Development for the production of low phosphorus steel in operations at Arcelor Mittal Tubarão[(•)]

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Abstract

The growing demand to produce steel with lower phosphorus (P) content happens in tandem with the increase in the content of this element in the ores used in the production of pig iron, leading to a constant evolution in the process of steel dephosphorization in BOF converters. Arcelor Mittal Tubarão (AMT), located in the municipality of Serra, Brazil, currently produces 5 million t of steel, but has an installed capacity of 7.5 million. This work aims at showing the development carried out in the dephosphorization of silicon-aluminium killed steel produced in the Arcelor Mittal Tubarão converters. The analysis of process variables such as flux addition, oxygen lance position and temperature at the end of blow are based on classical phosphorus partition models. The results compare phosphorus values in liquid steel before and after modifications in the variables and the refractory wear caused by the new procedures applied to AMT steelmaking converters .

Keywords

Dephosphorization; Steel; BOF converter.

Desarrollo para la producción de acero con bajo contenido de fósforo en las operaciones de Arcelor Mittal Tubarão

Resumen

Con la creciente demanda de aceros cada vez más bajos en fósforo (P), junto con el constante aumento en el contenido de este elemento en el mineral utilizado para producir arrabio, es necesario un proceso en constante evolución para la eliminación de fósforo del acero en los convertidores BOF. Este artículo tiene como objetivo mostrar el desarrollo para reducir el nivel de fósforo en el acero desoxidado con aluminio y silicio producido en los convertidores de Arcelor Mittal Tubarão (AMT), empresa ubicada en el municipio de Serra, Brasil. Este complejo produce 5 millones de toneladas pero tiene una capacidad instalada de 7,5 millones. El análisis de las variables del proceso tales como adición de fundentes, temperatura y el patrón de soplado, se basó en los modelos clásicos de la partición de fósforo. Los resultados presentados comparan los valores de fósforo obtenidos en el acero líquido antes y después de los cambios realizados, y analiza el desgaste de refractarios en los convertidores.

Palabras clave

Eliminación de fósforo; Aceros; Convertidores BOF.

1. INTRODUCTION

In most steel grades, the phosphorus is considered an undesirable element, which must be reduced as much as possible. The most common way to reduce this element in fully integrated steel-making companies is during the oxygen blowing process in the converters. This paper presents the production development of silicon-aluminium killed steel with phosphorus content below current standards in the final product (slab). Therefore, the purpose of this study is to evaluate the steel dephosphorization process performance of Arcelor Mittal Tubarão converters to meet the demand for low phosphorus, lower than 0.015 % for silicon-aluminium killed steel with manganese higher than 1.0 % in the final product.

Several authors referred to in this paper have studied the process of steel dephosphorization, working with the phosphorus partition coefficient (Lp) at the end of the blow, where (Lp) = the correlation between phosphorus content in the slag divided by the percentage of this element in steel.

Baljiva[1], Suito and Inoue[2] considered $Lp = \dfrac{(\% \, P_2O_5)}{[\% \, P]^2}$;

Healy[3] and Turkdogan[4] considered $Lp = \dfrac{(\% \, P)}{[\% \, P]}$

These studies try to correlate this parameter with process variables such as the addition of fluxes in the converters (e.g. lime, dolomite, fluorspar), the slag chemical composition at the end of the blow (e.g.: % total Fe, % FeO, % P_2O_5, % MnO, % MgO, % CaO, % SiO_2) and blowing patterns.

The dephosphorization reaction could be considered as[1 and 2]:

$$2\underline{P} + 5(FeO) + 3(CaO) = 5Fe_{(l)} + (3CaO.P_2O_5)_{(s)} \quad (1)$$
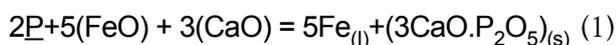
Balajiva[1] suggests a correlation between the phosphorus partition coefficient (Lp) with CaO (lime), the percentage of total Fe in slag and temperature, i.e.:

$$\log Lp = 11.80 \log (\% \, CaO) - 5 \log (\% \, Fe_t) - C \quad (2)$$

where: $Lp = \dfrac{(\% \, P_2O_5)}{[\% \, P]^2}$

where C, is a constant for a given melt temperature: $C = 21.13$; 21.51 and 21.92 for the melt temperatures of 1550 °C, 1585 °C and 1635 °C respectively.

The elements or compounds in parentheses are present in the slag and the elements in brackets are dissolved in the steel.

Suito and Inoue[2] changed this formulation, inserting other slag oxides contribution such as (% MgO, % P_2O_5, % MnO, % CaF_2 and % Al_2O_3), obtaining the following equation:

$$\log Lp = 0.145 \, (\% \, CaO) + 0.3 \, (\% \, MgO) +$$
$$+ 0.5 \, (\% \, P_2O_5) + 0.3 \, (\% \, MnO) +$$
$$+ 1.2 \, (\% \, CaF_2) - 0.2 \, (Al_2O_3) + \quad (3)$$
$$\dfrac{22810}{T} - 20.51 - 5 \log (\% \, Fe_t)$$

For Healy[3] and Turkdogan[4] the dephosphorization reaction could be considered as:

$$\underline{P} + 5/2 \, (FeO) + 3/2 \, (CaO) = 2.5 \, Fe_t +$$
$$(1.5CaO.PO_{2.5})_{(s)} \quad (4)$$
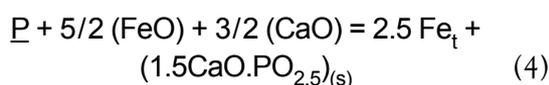
Healy[3] proposes a new formulation for (Lp):

$$\log Lp = 0.08 \cdot (\% \, CaO) + 2.5 \cdot \log (\% \, Fe_{total}) + \quad (5)$$
$$\dfrac{22350}{T} - 16 \pm 0.4$$

where: $Lp = \dfrac{(\% \, P)}{(\% \, P)}$

Considering equations (3) and (5), it could be noticed that an increase in basicity, the iron content in the slag and the reduction of temperature enhance the dephosphorization process, as observed by the increase of the phosphorus partition coefficient.

Turkdogan[4] proposed a correlation of the phosphorus partition coefficient, considering the reaction (6) with a new variable which aims at measuring the slag basic oxides (BO), as follows:

$$[P] + 5/2 \, [O] + 3/2(O^{-2}) = (\cdot PO_4^{-3}) \quad (6)$$
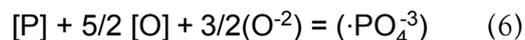
where: $Lp = \dfrac{(\% \, P)}{[\% \, P]}$

$$\log (Lp) = 0.071BO + 2.5\log [\% \, P] + \dfrac{21740}{T} - 9.87 \quad (7)$$

where BO is defined in equation (8):

$$BO = (\% \, CaO) + (\% \, CaF_2) + 0.3 \cdot (\% \, MgO) \quad (8)$$

Equation (7) intends to provide the capacity to absorb phosphorus from the slag in terms of basic oxides, where CaF_2 has the same weight as CaO and MgO is 1/3 of the CaO weight. Therefore, fluorspar, as well as the reduction of slag viscosity increasing the reaction kinetics have the same effect in improving the thermodynamic conditions as the CaO [4].

Notice that an increase in basic oxides and a fall in temperature both decrease the activity coefficient of P_2O_5 favoring dephosphorization. Turkdogan and Pearson[5] proposed that the Raoultian activity coefficient "γ_{FeO}" decreases with increasing binary slag basicity (B = % CaO / % SiO_2), as shown in table I.

According to the author, a decrease in the "γ_{FeO}" makes the Raoultian activity of FeO "a_{FeO}" also decrease, which causes the reaction (4) to occur towards the decomposition of CaO P_2O_5, which would result in a reduction of the slag capacity to retain phosphorus.

Table I. Effect of slag basicity on FeO activity coefficient

Tabla I. Efecto de la basicidad de la escoria en el coeficiente de actividad de FeO

B = % CaO / % SiO₂	2.0	2.5	3.0	3.5	4.0
γ_{FeO}	2.00	1.33	1.11	0.98	0.87

Turkdogan[4] affirms, however, that the slag basicity is not the most appropriate parameter to describe the dependence of the phosphorus absorption capacity of the slag. "BO" would be more important.

However, according to Balajiva[1], there is an optimum relation between the % FeO in slag, basicity and the phosphorus partition coefficient (Lp) between slag and metal, as shown in figure 1.
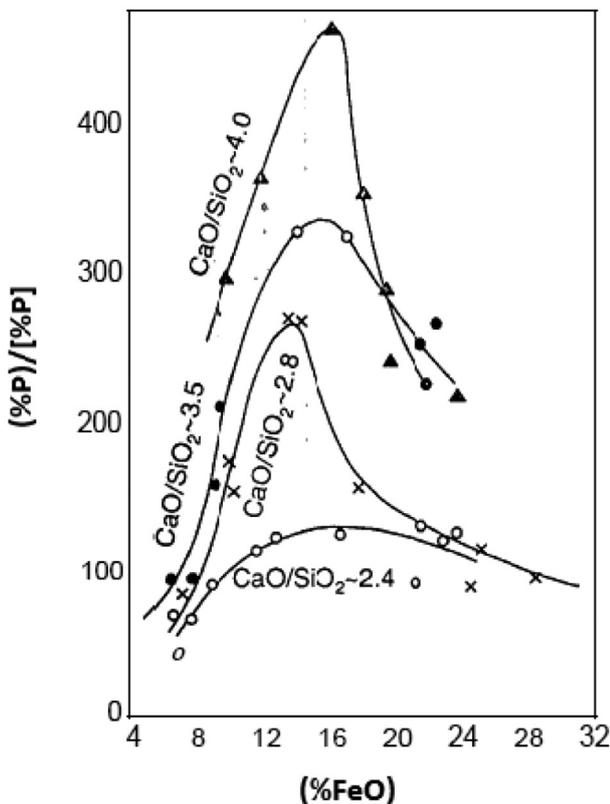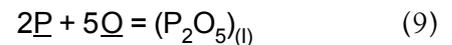

Figure 1. Relation between the % FeO in slag, basicity and phosphorus partition $L_P = \dfrac{(\% \, P)}{[\% \, P]}$.

Figura 1. Relación entre el % FeO en la escoria, basicidad y coeficiente de partición del fósforo $Lp = \dfrac{(\% \, P)}{[\% \, P]}$.

Turkdogan and Pearson[5] considered the formation reaction of P_2O_5 in slag as:

$$2\underline{P} + 5\underline{O} = (P_2O_5)_{(l)} \qquad (9)$$

They also established the expression of the P_2O_5 activity coefficient:

$$\log \gamma_{(P_2O_5)} = -1.12 \, (22.X_{(CaO)} + 15.X_{(MgO)} + \\ + 13.X_{(MnO)} + 12.X_{(FeO)} - 2X_{(SiO_2)} - 42000/T + (10) \\ + 23.58$$

Notice that as a result of the increase in basicity of FeO content in slag and a fall in temperature, the P_2O_5 activity coefficient decreases, favouring dephosphorization.

2. EXPERIMENTAL

In order to develop low phosphorus steel, 12 heats were produced. Changes in the process were based on some of the parameters mentioned before, with focus on variables which enhance the removal of phosphorus during the production process. The methodology was based on current results of phosphorus content in normal grades of steel, changing the process variables in order to increase the phosphorus partition coefficient.

For the production of steel in development, the phosphorus content must be around 50 to 60 ppm lower than the phosphorus specification of the final product, which is of 150 ppm, due to the contamination that may occur from the slag carried over from the converter heat tapping to the ladle, and also from the pick-up of phosphorus content in the Mn-Fe-alloy, which is usually added to these steel grades.

The main actions in the process variables in order to achieve the phosphorus partition are described below.

As mentioned before, from all the expressions applied to describe the phosphorus partition

coefficient, oxidized iron is the variable that affects positively the removal of phosphorus. Thus, it was aimed to achieve lower carbon content in the end of the blow. In fact, oxygen mass balance calculations were made in order to obtain an excess of blown oxygen volume, which allows higher oxidation of carbon, silicon and manganese, also a larger amount of iron oxide in the slag, as it can be seen in table II.

The effect of increasing the amount of flux used during the oxygen blowing was also analysed based on the Turkdogan[4] model (Ec. (7) and (8)). In this case, the CaO quantities were increased by adding lime, and also fluorspar (CaF$_2$) to speed highly basic slag formation. Regarding Si-Al killed steel grades with high manganese, the increase in lime was, on average, of 3 kg/t of steel produced and the fluorspar was of approximately 1 kg/t of liquid steel. The average net result (Table II) was an increase in basicity (% CaO / % SiO$_2$).

Temperature is a highlighted item in all the models showed before and it is inversely proportional to the phosphorus partition coefficient, i.e., lower temperatures enhance the phosphorus removal from the steel. Despite this, high additions of manganese alloys in the bath after steel tapping push the temperature to higher values compared with current grades of steel, to compensate the heat loss. Thus, it was not possible to reduce the temperature values at the end of the blow.

Table III shows the summary of the actions taken in process variables and the impact on the partition coefficient based on the mentioned authors[1-5]. All the changes shown in table III were performed simultaneously on all 22 heats. Throughout the production process, all fluxes and materials are added by weighing on certified scales and the data are recorded in the computers in the process. All the process information presented in this report was collected from this database.

Temperature measurements and steel samples were collected by using probes connected to a sub lance which is inserted in the liquid steel bath during and at the end of the blowing. The phosphorus content in steel was analysed at the AMT chemical laboratory by optical spectroscopy and slag samples were analysed using an X-ray diffractometer.

3. RESULTS AND DISCUSSION

The results of the phosphorus evolution from hot metal to the final product (slab) in the different experimental heats, after the changes, shown in table III, are shown in figure 2. As it can be seen, there was a strong removal of phosphorus in the stage of oxygen blowing and after a phosphorus reversion in the following process. That occurred because of the slag carried over during the tapping process and from the pick-up of residual phosphorus of Fe-alloys added. The maximum phosphorus reversion for high Si-Mn-Al killed steel was observed to be of 60 ppm.
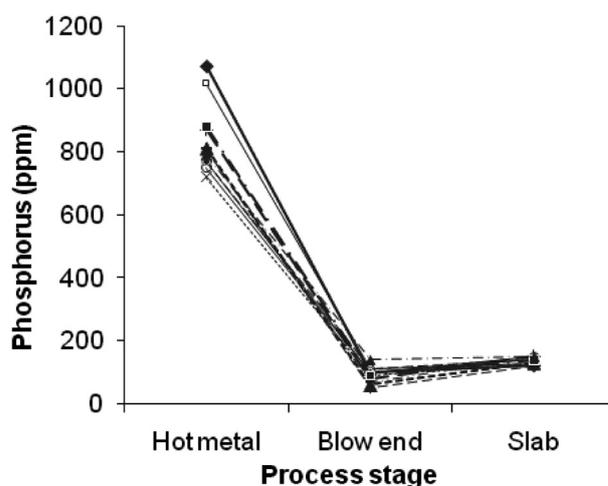
Table II. Average compositions values of hot metal and final slag

Tabla II. Valores medios de la composición del arrabio y escoria final

Data	Current	Experimental
Hot metal composition		
% C	4.55	4.49
% Si	0.19	0.18
% Mn	0.45	0.45
% P	0.08	0.08
End point slag data		
Binary basicity	3.88	4.27
% MgO	8.77	7.98
% FeO	28.24	33.77
% CaO	42.68	41.53
% Al$_2$O$_3$	1.86	1.27
% MnO	4.80	3.61
% P$_2$O$_5$	1.87	1.48
% CaF2(*)	~0.20	~1.00

Figure 2. Phosphorus content evolution from hot metal to slabs in the experimental heats.

Figura 2. Evolución del contenido de fósforo desde el arrabio al término del soplado y contenido final en la colada continua.

Table III. Summary of actions in the process and its impact on the phosphorus partition coefficient

Tabla III. Resumen de las acciones en el proceso y su impacto en el coeficiente de partición de fósforo

Variables	Action	How	Result measurement	Impact on P (partition coefficient)
Steel oxidation	To increase oxygen volume	Add more 3 Nm^3/t of steel	% FeO and % Fe_T slag result	↑
	To modify the height of oxygen lance standard	To raise the lance between 200 to 400 mm		↑
Fluxes consumption	To increase lime addition	Add more 3 kg/t of steel	Flux weight	↑
	To increase fluorspar addition	Add more 1 kg/t steel		↓
Temperature	To increase temperature in the end of the blow	According to Fe-Mn addition	Temperature measurement	↓

The results of the average values in the end of the blow and in the slab of current and experimental heats, are shown in table IV.

The phosphorus removal efficiency in the experimental heats is compared to the current ones through figure 3. Actually, it is observed that in general, phosphorus partition coefficients (Lp) were higher than the current ones, endorsing the plan of action reported in table 2. This result is due to an increase of % FeO in the slag, the higher addition of CaF_2, as well as to an increase in the oxygen available to form P_2O_5, as shown in table II. All these actions

Table IV. Average values in the end of the blow and in the slab of current and experimental heats

Tabla IV. Valores medios al término del soplado y el contenido final en la colada continua en las coladas de operación de prueba y las regulares

Data	Current	Experimental
End point steel		
% C	0.049	0.042
O (ppm)	873	903
T (°C)	>1680 ºC	>1680 ºC
% P	0.0140 (σ = 0.004)*	0.0093 (σ = 0.002)
Lp	55	68
Final P content in the slab (average)	0.017 (σ = 0.003)*	0.013 (σ = 0.002)*

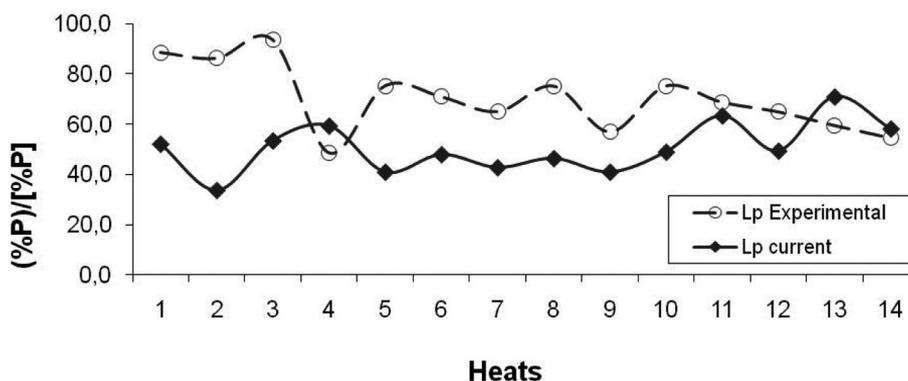* Predicted by mass balance; σ: standard deviation.

Figure 3. Phosphorus partition coefficient in the converter, in the current and experimental heats, where $Lp = \dfrac{(\% \, P)}{[\% \, P]}$.

Figura 3. Coeficiente de partición del fósforo en las coladas de operación de prueba y las regulares, donde $Lp = \dfrac{(\% \, P)}{[\% \, P]}$.

associated decreased slag viscosity and enhanced dephosphorization kinetics. On the other hand, an increase in the addition of CaO, supports the dephosphorization thermodynamically, by reducing the P_2O_5 activity, also offering a higher amount of CaO to fix the P_2O_5 in slag, according to reaction: $P_2O_5 + 3CaO = P_2O_5 \cdot 3CaO$.

The results reassure the relation of empirical models to describe the phosphorus partition coefficient, despite the wide dispersion when compared to industrial data.

Figure 4 shows the distribution of phosphorus content at the end of blow of current and experimental heats. As can be seen in the figure, phosphorus occurrence frequency is lower than 0.015 % was always higher than the experimental heats, and the occurrence of phosphorus above 0.015 %, was always higher than the current ones. These results show that the process changes, according to table III, were effective to ensure results below or equal to 0.015 % of phosphorus content in the final product (slab). This occurred due to the same reasons aforementioned.
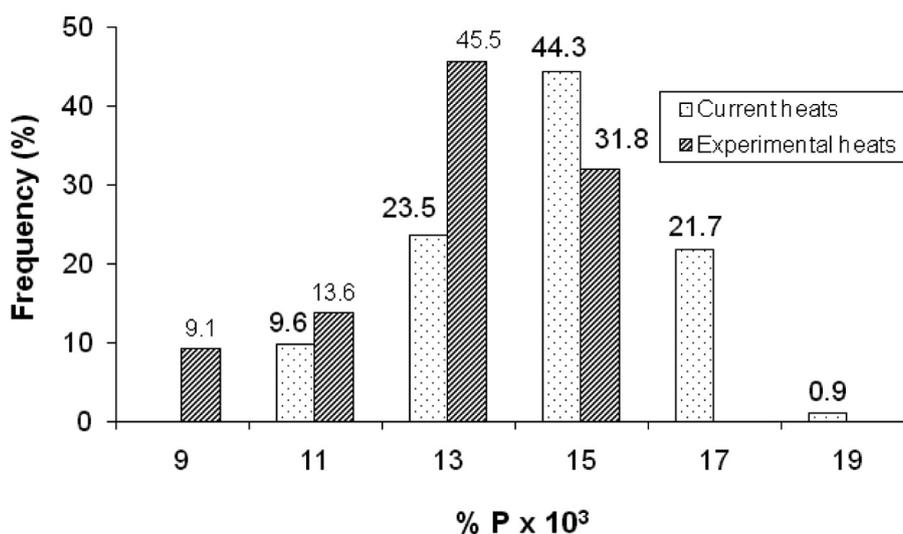

Figure 4. Frequency of phosphorus content in the final product (slab) comparing current heats with experimental heats.

Figura 4. Distribución de la composición de fósforo en las coladas de operación de prueba y las regulares.

Despite the good results of the tests regarding the phosphorus content at the end of the blow for experimental heats, the converter refractory wear index, evaluated from bricks thickness measurements, was significantly higher than in the current heats, as it can be seen in figure 5. This undesirable effect is due to the higher FeO content in slag, and also the increase in fluorspar addition. Both procedures aim to decrease slag viscosity, which increases refractory wear. High temperatures at the end of the blow also contribute to increase refractory wear.
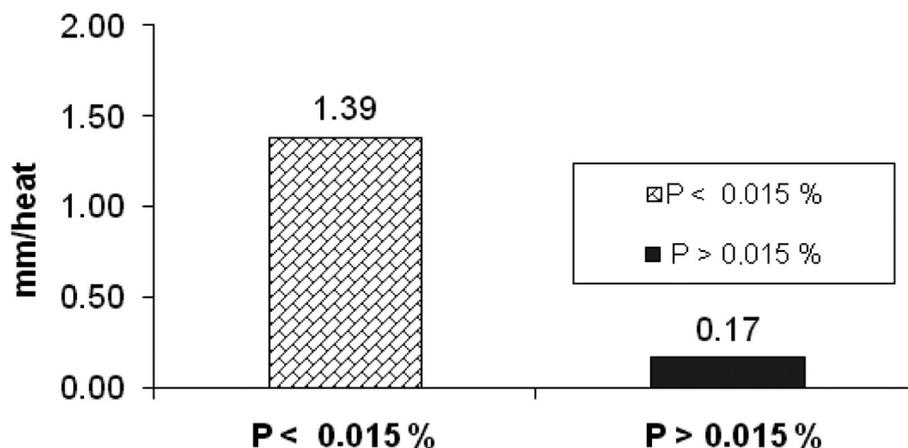

Figure 5. Refractory wear rate in converters for current heats (P ≥ 0.015) and experimental heats (P ≤ 0.015).

Figura 5. Desgaste refractario de los convertidores en las coladas de operación de prueba (P ≤ 0,015) y las regulares (P ≥ 0,015).

4. CONCLUSIONS

— The dephosphorization results of experimental heats were significantly higher than the current ones.
— Higher phosphorus removal in the experimental heats is mainly due to:
   An increase of oxidation level of the system; Changes made in the process, such as the increase of oxygen volume and blow pattern modification (changes in the oxygen lance height), were effective for this item.
   Higher additions of fluxes; The increase in lime and fluorspar additions were also satisfactory in the achieving the expected results.
— These results are consistent with the available models proposed in the literature describing the phosphorus partition coefficient equilibrium, as shown in this paper.
— The side effect of increasing the efficiency of phosphorus removal was the raise of the refractory wear rate in the converters, due to an increase of slag oxidation, the presence of fluorspar, both associated with higher temperatures at the end of the blow.

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