TECHNOLOGY CONSIDERATIONS FOR THE REMOVAL OF PHOSPHORUS*

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Abstract

Phosphorus is a problematic impurity that has challenged steelmakers for decades. Steel producers have developed specific technologies to eliminate phosphorus prior to and during steelmaking. These process technologies reduce phosphorus to various degrees and increase the cost of making steel. The state-of-the art dephosphorization technologies are described and operating costs compared for each of the established technologies. Costs are discussed in terms of price penalties for high P iron ore and selling premiums for low P steel. From this, strategies to control P in a cost effective manner are described.

Keywords: Dephosphorization; BOF steelmaking; Hot metal pretreatment.

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1 INTRODUCTION

Demand for steel with improved physical and mechanical properties is increasing and many of these grades require low phosphorus content. A wide variety of steel products are produced with <0.02%P and some seamless pipe grades and plate grades require phosphorus <0.01%P. Case studies comparing six (6) process technologies to reduce phosphorus are described including the related treatment cost and final steel phosphorus content. Iron ore price penalties/premiums for P content; additional steel treatment costs and low-P steel price premiums are compared to put the cost of phosphorus removal into context. From this, suitable processing technologies to control P in a cost effective manner are identified to meet the growing demand for low phosphorus steel products.

2 PHOSPHORUS REMOVAL TECHNOLOGY

Phosphorus is typically found in the ferrous charge materials to the blast furnace but can also be contained in coke, flux and pulverized injected coal (PCI). With the strongly reducing nature of the blast furnace, 97% of the input phosphorus reports to the hot metal (HM).
In order to remove phosphorus, oxidizing conditions such as those present in BOF steelmaking are required. The dephosphorization reaction is illustrated by Equation (1):

$$2\,[P] + 5\,(FeO) + n(CaO) \leftrightarrow (nCaO \times P_2O_5) + 5[Fe] \qquad (1)$$

In Equation (1), the slag phase is represented by ( ) and the metal phase in represented by [ ]. The fundamentals of phosphorus removal and the factors that favor dephosphorization are extensively discussed in literature.[1,2] In BOF steelmaking, the phosphorus partition between the slag and metal phase is expressed as a partition coefficient, L_p described by Equation (2).

$$L_p = \frac{\%(P_2O_5)}{\%[P]} \qquad (2)$$

Many empirical equations have been developed to estimate L_p. Twenty four (24) different equations are provided by Urban et al.; these illustrate the challenges to accurately estimate L_p in non-equilibrium steelmaking conditions.[1] Conditions that increase L_p are low temperature, high activity of FeO in slag, low activity of P_2O_5 in slag, high slag basicity and low slag MgO content.[1,2]
The BOF process is challenged to produce low phosphorus levels, <0.02%P needed for more demanding steel grades especially at a time when hot metal phosphorus was increasing. Historically, steel producers used a double slag practice where the decarburization process is interrupted, high phosphorus slag removed and decarburization restarted with fresh fluxes added. While phosphorus was reduced, the cost and more importantly BOF productivity losses were too large for this practice to be widely adopted. In the 1970s, steelmakers developed combined blowing processes where nitrogen and argon stirring gases were blown through tuyeres or porous elements located in the BOF vessel bottom to reduce FeO in slag, and increase process yield. Phosphorus removal improved as the stirring increased the interaction of the FeO rich slag and P containing liquid steel.

Hot metal pretreatment emerged in Japan as a new technology to reduce phosphorus prior to BOF steelmaking in the late 1980s. As silicon is more easily oxidized than phosphorus, hot metal silicon must first be reduced to <0.15% before meaningful phosphorus removal can be achieved. Separate refining stages to remove silicon from hot metal were developed initially using sinter fines and later with gaseous oxygen to reduce hot metal temperature losses. Once silicon is reduced, the silica rich slag is discarded and an oxidizing reagent such as sinter fines and lime fluxes are added to reduce phosphorus. In 1982, Nippon Steel Corporation commercialized its Optimum Refining Process (ORP) to reduce silicon, phosphorus and sulfur prior to BOF steelmaking (Figure 1).

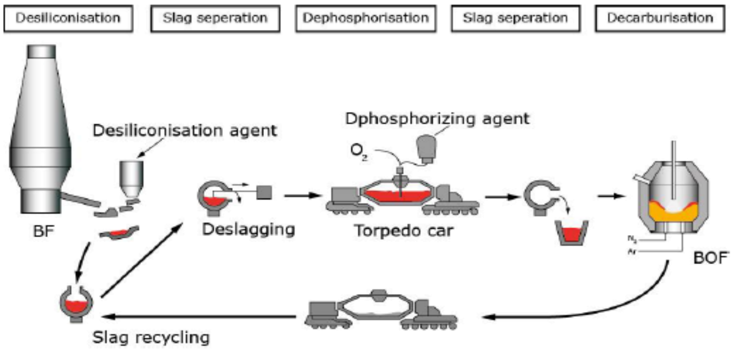

Figure 1. Nippon Steel’s Optimum Refining Process (ORP) circa 1982. [3]

The pretreatment cost of ORP was high due to large reagent consumption, temperature losses, refractory consumption and need for a large torpedo ladle fleet. Nippon Steel ultimately decided to use a specially designed BOF converter to remove phosphorus. This provided a large free board volume, and the agitation of the hot metal was much stronger by blowing oxygen from the top of the furnace.[4] In 1987, the single refining process (SRP) using two converters in series was developed at Nippon Steel’s Kashima Works. In the SRP, one converter is assigned for De-P and the other for De-C. Molten slag from the De-C converter is charged back to the De-P converter so that high FeO containing de-carburization slag can be used as a reagent to remove phosphorus in the inbound hot metal. This countercurrent flow of liquid steel and molten slag used in the SRP is presented in Figure 2 below.

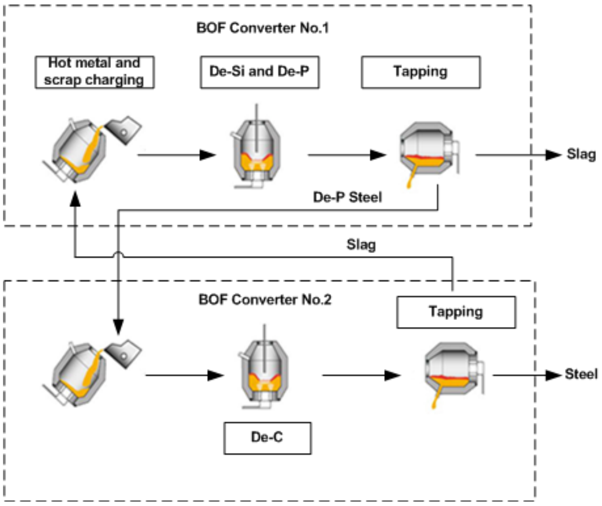

Figure 2. Single Refining Process (SRP) Developed by Nippon Steel, circa 1987. [3,4]

In 1989, another technology to reduce P in BOF steelmaking was developed at Nippon Steel's Nagoya Works and was named the 'LD Optimized Refining Process' (LD-ORP) – Figure 3.

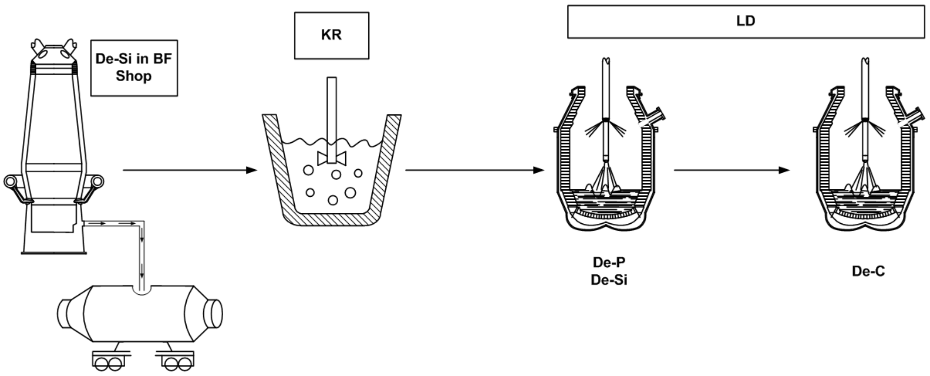

Figure 3. Nippon Steel's LD-ORP, circa 1989 [4].

With the LD-ORP/SRP technologies, the consumption of lime was reduced and the steel yield increased compared to torpedo ladle treatment.[4] Nippon Steel and other Japanese steel producers abandoned the torpedo ladle De-P treatments to reduce costs and improve performance. A modified steelmaking process known as the multi-refining process (MURC) emerged where De-P and De-C were completed in a single vessel. MURC is essentially a double slag practice completed in a single BOF and does not require the additional BOF converter used in the SRP.

The SRP is an elegant and efficient method that uses the principles of the double slag practice. This countercurrent approach avoids the need to make a new slag from cold fluxes that adds processing time to the traditional double slag practice. Additional operating costs are minimal as only a small amount of fresh fluxes are required.

The usage trend in various phosphorus treatment technologies from the early 1990s is presented in Figure 4.[4]

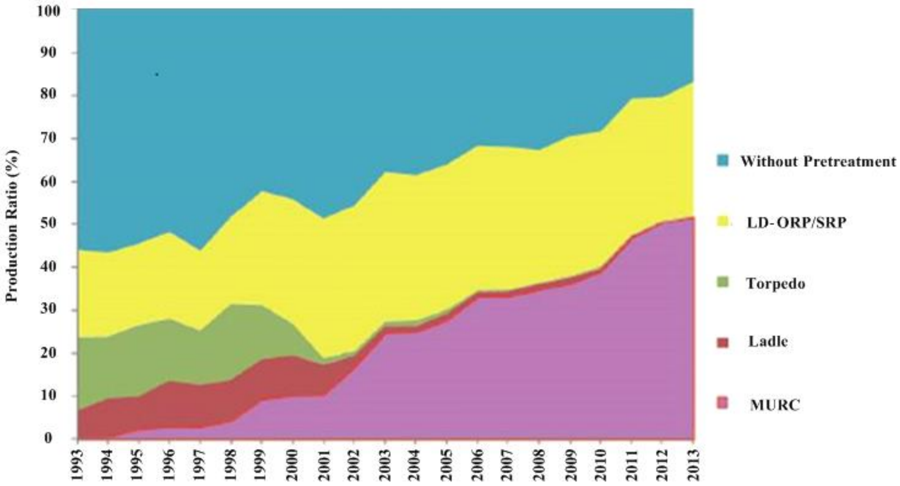

Figure 4. The Evolution of De-P Hot Metal Treatment at NSSC. [4]

Some interesting trends can be seen in the evolution of practices at Nippon Steel Sumitomo Corp. In 2013, approximately 50% of the hot metal is dephosphorized using the MURC process (i.e. double slag practice in a single BOF converter) and

30% using the LD-ORP/SRP process (i.e. using two BOF converters). Interestingly, for about 20% of the time, no De-P treatment was necessary. The use of torpedo and transfer ladles for De-P has stopped in place of the BOF converter practices.

3 CASE STUDY

Two case studies representing different iron ore sources were prepared. Both cases consider a blast furnace charge of 70% sinter, 20% pellets and 10% lump ores. In Case 1, sintering fines with low P content of 0.060%P were used while Case 2 considered sintering fines with 0.080%P. Table 1 details the blast furnace burden, phosphorus input assumptions and resulting hot metal phosphorus assuming 97% phosphorus recovery to hot metal for both cases.

Table 1. Blast Furnace Operation for Low P Sinter and High P Sinter

Item	Consumption (kg/t HM)	Case 1: Low P Sinter		Case 2: High P Sinter	
		%P	Input P (kg/t)	%P	Input P (kg/t)
Inputs					
Pellets	160	0.045	0.072	0.045	0.072
Lump	320	0.050	0.160	0.050	0.160
Sinter	1120	0.060	0.672	0.080	0.896
Coke	369	0.025	0.092	0.025	0.092
PCI	149	0.030	0.045	0.030	0.045
Total P Input			1.04		1.27
Output					
Hot Metal	1000	0.101	1.01	0.123	1.23

Two different BOF hot metal-to-scrap ratios were considered to cover a number of operating scenarios. Details of the assumed charge mixes are provided in Table 2 below.

Table 2. BOF Steelmaking Inputs for Case Studies 1 and 2

Item	Case 1 – Low P Sinter		Case 2 – High P Sinter	
Hot Metal to Scrap Ratio	90% Hot Metal and 10% Scrap	80% Hot Metal and 20% Scrap	90% Hot Metal and 10% Scrap	80% Hot Metal and 20% Scrap
Hot Metal Silicon	0.38%	0.38%	0.38%	0.38%
Hot Metal Phosphorus	0.101%	0.101%	0.123%	0.123%
Scrap Phosphorus	0.035%	0.035%	0.035%	0.035%

An Excel based model was used to compare dephosphorization performance and costs for Cases 1 and 2 using six (6) different BOF treatment technologies. The technologies are described below in Table 3.

Table 3. Treatment Technologies Evaluated to Reduce Phosphorus in Hot Metal

Treatment Technology		Comment	Industrial Acronyms
1	Top Blown BOF	Oxygen injection through a top lance	BOF
2	Combined Blown BOF	Gas injection using either refractory	Many

	Treatment Technology	Comment	Industrial Acronyms
		elements or tuyeres	processes available
3	Combined Blown BOF with Enhanced Slag	As in Case 2 but with additional fluxes added	As above
4	Combined Blown BOF with Double Slag Practice	BOF slag removed partially through refining, fluxes added and De-C completed	MURC
5	Combined Blown BOF with Hot Metal Pre-treatment	Hot metal P level is reduced prior to steelmaking in torpedo or transfer ladle	ORP
6	Two BOF Converter Process	Two converters are used in series with countercurrent transfer of liquid steel and molten slag	LD-ORP SRP

The slag weight was determined based on the hot metal silicon content and steelmaking basicity ratio. The process parameters and estimated phosphorus partition coefficient, L_p for each technology is shown in Table 4.

Table 4. BOF Steelmaking Process Parameters

	Top Blown BOF	Combined Blown BOF	Combined Blown BOF with Enhanced Slag	Combined Blown BOF with Double Slag Practice	Combined Blown BOF with Hot Metal Pre-treatment	Two BOF Converter Process
Basicity Ratio	3	3	3.5	3	3	3
Slag Weight (kg/t)	53	53	62	53	53	53 (De-P BOF) 35 (De-C BOF)
L_p	55	80	80	80	80	80

The difference between the combined blown BOF and the same case with enhanced slag is the use of a larger amount of flux, and higher slag rate. This favors dephosphorization hence a lower final phosphorus in the tapped steel is realized. In the double slag practice, the first blow is assumed to achieve 35% phosphorus reduction. The second blow then proceeds per the combined blown BOF practice. One of the disadvantages of a double slag process is the productivity loss, due to the increased tap-to-tap time which is around 10 minutes.[5] For the case with hot metal pre-treatment, 70% phosphorus reduction was assumed in the pretreatment stage. The subsequent BOF treatment followed the same practice as the combined blown BOF process.

4 RESULTS AND DISCUSSION

The final phosphorus levels in the tapped liquid steel for the six (6) different BOF treatment technologies are presented in Figure 5.

The relative performance of each treatment technology reflects the changes in L_p and slag volume for each case. The combined blown BOF could only reach <0.02%P in Case 1 when low phosphorus sinter was used. Employing an enhanced slag practice only produced steel <0.02%P for Case 1 with low phosphorus sinter and in Case 2 when the hot metal ratio was limited to 80% hot metal. The lowest steel phosphorus content was achieved using two BOF converters in series closely followed by pretreatment of hot metal. The only time that steel with 0.005%P was produced was when the two BOF converter practice was used for Case 1 with low phosphorus sinter and 80% hot metal ratio.

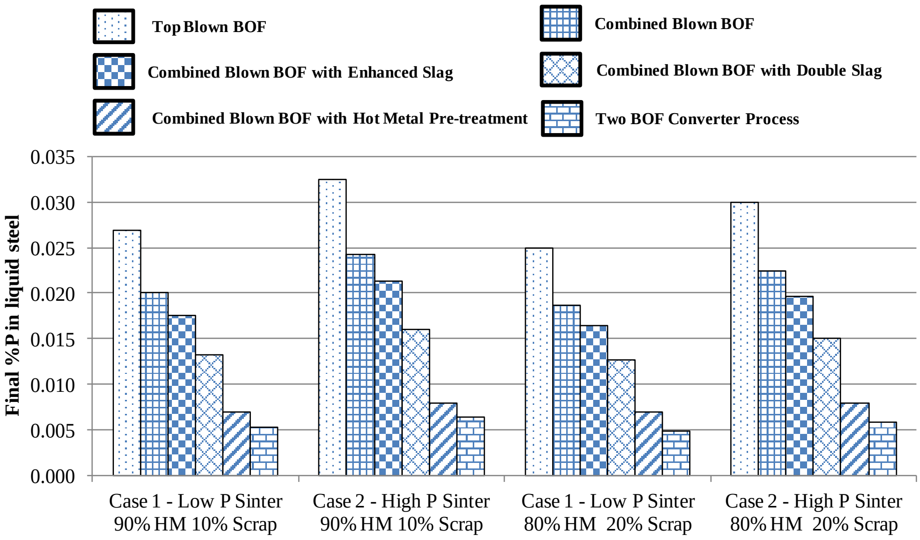

Figure 5. Final %P in Liquid Steel Achieved using the Six (6) Different BOF Treatment Technologies.

The use of two BOF converters in series is a powerful practice to remove phosphorus. In the first BOF converter phosphorus is reduced to less than <0.03%P. Phosphorus is further reduced in the second BOF converter to produce ultra-low phosphorus levels (<0.01%P) in the tapped steel. The final phosphorus in steel was <0.007%P for both cases and sensitivity to input phosphorus or hot metal ratio was minimal. The use of two BOF converters in series is a paradigm change to removing phosphorus compared to the other BOF refining approaches.

Many high performance steel grades require phosphorus in liquid steel between 0.01-0.02%P. This can be a problematic target for the BOF treatment processes studied. Lower phosphorus in the hot metal may be needed to consistently meet this phosphorus specification. Longer processing times using enhanced slag or a double slag practice can be expected to consistently produce liquid steel <0.02%P.

4.1 Techno-Economic Analysis

The operating cost to remove phosphorus for Case 1 - low P sinter with 90%HM and 10% scrap - was selected for the techno-economic analysis. Factors that were considered included the flux, refractory, slag disposal and yield loss costs, as well as the BOF productivity impact. The combined blown BOF was considered as a base case. The relative treatment cost for each technology is shown in Table 5.

The two BOF converter process lowers the cost to produce steel as productivity gains are achieved and consumable costs are virtually zero. The use of pretreated hot metal only slightly increased steel costs. The combined blown BOF with enhanced slag increased costs due to additional flux costs and a greater yield loss. For the double slag practice, the high FeO slag from De-C stage is usually recycled to the De-P/De-Si stage of the next heat, and therefore no yield losses compared to the base case were considered. Productivity penalties associated with the double slag practice confirm the large disadvantages with this approach.

Table 5. Case 1 Treatment Costs to Reduce Phosphorus per tonne of Liquid Steel – 90% Hot Metal

BOF Treatment Technology	Treatment Cost ($/t-LS)	Productivity Benefit or Penalty ($/t-LS)	Total Treatment Cost ($/t-LS)
Combined Blown BOF	Base	Base	Base
Combined Blown BOF with Enhanced Slag	1.58	5.26	6.84
Combined Blown BOF with Double Slag Practice	2.25	33.33	35.58
Combined Blown BOF with Hot Metal Pretreatment	5.27	(4.76)	0.51
Two BOF Converters	0.00	(4.76)	(4.76)

Capital costs were also considered. The two BOF converter process requires an additional blowing stand and off-gas system making this the most expensive technology to adopt, estimated at $100 M. A hot metal pretreatment station was estimated to cost around $15 M for the facility, additional costs for extra torpedo or transfer ladles may be required. Converting from top blown to a combined blown BOF is estimated at $15-30M per converter. With such a high investment cost, the motivation for implementing the two BOF converter process is two-fold; first to provide the maximum flexibility on the phosphorus input from hot metal and secondly, the two BOF converter process can easily produce large amounts of ultra-low phosphorus steel for demanding applications.

4.2 Steel and Iron Ore Price Premiums and Phosphorus Content

Steel with low phosphorus content and related property improvements commands a premium price when sold in the market place. In Europe, published price premiums range from 10 to 200 EUR/t for low phosphorus steel grades.[6]

Hatch estimated that ArcelorMittal Europe's price premium for low phosphorus grades (0.02-0.03 %P) is about 50 EUR/t (55 USD/t). Expressed on an iron ore basis, the premium is ~ 30 USD/t iron ore. Such a selling advantage can allow a steel producer to pay extra for the lower phosphorus iron ore needed to make low phosphorus steel products. The quantities of premium steel products can be significant; Hatch estimates that about 30% of the steel sold in China and up to 50% of the steel sold in the Japan-Korea-Taiwan and European regions requires low phosphorus content, < 0.03%P.

Major iron ore price index compilers (Platts, TSI and MB) publish price adjustments for a number of constituents including iron, silica, alumina and phosphorus. In October 2015, Platts' price adjustment for phosphorus was $0.35 per 0.01%P per tonne of iron ore working from a base of 0.1%P.[7] The ore price premium is about $1.00 to $1.80 per tonne for low phosphorus iron ore, more than an order of magnitude less than the price premiums when the resulting steel is ultimately sold. Conversely, should the steel producer be unable to buy the needed low-P iron ore, an opportunity to sell steel into premium markets with associated higher margins will be missed. With increasing phosphorus in major ore resources such as Australia's Pilbara region, more aggressive BOF technologies are required to produce the low phosphorus steels, see Figure 6.

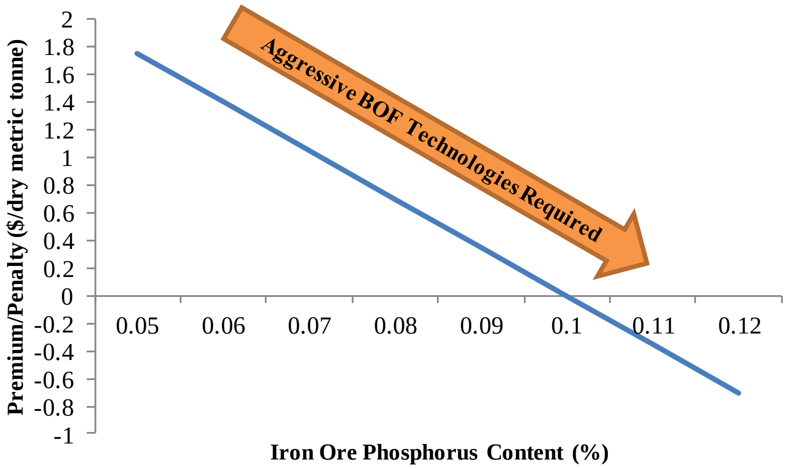

Figure 6: Iron Ore Premium based on %P and on a dry metric tonne basis.

For the treatment costs provided in Table 5 for Case 1, an additional $2.76 per tonne of steel treated must be added to reflect the cost to buy-in the 0.060%P sinter fines on which Case 1 is based. The treatment costs for Case 1 are restated in Table 6.

Table 6. Case 1 Treatment Costs including Iron Ore Price Premium per tonne of Liquid Steel – 90% Hot Metal

BOF Treatment Technology	Treatment Cost ($/t-LS)	Productivity Benefit or Penalty ($/t-LS)	Iron Ore Price Premium for 0.06%P ($/t-LS)	Total Treatment Cost ($/t-LS)
Combined Blown BOF	Base	Base	2.76	2.76
Combined Blown BOF with Enhanced Slag	1.58	5.26	2.76	9.60
Combined Blown BOF with Double Slag Practice	2.25	33.33	2.76	38.34
Combined Blown BOF with Hot Metal Pretreatment	5.27	(4.76)	2.76	3.27
Two BOF Converters	0.00	(4.76)	2.76	(2.00)

For Case 1, the combined blown BOF converter is able to produce steel with 0.02%P using low-P sinter fines for $2.76/t-LS. Plants with the two BOF converters in series or hot metal pretreatment facilities can purchase high P iron ore and save the $2.76/t-LS premium for low-P sinter fines and easily produce steel <0.02%. This provides an operating cost advantage of $2.25/t-LS for hot metal pretreatment and $7.52/t-LS for two BOF converters compared to combined blown BOF treatment route with low-P sintering fines. The greatest cost advantage for hot metal pretreatment and two BOF converters is from productivity improvements associated with shorter blowing cycles.

The changing iron ore market with increasing availability of low-P iron concentrates offers another route to reduce steel phosphorus. Adding low-P concentrates to the sinter blend using intensive mixing and micro-pelletizing can be an interesting option compared to the high investment cost for conversion to a two BOF converter process route.

5 CONCLUSION

Low phosphorus, high performance steel commands a significant price premium for the steel producer. Many higher performance steel grades require phosphorus in liquid steel between 0.01-0.03%P. This can be a problematic for the BOF treatment processes and limits on the hot metal phosphorus content are needed to meet this phosphorus specification. Aggressive technologies such as two BOF converters operating in series can easily make low phosphorus steel from relatively high phosphorus containing iron ores.

Ultra-low phosphorus steel, <0.010%P can only be achieved with the two BOF converter process or using pretreated low-P hot metal. The two BOF converter process is a powerful technology to remove phosphorus that has been successfully implemented in Japan-Korea-Taiwan and by a few Chinese steel companies. With its high capital cost, adoption of the two BOF converter process route has been slow outside the Japan-Korea-Taiwan region.

Combined blown BOF refining will continue to be a viable technology for producing low phosphorus steel required by the marketplace. European steelmakers produce many high performance steel products using combined blown BOF converters and with control of the phosphorus input. Low phosphorus iron ore concentrates will be increasingly added to sinter blends to reduce phosphorus in the steelmaking process. The steelmaker profits from producing high quality low phosphorus steel, with profit margins that are an order of magnitude larger than iron ore premiums and extra treatment costs.

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