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TITANIUM GOIÁS - DECADES OF EXPERIENCE IN MARKETING OF ILMENITE FOR BLAST FURNACES IN BRAZIL[1]

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Abstract

Since the late 90's, most of the large blast furnaces of steel plants in Brazil, following the global trend, surpassed 2.3 t/day.m3 of productivity. The intensive use of oxygen enrichment of the blast for use of auxiliary fuels injections in the tuyeres helps to achieve unimagined productivity. Even in the 90's, AK Steel, U.S., reaches in his Blast Furnace No. 3, the astonishing pace of 4.0 t/24 hours.m^3 (work volume) of productivity, showing that it can operate continuously blast furnaces with productivity up 3.0 t/day.m^3. However, experience has shown that these results relates to the cost too expensive wear of the walls of the crucible (hearth) and its consequences in the short and medium term (loss of revenue and increased cost of production). This paper aims to show that it is possible to operate continuously and efficiently blast furnaces with high productivity, without the crucible becomes a limiting factor of the process, even after have already suffered considerable wear. To this end, the long experience of Titanium Goiás with marketing titanium magnetite (ilmenite) for large blast furnaces are presented as evidence of the effectiveness of titanium exclusively in charge of the blast furnace, as a protective agent of the crucible.

Key word: Titanium; Ilmenite; Titanium magnetite; Crucible (hearth); Blast furnace.

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1 INTRODUCTION

From the 1990s, the blast furnaces around the world have increased their productivity. One of the factors that contributed to this increase was the intensive use of the auxiliary fuel injection tuyeres, forcing the use of higher rates of air enrichment with oxygen. Figure 1, shows the evolution of the productivity of Blast Furnace # 3 of AK Steel, during the 1990s, according Frueham.(1)

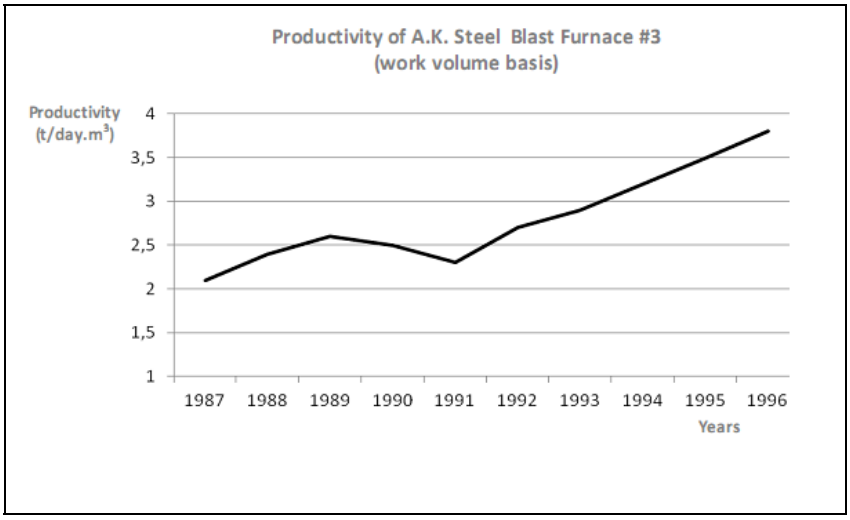

Figure 1: Evolution of the productivity of Blast Furnace # 3 of AK Steel, with ilmenite in the charge and intensive use of natural gas, oxygen and metallic charge.

Figure 2 shows the evolution of Japanese productivity of blast furnaces with the use of coal injection, a trend followed by most large blast furnaces in the world in a similar period.

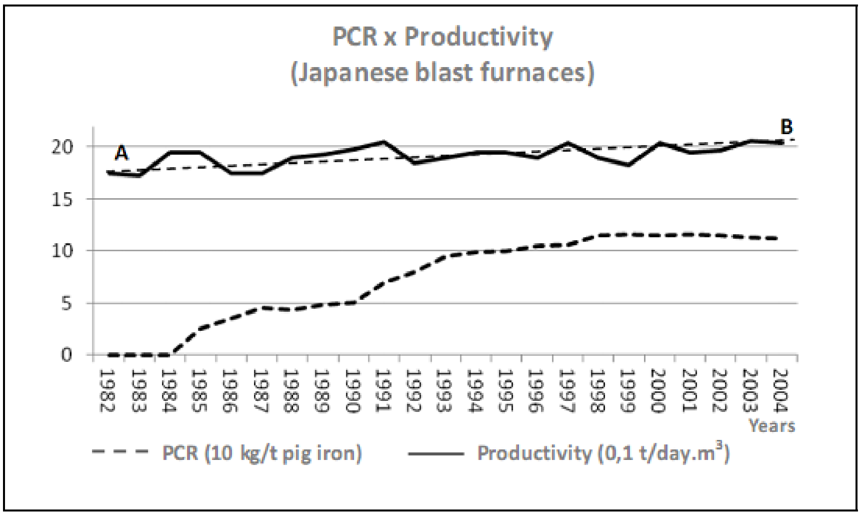

Figure 2: Evolution of the productivity of blast furnaces Japanese (trendline AB), with the intensive coal injection in the tuyeres (10 kg / t pig iron) and enriching the air with oxygen.

However, this increase in productivity has a price. Research has shown that increasing the productivity of a blast furnace is an important condition in the incidence of wear of the hearth. Santos,(2) in his Master's thesis, highlights the research Shinotake et al.,(3) which led him to some factors that contribute to the

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crucible erosion through increased productivity. According to these researchers, the main factors are:

- The flow and temperature of the pig iron along the wall of the crucible increases with increased productivity;
- Transfer of heat by convection also increases with increased productivity;
- And, consequently, the heat flux through the walls of the crucible increases.

Through the model, these researchers established relationships between the productivity of blast furnace and the temperature in the crucible. An example of this relationship is shown in Figure 3, based on an initial temperature of 1390°F.

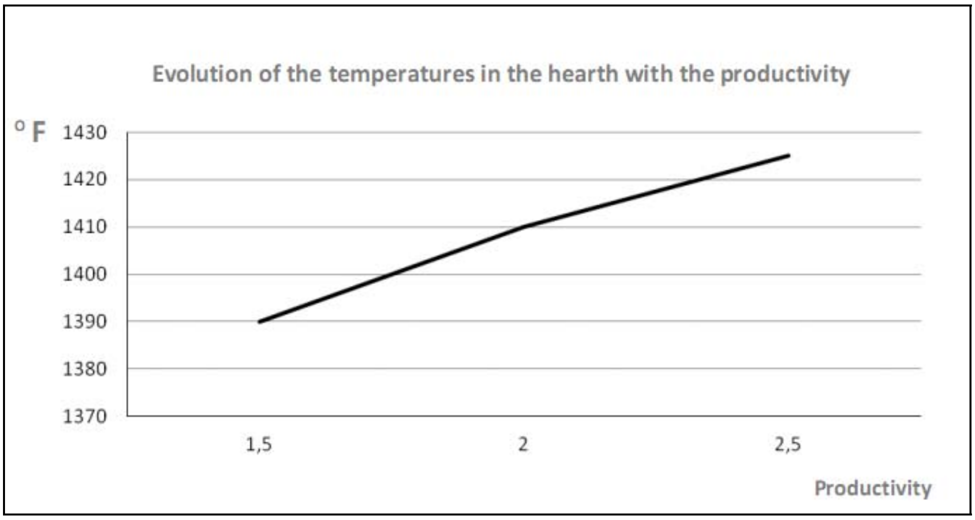

Figure 3: Correlation between temperature and productivity in the hearth of the blast furnace.

A fact that supports this relationship between productivity and increased wear of the crucible is that, in general, the blast furnaces that operate with higher productivity have lower campaign. Therefore, even based on the work of Santos,(2) Zubimendi et al.(4) listed the reasons for termination of the campaign of 100 blast furnaces between 1986 and 2000, during which there was a significant increase in the productivity of large blast furnace throughout the world. The main cause of closure of blast furnace campaign was wearing in the hearth (crucible), as shown in the graph in Figure 4.

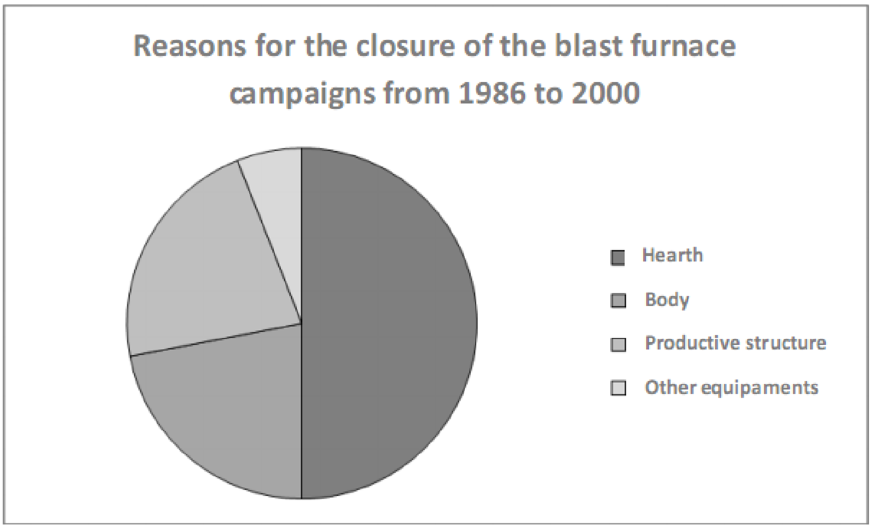

Figure 4: Major causes of foreclosure campaign blast furnace in the period 1986-200.

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Another factor that indirectly tends to cause wear in the crucible is the permeability of the load, mainly governed by the quality of coke, the only load to remain solid in the entire loading column. Currently, with the aim of reducing costs by increasing the incomes of various raw materials, we seek to maximize the screening process, taking advantage of materials that, by its small size, anteriorly were being diverted to units of agglomeration (sintering). So, now are common uses of small coke and small sinter in loads of blast furnaces, while the use of coal injection in the tuyeres. Research has shown that the technique of coal injection tends to reduce of size of the coke during its descent from top of blast furnace to the crucible, which tends to further reduce permeability of the load. The low permeability of the load and the reduction of voids in the structure of the "dead man" in the crucible does the flow of iron in the crucible be conducted irregularly and around the "dead man". This process increases the wear in the region between the walls and bottom of the crucible (forming the so-called "elephant's foot"), which intensifies when trying to achieve higher productivity.

2 WEAR MECHANISMS

Studies show that the wear of the crucible presents most frequently in two configurations. Figure 05, below, shows these two formats, based on the dissertation of Santos (2) and whose predominance was identified by studies Kolijn et al. (5)

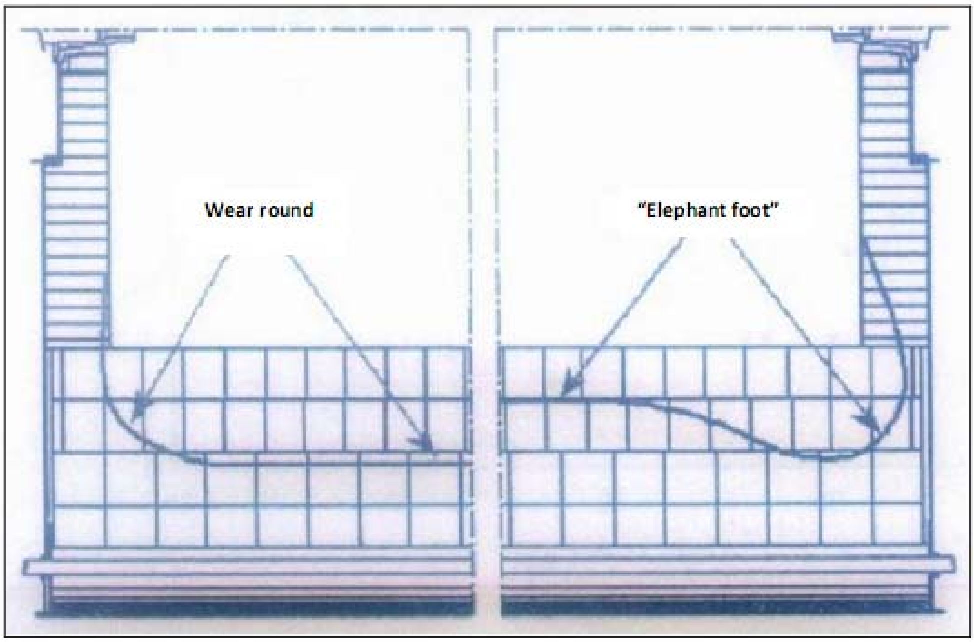

Figure 5: Settings of wear of the crucible of a blast furnace.

These settings have different causes.
The wear round occurs mainly when, on a good permeability of the structure of coke in the furnace ("dead man"), there are conditions for this structure is peel off the bottom (float in the pig iron).
In the case of the setting in "elephant foot (or paw) ", the permeability of the structure of coke is low due, among other factors, the low quality of the coke loaded. Researchers have also demonstrated that the crucible wear mechanism which occurs naturally in the blast furnace follows a process with three step, as shown in Figure 6.

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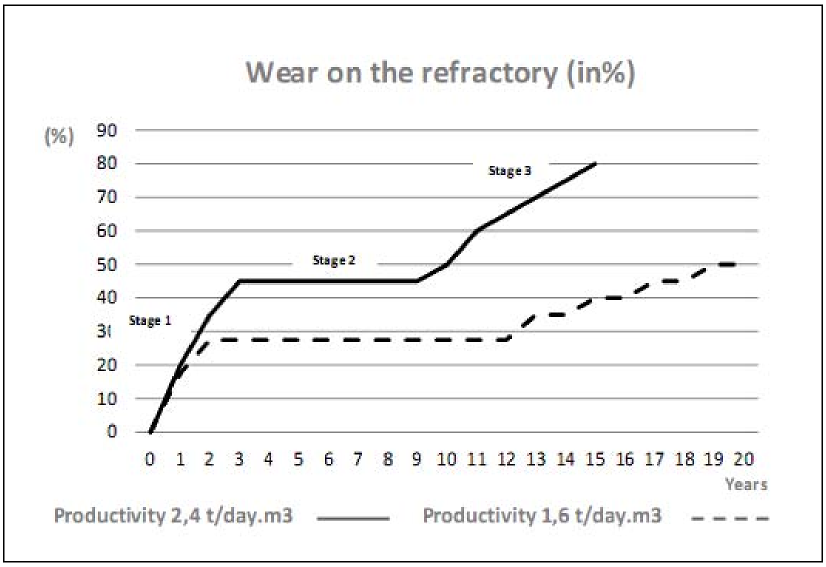

Figure 6: Mechanism of wear (relative) of crucible's refractory of a blast furnace. It also shows that productivity increases wear.

In the first stage, the erosion occurs by direct attack on the refractory surface and chipping (spalling).
In the second step, with the possibility of forming a layer of solidified pig iron, the erosion occurs in much lower speed, while maintaining the substantially constant wall thickness.
In the third stage, however, a prolonged exposure to high temperatures leads, again, to spalling of the material and to a condition that impairs the safe operation of the blast furnace.
As already mentioned, Figure 6 also shows that the increase in productivity accelerates this process. The process of erosion occurs by two mechanisms:

- Penetration of iron in the pores of the carbon block → solubilization of carbon in this iron → solidification in the isotherm of 1150°C with swelling → opening cracks for new penetrations, with the isotherm of 1150°C moving to the cold face of the refractory;
- Penetration vapor of elements such as alkali and Zn in the pores and crevices of the carbon block → This elements are deposited by condensation at temperatures around 800°C → with time, these elements are combined with substances present in the block forming liquid phases that accumulate to the volume to determine the collapse of the microstructure by chipping (spalling) → this mechanism affect the heat transfer to the cooling system, increasing the temperature in the hot face of the block and accelerate wear → the isotherm of 1150°C is approaching more and more the cold face of the block increasing the penetration of hot metal, closing both mechanisms.

3 CONTROL OF THE WEAR

The control wear of the crucible, like any control that you want effective, it must be done through actions in four phases: a) planning; b) execution of actions; c) verification of the results and d) review and possible amendments to the plan actions.
Kolijn [(5)] listed a series of actions that, if applied in practice, tend to reduce the marked wear of the crucible, increasing the campaign of the blast furnce. They are:

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3.1 Keep the Crucible as Empty as Possible

- This requires a better control of the length of the tap hole protecting the walls of the holes, in the region;
- Improve the operation of blast furnace, avoiding sudden changes in temperature, pressure, composition, and reducing the possibility of undesirable inputs of water in the crucible;
- Reduces the stresses to which the hearth is subject (lower residence time of material in the crucible).

3.2 Maintain High Quality Coke

- This requires maintaining a high hot resistance (CSR) and high cold resistance (DI);
- It also forces to control the reactivity, to prevent degradation by CO_2;
- Forces the control of the average size of the total coke loaded (including small-coke).

3.3 Maintain a Good System to Detect Water Leaks in Cooling System

- This forces them to maintain a continuous system and with ability to precisely locate the leak;
- Forces also keep operators trained to detect (including visual detection) and elimination of leaks;
- Forces to maintain stocks of spare parts in adequate quantity and quality.

3.4 Maintain an Excellent Cooling in the region of Each Tap Hole

- This requires a better control of the length of the hole protecting the walls of the tap holes in the region;
- It also obliges to keep casting (drills) and closing (mud gun) assessed as to their positions and angles of incidence with respect to the mouths of the tap holes;
- It also obliges to maintain tap holes without breaks or cracks.

3.5 Use Tuyere Diameter Suitable for the Planned Operation

- This requires a stock of tuyeres also suitable for the planned operation;
- This allows, in case of wear already present, to selectively close to the diameter of some tuyeres on the affected area.

3.6 Use ilmenite (TiO_2) on charge

- This forces you to choose one of the approaches to the use of ilmenite in charge of the blast furnace (preventive approach or corrective approach);
- This forces you to choose which form it will load the ilmenite (tunnelvision directly into the blast furnace or fine agglomerated in sintering or pelleting plants);
- This also forces you to choose which load iron ore blast furnace will be partially replaced by ilmenite (pellet or hematite);

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- It also requires to maintain a reliable system of checking temperature of the hearth, especially in regions affected by pronounced wear.

4 PROTECTION MECHANISMS WITH THE USE OF ILMENITE IN CHARGE

During his campaign, a blast furnace suffers a natural wear of his crucible. We have seen that this process can be enhanced by actions widely used today. Thus, two approaches should be considered when looking for protection of the crucible using ilmenite in the load.
First, ilmenite can be charged at a rate of 5 kg of TiO_2/ ton of pig iron from the second year of operation. This is a preventive approach, where the goal is to prevent the wear. This measure aims, mainly, the increase of the campaign, even if using high productivities.
In another approach, the wear is already present and its consequences may or may not be being felt in the operating performance of the oven. Furnaces with marked wear in the crucible tend to a lower productivity and to higher fuel consumption. Moreover, there is the risk of a serious accident and permanent closure of the campaign. In this case, ilmenite can be charged at a rate of 5 to 20 TiO 2 / t pig iron. This approach is thus a corrective action. Table 01 illustrates the characteristics of the two approaches.

Table 1: Forms of use of ilmenite in charge of the blast furnace, according to the desired objective

Forms of use	TiO_2 (kg/t pig iron)	% Ti in pig iron	% Ti in slag
Preventive	5 a 10	0,05 a 0,1	1,0 a 1,5
Corrective	10 a 20	0,1 a 0,3	1,5 a 3,0

The specific consumption should be adopted depending on the values and trends of the temperature of the hearth in the affected regions.
A summary of the protection mechanism can be described by the following sequence:

- TiO_2 introduced in the load is reduced to Ti when the load, in the downward movement, reaches the bosh of the blast furnace;
- as the Ti in solution in iron advances to the hearth, will form TiC, TiN and predominantly Ti (CN). These compounds of Ti remain in solution on iron, mainly a function of temperature. Thus, in regions near the tuyeres, the solubilities of carbides, nitrides and carbonitrides of Ti in the pig iron are larger;
- as the pig moves away from the tuyeres into the lower regions of the crucible, the temperatures drop, causing the fall of the solubilities of carbides, nitrides and carbonitrides, which are poured. Part of these precipitates is again oxidized, leaving the furnace through the slag. Another part comes out in pig;
- the predominance of Ti (CN) makes this compound remains in solution longer in the pig, reaching the lower and colder regions of the crucible, where it will set selectively in locations where temperatures and motion of the pig are low enough to precipitate the Ti (CN) and solidify the pig that still retains Ti (CN) in solution. This binding is selective to form the protection of the worn areas.

The graph of figure 7 illustrates the steps III and IV of the summary above.

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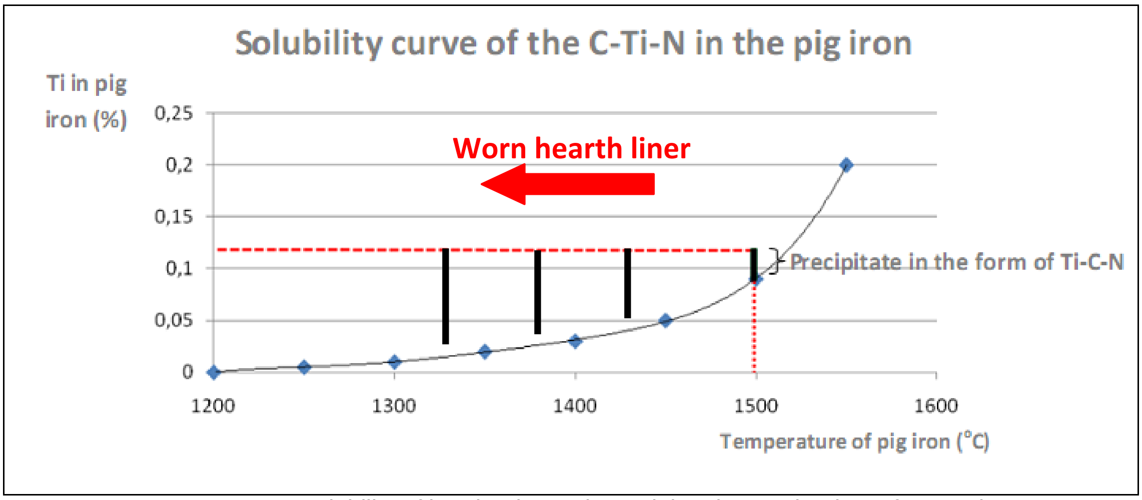

Figure 7: Curve solubility of iron in Ti-CN, determining the mechanism of protection.

Thus, for a pig iron with a given content of Ti, when its temperature drops, more Ti-CN precipitates. And by this mechanism, the protection extends to channels (principal and secondary), the spouts, torpedoes and the ladles.

5 A HISTORICAL SUMMARY OF TITANIUM GOIÁS

In 1974, a metallurgical engineer and a mechanical engineer initiated activities in the field of briquetting equipment manufacturing and processing various materials, including soda ash, used in the desulfurization of pig iron in the integrated steel plants. Between 1976 and 1977, they made these professional services to a steel plant of Siderbrás Group (hereinafter referred to as Plant A) and were consulted about the possibility of providing ilmenite for continuous use in blast furnaces of that plant. The main objective was to boost the campaigns of the blast furnaces that at that time already had high yields, comparable to the Japanese results, but with limited campaigns.
Then, a geologist was called to research and identify the main occurrences of ilmenite throughout the national territory. In 1979, it was began the production of granular ilmenite for the Plant A, where was used titanium as protection for the crucibles of the blast furnaces, using ilmenite in the load.
In 1989, after ten years of continuous supply to that same plant, born Titanium Goiás.

6 THE EXPERIENCE OF PLANT A IN THE USE OF ILMENITE IN THEIR BLAST FURNACES (1979-1996)

This plant was a pioneer in the conscious use of titanium in charge of its blast furnaces. It was also a pioneer in adopting the philosophy of preventive use of titanium in order to protect the hearth. It can be said with certainty that this pioneering was not restricted to the national level, since few plants in the world adopted the technique of using ilmenite in charge of the blast furnace, from the second year of the campaign, before any sign wear of the hearth. As already mentioned, in 1979, the Plant A, operating its blast furnaces with high yields for the season (above 2.0 t/days.m^3), developed a plan to boost the campaigns of its blast furnaces, without reducing yields. And the core of this plane was the use of ilmenite in charge of each blast furnace, at an appropriate rate, to prevent excessive wear. The results of the

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implementation of this plan, which involved the Titanium Goiás, can be seen in the graphs of Figures 8, 9 and 10.

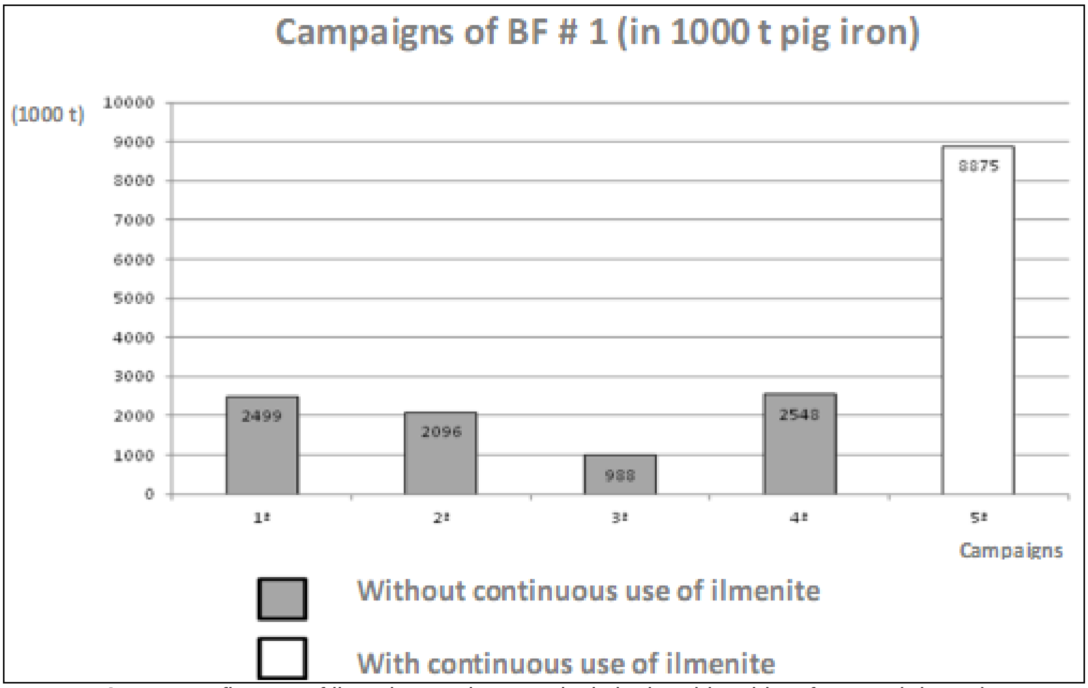

Figure 8: Influence of ilmenite used preventively in the oldest blast furnace (Plant A).

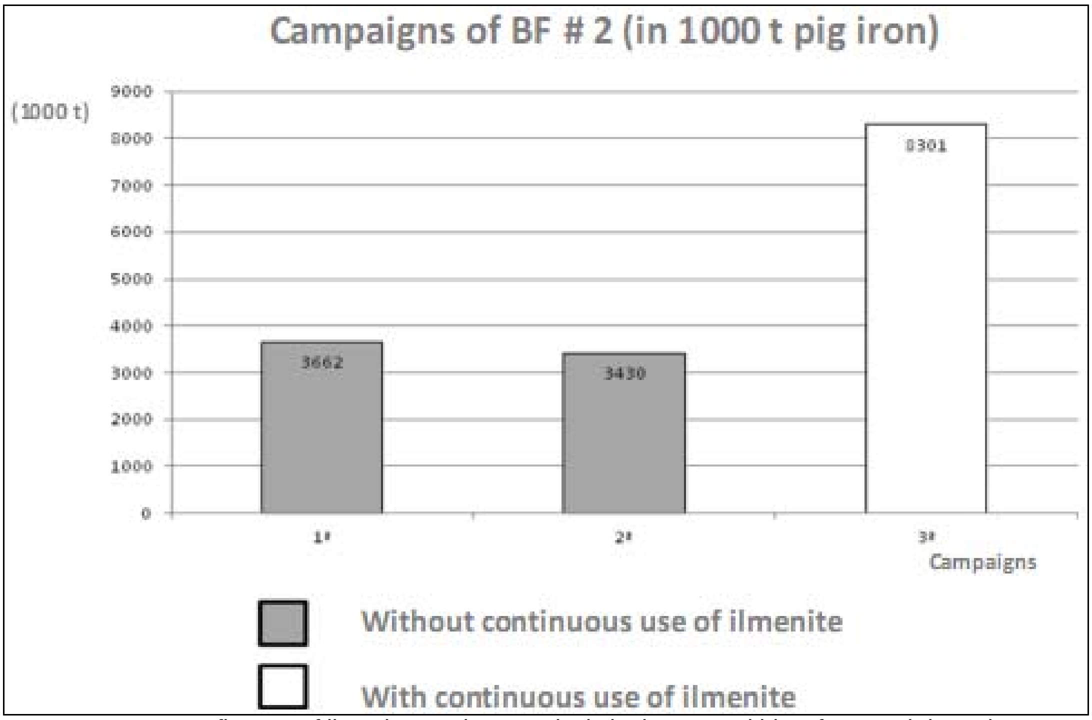

Figure 9: Influence of ilmenite used preventively in the second blast furnace (Plant A).

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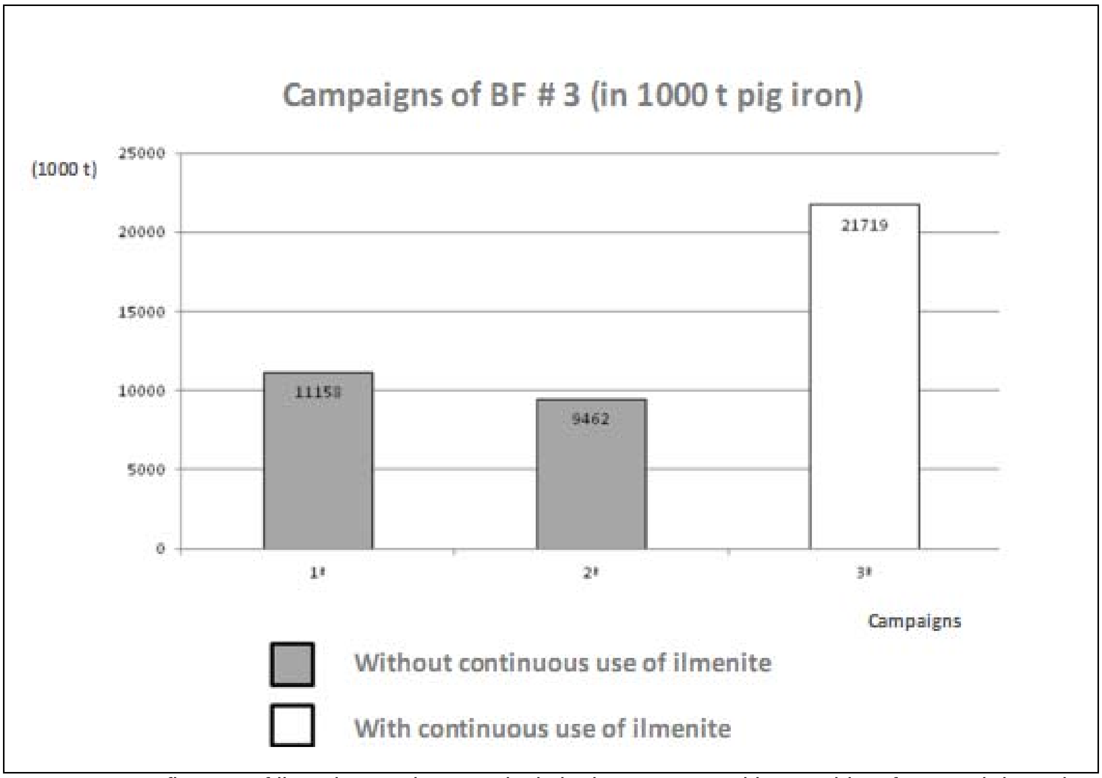

Figure 10: Influence of ilmenite used preventively in the newest and largest blast furnace (Plant A).

Continued use of ilmenite in charge of blast furnaces, from the 2nd year of the campaign, nearly tripled the campaigns of the blast furnaces of the Plant A.

7 THE EXPERIENCE OF PLANT B IN THE USE OF ILMENITE IN ITS LARGEST BLAST FURNACE (1998-2001)

From mid-1998 the temperatures of the crucible of the biggest blast furnace of Plant B began to rise, reaching 700ºC at the end of that year, causing losses of production. In the period 1999 to 2001, the furnace was operated using ilmenite of Titanium Goiás in charge, reaching rates of over 20 kg of TiO_2/t pig iron, without any problems in the operation. Not even any record of complaints about the quality of slag distributed to the two cement plants that received the granulated slag. In fact, it was found later that the slag granulated coming from a blast furnace working with ilmenite for the protection of crucible produces cement with greater resistance.
In 2000, in the period of use of ilmenite with even a higher rate of TiO_2 to 15 kg/t pig iron, the furnace broke historical records of production and lower fuel-rate, the best results until the end of his campaign in 2001. In 2001, two months before the blow-out, the ilmenite was removed from the charge to facilitate the dismantling of the hearth and still during the operation of demolition, a large plate of titanium carbonitride has been found protecting walls and entire bottom of the hearth. The graphs of Figures 11 and 12 illustrate, by records of the maximum temperature of the hearth and consumption of ilmenite, the wear process and recovery with the use of ilmenite in charge of the blast furnace.

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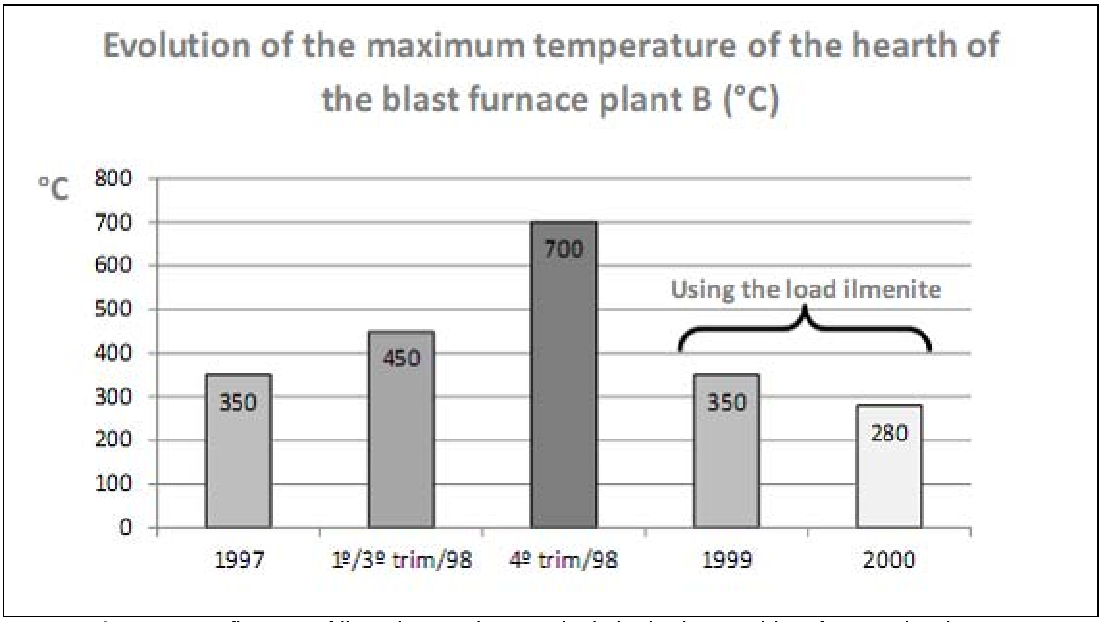

Figure 11: Influence of ilmenite used correctively in the largest blast furnace in Plant B.

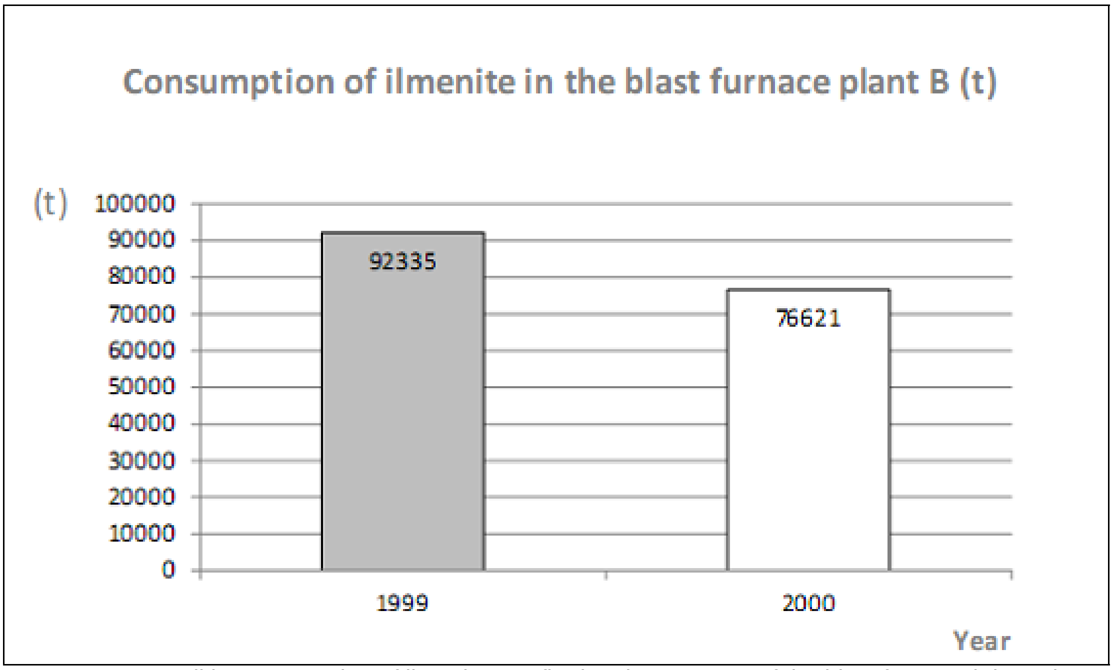

Figure 12: Fall in consumption of ilmenite, confirming the recovery of the blast furnace (Plant B).

8 THE EXPERIENCE OF PLANT B IN THE USE OF ILMENITE IN ITS LARGEST BLAST FURNACE (2006)

In 2006, during the shutdown of its largest blast furnace, Plant B, taking advantage of the availability of sintering plants, bought sinter-feed of ilmenite to produce self-sufficient in titanium sinter. Thus, this plant could research, design and produce a self-sufficient in titanium sinter, with sufficient strength to not only be used with success in your blast furnaces, but also strong enough to be stored.
The consumption profile, indicated by the acquisitions in 2006 shows that the Plant B certainly succeeded in producing a self-sufficient in titanium sinter using sinter-feed of Titânio Goiás.

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The graphs in Figures 13 and 14 illustrate the clear preference for sinter-feed, a fact not only characterized by the relative quantities (between lump and sinter-feed), but also by the characteristics of the programming of the orders of sinter-feed (frequency of orders).

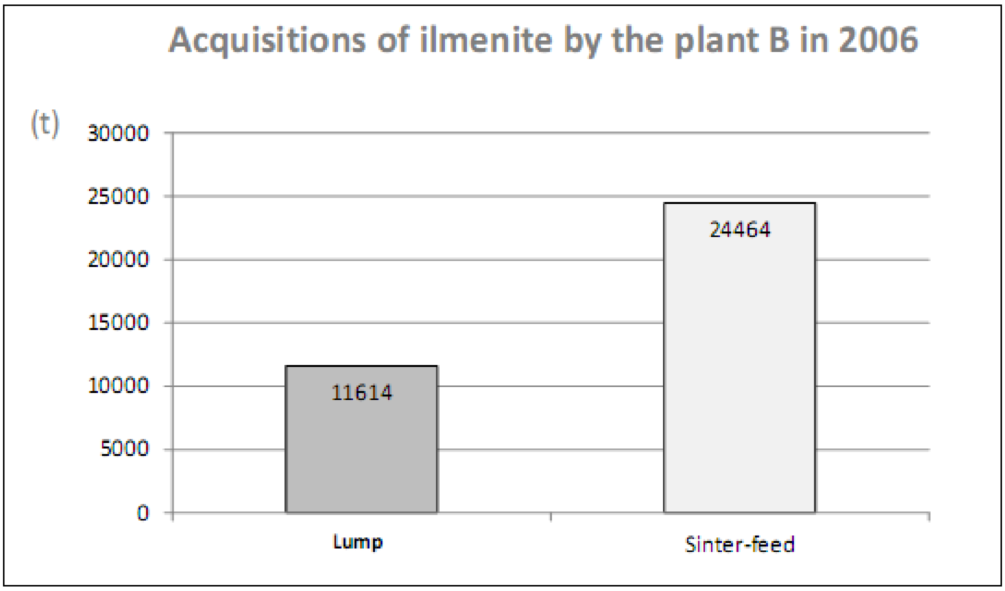

Figure 13: Purchases of ilmenite by Plant B, indicating a preference for sinter feed.

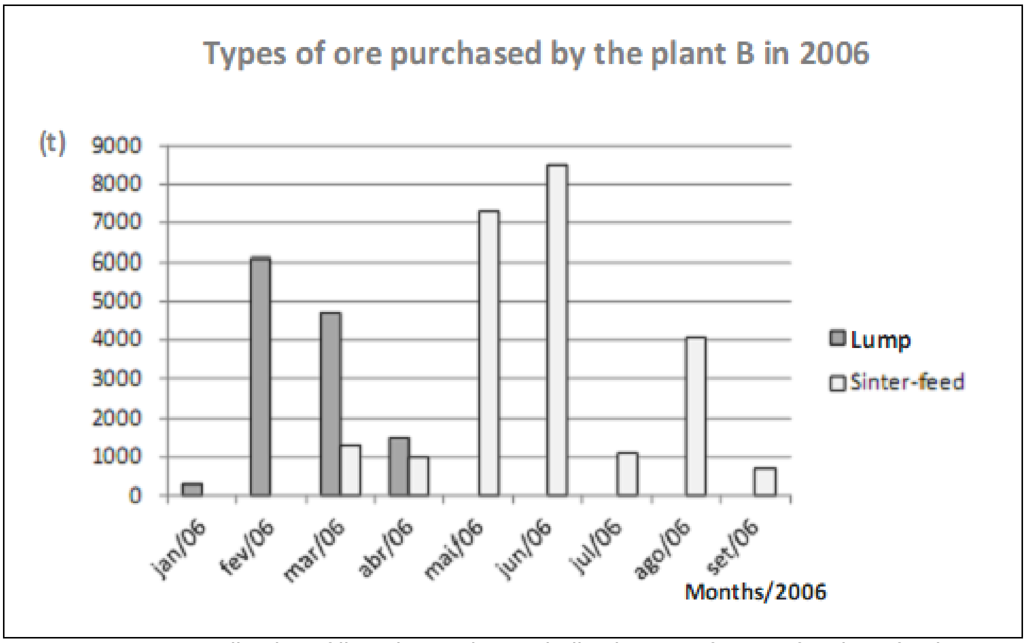

Figure 14: Deliveries of ilmenite to Plant B, indicating a preference for sinter feed.

9 CONSUMPTION OF MAJOR CLIENTS SINCE 1998

Since 1998, the Titanium Goiás started supplying of ilmenite to most Brazilian steel plants and one outside the country. Table 02 shows the supplies made by Titanium Goiás, in the period from 1998 to 2011 for various clients.

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Table 2: Supplies of ilmenite for titanium Goiás in the period 1998 to 2011

Supply of ilmenite by Titânio Goiás (in t)					
Year	Plant A	Plant B	Plant C	Plant D	Plant E
1998	1.624				
1999	1.698	92.335	12.555		
2000	11.925	76.621	18.990		
2001					
2002	22.560		10.096	23.193	
2003	8.747		12.794	9906	12.376
2004			27.471		38.916
2005			33.824	9840	2.618
2006	19.003	36.078	15.791	2850	
2007	25.965				
2008	1.868	14.995		4680	
2009					
2010		20.016			
2011		9.097			
Total	93.390	249.142	131.521	50.469	53.910

10 MYTHS ABOUT THE USE OF ILMENITE

In these decades, the Titanium Goiás has acquired a great experience, analyzing the behavior of their customers. Although have no direct access to results, some conclusions could be drawn from information obtained of techno-commercial relationship with their customers. Thus, we have listed below some concerns with respect to our customers and our products. Our experience has shown that, in most cases, results in loss of opportunity for capital gains.

10.1 Myth nº 1: "That the Ilmenite is an Expensive Raw Material"

This statement is not true because the ilmenite is used at very low rates compared with other materials and it also replaces part of the iron ore in the load. This double feature - low power and substitutability - makes of the ilmenite the load cheaper of the blast furnace. We must remember that the function of ilmenite is to protect the hearth. The content of 50% iron is an extra advantage that should be considered in the economic balance. Table 3 illustrates the actual specific cost of ilmenite, when replaces partially the pellet.

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Table 3: Evaluation of the real cost of ilmenite of Titânio Goiás

Raw Material	% Fe	Consumption (t / t pig iron)	Participation in load ore	Unit cost (R$/t)	Participation in the cost (R$/ t pig)
Ilmenite	50	+ 0,025	+ 1,5 %	370 (*)	+ 9,25
Pellets	67	- 0,019	- 1,1 %	370 (**)	- 7,03
Variation	-	-	+ 0,4%	-	+ 2,22

(*) Ex-work = R$ 260/ t + Freight = R$110/t (**) Ex-work = R$ 310/ t + Freight = R$ 60/ t

Analyzing the Table 3, we can see that all ilmenite replaces only a small and insignificant portion of the pellets, but this substitution is sufficient to reduce the price of ilmenite in approximately 76%. Then, in the example shown in the table, the real unit cost of ilmenite would be only 24% of the price, ie R$ 370 x 0.24 = R $ 88.80/t, which, effectively, will be paying the protection of the hearth.

10.2 Myth N^o 2: "That the Ilmenite in the Load Causes an Increase of the Fuel-Rate and Operational Difficulties"

As already mentioned, the Plant B, operating with large amounts of ilmenite in the load (TiO_2 ranging from 15 to over 20 kg / t pig iron) during the year 2000, the last year of his campaign, reached historical records of fuel-rate and productivity.
The Plant A also bears witness that such a statement is inconsistent with reality. For over 15 years, its blast furnaces operated with ilmenite in charge, achieving the best operating results in Brazil.

10.3 Myth N^o 3: "That the Ilmenite in Large Quantities in the Load Affects the Slag Causing Complaints from Cement Plants"

During the two years that the Plant B operated with high rates of ilmenite in the load of your furnace, reaching values of up to 20 kg/ t pig iron, there was not one complaint of cement factories.

10.4 Myth N^o 4: "That the Ilmenite can not be Used as Sinter-Feed"

It is important to mention that the ilmenite of Titânio Goiás is a magnetite (an iron ore). It is different from the TiO_2 sand-rich targets experiments unsuccessful in sintering process. As already shown, the Plant B, in 2006, acquired a large amount of sinter-feed, superior even to the amount of lump, which in itself indicates that succeeded in producing sinter self-sufficient in titanium.
The acquisition of sinter-feed for seven consecutive months and the option for sinter-feed in place of the lump are clear indications that the Plant B was successful in producing a self-sufficient in Ti sinter, and strong enough to be stored, as the amount purchased was much greater than necessary for use in the single blast furnace that was operating at period in which the sintering plants were idle.

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10.5 Myth Nº 5: "That the Ilmenite can be Injected Into the Tuyeres in Order to Protect the Crucible"

The graph in figure 17 shows the average content of Ti in the pig iron, recorded from samples of running in 72 hours of operation in three completely different situations in a blast furnace of a Brazilian plant. In one, Ti is not being introduced into the process. It is the baseline. The other two refer, respectively, in the introduction by injection tuyeres and the introduction by load (lump of ilmenite).

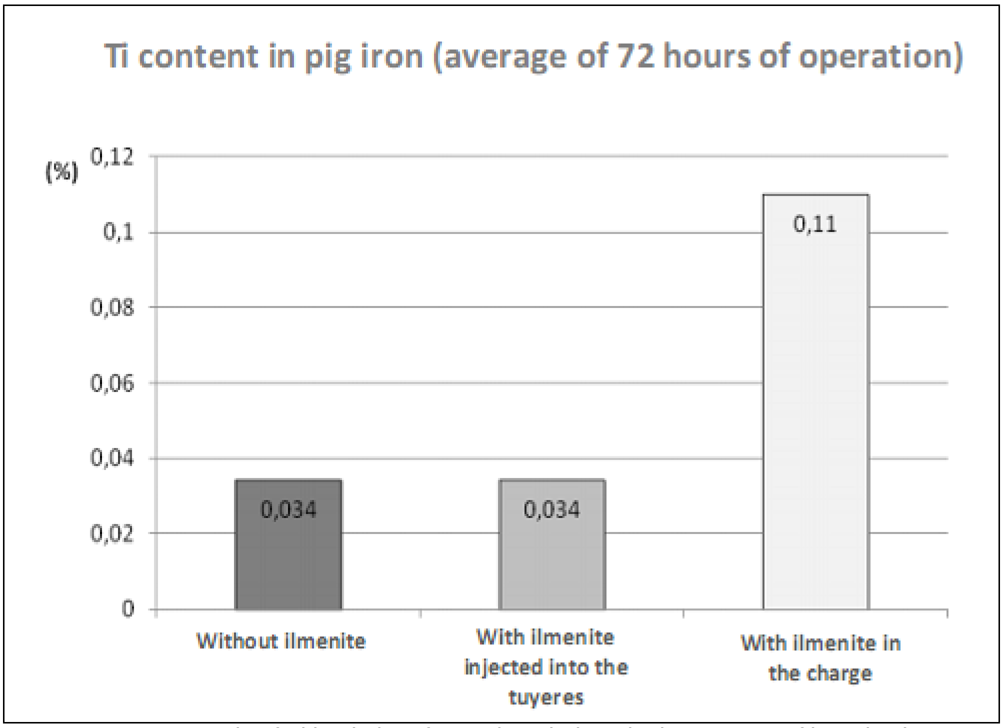

Figure 17: Levels of Ti in pig iron for each technique in the process of introduction.

It is clearly seen that there is no difference between the baseline (without Ti) and corresponding to the tuyere injections. Moreover, Ti loaded at a rate of 5 to 10 kg of TiO_2 / t pig iron resulted in a content which corresponds to three times the values observed in the other two. As seen in figure 7, is required content of Ti in iron above the solubility curve in the range of casting temperatures so that a portion of the Ti-CN stay in the blast furnace and do not leave during the runnings. If the Ti content is below the curve, all the Ti contained in the pig iron exits the furnace during runnings. Mainly in blast furnaces that operate continuously open (no interval between runnings).

It should be noted also that the ilmenite, injected cold in the tuyeres and in much smaller quantity than is needed, has a specific gravity of about 4. Find it serious difficulties in developing the protection mechanism, since the iron has specific gravity of about 7.5. The trend is TiO_2 to be eliminated by slag. It is precisely for this reason that the average content of Ti pig during injections is presented near the Ti content while not introducing titanium in process.

Moreover, we have to consider that each tuyere injecting ilmenite represents a double pressure on the cost of energy, since it looses the opportunity to inject (even partially) a cheaper fuel (coal, for example), and ilmenite is injected cold and whose active ingredient (TiO2) is quite stable (requires a lot of energy to reduce Ti).

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11 CONCLUSION

Given the facts presented here, it is concluded that the use of the ilmenite of Titânio Goiás was effective to protect the hearth of several blast furnaces. The study showed that the advantages in the use of ilmenite in charge are numerous and not always are all considered when deciding to discontinue use as soon as the blast furnace to recover. One of these advantages, for example, is an extension of the protective effects in the channels, torpedoes and ladles. The efficiency factor of the technique of inserting titanium by ilmenite loaded by the blast furnace has its heart in the fact that the protective effects are expected to be achieved with a very low consumption of raw materials and because of its ability to partially replace another iron ore loaded. Thus, the expected effect is achieved with few side effects.
This lets you use the ilmenite as a regular load, following the example of Plant A in past periods, especially nowadays, when yields are rising increasingly.

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