BENEFITS FOR LD STEEL PLANT RESULTING FROM THE PARTIAL SUBSTITUTION OF MANGANESE BY SMALL ADDITIONS OF NIOBIUM*

Danilo Di Napoli Guzela[1]
Marcos A. Stuart Nogueira[2]
Antonio Augusto Gorni[3]
Marcelo Arantes Rebellato[4]

Abstract

Recent developments proved that it is possible to reduce manganese content by adding small amounts of niobium, keeping the same mechanical properties of structural steels plates. For low yield strength around 350 MPa, small additions of niobium like 0.010% are enough to maintain the same mechanical properties of the material even reducing 0.50% of manganese content. This results in reduction of the costs of alloying design, that must be analysed based on updated ferroalloy prices. This paper points the benefits that reductions of manganese content can bring to the steelmaker and to the quality of product. The reduction of manganese content results in less additions of FeMn, allowing to decrease the tapping temperature. This brings many benefits, e.g., regarding the consumption of refractories of LD furnace and ladle, the increase of metallic yield, the reduction of amount of aluminum as deoxidizer, of absorbed hydrogen and nitrogen, and of macro segregation. This paper presents a simulation that considered the reduction of Mn contents from 1.40% to 0.90% associated with the addition of 0.010% Nb, resulting on the reduction of 15ºC in tapping temperature, which brings savings of 8.6 kg/t of FeSiMn; 0.050 kg of ladle lining/t of liquid steel; increase of 0.75% in metallic yield; savings of 0.135 kg/ t of aluminum as deoxidizer; reduction of 13 ppm of phosphorous, of 1.6 ppm of hydrogen and 8.7 ppm of nitrogen.

Keywords: Niobium microalloyed structural steel; manganese; alloy design; secondary refining

1 *Metallurgical Engineer, Steelmaking and Continuous Casting Consultant, Santos, SP, Brazil.*
2 *M.Sc., Metallurgical Engineer, Steel Technology Consultant, São Paulo, SP, Brazil.*
3 *PhD, MSc, Materials Engineer, Hot Rolling Consultant, São Vicente, SP, Brazil.*
4 *Metallurgical Engineer, Consultant, RMS – Rolling Mill Solutions, São Paulo, SP, Brazil.*

1 INTRODUCTION

Since the beginning of its activities in Araxá, CBMM strives to provide technology to develop applications where niobium can increase the performance, the life cycle or reduce the costs of the components where it is applied. For this purpose, CBMM provides the technology that can help to overcome the main challenges worldwide: growing wisely and in a sustainable way. CBMM has a technical group acting together with steelmakers, research universities, institutes and end users. The company started a program for partial substitution of manganese by small additions of niobium in structural steels aiming to reduce the natural resources consumption by using the proper alloy design. The idea was based on the equivalence ratio of Mn and Nb contents for plates, developed by Morozov and presented at Figures 1 and 2 [1]. He and coauthors, studying low alloy steels, realized that there was a clear relation between manganese and niobium contents for the same mechanical properties (Figure 1). For low values of yield strength, 350 MPa, very small additions of niobium (0.010%) are enough to allow considerable reductions of manganese content (0.50%) (Figure 2).

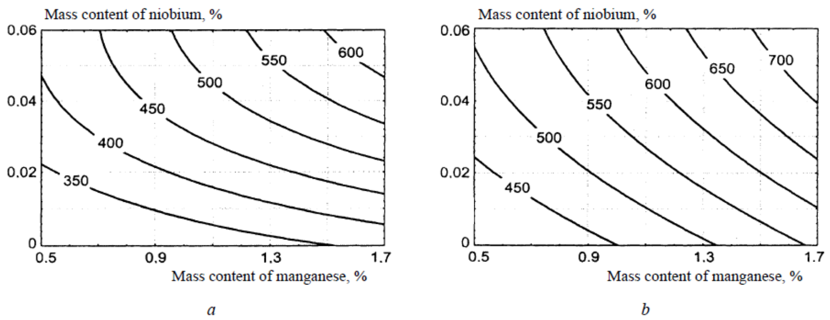


Figure 1. Relationship between manganese and niobium contents for the same values of yield strength (a) and tensile strength (b) for plates from 8 to 12 mm [1].

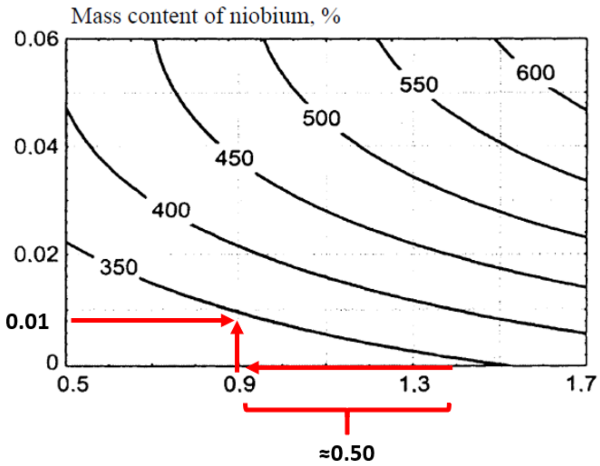


Figure 2. Example showing that a reduction of Mn content from 1.4 % to 0.9% can be compensated by adding 0.010% Nb, keeping 350 MPa of yield strength [1].

A significant cost reduction due to the decrease of manganese consumption has been enabled through the adoption of this concept [2,3]. The objective of this paper is to show the benefits the reduction of manganese contents can bring to the melting shop processes.

* *Technical contribution to the 51º Seminário de Fusão, Refino & Solidificação de Metais, part of the ABM Week 6th edition, June 7th-9th, 2022, São Paulo, SP, Brazil.*

2 EFFECT OF FERROALLOY ADDITION ON THE TEMPERATURE OF LIQUID STEEL IN THE LADLE

During and after the tapping of liquid steel from the LD furnace into the ladle, the temperature of the liquid steel is influenced by some factors, such as heat conduction through the refractory lining, radiation, convection losses to the environment (by the slag and metallic structure of the ladle) and alloy dissolution. Each alloy added causes different thermal effects when dissolved in steel, as they have different chill factors. The chill factors represent the thermal effect of each alloy on the temperature of the metal bath, when dissolution and oxidation reactions occur in the steel. The dissolution of silicon and aluminum in steel, for example, are exothermic, resulting in the heating of the metallic bath, unlike the dissolution of manganese alloys, which are endothermic, causing a decrease in temperature [4].
Steel grades with high Mn contents require high tapping temperatures from the LD furnace to the ladle to compensate for the thermal loss caused by the addition of Mn alloys (e.g., FeMnHC or FeSiMn). High tapping temperatures result in high material consumption and accelerate the damage of furnace lining; lengthen operation time and increase the cost of steelmaking. In addition, non-metallic inclusions in molten steel are more difficult to control, and finally affect the quality of the steel products. For structural flat products up to 355 MPa yield strength, large amounts of Mn ferroalloys need to be added to the liquid steel to reach the required Mn content. The reduction of the necessary additions of FeMn alloys will lead to a reduction in the LD furnace tapping temperatures. This temperature reduction will open the door to other opportunities to reduce the cost of steel production in the melt shop. Figure 3 shows the savings of FeMnHC addition due to the reduction of manganese content of the steel. Figure 4 shows the resulting reduction of tapping temperature of LD furnace. This will result in cost reductions of various KPIs of LD furnace process and equipment, as will be presented.

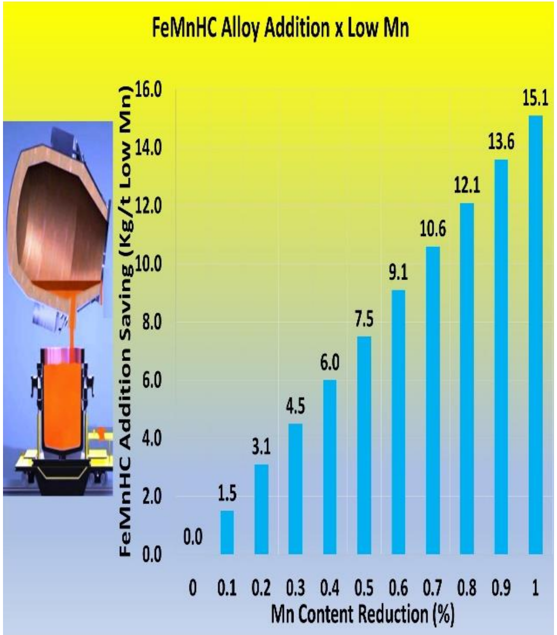


Figure 3. FeMn savings as function of lower Mn.

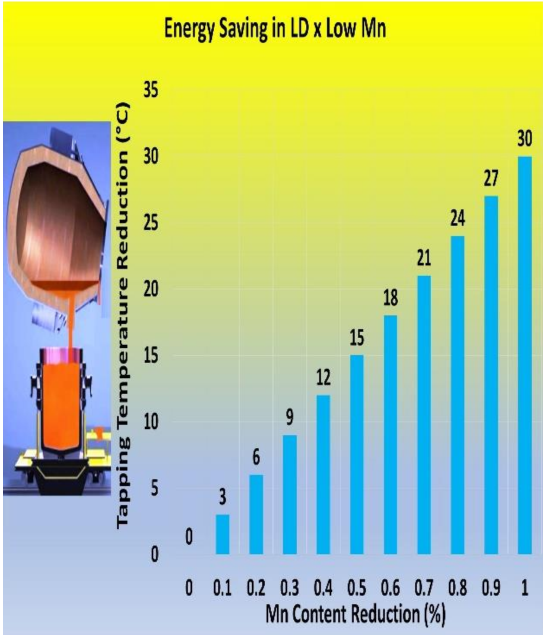


Figure 4. Energy saving in LD as function of lower Mn.

3 DEVELOPMENT

3.1 Effect of Mn content on LD furnace lining refractory life

3.1.1 LD furnace with “Slag Splashing” technology

Lining life is a technical and economic concern of oxygen steelmaking. An increase in lining life can not only decrease refractory consumption and reduce smelting cost, but it can also promote efficient production and increase steel yield. A technology known as “slag splashing” is a simple and effective method to increase the life span of LD furnace lining. The slag splashing was introduced in USA in 1993 and in China in 1995; it is now used for more than 95% of steel produced by the LD process in China. Slag splashing is the result of the interaction between a top blown gas jet (nitrogen generally) and liquid slag. The top blown gas jet impinges on the bath surface, producing a jet impact zone and making slag splash by a reflex force. Slag is splashed along the edge of the jet impact zone mostly (Figure 5) [5]. A slag coating on the furnace stays on the lining refractory. With enough know-how, up to 60,000 heats with one vessel lining have been realized. Slag splashing is directly associated with factors such as slag properties and amount, lance height and tapping temperature. Tapping temperatures tend to be higher in steels with high Mn content and in cases where there is a lack of secondary refining facilities to heat liquid steel (e.g., ladle furnace). During splashing, if the temperature of the liquid steel is too high, slag is not distributed uniformly and tends to build up in the bottom of the vessel. Figure 6 shows the effect of steel tapping temperature on refractory life [6]. Figure 7 shows the Mn content reduction on the potential reduction in LD refractory consumption by reducing the tapping temperature.

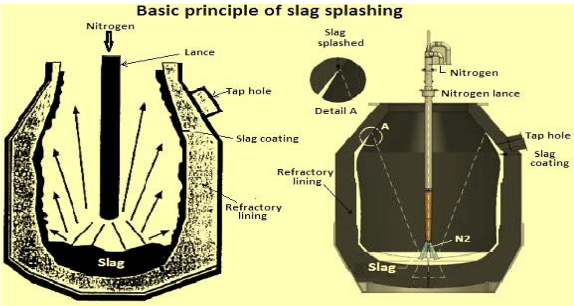


Figure 5. Basic principle of slag splashing [5].

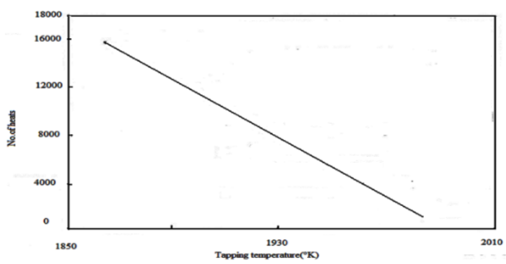


Figure 6. Effect of steel tapping temperature on refractory life [6].

3.1.1 LD furnace with “Gunning Repair” technology

A technique to extend the vessel lining service life is the gunning of pre-worn areas with special gunning mixes. Accurate gunning leads to a uniform lining wear rate and maximizes utilization of all refractory materials of the vessel. Accelerated wear is also experienced in the trunnion areas of any oxygen furnace, mainly because this area is the most difficult to coat with protective slag. Figure 8 illustrates one furnace campaign in which rapid trunnion wear was experienced in the first 500 heats [7]. Prolonged lining life, no doubt, increases the availability of the LD furnace, but extending its useful life using the gunning technique increases the cost of the refractory from 5000-6000 heats (Figure 9) [8]. The reduction of manganese content of the steel allows to reduce the tapping temperature. Consequently, the protection repair will have less damage due to the action of the liquid steel, increasing service life for the lining refractory (Figure 10).

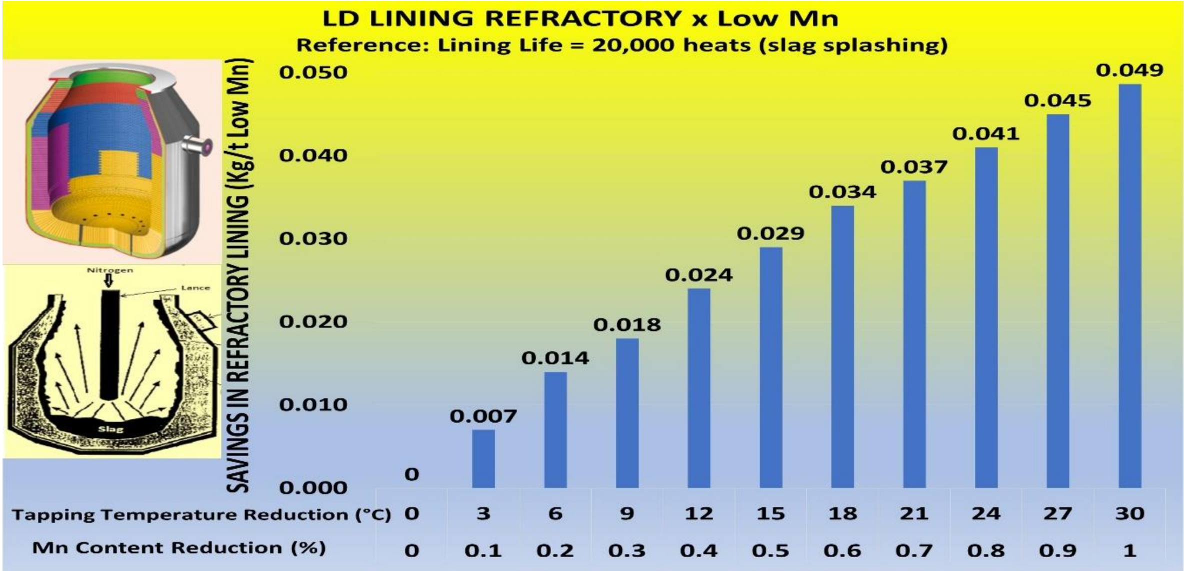
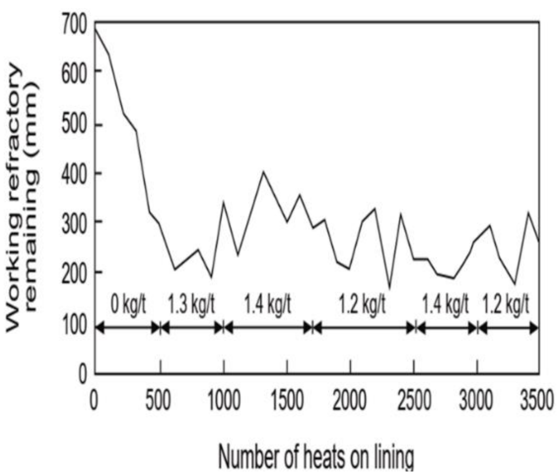


Figure 7. Refractory lining saving in LD furnace as function of Mn content reduction.



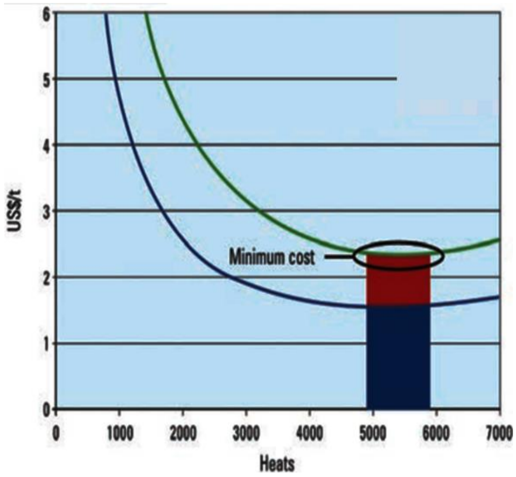


Figure 8. Wear and gunning rate in the trunnion area [7]. **Figure 9**. Optimum LD furnace cost as a function of the number of heats [8].

3.2 Steel ladle lining refractory life and low manganese

There are many variables that influence the life of the steel ladle lining refractory life just like occurs in the LD furnace. The tapping temperature is one of these variables, as shown in Figure 11 [9]. In this case, too, the adoption of Low Mn technology will lead to a reduction of refractory costs (Figure 12).

3.3 Metallic yield and low manganese

The index FeT (that is, *FeT= 0.8*% FeO*) in the slag represents the amount of iron that was oxidized during the blowing of oxygen in the LD furnace and that became part of slag [10]. Tapping temperature influences the FeT content, as shown in figure 13. The higher the FeT content in the slag, the lower will be the metallic yield, since a greater portion of iron was oxidized and migrated to the slag, rather than remaining in the liquid steel. The use of *lower tapping temperatures* should be aimed for increasing the metallic yield as well. The reduction of Mn on alloy design leads to the increase of metallic yield (Figure 14).

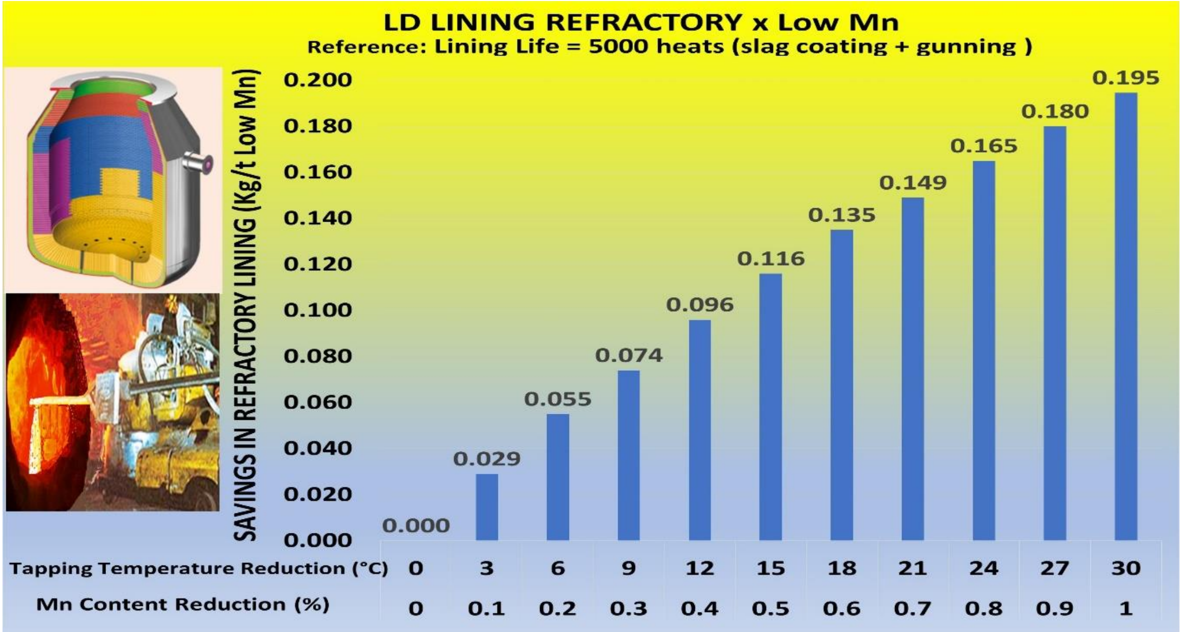


Figure 10. Refractory lining saving in LD furnace as function of Mn content reduction.

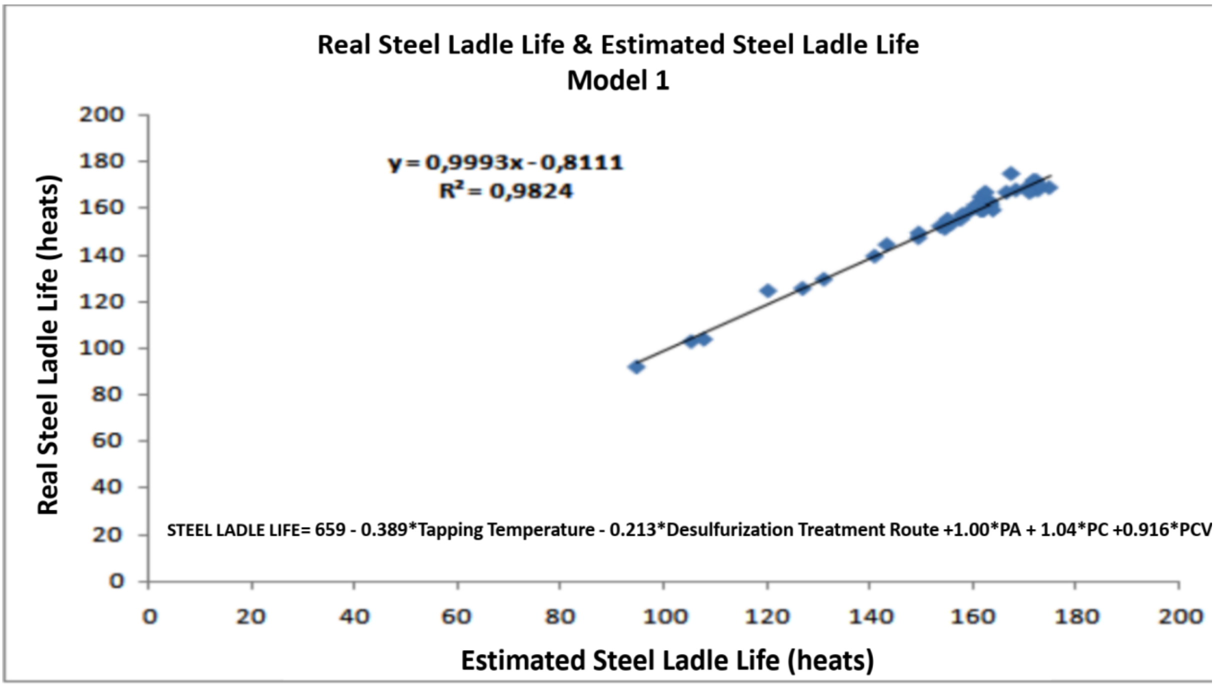


Figure 11. Tapping temperature influence on steel ladle lining refractory life [9].

3.4 Aluminum addition and low manganese

Temperature also influences the dissolved oxygen content of the steel, as shown in Figure 15 [11]. Higher tapping temperatures lead to higher dissolved oxygen contents in the metallic bath, increasing the need of aluminum to reduce its oxygen content. The decrease of Mn content allows to adopt lower tapping temperatures and so less aluminum is necessary (Figure 16).

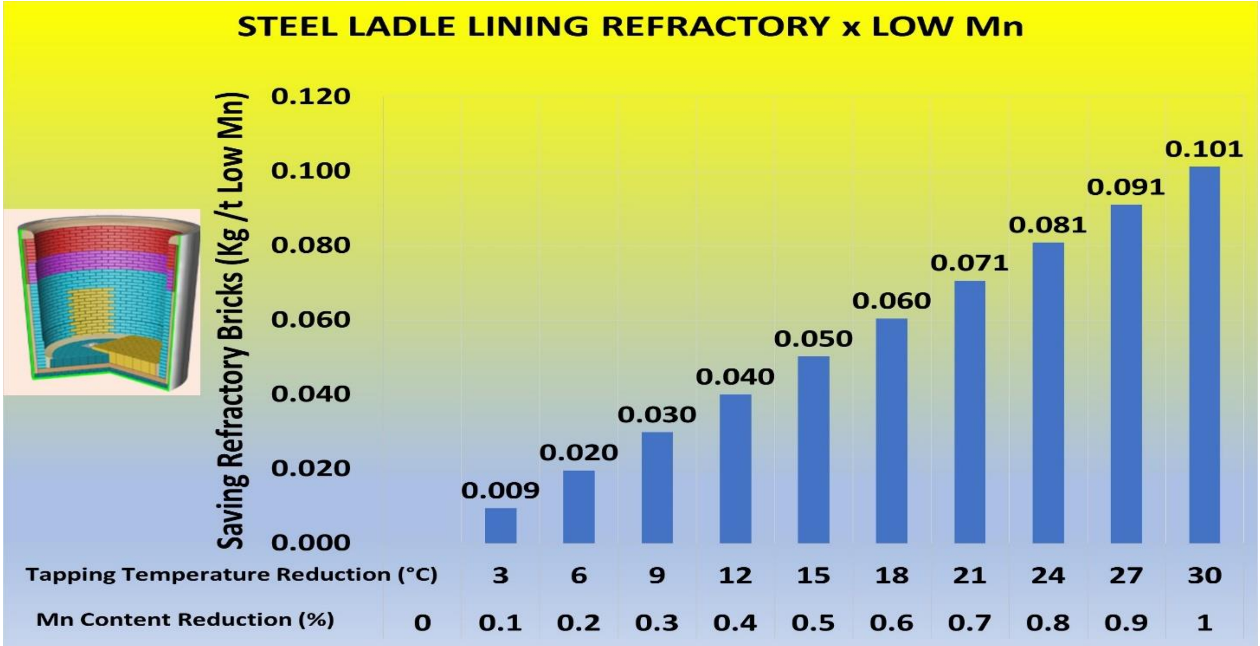


Figure 12. Refractory lining saving in steel ladle as function of Mn content reduction.

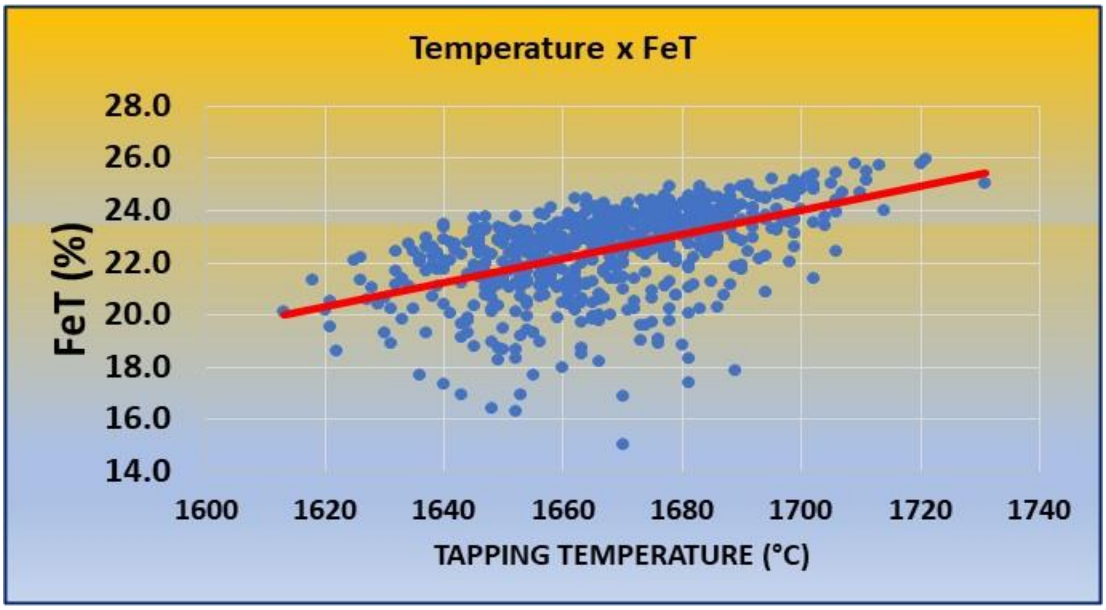


Figure 13. Tapping temperature influence on FeT in the slag.

3.5 Phosphorus content and low manganese

Dephosphorization of steels has become a very important metallurgical technique in steelmaking process to produce high quality steels. P content is controlled by the reactions in the LD furnace, mainly due to the composition of the slag and the temperature, as shown in Figure 17 [12]. Lower tapping temperatures means lower phosphorus contents in steel (Figure 18).

3.6 Hydrogen content and low manganese

The deleterious effect of hydrogen on steels is well known, especially in high grade steels where hydrogen induced cracks (HIC) can occur. Therefore, every effort should be made to avoid H pick up in steel. There are numerous sources of hydrogen in liquid steel, being ferroalloys an important source to be considered. The addition of some types of ferroalloys, in special, FeMn, causes incorporation of hydrogen in the liquid steel due to their hydrogen and moisture contents, as shown in Figure 19 [13]. Therefore, by reducing the addition of Mn ferroalloys, hydrogen content in steel can be decreased (Figure 20).

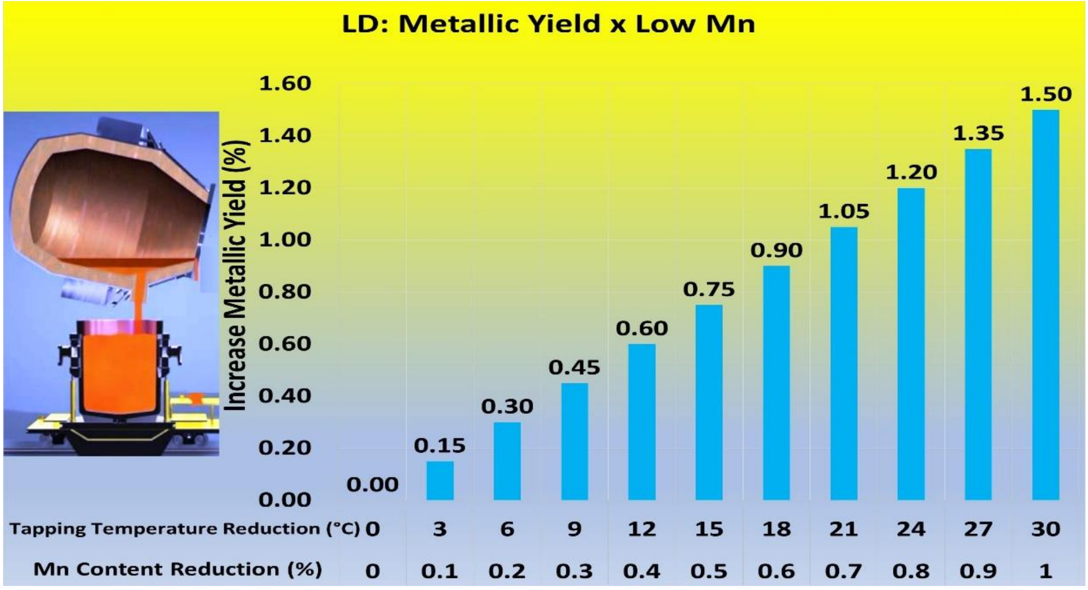


Figure 14. Increase in the LD furnace metallic yield as function of Mn content reduction.

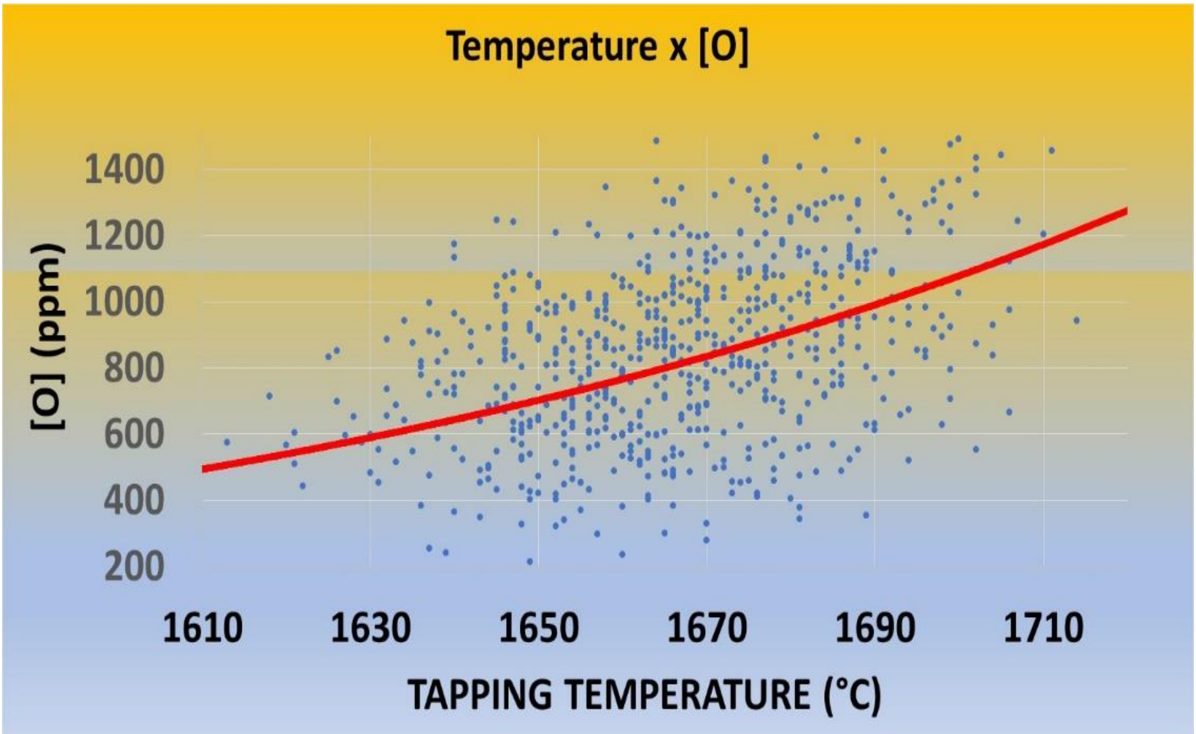


Figure 15. Tapping temperature influence on O content.

3.7 Nitrogen content and low manganese

Ferroalloys, particularly ferrovanadium, ferrochrome, and *ferromanganese*, are major sources of nitrogen that must be considered in any nitrogen control program. In the melting of low and medium carbon steels, these ferroalloys are added in the ladle and directly increase the nitrogen content of the steel. This pickup can be in the range of 10-20 ppm N, depending on the type and amount of ferroalloy added. Typical nitrogen analysis for ferroalloys, by manufacturing process, are shown in Table 1 [14]. Therefore, by reducing the addition of Mn alloys, N in steel will decrease (Figure 21).

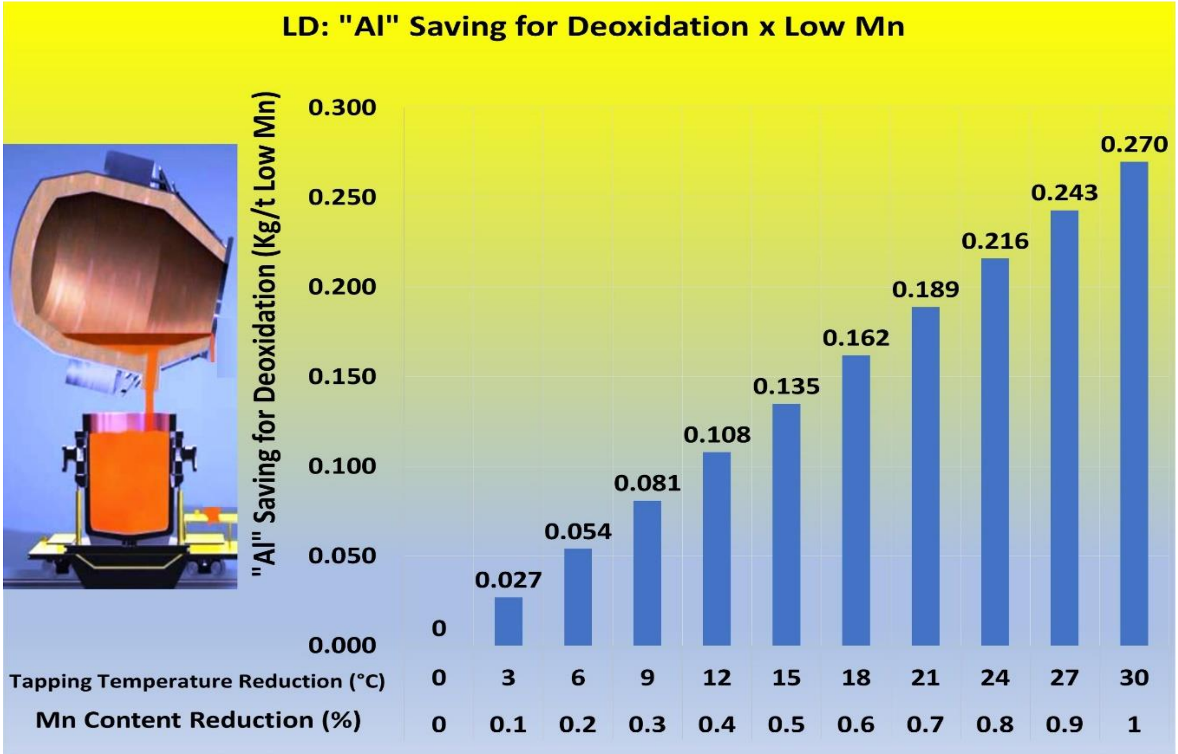


Figure 16. Decrease of the deoxidizer Al due to the reduction of tapping temperature at LD furnace.

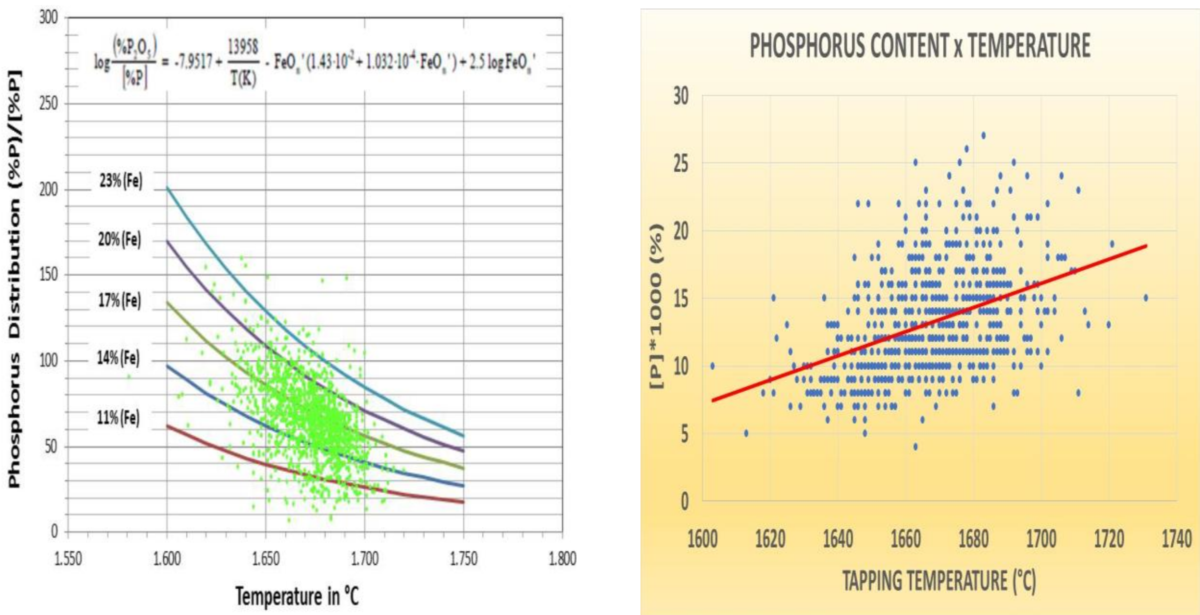


Figure 17. Tapping temperature influence on P contents [12].

3.8 Manganese segregation in continuous casting

High strength steels with high manganese content offer an exceptional balance of strength and ductility. However, the occurrence of segregation in these steels, particularly at the strand centerline, leads to quality control issues in slabs continuously cast. Moreover, segregation of manganese during the continuous casting process can lead to the formation of detrimental microstructural banding in subsequent manufacturing operations. The Figure 22 shows that Mn centerline segregation in the continuous casting slab grows exponentially with the increase in its content (red curve) (15). Reducing Mn content results on the reduction of centerline segregation, improving slab quality (Figure 23).

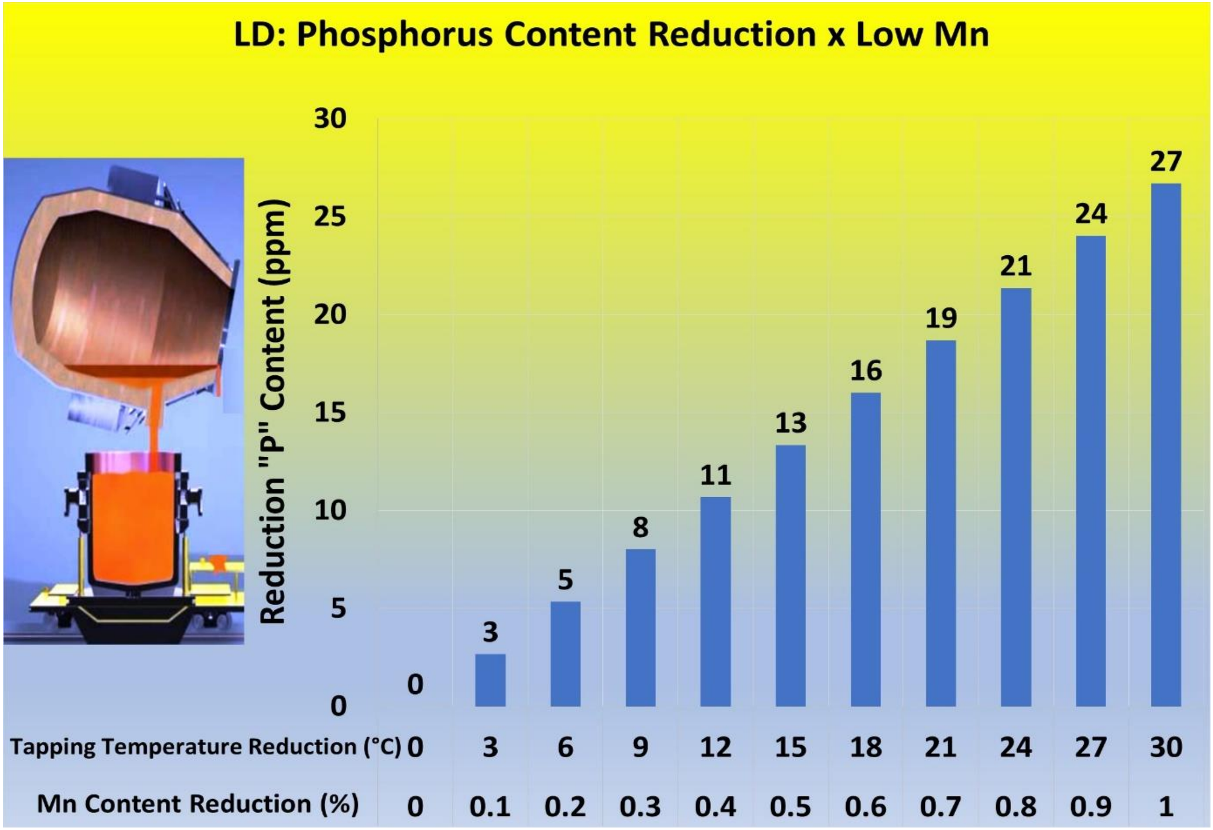


Figure 18. P content reduction as function of Mn content decrease.

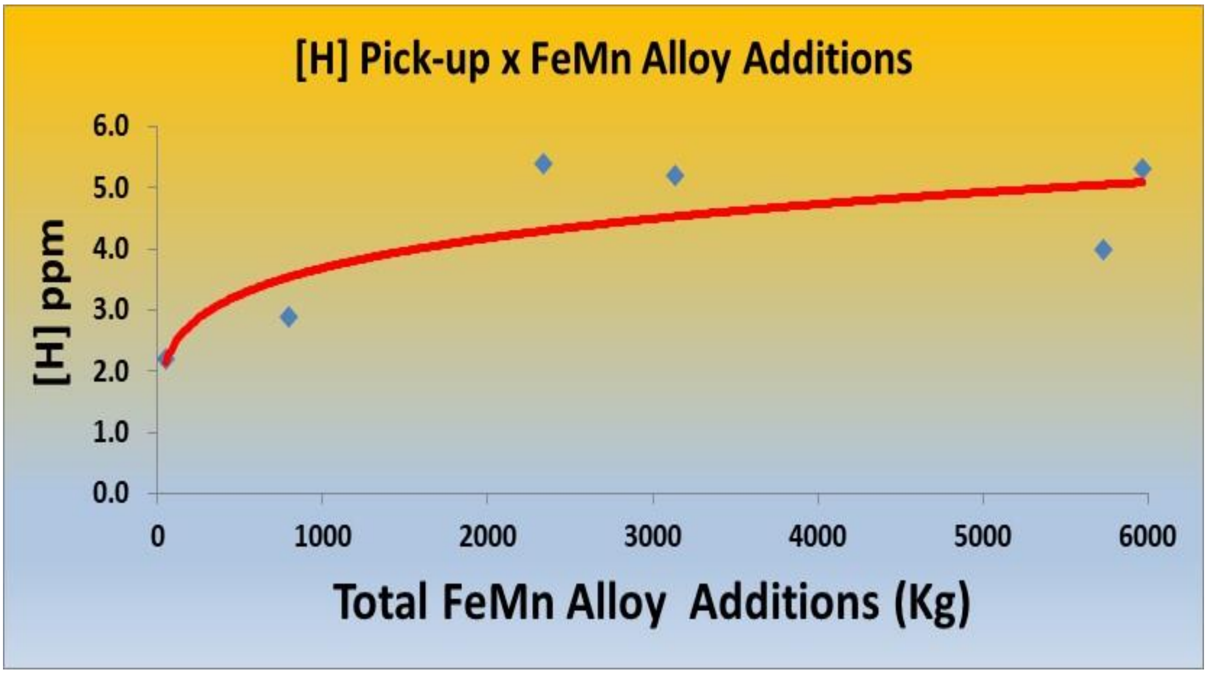


Figure 19. FeMn influence on H content [13].

* Technical contribution to the 51º Seminário de Fusão, Refino & Solidificação de Metais, part of the ABM Week 6th edition, June 7th-9th, 2022, São Paulo, SP, Brazil.

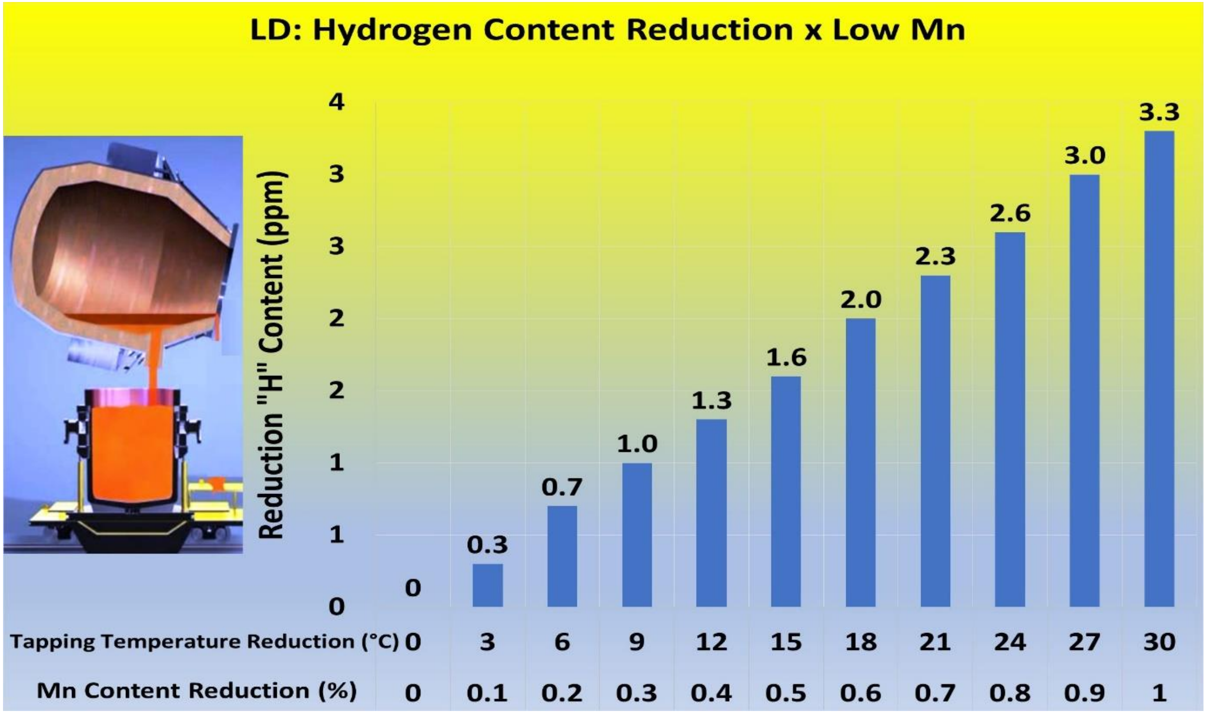


Figure 20. H content reduction (ppm) as function of Mn content decrease.

Table 1. Nitrogen content of various ferroalloys and processes [14].

Various Ferroalloys(Process)	N, ppm	Various Ferroalloys (Process)	N, ppm
Manganese (Electrolytic)	30-100	75 percent FeSi	70
Nickel (Electrolytic)	30	80 percent FeV (Aluminothermic)	200 max.
Cr (Electrolytic)	200-500	55 percent FeV (Silicothermic)	60 max.
Charge Cr	300-400	Ferromanganese (Blast Furnace)	200-500
Low C- FeCr (Silicothermic)	1 000	Ferromanganese (Silicothermic)	300-500
Raw aluminum	30	Ferromanganese (Aluminothermic)	600-800
95 percent recycled aluminum	5	FeMo	110
SiCa	310	FeTi	220
MnSi	190	FeW	10

4 EXAMPLE OF POTENTIAL GAINS WITH LOW MANGANESE TECHNOLOGY

Considering all these KPIs in a computer program one can get a summary of improvements that the reduction of Mn content from 1.40% to 0.90% with the addition of 0.010%Nb can bring for structural steel production (Table 2). This reduction of Mn allows the decrease the FeSiMn addition in 8.651 Kg/t, which implies in 15°C of tapping temperature reduction, which results on savings of 0.116 kg of LD furnace lining/t of produced steel (when applying the gunning technique), 0.050 kg of ladle lining/t of produced steel, increase of 0.75% of metallic yield and savings of 0.135 kg/ t of aluminum, as presented at Table 2.

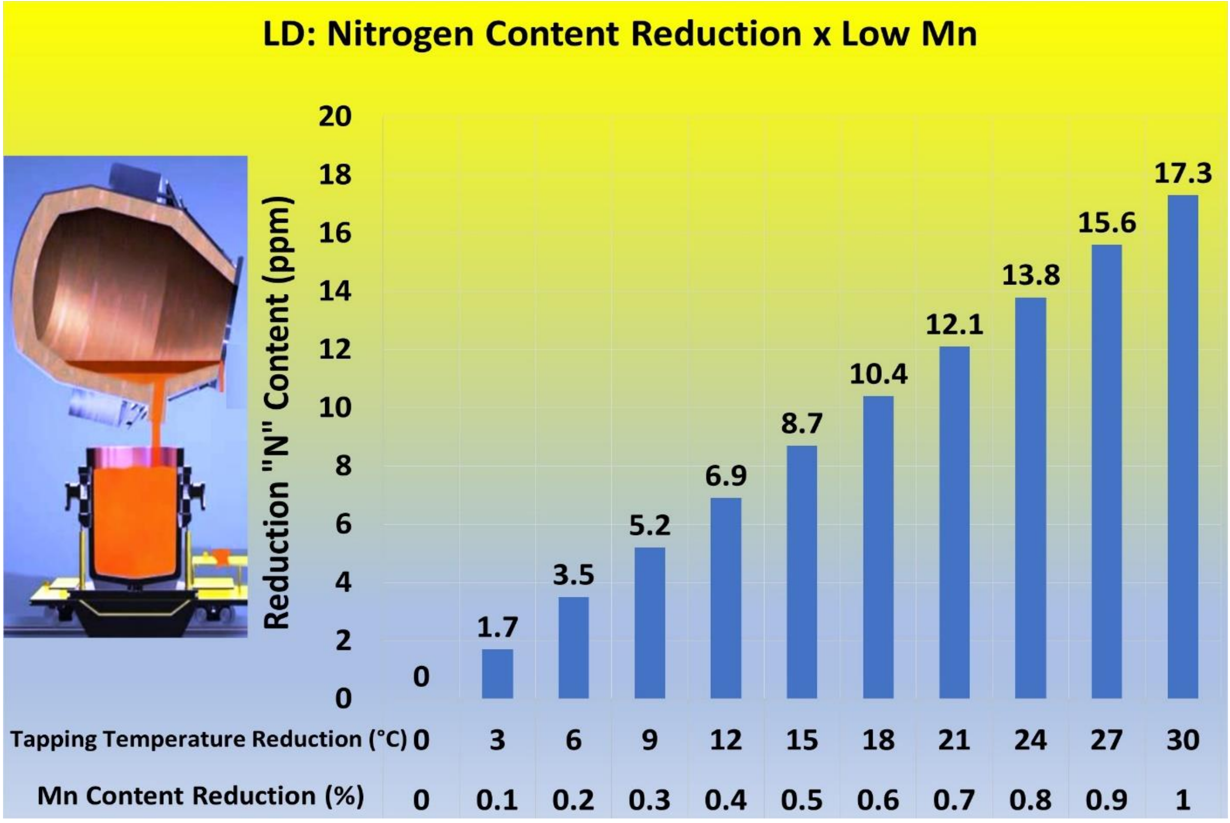


Figure 21. N content reduction (ppm) as function of Mn content decrease.

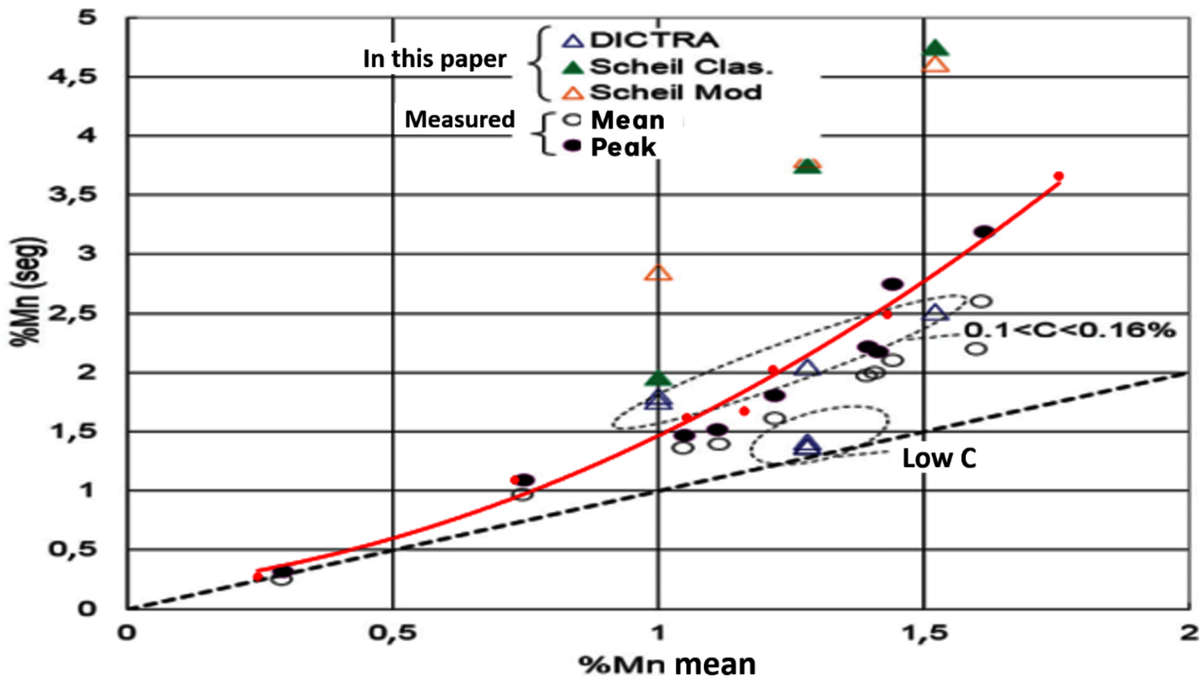


Figure 22. Segregated Mn content during continuous casting as a function of its nominal content [15].

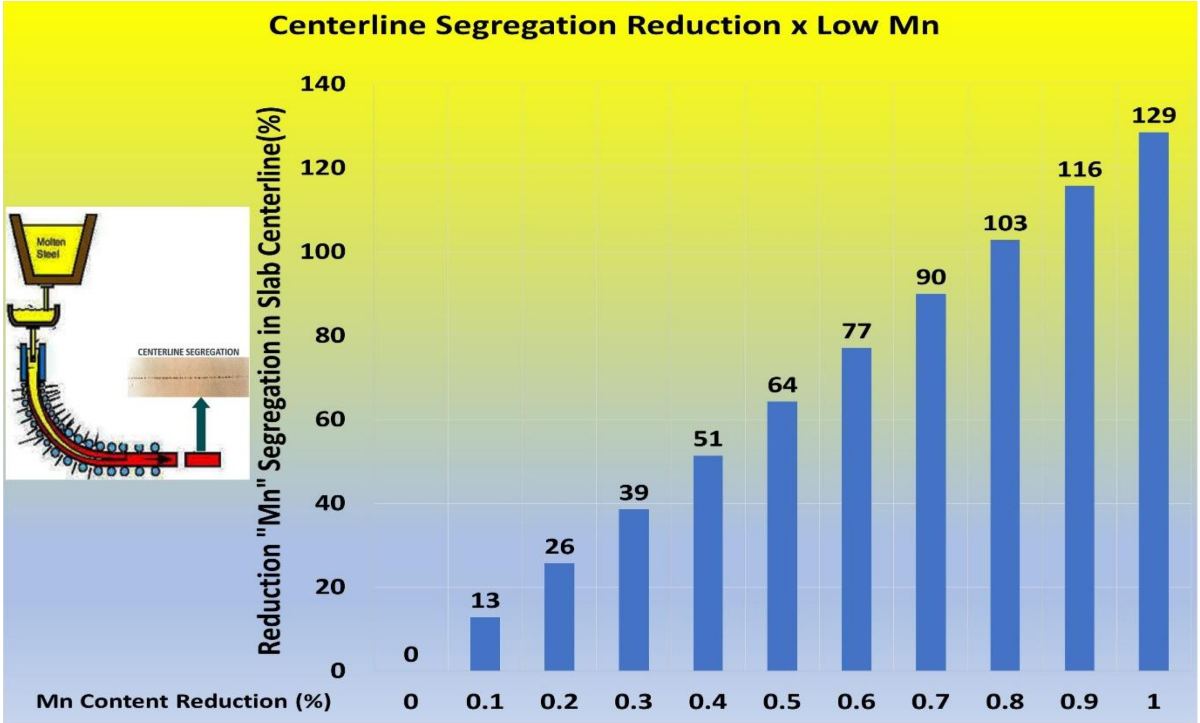


Figure 23. Centerline segregation percentage reduction as function of Mn content decrease.

Table 2. Simulation of the benefits that reduction of manganese content from 1.40% to 0.90% by adding 0.010%Nb can bring to the production of structural steel.

EXAMPLE OF POTENTIAL GAINS WITH LOW Mn TECHNOLOGY																
"TRADITIONAL" Q 345	ELEMENT	C	Mn	Si	P	S	Cu	Ni	Nb	V	Ti	Al	B	Cr	Mo	N
	%	0.16	1.40	0.25	0.020	0.005	0.000	0.000	0.000	0.000	0.000	0.025	0.000	0.00	0.00	0.005
"NEW"Q 345	ELEMENT	C	Mn	Si	P	S	Cu	Ni	Nb	V	Ti	Al	B	Cr	Mo	N
	%	0.16	0.90	0.25	0.020	0.005	0.000	0.000	0.010	0.000	0.000	0.025	0.000	0.00	0.00	0.005

Addition Savings: FeSiMn		Kg / t LOW Mn	8.651
Tapping Temperature Reduction		° C	15
Saving LD Lining Refractory Consumption	SLAG SPLASHING	Kg / t LOW Mn	0.029
	GUNNING	Kg / t LOW Mn	0.116
Saving Steel Ladle Lining Refractory Consumption		Kg / t LOW Mn	0.050
Increase LD Metallic Yield		%	0.75
Addition Savings: Al for deoxidation		Kg / t LOW Mn	0.135
"P" Content Reduction at Tapping		ppm	13
"H" Content Reduction in the Ladle		ppm	1.6
"N" Content Reduction in the Ladle		ppm	8.7
Manganese Centerline Segregation Reduction		%	64

5 CONCLUSION

Recent developments proved that it is possible to reduce manganese content in structural steel plates by adding a small amount of niobium and keeping the same mechanical properties. For low values of yield strength, like 350 MPa, small additions of niobium like 0.010% are enough to keep the same mechanical properties of material even reducing 0.50% of manganese. Normally there are reductions of alloy design costs that must be analysed based on updated ferroalloy prices. Once the reduction of Mn content results in less additions of FeMn, the tapping temperature can be decreased, bringing the following advantages for the steel production:

- Reduction of refractory lining in the LD furnace,
- Reduction of refractory lining in ladle,
- Increase of metallic yield,
- Reduction of amount of aluminum as deoxidizer,
- Reduction of absorbed hydrogen and nitrogen,
- Reduction of macro segregation.

The presented simulation example, that considered the reduction of Mn contents from 1.40% to 0.90% associated with the addition of 0.010%Nb, resulted on the reduction of 15^{0}C of tapping temperature, bringing savings of:

- 0.050 kg of ladle lining/t of produced steel,
- Increase of 0.75% of metallic yield,
- Saving of 0.135 kg/t of aluminum as a deoxidizer,
- Reduction of 13 ppm of phosphorous,
- Reduction of 1.6 ppm of hydrogen and 8.7 ppm of nitrogen.

Acknowledgments

The authors are grateful to CBMM for its kind support during the elaboration of this paper.

REFERENCES

1. Morozov YuD, Stepashin AM, Aleksandrov SV. Effect of Manganese and Niobium and Rolling Conditions on the Properties of Low-Alloy Steel. Metallurgist. 2002;46(5-6):152-156.
2. Barbosa R, Rodriguez-Ibabe J, Stalheim D, Rebellato MA. Alloy Cost Optimization Through Proper Metallurgical Development of Strength and Ductility Properties in Structural Steels. In: Association for Iron and Steel Technology. *The Iron & Steel Technology Conference and Exposition, AISTech 2018, May 7 to 10, Philadelphia PA, U.S.A.* 2018. pp 2753-2762.
3. Gorni AA, Rebellato MA, Silvestre LM. Substituição Parcial do Manganês pelo Nióbio em Aços Estruturais de Baixo Carbono. In: *Rede PDIMat. II Congresso Brasileiro de Engenharia da Rede PDIMat – engBrasil 2021, 24 a 26 de Novembro de 2021, Evento Virtual*. 2021. 12 p.
4. Stragliotto BV, Deisi V, Bielefeldt WV, Vilela ACF, Trindade LB, Contini AC, Machado FD. Modelo de Previsão de Temperatura de Chegada no Forno-Panela do Aço Líquido em Aciaria Elétrica. In: Associação Brasileira de Metalurgia, Materiais e Mineração. *48º Seminário de Aciaria, Fundição e Metalurgia de Não-Ferrosos, 2 a 6 de Outubro de 2017, São Paulo, Brasil*. 2017. pp 623-636.
5. Sarna SK. Slag splashing technique in converter operation. Ispat Guru. Available from https://www.ispatguru.com/slag-splashing-technique-in-converter-operation/. [Accessed 7th December 2021]
6. Guo HM, Yang J. Research of BOF Protection Technology by Slag Splashing. Materials Science Forum. 2009; 620-622:45-48.

7. Hubble H. Refractories for Oxygen Steelmaking. In: *The Making, Shaping and Treating of Steel*. 11th Edition. Pittsburgh: The AISE Steel Foundation; 1998. pp 227-230.
8. Junger HJ, Jandi C, Cappel J. Relationships Between Basic Oxygen Furnace Maintenance Strategies and Steelmaking Productivity. Iron and Steel Engineer. 2008;5(11):29-35.
9. Borges RAA. Análise Multivariada de Fatores que Afetam o Desgaste (Vida) do Revestimento Refratário das Panelas de Aço na Aciaria da Usina de Cubatão Usiminas. Dissertação de Mestrado. São Paulo. Escola Politécnica da USP; 2016.
10. Henriques HB, Kirmse OJ. Steel Yield at AMT: Understanding, Managing and Optimizing. In: Associação Brasileira de Metalurgia, Materiais e Mineração. *47th Steelmaking, Casting and Non-Ferrous Metallurgy Seminar, September 27 to 19, 2016, Rio de Janeiro, Brazil*. 2016. pp 828-838.
11. Saldanha, FA. Estudo de Equilíbrios Químicos Relevantes em Aciaria Através do Software FactSage Education 8.0. Trabalho de Conclusão de Curso. Fortaleza. Universidade Federal do Ceará, 2020.
12. Cappel J, Huesken R, Guogang Z. Experience with Long BOF Campaign Life and TBM Bottom Stirring Technology at Baosteel Meishan in China. Stahl und Eisen. 2012; 132(11):61-78.
13. Henriques HB. Estudo da Incorporação de Hidrogênio no Aço Líquido. Dissertação de Mestrado. Ouro Preto. Universidade Federal de Ouro Preto; 2010.
14. Huo F. The Use of Iron Carbide for the Removal of Nitrogen from Molten Steel, Master of Engineering (Hons.) Thesis. Wollongong. University of Wollongong, 1997.
15. Costa e Silva ALV. Segregation in HSLA Steels for Sour Service: An Evaluation Using Computational Thermodynamics. Tecnologia em Metalurgia, Materiais e Mineração. 2014;11(1):3-13.