THE INCREASING IMPORTANCE OF BOF ENDPOINT CONTROL WHEN USING HIGHER PHOSPHPOROUS CONTAINING HM[1]

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Abstract

In the face of escalating raw material costs, BOF shops are being forced to operate at higher than traditional [P] "[P]" loadings which can impact turndown performance especially for lower [P] grades. This paper discusses the factors affecting [P] removal and reversion including the importance of controlling slag chemistry, the increasing need for effective carbon and temperature endpoint control and the need to minimize slag carryover especially when operating with higher [P] HM. A carbon, temperature, [P] endpoint control model was developed using online off-gas analysis, temperature and flow measurements. Model predictions were verified against in-blow and turndown chemistries and used to confirm the key factors needed to control turndown [P] levels. The aim is to define an enhanced single blow practice that is effective for processing higher [P] HM.

Key words: Phoshporous; BOF; Slag chemistry; End-point control; Slag carryover.

A CRESCENTE IMPORTÂNCIA DO CONTROLE DO PONTO FINAL NO BOF UTILIZANDO GUSA LÍQUIDO COM ALTOS TEORES DE FÓSFORO

Resumo

Com a escalada dos custos de matérias primas, as aciarias com BOF estão sendo forçadas a operar com carregamentos de [P] maiores que o tradicional, o que pode reduzir o desempenho especialmente para graus de [P] mais baixo. Este trabalho discute os fatores que afetam a remoção e reversão de [P] incluindo a importância do controle da composição da escória, a maior necessidade de um controle efetivo do ponto final de carbono e temperatura e a necessidade de minimizar o arraste de escória sobretudo na operação com gusa líquido com [P] mais alto. Um modelo de controle do ponto final de carbono, temperatura, [P] foi desenvolvido utilizando a análise dos gases de exaustão e medições de temperatura e vazão em tempo real. As previsões do modelo foram verificadas em sopros e composições reduzidas e utilizadas para confirmar os fatores chave necessários para controlar a redução dos níveis de [P]. O objetivo é definir uma prática aprimorada de sopro simples que seja efetiva para processar gusa líquido com alto [P].

Palavras-chave: Fósforo; BOF; Composição da escória; Controle do ponto final; Arraste de escória.

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1 INTRODUCTION

For the majority of grades phosphorous ("[P]") is considered a highly detrimental impurity with well defined maximum limits. Recently, demand for low [P] containing steels (≤ 0.015% [P] max) has been on the increase for many flat roll and automotive applications.

In this tightening [P] backdrop, steelmakers are also under intense economic pressures due to rapidly increasing prices for higher quality iron ore and coal. Faced with escalating raw material costs, many steelmakers are considering lower priced iron ores and coals that often contain elevated [P] levels. Since virtually 100% of the [P] entering the blast furnace charge will be recovered in the hot metal ("HM"), to facilitate tightening [P] specifications as well as the need to relax raw material [P] levels, it is increasingly important to review methods for controlling [P] levels in tapped steel.

Historically two practices have been used to process high [P] HM:

- external HM treatment - used particularly in Asia to remove silicon, [P] and sulfur prior to converter steelmaking;[1]
- double slag practice - dephosphorization occurs in two steps. The heat is interrupted early to mid-blow to remove the initial slag. Even though this slag has a lower basicity, it can effectively remove some [P] because early blow melt temperatures are lower and FeO contents are higher both of which favor dephosphorization. The second higher basicity slag is designed to bring the heat to the final aim [%P] at the end of the blow.

While these methods are technically capable of achieving turndown [P] levels of ≤ 0.015% in shops with highly elevated HM [P], both approaches are not without issue. External HM treatment suffers from increased process complexity, excessive heat losses, which adversely affect HM temperature and scrap melting, long processing times, increased yield losses and the use of highly reactive reagents that can be toxic and can accelerate refractory wear.[2] While a double slag practice is effective for removing [P] and can avoid excessive slag volumes and associated slopping problems, it can increase heat times by ~50% and increase yield losses thereby add operating cost and diminish productivity.[3]

In many instances especially where [P] loadings are increased but are not extreme, a better, more cost effective approach is to establish a single blow practice with enhanced dephosphorization capabilities.

1.1 Operating Data

Operating data indicate that the actual in-blow Partition Ratio between slag and metal (Equation 3) is well below that predicted for equilibrium conditions.[4] For vessels equipped with bottom stirring, the BOF process operates much closer to chemical equilibrium. Hence, bottom stirring if available can be an effective method to enhance in-converter dephosphorization and can be used in combination with external treatments or a double slag practice when needed to achieve low [%P] levels when processing high [P] containing HM.[2,5] Since combined blowing is only employed on about 60% of the BOF vessels worldwide,[2] improved practices must also be established for top blown converters as well.

This paper discusses factors affecting [P] removal during oxygen steelmaking with the objective of determining an enhanced dephosphorization practice applicable to both conventional top blowing and to combined blowing BOF converters. The

ultimate aim is define an optimum single blow enhanced dephosphorization practice that can be used to effectively process higher [P] HM.

Attention is paid to slag chemistry control, carbon & temperature endpoint control and slag carry-over control.

2 [P] CHEMISTRY IN BOF STEELMAKING

[P] is removed under oxidizing conditions during the steelmaking process according to Reaction 1:

$$2\ [P]\ +\ 5\ [O] = \quad (P_2O_5)_{slag} \tag{1}$$

Where [ ] denotes the species is dissolved in the steel bath and ( ) means the species is in the slag phase. The Phosphorous Partition Ratio ("PR") given in Equation 2 is the ratio of %P contained in the slag over %P contained in the steel bath:

$$PR\ =\ (wt\%\ P_2O_5)_{slag}\ /\ [wt\%\ P]_{metal} \tag{2}$$

Effective [P] control depends on establishing BOF steelmaking conditions that will increase the PR, improve reaction kinetics and minimize [P] reversion from the slag back to the metal.

2.1 Thermodynamic Factors Promoting [P] Removal

The following factors enhance dephosphorization in BOF steelmaking.

2.1.1 A basic slag rich in dissolved CaO

Since (P_2O_5) is acidic, the thermodynamic driving force for Reaction 1 and (P_2O_5) absorption into the slag phase is favored with increasing slag basicity. Based on ionic slag theory, CaO is about 30 times more effective than MgO for increasing the dephosphorizing power of the slag.[6] Hence, to maximize [P] removal it is beneficial to control basicity with CaO rather than MgO.

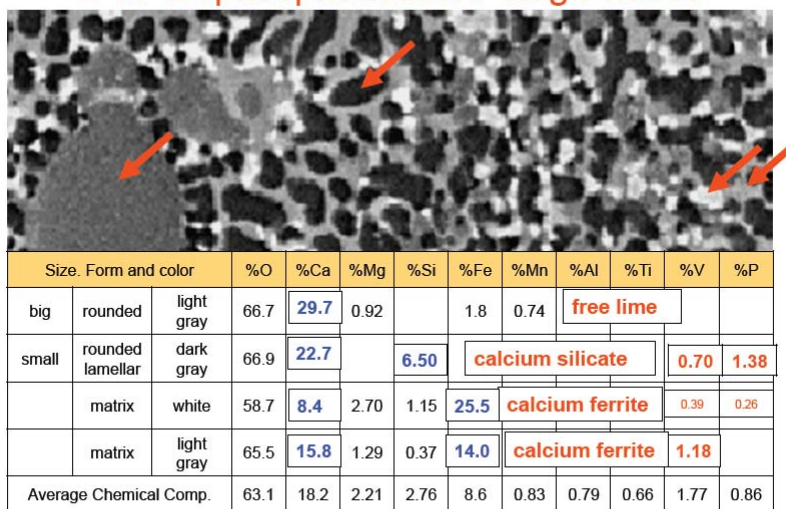| CaO	MgO	MnO	FeO
30,000	1,000	3	1

These data also indicate that MnO and FeO have a relatively insignificant effect on the slag's chemical dephosphorizing power. However as discussed below, (FeO) remains an important factor because it determines the near end of blow oxygen potential of the steel [O] which is necessary for oxidation of [P] by Reaction 1.

The form of CaO in the slag also impacts the slag's dephosphorization capacity. Figure 1 shows a microscopic, x-ray analysis of typical BOF slag and confirms that [P] is largely contained in the calcium silicate phase and that free CaO phase contains essentially no [P].

Hence, it can be concluded that a basic slag rich in "dissolved" CaO is the most effective for [P] removal and that the presence of large quantities of undissolved flux have little dephosphorization benefit.

BOF Dephosphorisation: Slag Phases

Size. Form and color			%O	%Ca	%Mg	%Si	%Fe	%Mn	%Al	%Ti	%V	%P
big	rounded	light gray	66.7	29.7	0.92		1.8	0.74	free lime			
small	rounded lamellar	dark gray	66.9	22.7		6.50	calcium silicate				0.70	1.38
	matrix	white	58.7	8.4	2.70	1.15	25.5	calcium ferrite			0.39	0.26
	matrix	light gray	65.5	15.8	1.29	0.37	14.0	calcium ferrite			1.18	
Average Chemical Comp.			63.1	18.2	2.21	2.76	8.6	0.83	0.79	0.66	1.77	0.86

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Figure 1. Microscopic & X-ray Analysis of BOF Slag.[7]

2.1.2 Minimizing tap temperature

Thermodynamically, the oxidation of [P] to (P_2O_5) by Reaction 1 is strongly dependent on metal/slag temperatures – the PR increases sharply with decreasing temperatures. As indicated in Table 1, the equilibrium PR increases by almost 100% by decreasing the tap temperature from 1700 °C to 1650 °C.

Table 1. Equilibrium Partition Ratios as a function of Bath/Slag Temperatures[8]

Tap Temperature	1.700°C	1.675°C	1.650°C
Equilibrium Partition Ratio (wt% P_2O_5) slag/ [wt% P] metal	286	205	148

An effective [P] removal strategy necessitates avoiding "over-blowing" heats, which increases tap temperatures sharply through excessive end-of-blow [Fe] oxidation.

2.1.3 A high oxygen potential in the metal [O] to oxidize the [P] into the slag

According to Reaction 1, the oxidation of [P] to (P_2O_5) is favored by a high [O] potential in the metal. For this reason, [P] oxidation occurs near the end of the blow when the [O] potential of the steel is increasing as decarburization rates slow and [Fe] oxidation accelerates forming increased amounts of (%FeO) in the slag.
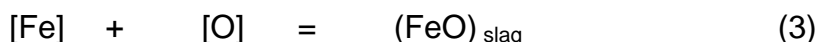
$$[Fe] + [O] = (FeO)_{slag} \qquad (3)$$

Figure 2 indicates there is an optimum % FeO in the slag at which the PR is maximized.[6]
The earlier work of Balajiva, Quarrell and Vajragupta[9] which is depicted in Figure 2 was based only on Fe^{+2} and showed that the maximum PR occurs at about 16% FeO in the slag. However, further studies by Selin[10] which factored in both Fe^{+2} and Fe^{+3} in the slag indicates that the maximum PR shifts upwards to between 20% - 22% FeO. It is evident from Figure 2 that increasing the V-Ratio (i.e. CaO/SiO_2) in the

slag will increase the PR. However, when assessing the V-Ratio it is best to consider only dissolved CaO since free CaO is not very effective for removing [P] (Figure 1).
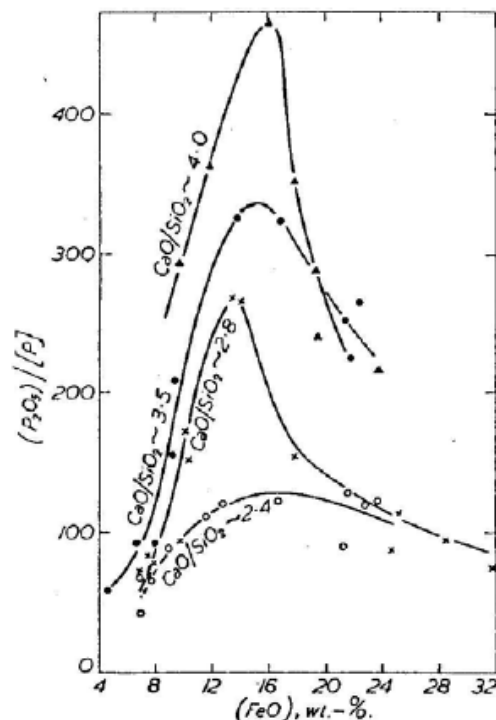

Figure 2. Effect of the CaO to SiO$_2$ Ratio on the PR at various FeO Levels.

The effect of FeO is explained as follows; the [O] potential of the steel increases with increasing (FeO) through Reaction 3 which causes a corresponding increase the PR. However, the increasing amount of FeO created during the blow increases the slag volume and effectively results in a decrease in the mass% CaO in the slag due to a dilution effect. At some point the effect of decreasing the mass% of dissolved (%CaO) in the slag starts to outweigh the positive effect of increasing [O] from. increasing %FeO thereby causing the [P] PR to peak and then to decrease.

2.2 Kinetic Factors Hindering [P] Removal

Figure 3 shows that the actual [P] PR determined by in-blow slag and metal sampling increases during the blow however it is much lower than expected based on thermodynamic equilibrium especially in the latter half of the blow. For slags with a V-Ratio of about 3, the actual BOF PR in practice is only about 70 – 90 which is 2.5 to 3 times lower than expected from thermodynamics.

Through an analysis of published literature, Swinnerton[11] concluded that the majority of dephosphorization occurs between molten steel and slag droplets within the emulsion. The rate limiting step can be attributed to diminished mass transfer, which slows kinetics particularly due to the formation of a dry slag at mid-blow and reduced stirring near the end-of-blow when CO generation is curtailed.

In vessels equipped for combined top and bottom blowing, the increased level of stirring enhances reaction kinetics and thereby allows for higher PR than obtained in top blown converters.[2,5] Hrabal and Marin[7] report that the improved kinetics with combined blowing can increase the PR by between about 35%-40% for low and high carbon steels.
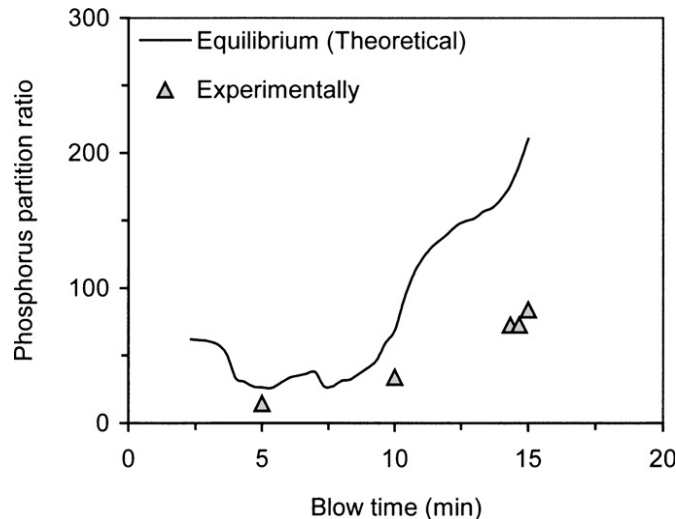
Figure 3. Comparison between the Actual & Theoretical Partition Ratio as measured at Tata Steel.[4]

2.2.1 Dephosphorization - characterization from start to end of blow

Based on the thermodynamic and kinetic factors discussed herein, the following is typical for [P] from start to end of blow.

2.2.1.1 Stage 1: early-blow dephosphorization

As shown in Figure 4, initially [P] levels in the steel decrease rapidly during the first 20%-30% of the blow. Early-blow dephosphorization is promoted by:

- a rapid dissolution of (CaO) into the slag due to the early oxidation of Si and Mn and the corresponding fluxing effects of SiO_2 and MnO;
- the presence of relatively high (FeO) levels early in the blow;
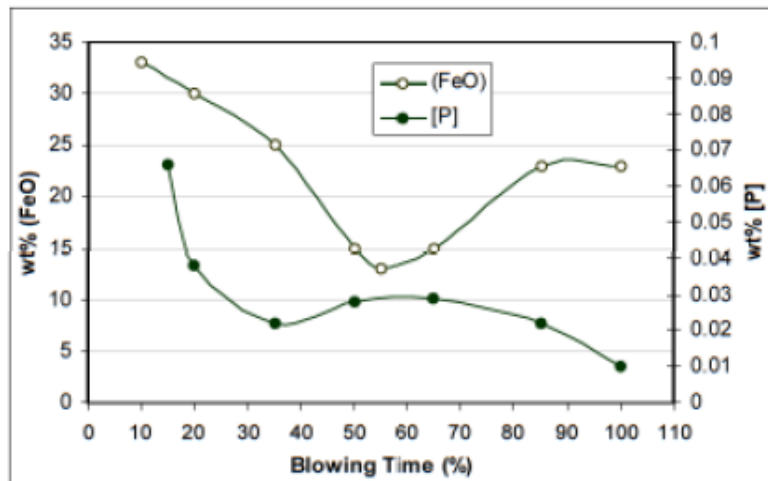- low bath temperatures in the early blow due to scrap and flux additions.

Figure 4. Slag (FeO) and metal [P] as a function of blowing time determined by in-converter sampling at Blue Scope Steel Port Kembla.[11]

2.2.1.2 Stage 2: mid-blow [P] reversion

As the blow progresses, conditions change that result in mid-blow [P] reversion, i.e. a portion of the (P_2O_5) in the slag reverts back to increase the [P] content of the steel bath. The dual slag practice is designed to take advantage of the early blow Stage 1 dephosphorization by deslagging the vessel before Stage 2 reversion.

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Typically mid-blow [P] reversion is a result of several factors:
- Bath temperatures steadily increase during the blow which reduces PR;
- the [O] potential in the bath declines as decarburization rates accelerate;
- the decrease in (FeO) causes a "dry" slag which reduces the amount of dissolved CaO and also hinders dephosphorization reaction kinetics.

2.2.1.3 Stage 3: near end-of-blow dephosphorization
Near end of blow, [P] levels in the metal once again begin to decrease due to:
- Rapid dissolution of CaO into the slag which increases the effective V-Ratio;
- an increase in the slag volume;
- an increase in the [O] potential of the steel bath as the BOF reaction mechanism switches from primarily decarburization to an increasing amount of [Fe} oxidation.

2.2.1.4 Stage 4: [P] reversion from over-blowing and/or excessive slag carryover
Poor end-point control and tapping practice can result in [P] reversion from the slag back to the metal thereby off-setting some of the benefits achieved with a good in-blow dephosphorization practice.

As shown in Figure 5, based on an analysis of over 5,000 heats Tripathy *et al.*[8] confirmed that prolonging the blow to less than 0.040-0.045% [%C] will result in [P] reversion and a corresponding increase in turn down [%P] levels.

End-of--blow [P] reversion is due to over-blowing which causes:
- A decrease in the [P] PR due to the (CaO) mass % dilution effect as (FeO) levels exceeds the optimal 20-22% threshold;[10]
- a decrease in the PR from increasing in bath temperature caused by the highly exothermic oxidation of [Fe] to (FeO).
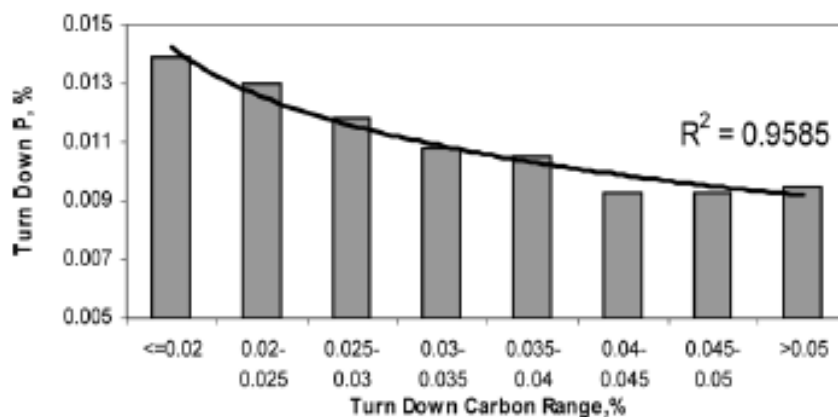

Figure 5. The effect of turn down [%C] on turn down [%P] as determined from an analysis of over 5,000 heats.[8]

Substantial [P] reversion will also take place in the ladle if tap alloys to reduce after tap [O] are added in the presence of significant quantities of (P_2O_5) enriched BOF slag.[3] Minimizing the carryover quantity of (P_2O_5) enriched slag into the ladle and the degree of over-blowing are important factors to reduce in-ladle [P] reversion.

2.3 Tenova Goodfellow's i BOF® Technology

i BOF® is a modular technology package designed to improve operating control.

2.3.1 Module 1 - EFSOP® end-point detection

Uses a combination of Tenova Goodfellow's EFSOP® off-gas analysis system proven in over 60 steelmaking installations together with proprietary process models and off-gas sensors. Module 1 significantly improves carbon and temperature end-point control thereby lowering conversion costs (reduced O_2, refractory, consumables & tap alloys), increases productivity (fewer reblows & delays) and increases % yield (lower FeO).

2.3.2 Module 2 - early warning slop detection

Uses advanced sensors together with proprietary software to continuously monitor high and low frequency changes in lance vibration. Tenova Goodfellow's proprietary software interprets the signals in real-time to obtain an 20-40 second advance warning of the onset of a slop event as well as an indication of slop severity. The system is designed for dynamic lance height and O_2 flow control to rapidly mitigate the effects of a slop.
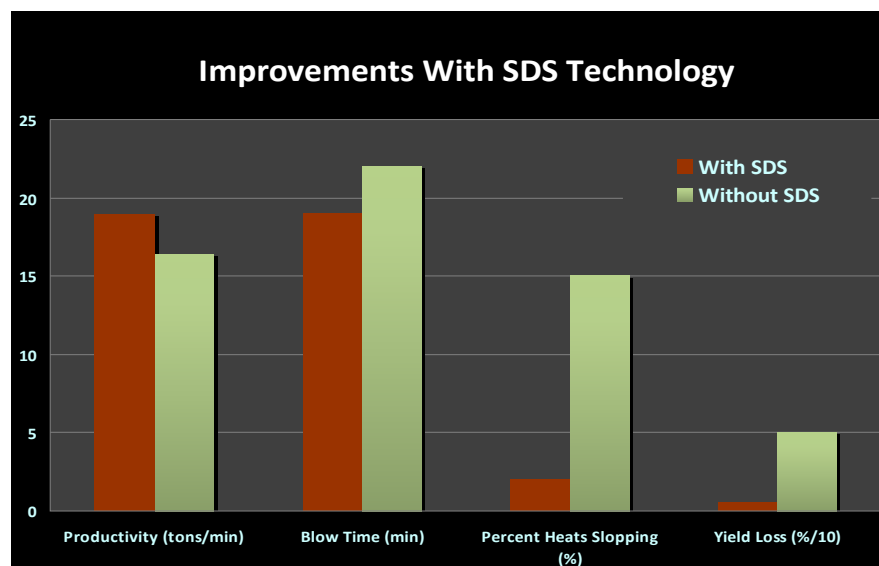

Figure 6. Productivity & Yield Improvements with Slop Detection Technology.[12]

2.3.3 Module 3 - optimized post combustion

Enhances "in-BOF" post combustion for increased scrap melting by using a combination of Tenova Goodfellow's industry proven EFSOP® off-gas analysis system together with dual flow lance technology.

2.3.4 Module 4 - automated tapping control

Provides control technology for operator assist or for fully automated tapping control to improve safety, minimize slag carry-over and reduce operating cost.
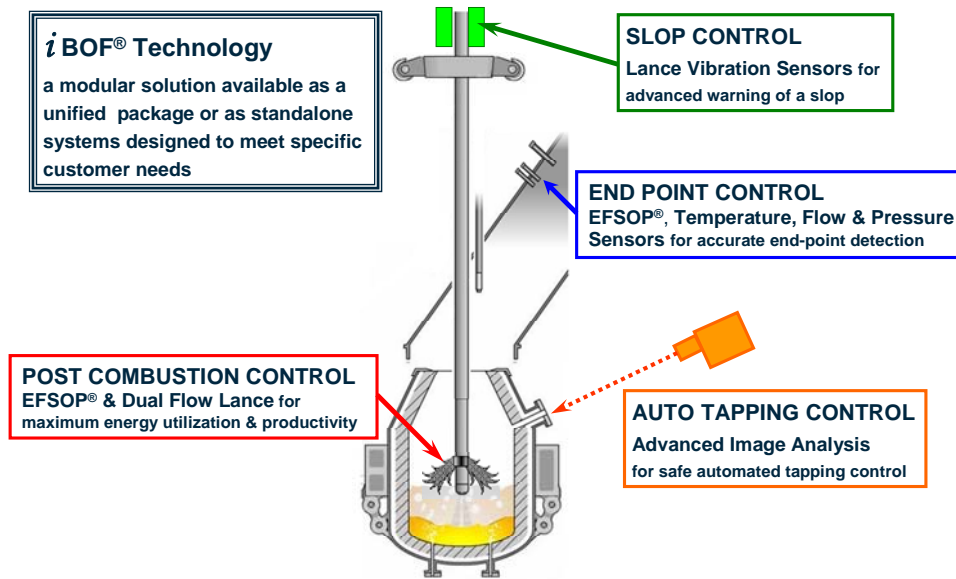
Figure 7. i BOF**®** Technology; off-gas analysis plus advanced sensors & dynamic process models.

2.4 i BOF® Technology for Enhanced [P] Control

Tenova Goodfellow's i BOF® technology package is ideally suited for BOF shops that require enhanced dephosphorization in response to increased HM [P] levels and/or lower aim [P] levels.

2.4.1 Module 1 [P], [C] & temperature endpoint control

Since final [P] levels are established right at the end of blow, avoiding both "under-blowing" and "over-blowing" situations is critical for effective [P] control.

Failing to turn down at the correct [C] and temperature is a critical mistake and can negate the benefits of a good [P] control slag practice. Turning down "too early" is particularly critical when HM [P] levels are increased. An early end to the blow can result in reblows not only for [C] and temperature but also for [P].

To better understand the impact of turn down practice on [P] control at various HM [P] levels, Tenova Goodfellow developed a comprehensive in-blow and end-of-blow BOF process control model. To enable the model to be fully predictive under varying process conditions and avoid the problems normally encountered with statistical based models, the i BOF® process model is based on thermodynamic and kinetic fundamentals employing a real-time heat and mass balance for the BOF operation. As such, the i BOF® process model can be used not only for real-time BOF end point detection and control but also to simulate and investigate the effects of HM and BOF practice changes.

Figures 8a and 8b compare model predictions (solid lines) with actual in-blow and end-of-blow [C] & [P] analysis from a 200 MT top blown BOF converter (data points) for both normal and elevated HM [P] levels. Figure 8a shows the endpoint window to hit $\leq$ 0.015% [P] at turn down is quite wide when utilizing a normal North American HM [P] level of 0.04%. Under such circumstances, reblows for [P] are very rare.

However as shown in Figure 8b, the endpoint window to hit $\leq$ 0.015% [P] narrows considerably when the HM [P] is increased to 0.1%. Additional increases in HM [P] levels will tighten the turn down window even further. Under such elevated [P] conditions, without an effective endpoint control model turning down too early

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becomes increasingly problematic. As shown in Figure 5 earlier, "over-blowing" is also problematic since it results in [P] reversion back to the metal thereby once again negating the benefits of a good slag practice.

Figures 9 shows the i BOF® endpoint model predictions for slag chemistry and the effect on metal chemistry of over-blowing a heat when using a low [P] HM. The model confirms the expected result, extending the blow dramatically reduces yield through rapidly increasing FeO which in turn results in [P] reversion.

i BOF® Module 1 provides proven effective endpoint control to avoid both early and late turn downs which is increasingly critical for effective [P] control when using high [P] HM.
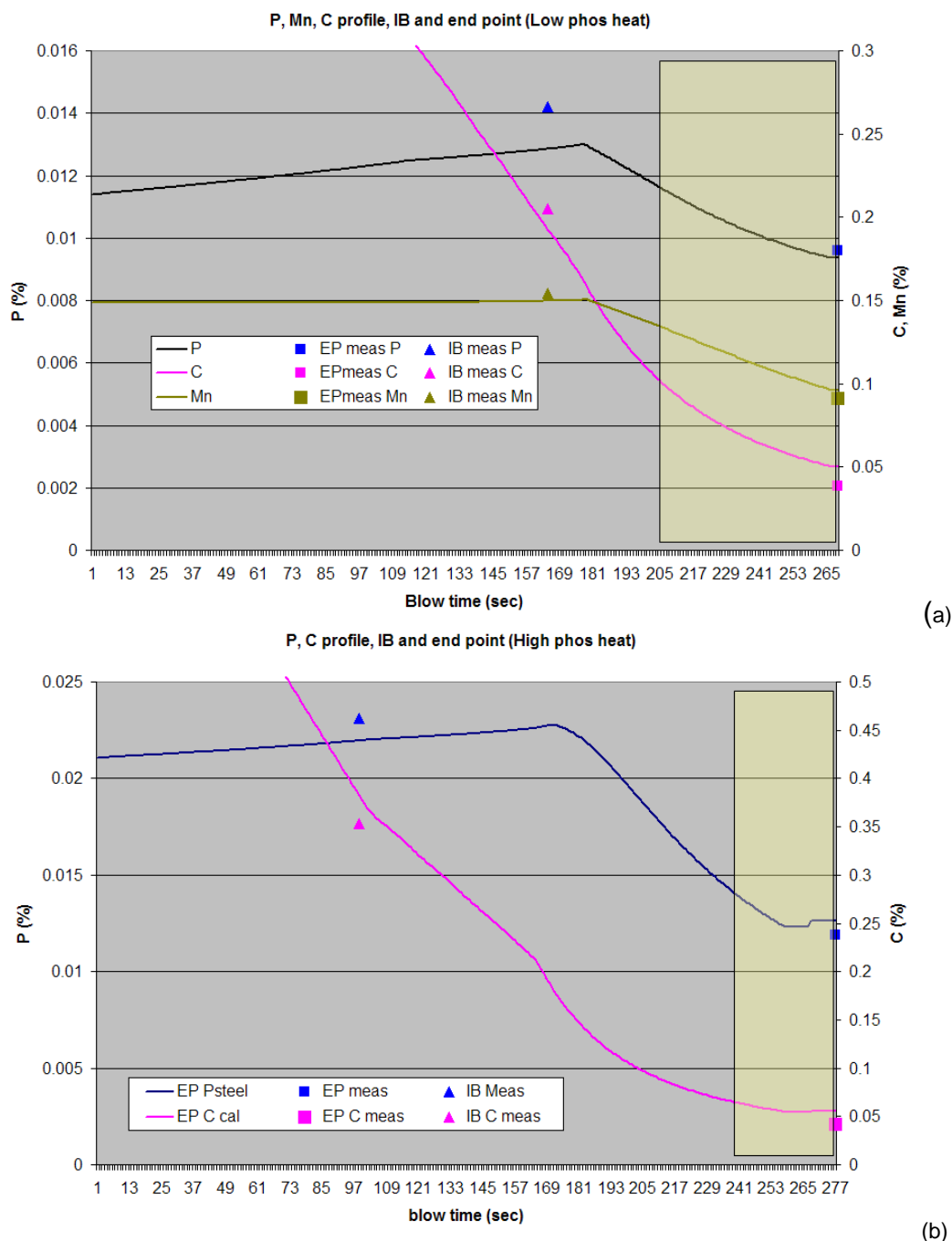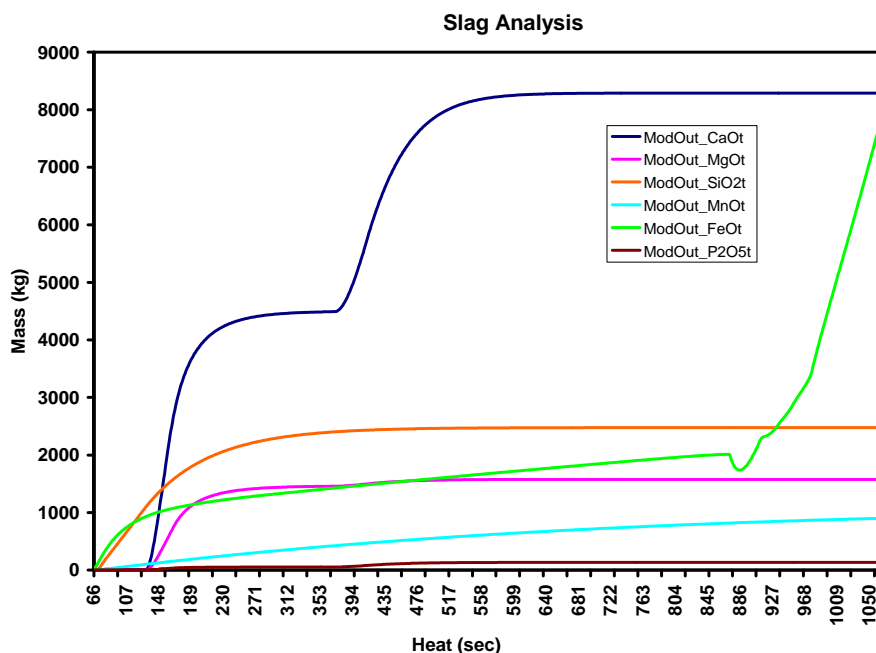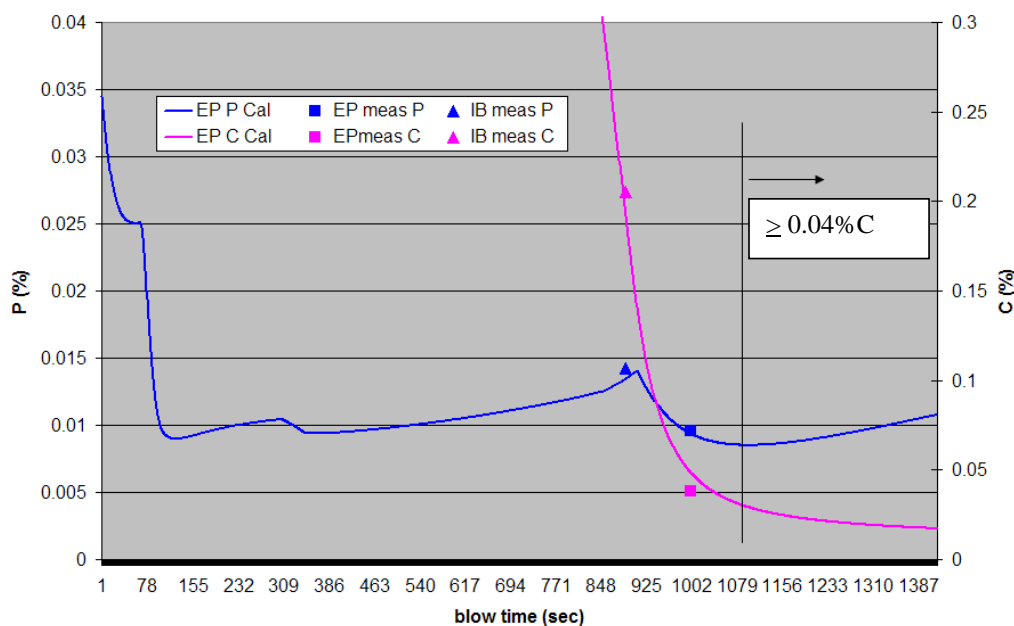

Figure 8. i BOF® Model. (a) predictions compared to in-blow and post-blow melt samples for normal; and (b) elevated HM [P] levels**.**

(a)

(b)

Figure 19. i BOF® Model. (a) predicted slag chemistry; and (b) [P] reversion when over-blowing with 0.04% [P] HM heats.

2.4.2 Module 2 - slop detection

Optimized slag chemistry control together with effective endpoint control are the cornerstones of a good [P] control strategy. Maintaining a slag rich in dissolved CaO with a V-Ratio of about 3 and MgO additions curtailed to levels no higher than required to minimize refractory wear will enhance the PR. Real-time slop detection and mitigation technology become more critical as slag volumes increase when utilizing HM with increasingly elevated [P] levels. Tenova Goodfellow's Slop Detection technology is designed to provide a 20-40 second advance warning of the onset of a slop together with dynamic control of both the lance height and O₂ flow rate thereby providing an effective real-time slop detection & mitigation strategy.
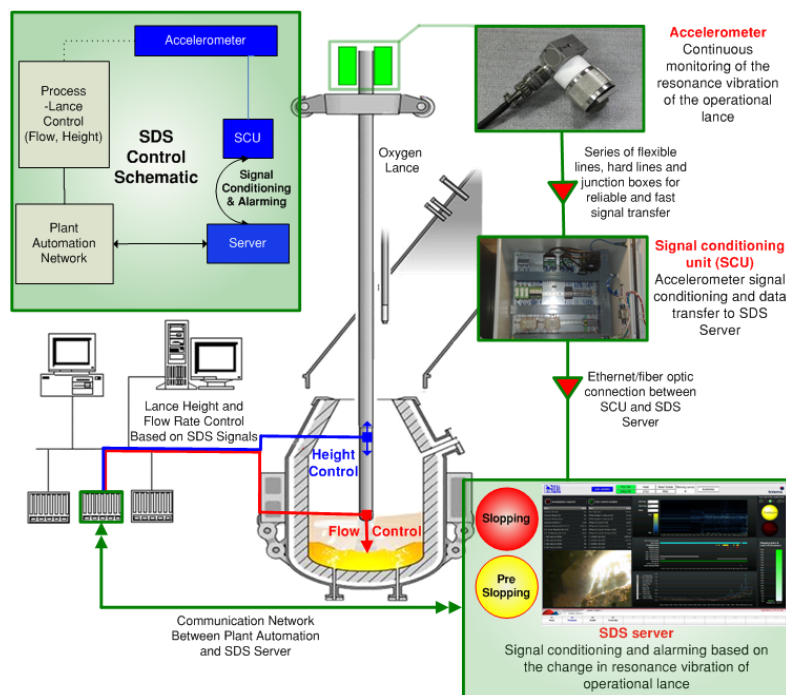
Figure 11. i BOF® Module 2 Real-time Slop Detection Technology (SDS).

2.4.3 Module 4 - auto tapping

[P] reversion back to the metal can also take place in the ladle due to the addition of tap alloys to reduce after tap [O] levels. Chukwelebe et al.[3] reported that even when turn down [P] levels were maintained at 0.012% excessive BOF slag carryover increased ladle [P] to 0.021% after the first Ar stir.

Poor control of tapping allowing (P_2O_5) enriched slag carryover into the ladle will negate good slag and endpoint control practices. i BOF® Module 4 is designed to provide fully automatic tapping control to improve safety and for consistently low BOF slag carryover. The system controls the BOF tilting sequence through a set of cameras, in order to maintain a maximum steel depth over the tap hole and to reduce the slag carryover into the ladle. Simultaneously, the system controls ladle car movement according to the tilting position. An HMI tapping display allows operators to tap safely without having to approach the vessel.

The Module 4 auto tapping system facilitates decreased tap times for increased productivity as well reducing slag carryover to minimizing tap alloy additions and the risk of [P] reversion.
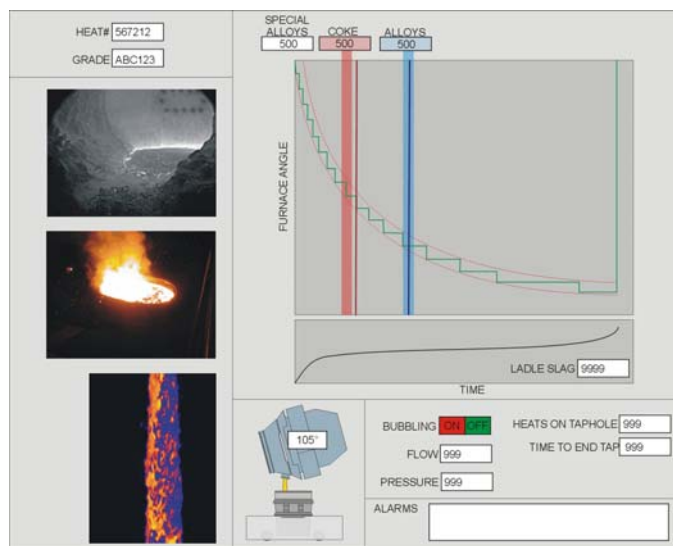
Figure 12. i BOF® Module 4 Auto Tapping HMI.

3 CONCLUSIONS

Steelmakers are increasingly turning to higher [P] containing iron ores which is forcing BOF shops to operate at higher than traditional [P] levels. While specialized practices have been developed for high [P] HM, they add complexity, decrease productivity & yield and increase operating cost. An enhanced dephosphorization single blow practice is preferable.

The cornerstones of an enhance dephosphorization practice include:

- optimized slag chemistry control - maintaining a slag rich in dissolved CaO with a V-Ratio of about 3 and MgO levels no higher than required to minimize refractory wear;
- effective endpoint control to avoid under and over blowing heats – as HM [P] levels increase, the turndown window to hit aim [P] specs diminishes thereby enhancing the need for effective endpoint control. Increasing HM [P] greatly exacerbates problems associated with turning down too early causing reblows for [C], T and [P]. "Over-blowing" is also problematic since blowing below 0.040-0.045% C results in lower yield and increased tap alloy additions but also in increased [P] levels from reversion; and
- effective tapping control to minimize slag carryover – Substantial [P] reversion will take place in the ladle if tap alloys are added in the presence of significant quantities of (P_2O_5) enriched BOF slag. Minimizing slag carryover into the ladle and the quantity of tap alloys by avoiding over-blowing are important factors to reduce in-ladle [P] reversion.

Tenova Goodfellow's i BOF® technology is ideal for achieving enhanced [P] control:

- module 1 Endpoint Control - provides effective real-time [P], [C] & T end-point control thereby avoiding both under and over blowing issues that affect turndown [P];
- module 2 Slop Detection - provides a 20-40 sec advance warning together with dynamic lance control to mitigate the effects from increased slopping events which often occur at the increased slag volumes customary with higher HM [P] levels;
- module 4 Auto Tapping - reduces slag carry-over to minimize in-ladle [P] reversion.

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