THE PRODUCTION OF STEELS APPLYING 100% DRI FOR NITROGEN REMOVAL

The Experience of ArcelorMittal Lázaro Cardenas Flat Carbon

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INTRODUCTION

In 1994, the electric steelmaking shop of ArcelorMittal Lázaro Cardenas Flat Carbon began using 100% DRI for some heats. Since then, it has become the normal practice. The main variables of DRI steelmaking, degree of metallization, carbon content, gangue content (especially acid gangue; $SiO_2 + Al_2O_3$) have been studied and evaluated extensively at AMLC-FC through the years. This analysis has allowed AMLC-FC to determine the most cost effective methods throughout the value chain of steel production. Each variable has a special impact in the final cost of the steel produced.

Usage of 100% DRI has been a very important tool for the production of clean steels, with very low tramp elements (Cu+Ni+Cr+Sn = 0.05%), as well as the production of steel with low nitrogen content (< 25 ppm at meltdown and 40 ppm in final product) for the API X steel grades. Table I shows the nitrogen requirements for some steel grades.

TABLE I *Nitrogen Requirements for Steel Applications*

Application	NItrogen Requirement (ppm)
Reinforcing Bar	120
Forging Grades	80
Cold Heading Quality	80
Low Carbon Wire	60
SBQ Wire	50
Hot Band (Commercial)	60
Hot Band (High Quality)	40
Deep Drawing for Automotive Parts	20
API X Steel Grades for Sour Gas Application	45

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Nitrogen control of steel grades produced in BOFs and in EAFs has been extensively studied, establishing a better understanding of the metallurgical basis. Table II indicates typical levels of nitrogen content, according to steelmaking method. In recent recent years, high carbon levels in DRI have been studied as a means of to CO evolution to remove nitrogen from the steel.

TABLE II *Nitrogen content for several technological routes for steel production.*

Process	Nitrogen Content at Steel Tap
EAF (Scrap Processed)	60-100 ppm
BOF	30 ppm
EAF with 100% DRI and 2.40% C	25 ppm
EAF with 100% DRI and 2.70% C	15 ppm

Since 2000, several trials were conducted melting DRI with differing %C (2.00- 2.20-2.40- 2.60 and 2.90%). These trials provided evidence that the high carbon in the DRI could decrease the nitrogen content in the steel. As these trials were carried out, the main goal was to increase the %C in the DRI in order to decrease the energy consumption in the EAF. The results obtained were in excellent agreement with the calculated expectations. Besides the benefit of decreasing the energy consumption, another important improvement was observed, namely the fact that the nitrogen content at meltdown was lower as the %C increased in the DRI. At that time, the main idea was to prove that the high %C in the DRI can be important to decrease the energy consumption of the EAF by means of increasing oxygen injection (the oxidation of carbon representing an important energy contribution). However, during these trials, the final nitrogen was very low when DRI with 2.90 %C was applied. The results showed the final nitrogen content at meltdown with this carbon content in the DRI was 7-12 ppm. The next charts show these results.

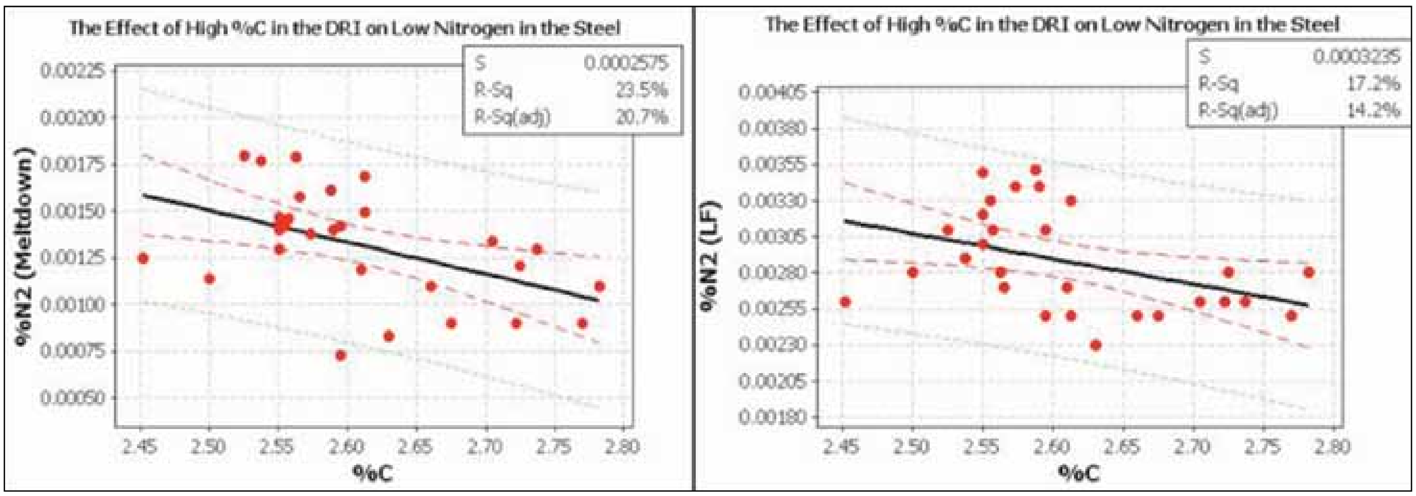

FIGURE 1 *Effect of High %C on the Nitrogen content at meltdown and at the Ladle Furnace.*

In previous research, Goldstein and Fruehan established the mechanism for nitrogen removal by applying large proportions of DRI. They established that nitrogen removal was possible due to the CO evolution by the carbon oxidation, and additionally that by applying big proportions of DRI, low nitrogen levels are possible via dilution. The observations indicate that the CO from DRI is evolved rapidly while the pellet remains buoyant in the slag phase. The rate of CO evolution from DRI at steelmaking temperatures is fast, controlled by heat transfer, and occurs at relatively low temperatures ranging between 800°C to 1200°C.

In the electric steelmaking shop at ArcelorMittal Lázaro Cardenas Flat Carbon, the normal practice is to feed 100% DRI for the production of steels that require low residual elements and low nitrogen content. A hot heel practice is always used. Prior to Power On, 5000 kg of DRI together with 1,000 kg of coke are fed onto the 50-60 ton of the hot heel that remains from the previous heat. Immediately a vigorous foaming slag formation takes place and allows the pre-deoxidation of the metal bath and decreases the %FeO in the slag. This practice is mandatory because 30 seconds after the Power On, the EAF reaches its highest active power (135 MW). The CO formation continues through all the heat because the DRI is fed to the EAF by continuous charging at a rate of 4500-5000 kg/minute. The %C in the DRI is 2.70%, therefore the carbon contribution by the DRI per minute is 135 kg.

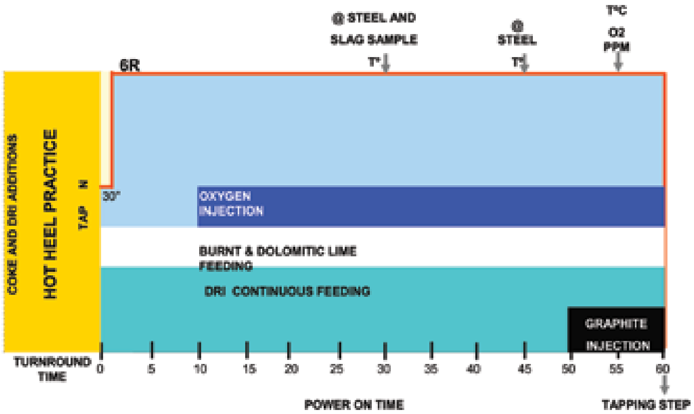

FIGURE 2 *Melting pattern used for 100% DRI melting.*

With this technology, there are several reactions responsible for the CO formation through the heat. They were explained by R. Morales in a previous document.

The first reaction takes place at the slag-metal interface during the addition of DRI and coke onto the hot heel in order to carry out the metal bath pre-deoxidation.

C + (FeO) = CO + Fe (1)

When the oxygen injection begins, there is a direct reaction between the gaseous oxygen and the carbon in the metal bath, taking place at the gas-metal interface.

$C + 1/2\ O_2 = CO$ (2)

The decarburization of the metallic charge promotes FeO formation. Lowering carbon level in the bath raises oxygen levels and vice versa. The next reaction is generated by the reduction of iron oxide by the carbon in the slag at the carbon-slag interface.

(FeO) + C = Fe + CO (3)

And, there are two reactions which consume CO. The first is reduction of iron oxide at the surface of a CO bubble, shown as Reaction (4). This can be controlled by an intermediate reaction which is shown as Reaction (5). Reactions (4) and (5) occur at the slag-gas and carbon-gas interfaces, respectively.

$(FeO) + CO = Fe + CO_2$ (4)
$CO_2 + C = 2CO$ (5)

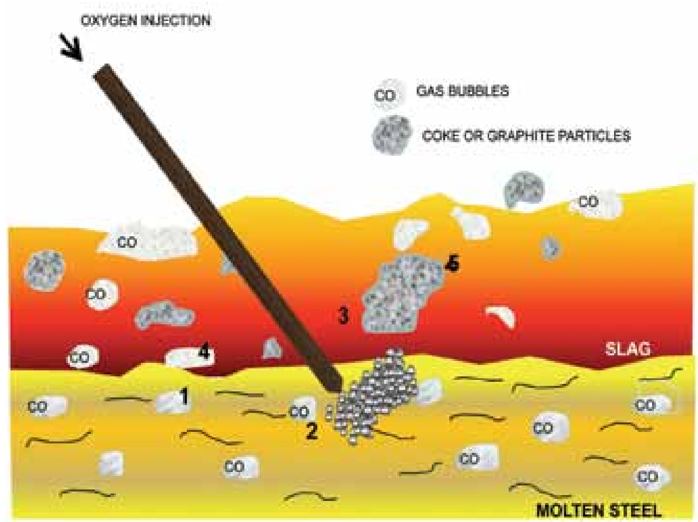

FIGURE 3 *Schematic representation of the chemical reactions that take place during slag foaming practice in the EAF. (Numbers in the figure refer to the chemical reactions described in the text.)*

All of the reactions promoting CO formation are important. They help avoid nitrogen pick up form the air. By means of continuous slag flushing, the dissolved gases collected in the slag are removed. DRI containing high carbon is the key to maintenance of proper slag foaming by means of CO evolution thoughout the heat.

NITROGEN CONTENT IN THE EAF RAW MATERIALS

In steels produced in an EAF, nitrogen comes from two main sources:

- From the scrap (mainly from purchased scraps)
- By air infiltration into the EAF

To assure low nitrogen content of the steel and to avoid sudden changes in nitrogen from the raw materials, all raw material inputs to steelmaking were sampled and analyzed. Results of these analyses are shown in Table III. (following page)

Based upon this analysis, care is taken to minimize addition of any materials that might represent an important nitrogen contribution.

TABLE III *Nitrogen Content in Raw Materials for Steelmaking*

Materials	ppm
Shredded Scrap	100
Internal Scrap	50
DRI	20
Coke	9000
Anthracite	10000
Graphite for Injection	13000
FeSi	320
SiMn	85
FeNb	270
FeMn LC	710
FeMn HC	140
FeMn Electrolytic (flakes)	45
CaF_2	3060
Fluxes	450

NITROGEN CONTROL DURING EAF STEELMAKING

To assure lowest nitrogen at meltdown, normal melting practice is to use 100% DRI, avoiding usage of purchased scrap. (In the AMLC EAF steelmaking shop only shredded scrap is used.) Also, coke addition at the beginning of the heat is controlled and graphite injection is completely avoided. When DRI with high carbon (>2.5%) is used, the CO formation is sufficient throughout the heat without any need for carbonaceous materials for foaming the slag.

As previously mentioned, a hot heel practice is implemented on 100% of the heats. Vigorous CO formation begins even before Power On of the EAF, minimizing nitrogen absorption of the steel. The CO bubbles adsorb nitrogen as they ascend to the surface, releasing the gases to the atmosphere. This CO formation helps to protect the metal bath from air infiltration, providing a barrier between the steel and the atmosphere.

EAF Closed Door Practice

This practice is very important to avoid nitrogen absorption from the atmosphere. At AMLC the only time the door is opened is after the 'peak' hour. Due to energy restrictions the steel shop works 22 hours per day, Monday-Friday. As stated earlier, never again, for the next 22 hours, is the EAF door opened. After tapping, coke and DRI are added to the hot heel to pre-deoxidize it. Then the DRI addition begins via continuous feed; 250 tons per heat. Maintenance of the bench of the working door is essential to keep the door closed as much as possible and to retain a sufficient slag volume.

EAF Tapping

Steel grades produced require high manganese (1.6% Mn). Therefore, addition of FeMn is mandatory. Table III shows the nitrogen composition of different FeMn alloys. Addition of 100 kg of Low Carbon FeMn increases steel nitrogen by about 5 ppm. FeMn electrolytic (flakes), normally used because of their low nitrogen content, increase the cost of the steel. High Carbon FeMn has low nitrogen content, but its addition will often over-carburize the steel. Charge mix selection is crucial to minimize nitrogen content and minimize costs.

Vacuum Degassing

100% of steel grades with nitrogen restrictions receive vacuum degassing treatment to achieve the lowest sulfur and to lower nitrogen. API X steel grades require 0.0024% S max and 45 ppm of nitrogen max. 100% DRI helps to tap the heats with low sulfur content (0.014%).

Vacuum Degassing

Special care must be taken during argon bubbling. An excessive flow rate causes an "eye" to form in the metal bath. This will promote nitrogen absorption from the atmosphere. Additionally, CaF_2 consumption must be minimized due to high nitrogen content. The Power On time must also be adjusted to avoid nitrogen dissociation. Addition of fluxes, carbon and manganese are minimized in order to avoid their nitrogen contributions.

Continuous Casting

Special care must be taken with the mechanism of the slide gate (ladle to tundish) to avoid infiltration of air. Argon bubbling for sealing in the long nozzle and SEN must be proper. An excessive argon flow will promote reoxidation of the steel and nitrogen pick up.

RESULTS

Melting 100% DRI with high %C (>2.5%) has allowed the production of steel grades demanding low nitrogen content. At present AMLC produces 1.4 million tons per year of API X grades, about 35% of its total output. In addition to using 100% DRI with high carbon, raw material selection is very important to assure low nitrogen content.

Figure 4 shows the results obtained regarding Nitrogen versus the carbon content of the DRI.

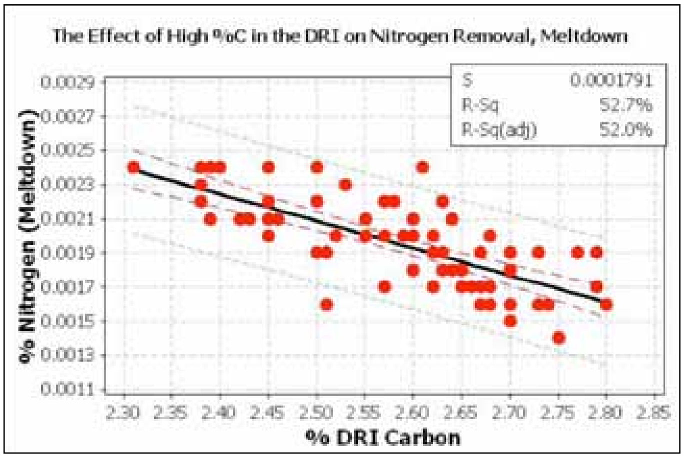

FIGURE 4 *The Effect of %C on nitrogen (100% DRI)*

API X grades require very low %S (0.0024% max). Usage of 100% DRI and proper selection of raw materials are extremely important, not only to avoid nitrogen content but also to avoid sulfur. All of these steels receive treatment at the vacuum degassing station. The effectiveness of nitrogen removal in the vacuum degasser depends on the sulfur level since sulfur is a surface active element. Once the first stage is concluded successfully, the next stage is to respect the fundamentals described during the vacuum degassing and ladle furnace treatment. Figure 5 shows the sulfur content in the different stages for steelmaking. It is important to see the sulfur removal in each process stage and the final %S in the steel.

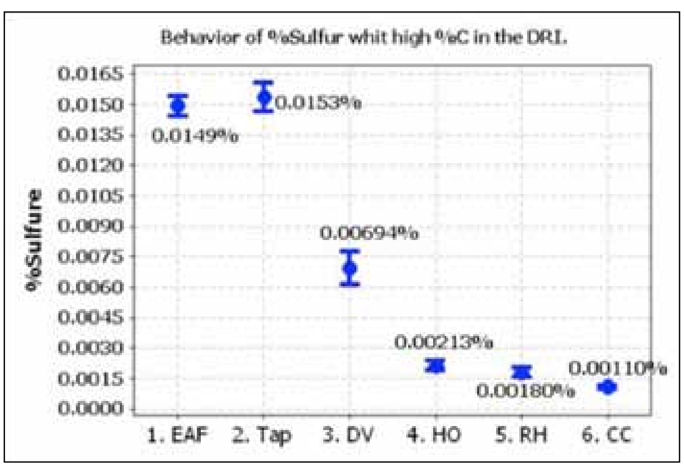

FIGURE 5 *Sulfur content in each process stage for steelmaking.*

To avoid nitrogen pick up in the ladle furnace, it is important to control the argon flow rate as well as to avoid fluxes (lime and CaF_2) and carbonaceous material additions. Power On time must also be controlled in order to avoid nitrogen dissociation. Figure 6 shows histograms of nitrogen content at EAF meltdown and at the end of the LF process. Figure 7 indicates the %S in the steel relative to the nitrogen obtained.

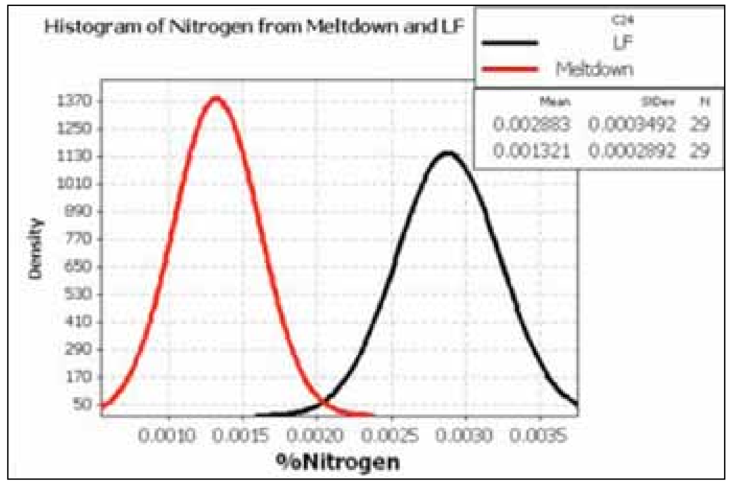

FIGURE 6 *Nitrogen content at EAF meltdown and at the end of the Ladle Furnace treatment*

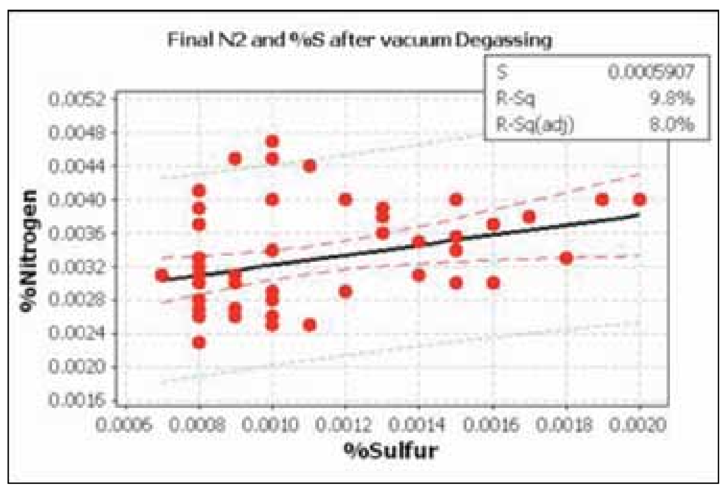

FIGURE 7 *Nitrogen and sulfur contents after vacuum degassing treatment using 100% DRI*

Nitrogen control for steelmaking is not easy unless the steelmaking shop has the proper equipment installed and the availability of low nitrogen raw materials. These are needed to control nitrogen from the beginning of the EAF process.

Figure 8 shows nitrogen content at each process stage.

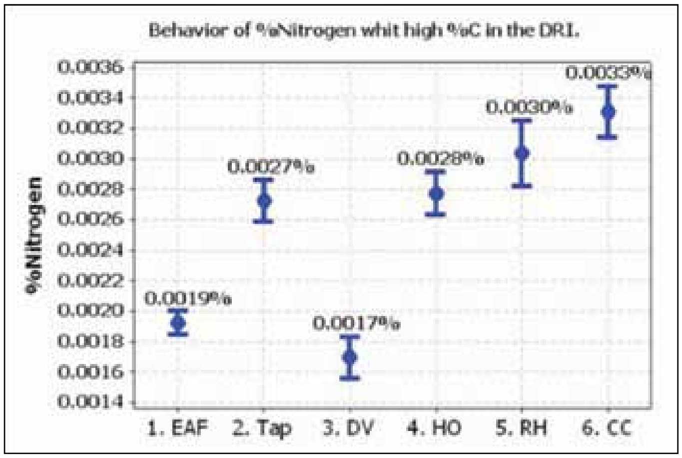

FIGURE 8 *Nitrogen behavior in each process stage (100% DRI)*

CONCLUSIONS

1. The usage of 100% DRI with high carbon (> 2.50%) is extremely important for the production of the steel grades that specify low nitrogen contents (< 45 ppm). Our experience allows us to produce 1.4 MT per year.

2. CO formation when DRI with high carbon (> 2.50%) is applied, promotes through all the heat vigorous CO formation. This CO formation helps to protect the metal bath from the air infiltration of the atmosphere providing a barrier between the steel and the atmosphere.

3. In 100% of the heats produced the hot heel practice is implemented. The vigorous CO formation takes place even before Power On of the EAF, preventing nitrogen absorption in the steel from this stage onward.

4. Proper selection of raw materials is very important in order to avoid sudden changes in the nitrogen content.

5. 100% of the steel grades with nitrogen restrictions receive VD treatment. Sulfur removal is extremely important in order to increase the efficiency of nitrogen removal in the VD process.

6. In continuous casting, argon bubbling for sealing the long nozzle and SEN must be appropriate. An excessive Air flow will promote the reoxidation of the steel and therefore cause an important nitrogen pick up.