all cost and logistics demands.

The removal of Phosphorus from the furnace charge is a well understood process and can be described by the De-Phos coefficient $L_P = (\%P_2O_5)/[\%P]$ which represents the distribution between slag and metal. The L_P depends on temperature of the melt, slag ($\%Fe_t$) content, slag V-ratio ($\%CaO)/(\%SiO_2)$, slag volume, slag ($\%MgO$) content and steel [$\%C$] content being the main parameters to be controlled during processing. Of course the total Phosphorus input into the system by the hot metal and the Phosphorus aim according to the steel product specification of the individual plant also play an important role. Furthermore the results also vary with the individual plant equipment available and the De-Phos strategy applied.

This paper reviews the metallurgical basics and discusses the different possibilities to succeed in the task by comparison of the result of various steel plants over the world and their different approach.

INTRODUCTION

Phosphorus because of its strong impact on steel properties is one of the most annoying elements in industrial stage production of steelmaking. Phosphorus in steel causes hot shortness, temper embrittlement, ductility, toughness reduction and is one of the most sensitive elements for grain boundary segregation [1], **Table 1** gives an overview [2].

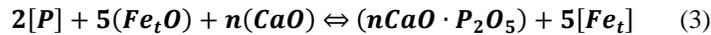
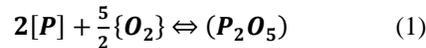
Property		Effect of Phosphorus
Strength		++ (ferrite strengthener)
Bake hardenability		+
Ductility		--
Fe-Zn galvanneal		may improve resistance to powdering
Phosphatability		+
Enamelling steels	Fish-scaling	-
	Pickling	+
Weldability		Not harmful for < 0,1 mass-%
Core loss in motor laminations		--
Fracture toughness		--

+ increase ++ strong increase - decrease -- strong decrease

Table 1: Effect of Phosphorus in Steel [2]

DE-P FUNDAMENTALS

Direct removal of Phosphorus with Oxygen into the BOF slag will not happen because of thermodynamic restrictions. Phosphorus Pent-Oxide P_2O_5 is not stable at steelmaking temperatures and will be reduced immediately after formation during hot metal refining, **Figure 1**. Therefore its activity must be reduced by offering of liquid CaO. Since the pure lime has a very high melting point of $> 2.800\text{ }^\circ\text{C}$ a flux must be used to liquefy the lime. This flux is Fe_tO in today's state-of-the-art operations. Of course SiO_2 also supports the solution of lime but lowers the activity. The general equations for the **reaction** are defined as follows:



The **equilibrium constant** for equation (3) is:

$$\log K_P = \frac{61.110}{T_K} - 23,3 \quad (4)$$

Other important factors are the **Phosphorus distribution** factors (5), (6) and the **De-P efficiency** factor (7):

$$L_P = \frac{(\%P)}{[P]} \quad (5)$$

$$L_{P_2O_5} = \frac{(\%P_2O_5)}{[P]} \quad (6)$$

$$\eta_P = \frac{[P]_{Initial} - [P]_{EOB}}{[P]_{Initial}} \quad (7)$$

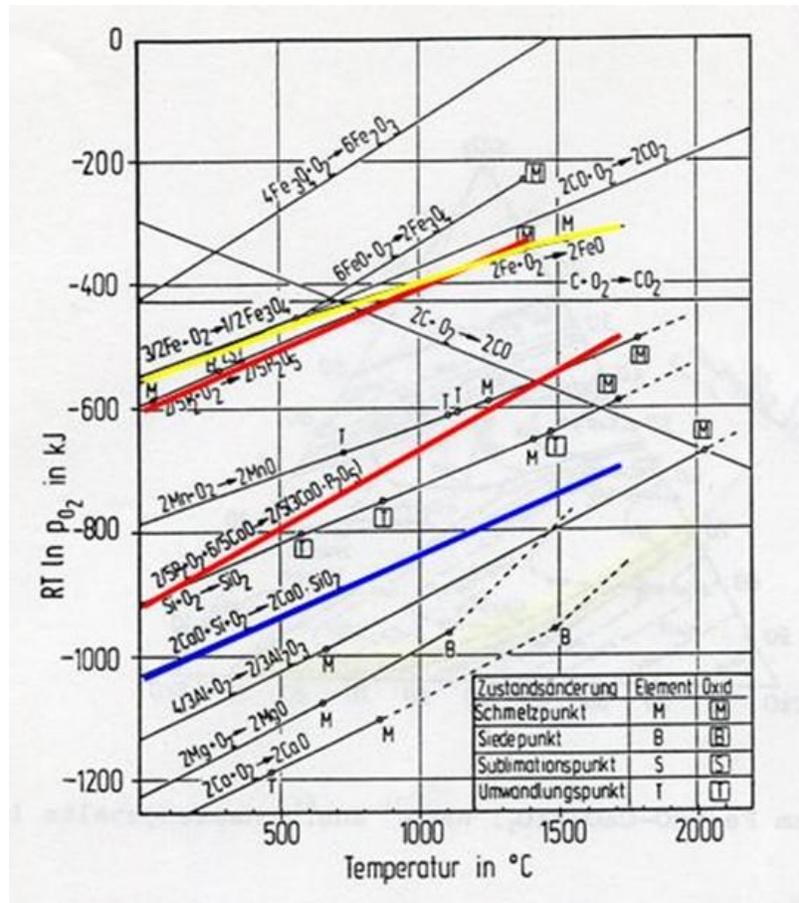


Figure 1: Richardson Diagram for Oxides [3]

The positive coefficient of the equilibrium constant K_p (4) shows, that the reaction is an exothermic reaction. Since the temperature is the denominator of the equation it is clear that with increasing temperature the reaction will move to the side of the reactants.

When looking into the phase diagram CaO–FeO–P₂O₅ it becomes evident, that equilibrium will be achieved at an sufficient CaO/P₂O₅-ratio > 3. Based on the reaction equation (1) it can be estimated that De-Phosphorization (De-P) is encouraged by:

- High oxidizing conditions in the BOF ($a_{FeO} \uparrow$)
- High lime activity in the slag ($a_{CaO} \uparrow$) and
- Low process temperature ($T_{EOB} \downarrow$)

Of course all other factors which enhance lime solution and increase the reaction surface between the metal and slag like reactivity/grain size of the lime or efficient bath stirring energy support the De-P process as well. The fundamentals and the relevant parameters of De-P in industrial application are very well investigated and understood.

Process Temperature T_{EOB} : As already mentioned before, the strongest influence on the achievable Phosphorus content of the steel melt is the temperature. It is well understood that De-P gives the best results in the temperature range of the hot metal (< 1.450°C), where hot metal pre-treatment is operated. The De-P starts immediately when the Silicon is oxidized from the metal.

In the later stage of the BOF-Process a low tapping temperature is favorable for Phosphorus control [4][5], **Figure 2**. Therefore it is understandable that operations equipped with ladles furnaces have a competitive advantage compared to plants which must guarantee the melt superheat for treatment based on the melting aggregate.

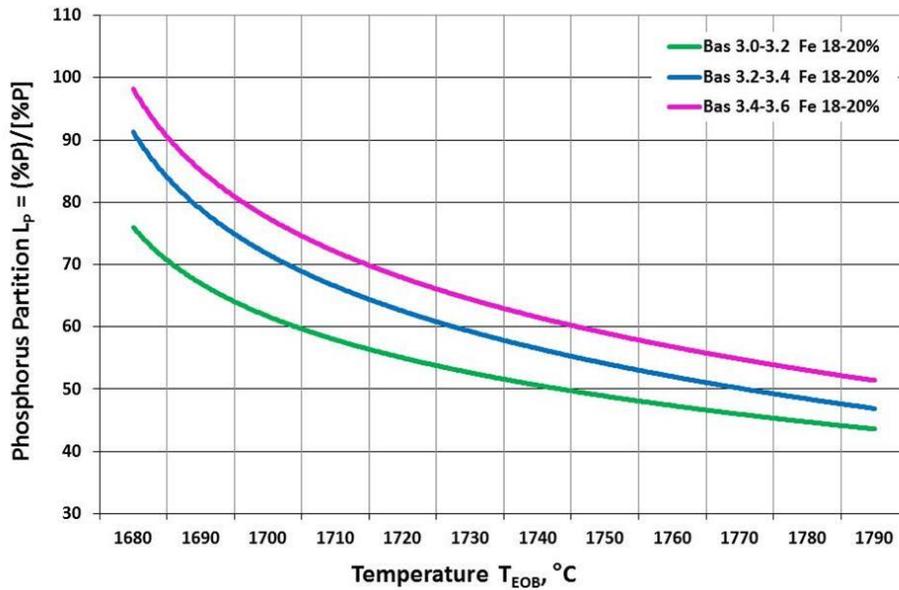


Figure 2: Phosphorus Control and Tapping Temperature

(%Fe₂O) content in the slag: Since the De-P reaction (1), (2) is not a direct reaction with the blow Oxygen, but with iron oxide in the slag, it is favorable to work at elevated (%Fe₂O) content. But, as shown in **Figure 3** [4][5], the L_p is initially enhanced with increasing (%Fe₂O) in the range of 15% to 20%, but this effect is reversed at higher content over 20%. Another negative effect on L_p must be mentioned which is the (%MnO)-content of the slag, which also has a declining effect on the L_p. The influence of the MnO is not so important in BOF steelmaking, since the (%MnO) levels are low < 5% in maximum, depending on the iron ore source for hot metal production.

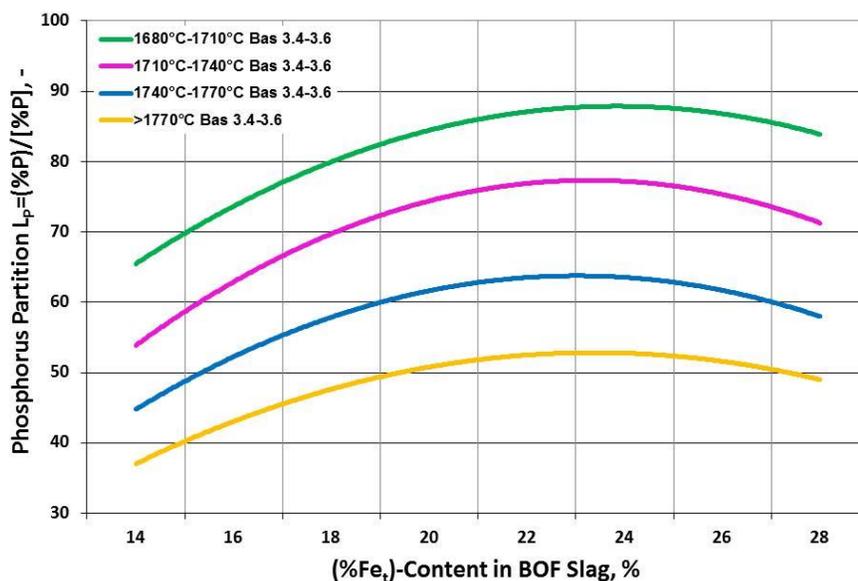


Figure 3: Total Iron Content in Slag (%Fe) and Phosphorus Distribution

Slag basicity (%CaO)/(%SiO₂): as mentioned before, free, liquid lime is needed to form a stable Phosphorus Oxide compound during the blow. The free lime available for this reaction can be described by using the slag basicity factor:

$$B_1 = \frac{(\%CaO)}{(\%SiO_2)} \quad (8)$$

who is a common factor to describe the lime surplus in the slag that overcompensates the Silica generation from the hot metal and scrap Silicon charge input to the process. **Figure 4** shows results HKM, It can be concluded, that a basicity increase up to a level of 4,0 will improve the Phosphorus partition [5][7]. Another investigation [6] shows that over a basicity of 4,0 the positive effect of the lime addition will be reversed.

$$B_2 = \frac{[(\%CaO)(\%MgO)]}{(\%SiO_2)} \quad (9)$$

Most properly at very high basicity the lime surplus is too high to be solute by the slag ($\%Fe_2O_3$) to liquid ($\%CaO$), which increases the viscosity and reduces the reactivity of the slag significantly.

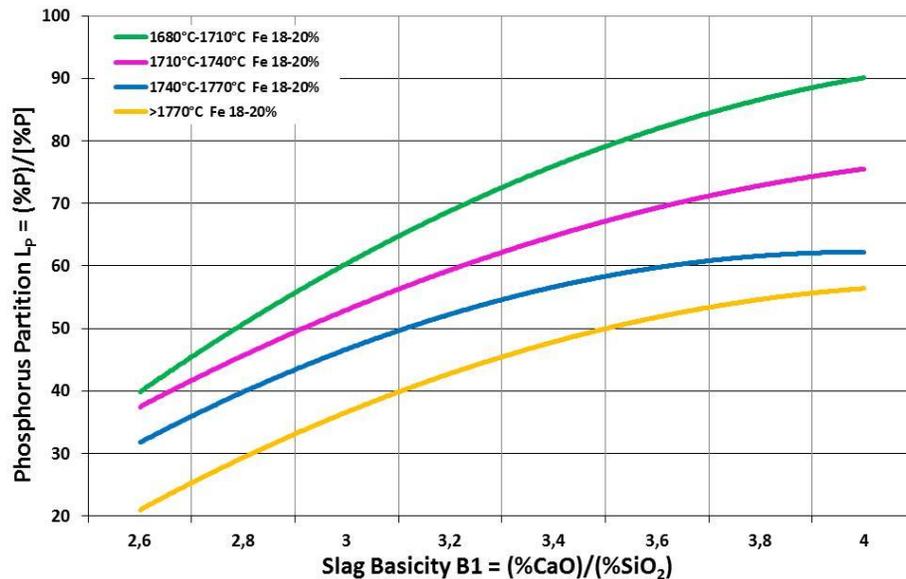


Figure 4: Phosphorus Partition L_P an Slag basicity B_1

Slag ($\%MgO$) content: The slag ($\%MgO$) content is an important factor to control the wear of the furnace refractory during operations and guarantee long vessel lining life times by using the slag splashing technology. In this application the BOF slags are enriched with ($\%MgO$) by using dolomite or MgO -Pellets/briquettes to increase the viscosity of the slag and to improve their sticking and melting properties.

Looking into the details it can be stated, that the slag liquidus and solidus temperature is influenced by the ($\%Fe_2O_3$), the ($\%MgO$) and the Basicity B_1 . ($\%Fe_2O_3$) strongly decreases the melting temperature and spreads the melting interval, which means the slag early starts to generate liquid fractions. The basicity is almost neutral with only slightly decrease in the melting temperature. The slag ($\%MgO$)-content generates a minimum melting temperature of the slag at 6-7%. At lower ($\%MgO$)-content the melting temperature increases quickly. At higher ($\%MgO$)-content the precipitation of solid MgO starts and the viscosity increases with negative impact on De-Phos-efficiency. These facts are important to know because they strongly influence the efficiency of slag splashing, which requires proper ($\%Fe_2O_3$) and ($\%MgO$) control. At the high ($\%MgO$) end the negative influence on the De-P efficiency must be taken into account.

It is clear understood that high ($\%MgO$)-content reduces the reactivity of the slag and according to that the efficiency of the De-P, as shown from laboratory trials in **Figure 5** below [5][6]. The “natural” ($\%MgO$)_n content (from charged lime and refractory wear) would reach up to 2,0-2,5%. The saturation content of ($\%MgO$)_s is varying with the slag basicity B_1 , but can be estimated at 5-6% at a basicity of 3,0. The figure shows a quick decline in the Phosphorus distribution factor L_P with increasing ($\%MgO$) content in the slag.

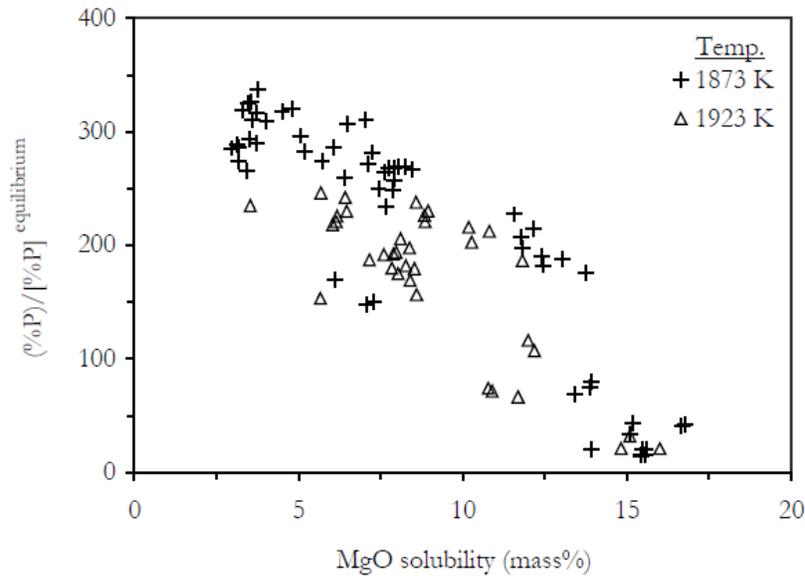


Figure 5: Slag (%MgO) Content and Phosphorus Distribution L_P [5][6]

Steel [%C] content: For the De-P reaction strong oxidizing conditions are favorable. Especially at the end of the blow the total Oxygen available for the reaction is of course dependent on total amount of Oxygen blown into and this influence can be described in the best way by the end of blow Carbon content $[\%C]_{EOB}$. The lower the $[\%C]_{EOB}$, the higher the $[\text{ppmO}]_{EOB}$. Both liquid steel components are linked together by the $[\%C][\text{ppmO}]$ -product, which is an operations constant describing the equilibrium stage at the end of the blow, **Figure 6**. The Oxygen content in the melt is directly linked to the $(\%Fe_tO)$ content in the slag.

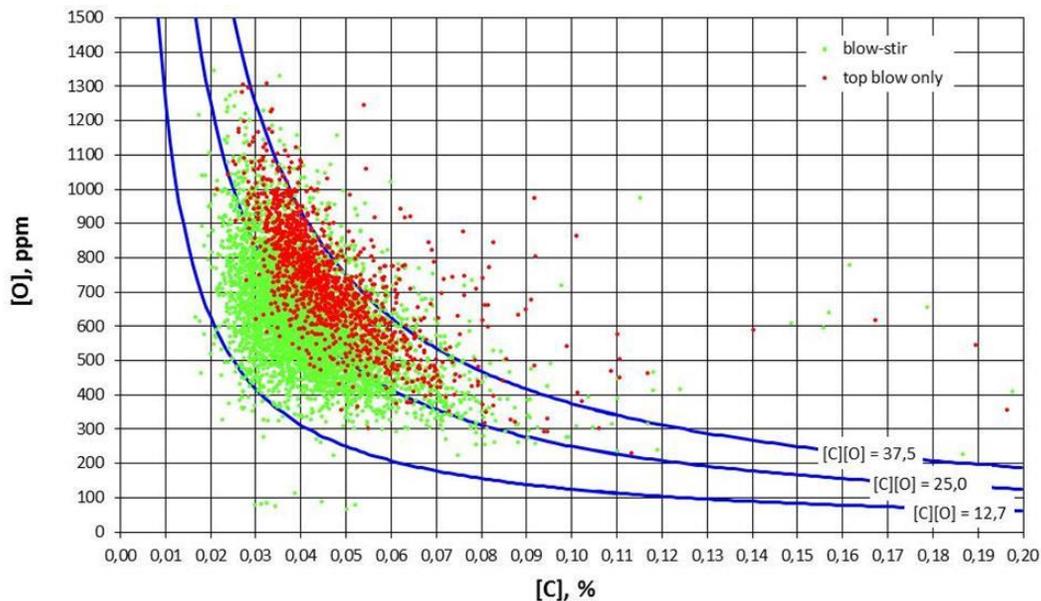


Figure 6: Carbon $[\%C]_{EOB}$ and Oxygen $[\text{ppmO}]_{EOB}$ Content at End of Blow [8]

It can be considered, that a general overblow of the heats to low Carbon content has the same effect on the De-P efficiency as a reblow because of too high Phos-content. The additional Oxygen offered to the melt increases the slag $(\%Fe_tO)$ and by that removes more Phosphorus from the melt into the slag. The aim for low Carbon content only offers additionally the possibility of more accurate temperature control.

Blowing conditions: The effect of the blowing conditions on the De-Phos result is shown in **Figure 7**. The figure shows the Phosphorus partition L_P and the total (%Fe_t) content of the slag during a regular furnace campaign. Both parameters are declining although the lance distance to the bath surface is always kept constant. Since in this particular BOF shop also the Oxygen flow rate is kept constant, the result must be interpreted as follows:

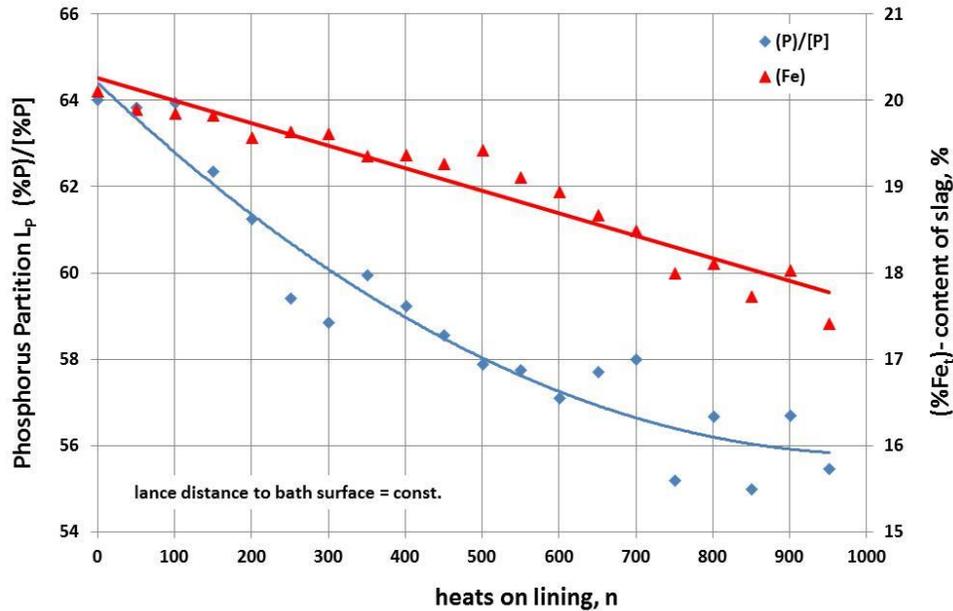


Figure 7: Phosphorus Partition, Slag Fe_t content and Converter life

With ongoing campaign life and the related refractory wear the bath gets flat, i.e. the bath diameter increases, but the bath height decreases. With a constant bath distance and flow rate the penetration depth of the jet remains constant. The (Fe_tO) generation during blowing is depending on the percentile ratio of the penetration depth on the bath height. The higher the percentile ratio, the “harder” is the blow. It is common understanding that hard blowing results in lower (Fe_tO) content. Because of the relation between L_P and (Fe_tO) described before, the L_P is reduced simultaneously. A dynamic blow control is required.

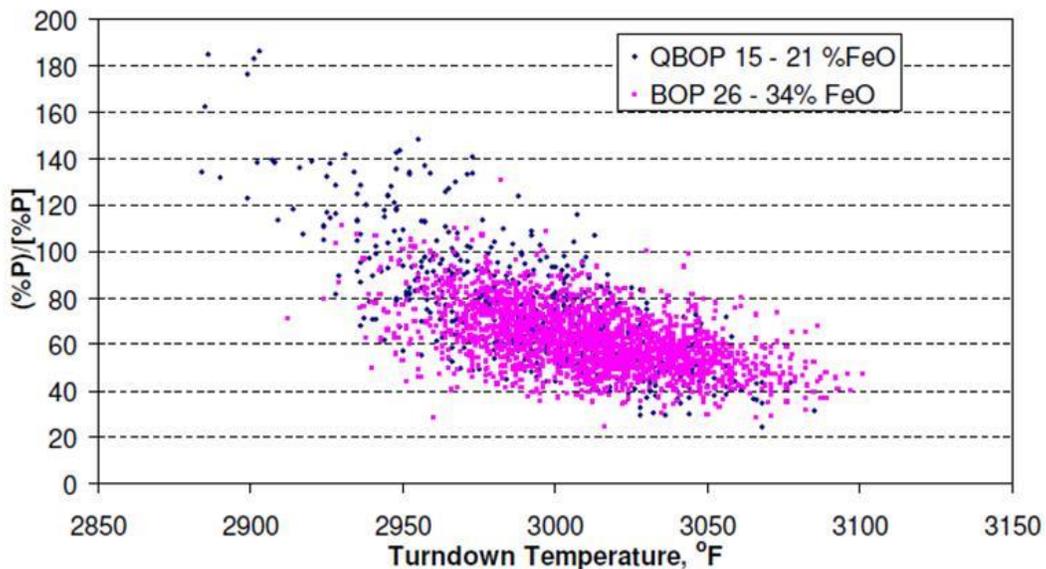


Figure 8: Stirring Intensity and Phosphorus Distribution L_P [9]

Mixing intensity: It is well known, that efficient De-P is also strongly dependent on the kinetics offered during blowing. Since the Phosphorus of low content (240 kg/heat at a 300 t heat and an $[P]_{INI}$ of 0,0800 %) which is even distributed in the huge volume of almost 43m³ shall be reduced to 30 kg/heat (= 0,0100 %) it is crucial to bring the phosphorus molecules to the slag metal interface in the BOF vessel.

This can be done weather by emulsification of slag droplets into the steel melt or by moving the melt from the vessel bottom to the surface where the slag is on top. Both cases require strong mixing behavior. **Figure 8** shows a direct comparison between a top- and a bottom blowing BOF operated in the USA. It becomes evident that the bottom blowing technology can achieve the same De-P efficiency as the top blowing vessel, but with significantly lower (%FeO) contents in the slag. The bottom blowing technology is known for its better mixing behavior.

Slag volume: In practical operation the tasks of the process normally are defined by the steel quality program (aim Carbon, aim Phosphorus and alloy content = tapping temperature). The slag composition is optimized for iron yield (%Fe_t) and low refractory wear (%MgO) and the basicity (B1) is restricted to save flux consumption. With all these limitations the achievable De-P distribution factor is also fixed within only small limits. To achieve the desired end of blow Phosphorus content in the steel the only way left to increase the removal efficiency η_P is to increase the slag volume. This is especially necessary in case of low Silicon content in the hot metal supplied from the blast furnaces. In this case the slag volume must be increased by using Silica flux or FeSi-fuel to increase the slag volume to a sufficient level.

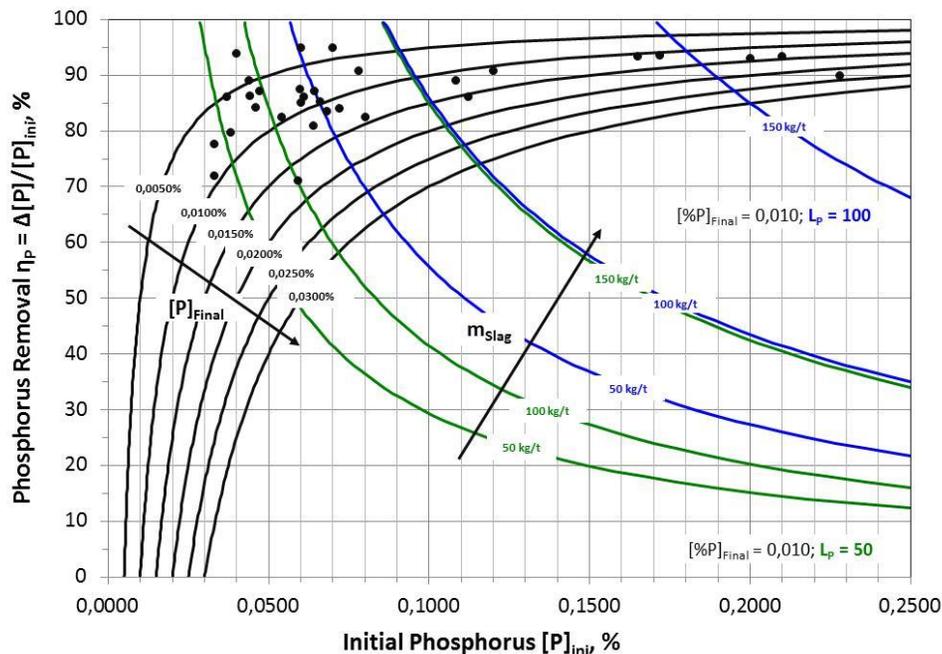


Figure 9: De-Phosphorization by Slag Volume

DE-P LITERATURE REVIEW

The distribution of Phosphorus between metal and slag is difficult to predict. A lot of models were investigated and published over the decades, **Table 2**, but all efforts to guarantee a steady-state operation towards the end of the blow will still result in varying process results from shop to shop. The reason is that under floor-shop condition there is always a lack between the ideal thermodynamic relations and their practical application. Differences are generated from slag temperature, composition and volume, turndown Carbon content and related slag (%Fe_tO) content, hot metal initial $[%P]_{HM}$ content, and the operations parameters like lance height, Oxygen flow rate, bottom stirring intensity and timing of the flux and iron ore additions. In consequence every individual plant usually develops its own blowing regime and practice based on the analysis of individual plant data. The selection of a general control model is not a simple task.

Source	Correlation Formula
Gemma 1987	$L \frac{(\%P)}{[\%P]} = -3,113 + \frac{8198,1}{T(K)} - 0,2075 * \log[\%C] + 0,3956 * \log(\%Fe_{\text{total}}) + 0,6639 * \log[(\%CaO)/(\%SiO_2)]$
Chukwulebe 1996	$L \frac{(\%P)}{[\%P]} = 5,41 - 0,00218 * T(K) + 0,00382 * (\%FeO) + 0,0228 * [(\%CaO)/(\%SiO_2)] - 0,0029 * (\%MgO)$
ESAI 2010	$L \frac{(\%P)}{[\%P]} = -5,71 - \frac{13590}{T(K)} + 0,384 * \log(\%Fe_{\text{total}}) + 0,431 * [(\%CaO)/(\%SiO_2)] - 0,361 * \log(\%MgO)$
Meishan 2011	$L \frac{(\%P)}{[\%P]} = -5,41 - \frac{10173}{T(K)} + 0,0088 * \log[\%C] + 0,855 * \log(\%Fe_{\text{total}}) + 0,346 * [(\%CaO)/(\%SiO_2)] - 0,144 * \log(\%MgO)$
Turkdogan 1996	$\log \frac{(\%P)}{[\%P]} = 10,6 + 2,5 * \log(\%FeO) + 0,5 * \log(\%P_2O_5) + 5,0 * \log(\%CaO)$
Balajiva 1946	$\log \frac{(\%P)}{[\%P]} = -0,36 - 0,5 * T(K) + 2,5 \log(\%FeO_n) + 5,9 \log(\%CaO) + 0,5 \log(P_2O_5)$
Ogawa 1993	$\log \frac{(\%P)}{[\%P]} = -8,55 + \frac{7710,2}{T(K)} + 2,5 \log * \left(\frac{\%FeO}{71,8} * 55,8 \right) + 0,0715 * (\%CaO + \%MgO) + \left(\frac{105,1}{T(K)} + 0,0723 \right) * [\%C]$
Balajiva 1947	$\log \frac{(\%P)}{[\%P]} = 5,9 \cdot \log(\%CaO) + 2,5 \cdot \log(\%FeO) + 0,5 \cdot \log(\%P_2O_5) - 0,5 \cdot C - 0,36$
Healy 1970	$\log \frac{(\%P)}{[\%P]} = -16 + \frac{22350}{T(K)} + 2,5 \log(\%Fe_{\text{total}}) + 0,08 * (\%CaO) \pm 0,4$
Suito 2006	$\log \frac{(\%P)}{[\%P]} = -10,52 + \frac{11570}{T(K)} + 2,5 \log(\%Fe_{\text{total}}) + 0,072 * \{(\%CaO) + 0,3 * (\%MgO)\}$
Bannenberg 1981	$\log \frac{(\%P_2O_5)}{[P]} = -0,69 + 2,5 \cdot \log(\%FeO_n)' - (\%FeO_n)' \cdot (1,55 \cdot 10^{-2} + 9,12 \cdot 10^{-5} \cdot (\%FeO_n)')$
Tata 2007	$\ln \frac{(\%P_2O_5)}{[P]} = \frac{20,254}{(T+273,15)} + 0,3638 \cdot \ln(\%FeO) - 0,0499 \cdot (\%MgO) - 6,299$
Bannenberg 1994	$L \frac{(\%P_2O_5)}{[\%P]} = -7,9517 - \frac{13958}{T(K)} - FeO_n' * (1,43 * 10^{-2} + 1,032 * 10^{-4} * FeO_n') + 2,5 * \log FeO_n'$
Suito 1995	$\log \frac{(\%P)}{[\%P] * (\%Fe_1)^{3/2}} = -10,52 + \frac{11570}{T(K)} + 0,72 * \{(\%CaO) + 0,3 * (\%MgO) + 0,6 * (\%P_2O_5 + \%MnO)\}$
Suito 1981	$\log \left(\frac{(\%P)}{[\%P] \cdot (\%Fe_1)^{2,2}} \right) = 0,072 \cdot [(\%CaO) + 0,3 \cdot (\%MgO) + 0,6 \cdot (\%P_2O_5) + 0,2 \cdot (\%MnO) + 1,2 \cdot (\%CaF_2) - 0,5 \cdot (\%Al_2O_3)] + \frac{11,570}{T} - 10,52$
Sobadi 2000	$\log(P_{O_2,3}) = \frac{1,400}{T} - 5,75 - \frac{2,59}{(\%SiO_2)} \cdot \{(\%CaO) + 0,33 \cdot (\%Me) + 0,55 \cdot (\%MgO) - 0,9 \cdot (\%Fe_1O) - 0,77 \cdot (\%PO_{2,3})\}$
Turkdogan 2000	$\log(\gamma P_2O_5) = -9,84 - 0,142 \cdot ((\%CaO) + 0,3 \cdot (\%MgO))$

Table 2: Various Formulas to describe the Phosphorus Partition Ratio

At the end the conclusion is, that every shop must develop its own De-P strategy and calculation model using the typical equation factors valid for operations in that particular shop. Which model type to be used can be discussed divergently. The recommendation from the authors is to use the simplest type of equation possible and to carry out a multivariate analysis with a sufficient volume of operation data. The influence factors on the Phos-partition should be implemented in the analysis according to their effect on the L_p . Of course the data collective must be controlled for inconsistency before the multivariate analysis.

DE-P PRACTICE

The operation practice of the BOF is not uniform in the different parts of the world. The practice can be differentiated in the European, Japanese and North American way, special converter technology completes the picture.

European BOF practice: In Europe the common technology is to process Fe-rich iron ores from Brazil, Canada and Australia, which result in a hot metal Phosphorus content between 0,060-0,090%. Almost all plants are operating a combined blowing process with top-lance and bottom stirring. The heat is blown down in a single stage process. Because of the production program alloy contents are high which causes high tapping temperatures and unfavorable De-P condition which are compensated with higher basicity and (%Fe₂O₃)-content. (%MgO)-enrichment and slag splashing is often not applied.

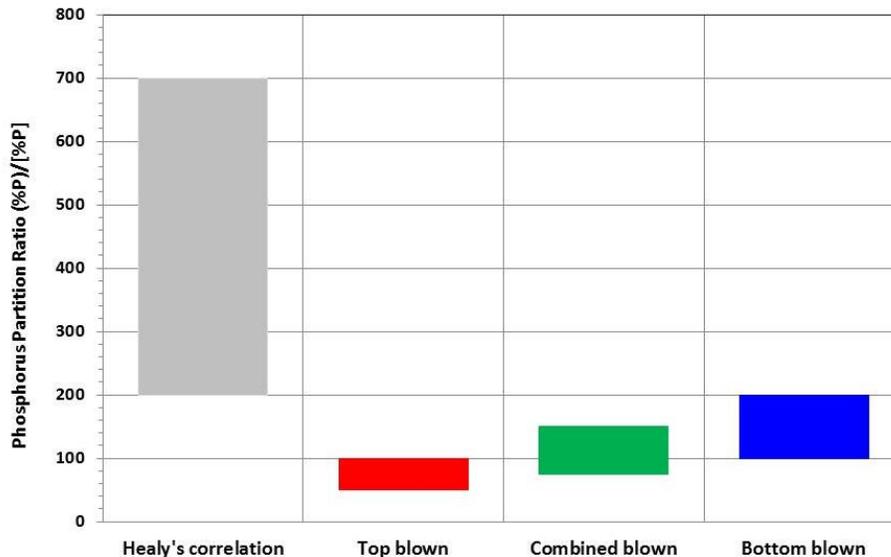


Figure 10: Comparison of Phosphorus partition ratio predicted by Healy's correlation with that practically attained during steelmaking [6], [10]

Japanese BOF practice: In Japan (and Korea and Taiwan) the Hot Metal Phosphorus is much higher with 0,090-0,120 % compared to the European condition. Therefore in almost all of the plants a double slag process whether as a Hot Metal pretreatment or a double BOF-process is applied to control the high Phosphorus content and to achieve very low final product [%P]-contents, which are used as a product differentiation attribute to the competitors in other regions. It should be mentioned, that NSSMC has developed and introduced a BOF lime injection technology to enhance the De-P partition by quick lime solution.

North American BOF practice: In North America the producers have the most comfortable situation with respect to the Hot Metal Phosphorus content, which is between 0,030-0,060%. These favorable conditions and the availability of secondary reheating units allow the steel plants to operate at low tapping temperature, low slag basicity, moderate (Fe₂O₃)-content and high (%MgO)-content as required for slag splashing. The poor kinetics of the top-blowing process is sufficient to guarantee the steel grade specification requirements.

Bottom and combined blowing BOF practice: The influence of the process type on the De-P behavior was reported earlier by Deo [6] and Basu [10]. **Figure 10** gives an indication of the results obtained in different process variants compared to the theoretical Healy correlation, mentioned in Table 2. It becomes evident that all industrial process results are below the thermodynamic potentials. Furthermore it is obvious that the mixing intensity increases the efficiency of the metallurgical reaction.

To demonstrate this estimated effect more in detail an investigation including the operations results from more than thirty BOF shops worldwide was carried out. The investigation includes all type of BOF Process available today, which are grouped in:

1. **Top-Blow & Slag Splash Shops:** Shops that are applying intensive slag splashing and top-blowing only.
2. **Blow-Stir & Slag Splash Shops:** Shops that are applying intensive slag splashing and use top-blowing and bottom stirring technology.
3. **Blow-Stir Shops:** Shops that use top-blowing and bottom stirring technology and do not apply slag splashing.
4. **Bottom-Blow & Slag Splash Shops:** Shops that use bottom blowing in combination with intensive slag splashing.

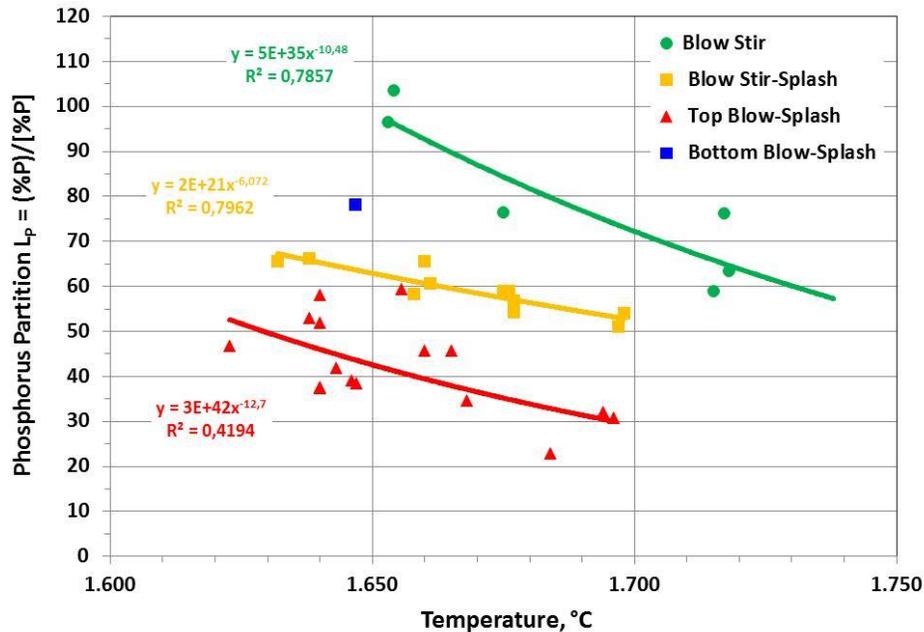


Figure 11: Phosphorus partition and BOF operation practice

The result of this investigation is shown in **Figure 11** below. According to the operation results the lowest Phos partitions are achieved in the top-blow & slag splash operation, represented by the red dots and trend line. The dominant effect of the tapping temperature on the partition ratio is evident. The variation in the results may be caused by the other factors ($\%Fe_tO$), ($\%MgO$), ($\%CaO$)/($\%SiO_2$), blowing conditions, etc. It is obvious that these shops are relying on ladle furnace availability because this is the only way to reduce the tapping temperatures to levels below $1.650\text{ }^\circ\text{C}$

On the other hand the shops which operate the Blow-Stir process and do not apply slag-splashing, represented by the green dots and trend line, achieve significantly higher De-Phos partition ratios. This effect allows them to operate at high tapping temperatures of $> 1.700\text{ }^\circ\text{C}$. It can be estimated, that due to the higher mixing energy of the combined process the Phos-Partition can be doubled compared to Top-Blow operation.

The shops which operate a Blow-stir process and do apply intensive slag-splashing are represented by the yellow dots and trend line. It becomes obvious that in this operation mode metallurgical efficiency is sacrificed by refractory campaign life. As often observed in industrial operation these plants try to compromise the benefits from all possible metallurgical options. If this strategy pays off must be calculated in detail and must be subject of further investigation.

It should be mentioned, that the bottom blowing process, represented by the blue dot again shows a clear improvement compared to the bottom stirring operations which results in higher De-Phos efficiency, lower slag (Fe_tO) content, lower slag volume and therefore higher yield and lower flux consumption. This process definitely is the process with the highest metallurgical and cost efficiency available in Oxygen steelmaking.

DE-P MODELLING

Based on the above mentioned relations, modelling of De-Phos always starts with the calculation of the Phosphorus removal level η_P (7), required to meet the specification of the melt. By using this equation and the formula for L_P (5) the slag volume can be calculated as follows:

$$m_{slag} = m_{steel} \times \frac{\eta_P \cdot [\%P]_{ini}}{L_P [\%P]_{steel}} \quad (10)$$

$$L_P = f(T_{aim}, [\%C]_{aim}, (\%MgO)_{aim}) \quad (11)$$

$$(\%Fe_tO)_{aim} = f([\text{ppmO}]_{aim}, T_{aim}) \quad (12)$$

$$[\%C]_{aim} \cdot [\text{ppmO}]_{aim} = \text{constant} \quad (13)$$

$$B1_{aim} = f(\%Fe_tO)_{aim} \quad (14)$$

The L_P formula developed for the special plant configuration is used to calculate the L_P value based on the aim temperature, aim [%C] and aim (%MgO) content. The tapping temperature is the result of the temperature control model of the plant and is determined according to the steel composition and the necessary metallurgical treatment. The (%MgO) content is adjusted according to the refractory maintenance strategy. The slag basicity is adjusted according to the aim iron content at the lime saturation line. The aim iron content is adjusted based on the aim [%C] content using the [ppmO] – (%Fe_tO) relation at the [%C][ppmO]-Product valid for the actual vessel operation.

The result of this model calculation is the slag volume which is necessary to remove the Phosphorus successfully from the melt, without any demand for reblow. Since this calculation already includes the basicity adjustment, no further corrections for Silicon are necessary. Strategies how to deal with a minimum and a maximum slag volume must be implemented further on. Variations from the model path are corrected by applying end point control technology.

Specialties (strategy applied at HKM):

Hüttenwerke Krupp-Mannesmann GmbH (HKM) has a unique plant configuration with two blowing stands and a change vessel system, as shown in the scheme in **Figure 12**. The process operated is blow-stir operation with automated blow end control and auto-tap practice. Because of this special plant configuration the process and the logistics in the plant are optimized for productivity. Production is operated continuously; maintenance is focused on scheduled stops which are also utilized to change out the vessels for refractory repair. The 3rd vessel is cleaned, knocked out and relined in a special relining stand located in a separate aisle without disturbing the operation at the blowing stand. The time required for a full vessel change out is 12h + 2h heating only from tapping out the last heat on the worn lining until the start of blow of the 1st heat on the new lining. To match the requirements of boiler maintenance with the vessel change out frequency the lining is balanced for 1.000 heats only.

To optimize the productivity, refractory maintenance is reduced to the minimum possible. Only the tap hole change out and mouth cleaning is applied in a furnace campaign. The vessel change-out is scheduled to fixed dates. As soon as the date has arrived, the vessel is taken out of service despite of the lining condition. Task of the scheduled maintenance is to guarantee the lowest possible break-down frequency during the regular operation periods of five weeks (~ 35 days*30 heats) in a row.

Since refractory consumption is not the focus of operations, it is also beneficial to take care for maximum yield by operation with a low slag process technology. Because of this task also the required De-P must be guaranteed at minimum possible lime consumption and lowest possible slag (%Fe_tO) content. Slag splashing is not necessary and is not applied. Also slag (%MgO) enrichment, as state-of-the-art in most of the BOF shops worldwide to increase the lining campaign life, is not applied. Therefore the influence of the slag (%MgO) on De-P is negligible.

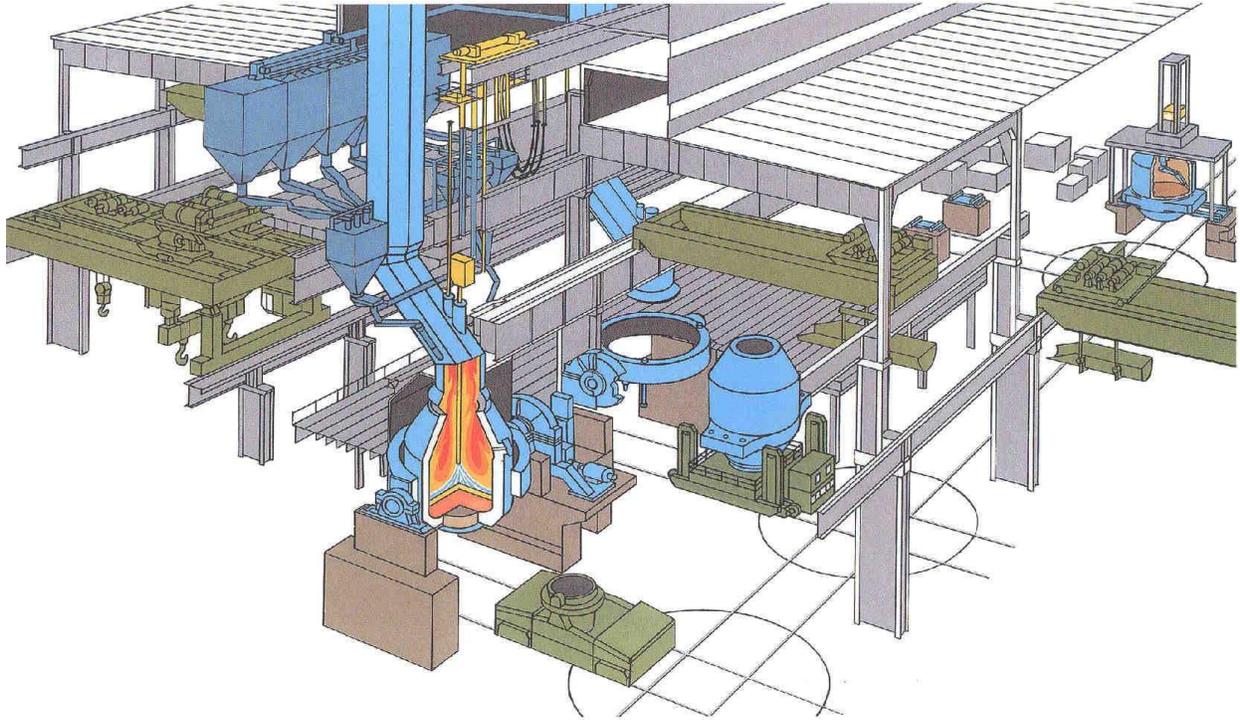


Figure 12: BOF vessel change out system at HKM

Of course it must be guaranteed that the refractory wear is controlled within the scheduled change-out periods. Because of this requirement a minimum slag basicity $B1 = (\%CaO)/(\%SiO_2)$ is adjusted, which is not described by a saturation function, but by an empiric equation (15) as defined below, which basically is a linear function of the tapping temperature, the Silicon charge with the Hot Metal and the steel Phosphorus content [%P].

$$\frac{(\%CaO)}{(\%SiO_2)_{min}} = k_1 * T + k_2 * \left(m_{Si} * \frac{100}{m_{HM}} - k_3 \right) + k_4 * \ln[\%P] + k_5 \quad (15)$$

The linear function is not directly proportional to the Hot Metal Silicon content. At high Silicon levels basicity is slightly decreasing. Low steel [%P]-requirement is recognized in this formula by a slag basicity increase factor. At HKM the negative impact on the refractory wear caused by lower basicity is overcompensated by the lower slag (%Fe_tO)-content accompanied with the lower basicity.

The upper limit for the slag basicity of course is the slag lime saturation, as shown in equation (16):

$$\left(\frac{(\%CaO)'_{sat}}{(\%SiO_2)'} \right)_{max} = \frac{(68,1 - (\%Fe_tO)' \cdot (0,3325 + 0,0024 \cdot (\%Fe_tO)'))}{(\%SiO_2)'} \quad (16)$$

with:

$$(\%CaO)_{sat} = 68,1 - (\%Fe_tO)' \cdot (0,3325 + 0,0024 \cdot (\%Fe_tO)') \quad (17)$$

The calculation method of the required slag volume is explained by a nomogram, **Figure 13**. In the first step the amount of Phosphorus to be converted from the metal to the slag is calculated, by using the lower left diagram. The upper left diagram converts the slag Phosphorus mass to a total slag mass by using the Phosphorus partition L_P as defined in equation (5).

For this purpose a Healy like formula for the Phosphorus partition was developed by multivariate regression analysis of a several 10.000 heat database.

$$\ln\left(\frac{(P)}{[P]}\right) = \frac{k1}{T} + k2 * \ln(Fe) + k3 * (Fe) + k4 * Bas + k5 * Bas^2 + k6 \quad (18)$$

As one can read from the equation, the Phosphorus partition is defined as a function of the temperature, the basicity and the slag (Fe₂O)₃-content. Since at HKM the temperature is a function of the secondary metallurgical treatment required by the grade specification and the basicity is operated in the savings mode, only the slag (%Fe₂O)₃ can be varied to change the Phosphorus partition. At HKM the aim (%Fe₂O)₃-content of the slag is calculated by formula 18 and achieved by adding Oxygen volume or iron ore amounts according to the tapping temperature, the aim Phosphorus content, basicity and slag amount.

In the upper right diagram in **Figure 13** the slag volume required for De-P is compared with the minimum slag volume and the maximum slag volume, three different results are possible:

1. The required De-P slag volume is lower than the minimum slag volume
2. The required De-P slag volume is in between the minimum slag volume and lime saturation and
3. The required De-P slag volume is bigger than the maximum slag volume at lime saturation.

In case of a calculation result according to #1, the slag volume for the heat is adjusted at the minimum slag basicity required for the lining wear control. In case of a calculation result according to #2, the slag volume is adjusted with basicity between the minimum and maximum basicity equivalent to the linear relation of the slag volumes. In case the calculation result requires #3, the slag is already lime saturated. In this case the slag volume must be increased by addition of lime and Silica flux. At HKM the practice is to add FeSi-fuel in these cases instead of gravel-gangue. Another alternative would be to increase the aim (%Fe₂O)₃-content, which is unlikely because of the related yield loss.

CONCLUSION

The De-Phosphorization reaction in the BOF process was exemplified. The chemical and thermodynamic basics of the reaction and the metallurgical parameters influencing the efficiency of the reaction were discussed in detail. The following conclusions can be summarized from the discussion:

1. The Phosphorus partition is a kinetic phenomenon rather than a chemical one.
2. BOF vessels equipped with combined blowing/stirring installations have kinetic advantages compared to only lance blowing vessels.
3. All industrial processes operated are far away from thermodynamic equilibrium which is a tribute to productivity.
4. Because of this fact always the individual vessel process characteristic is an integral element of the De-Phos modelling.
5. Since equilibrium based model do not represent the industrial process, empiric models based on statistical evaluation must be developed for De-Phos modeling.
6. Therefore every plant must develop its own De-Phos model adapted to the individual plant configuration on site.

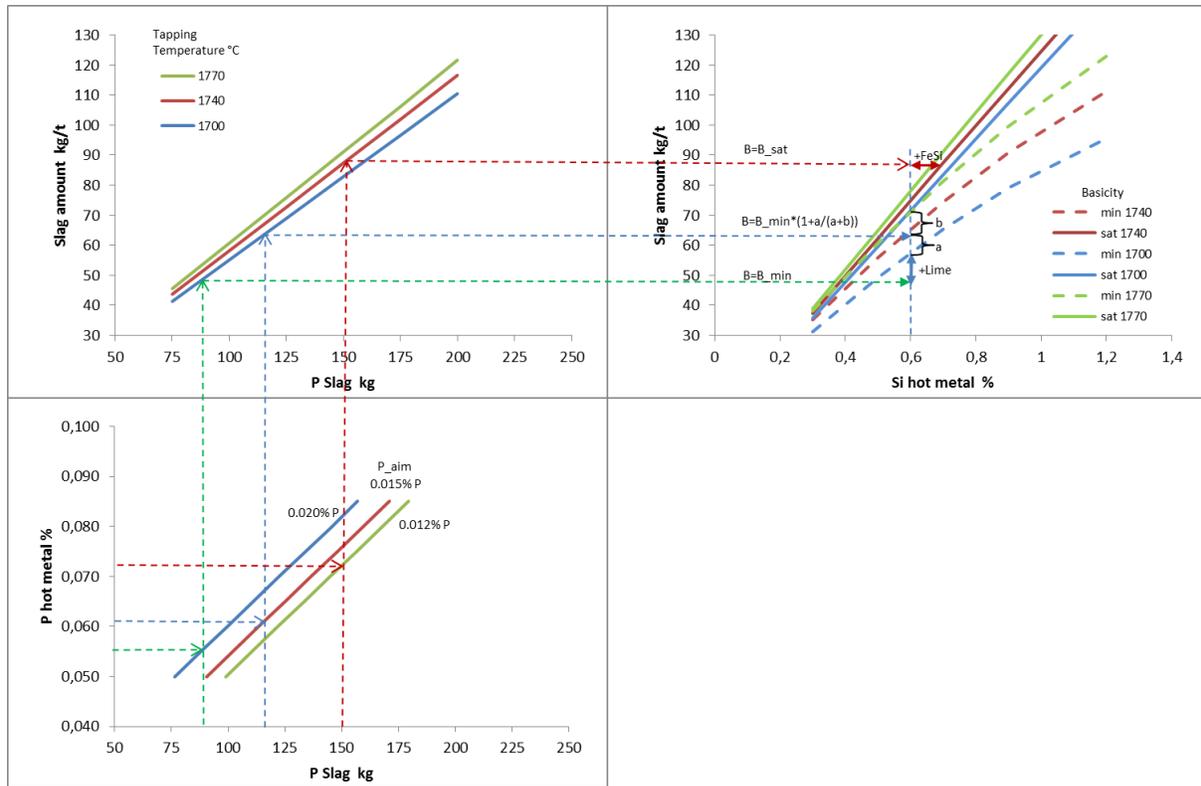


Figure 13: Nomogram for slag volume calculation at HKM

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