ANALYSIS OF FACTORS CONTRIBUTING TO CRUDE STEEL NITRIDATION IN BASIC OXYGEN FURNACE PRIOR TO TAPPING

[1]Jaroslav DEMETER, [1]Branislav BUĽKO, [1]Peter DEMETER, [1]Martina HRUBOVČÁKOVÁ, [1]Lukáš FOGARÁŠ, [1]Slavomír HUBATKA, [1]Andrii PYLYPENKO, [1]Peter ŠMIGURA

[1]Institute of Metallurgical Technologies and Digital Transformation, Faculty of Materials, Metallurgy and Recycling, Technical university of Košice, Slovak Republic EU, _jaroslav.demeter@tuke.sk_, _branislav.bulko@tuke.sk_, _peter.demeter@tuke.sk_, _martina.hrubovcakova@tuke.sk_, _lukas.fogaras@tuke.sk_, _slavomir.hubatka@tuke.sk_, _andrii.pylypenko@tuke.sk_, _peter.smigura@tuke.sk_

Abstract

Assessing and quantifying the impact of various factors on nitrogen content in metal is vital for optimizing technological and operational strategies to minimize or prevent nitridation in the final steel product. Recognizing how individual factors affect nitrogen levels is crucial for predicting nitrogen quantities during both production and processing stages within a closed production cycle. This study investigates the factors influencing nitrogen content in crude steel before tapping, using Cohen's distribution table and graphical analysis. Although the impact of after-blows on nitrogen content is well established, the paper also explores other factors contributing to nitridation before tapping from the basic oxygen furnace.

Keywords: Nitrogen, steel, nitridation factors, steel cleanliness, BOF

1.   INTRODUCTION

The presence of nitrogen in steel contributes to the brittleness of ferritic steels. The process by which nitrogen as a diatomic gases dissolve in molten steel can be represented by a chemical equation (1). In addition, the concentration of nitrogen in the steel can be quantified using Sievert's law, based on equation (2) [1].

$$\frac{1}{2}\{N_2\} = [N] \qquad \Delta H_{1600°C} = 479.632\ kJ.mol^{-1}; \ \Delta G_{1600°C} = 354.790\ kJ.mol^{-1} \tag{1}$$

$$\%[N] = K_N\left(p_{N_2}\right)^{\frac{1}{2}} \tag{2}$$

where: K_N - equilibrium constant of atomic nitrogen N

p_{N_2} - partial pressure of molecular nitrogen N_2

The amount of dissolved nitrogen in a metal is influenced by the square root of the equilibrium gas partial pressure. This relationship arises because diatomic gases form atomic solutions with metals [2]. Upon dissolution in the metal, the gas molecules undergo dissociation into individual atoms. As a result, the number of atoms dissolved in the metal is double that of the original molecules [3]. The applicability of Sieverts' law is limited to situations where no chemical reaction occurs between the gas and the metal. Furthermore, the solubility of nitrogen in steel is modulated by the presence of other alloying elements [4]. Predicting the nitrogen content of steel is complicated by the fact that it is influenced by a considerable number of active factors [5]. The nitrogen content in crude steel is significantly influenced by the specific process employed [6]. In the basic oxygen furnace, the nitrogen content primarily depends on the contamination of the oxygen jet. In the region where the oxygen and the melt come into contact, temperatures exceed 2000°C. In this region (known as the hot spot), the distribution of nitrogen between the gas phase and the metallic phase approaches equilibrium,

typically resulting in a nitrogen content of 0.002%–0.005%. In contrast, the electric arc furnace exhibits a more pronounced effect due to the active influence of the electric arc, leading to a higher nitrogen content in the metal, generally ranging from 0.007%–0.012% [7]. In addition, the nitrogen content in the oxygen used in both the bottom-blown and top-blown processes has contributed to elevated nitrogen levels [8]. The practice of reblow increases the likelihood of higher nitrogen concentrations in the molten steel [9-11]. The primary objective of this study is to investigate the various factors influencing the nitrogen content of crude steel produced in the basic oxygen furnace (BOF).

2.   SOURCE MATERISLS AND EXPERIMENTAL SETUP

The nitrogen content in crude steel was examined in the basic oxygen furnace prior to tapping. Samples were collected from the crude steel for analysis. Presence of the dissolved nitrogen was evaluated in the sample of crude steel in the certified quantometric laboratory of U. S. Steel Košice - Labortest, s.r.o. using the test method Thermal Conductivity Detection (standard ASTM E1019-18) with mass fraction range 0.0005 %–0.50 %.

The obtained results regarding nitrogen content in the metal were synchronized with databases containing information on the chemical composition, temperature, weight, and other relevant parameters recorded during specific stages of the manufacturing process. This synchronization was performed based on heat number and the designated sampling location.

In total, 66 crude steel samples were analysed. The measured nitrogen content values from these samples were synchronized with multiple databases based on the corresponding heat number. These databases included detailed information regarding the chemical composition, temperature, weight of the steel, and other relevant parameters. All gathered data were processed and evaluated using Microsoft Excel 365 with the advanced statistical add-in Lumivero XLSTAT 2019. The charts were created in StatSoft STATISTICA 7.0.

2.1   The Methodology for Factor Determination

All examined factors were included in a correlation matrix, which enables the identification of quantitative relationships, wherein changes in one variable correspond to changes in others. The mathematical expression describing this relationship is known as the regression function. The nature of correlation—positive or negative—can be determined based on the form of the regression function. An increasing regression function indicates a positive correlation, while a decreasing regression function signifies a negative correlation. The correlation coefficient for the statistical dataset falls within the closed interval <−1,1>. A correlation coefficient approaching the value of 1 indicates a stronger linear relationship between variables [12]. The correlation coefficient R quantifies the strength of the statistical relationship between two quantitative variables. The most frequently utilized form of this coefficient in statistical analyses is the Pearson correlation coefficient (3) [13].

$$R_{xy} = \frac{\sum x_i y_i - n\bar{x}\bar{y}}{(n-1)s_x s_y} \qquad (3)$$

where: n - number of parameters to be measured

X, Y - parameters that can be written as x_i and y_i and in this case i = 1, 2, 3, …, n

$\bar{x}, \bar{y}$ - average value of X and Y

s_x, s_y - standard divergence of X and Y

Based on equation (3), it is possible to identify and rank the factors that have the greatest influence on the nitrogen content at each stage of steel production within a BOF steelmaking process. The interpretation of the correlation coefficient R depends significantly on the context and characteristics of the analysed data. For instance, a correlation coefficient value of 0.8 would be considered relatively low when verifying a physical law using precise measurement instruments; however, the same value would be regarded as very high within the context of social sciences research [14]. Jacob Cohen developed a straightforward method for interpreting

correlation coefficients within the context of research studies (**Table 1**) [15]. The value of R^2, referred to as the coefficient of determination (4), represents the proportion of shared variability between two variables. The value of R^2 is highly dependent on the characteristics of the data that are being analysed and the interpretation of the obtained R^2 values primarily relies on the nature and context of the data under investigation [15,16].

Table 1 Cohen´s interpretation of correlation coefficients

Correlation coefficient	0 - 0.1	0.1 - 0.3	0.3 - 0.5	0.5 - 0.7	0.7 - 0.9	0.9 - 1
Correlation description	trivial, very small	a little, low	moderate	big, high	very big, very high	perfect, clear

$$R_{xy}^2 = 1 - \frac{s_{y|x}^2}{s_y^2} \qquad \text{or} \qquad R_{xy}^2 = 1 - \frac{s_{x|y}^2}{s_x^2} \tag{4}$$

where: $s_{x|y}^2, s_{y|x}^2$ - number of parameters to be measured

s_x^2, s_y^2 - parameters that can be written as x_i and y_i and in this case i = 1, 2, 3, …, n

3. RESULTS AND DISCUSSION

The correlation matrix generated by StatSoft STATISTICA 7.0 was used to rank the factors influencing the final nitrogen content at a specific production stage. By integrating of the correlation analysis and empirical finding, it is possible to identify the most significant influencing factors, which are represented as variables in subsequent complex statistical operations. A positive correlation coefficient indicates that an increase in the studied parameter corresponds to an increase in the nitrogen content.

The ranking of the most important factors influencing the nitrogen content in the crude steel after the BOF process is shown in **Table 2**. The results are obtained from regression analysis based on the correlation matrix generated using StatSoft STATISTICA 7.0 application.

Table 2 Sequence of factors influencing the nitrogen content in the crude steel after the BOF process prior to tapping

Sequence of effects	Factor	Correlation coefficient R	Coefficient of determination R²
1.	Reblow (s)	0.4291	0.1842
2.	Manganese content in steel (%)	−0.3017	0.0910
3.	Phosphorus content in steel (%)	−0.2339	0.0547
4.	Carbon content in steel (%)	−0.2055	0.0422
5.	Briquettes (kg)	−0.1594	0.0254
6.	Tapping temperature (°C)	0.1457	0.0212
7.	Time of oxygen blowing (s)	−0.1314	0.0173

According to Cohen's classification, the obtained correlation coefficients can be interpreted as ranging from small to medium. Nevertheless, it is important to consider the non-stationary characteristics inherent in data from integrated systems, as well as the operational nature of the dataset. In the context of the present study, the attainment of moderate correlation coefficients is indicative of a substantial level of success. As illustrated in **Figure 1** – **Figure 5**, the impact of certain parameters from **Table 2** on the subsequent nitrogen content in steel following its fabrication in a basic oxygen furnace (BOF) within a closed production cycle is presented through graphical representations.
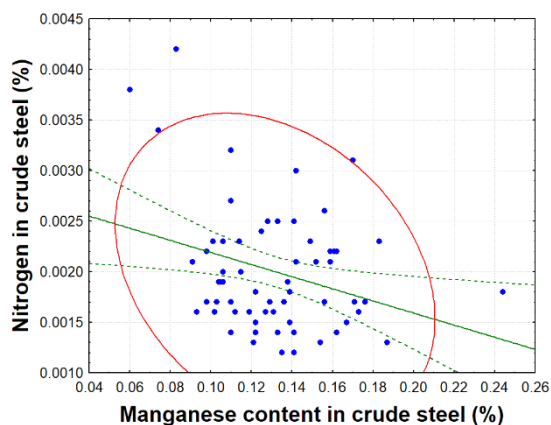
Figure 1 Relationship between the Manganese content in crude steel and the Nitrogen content in crude steel prior to tapping.
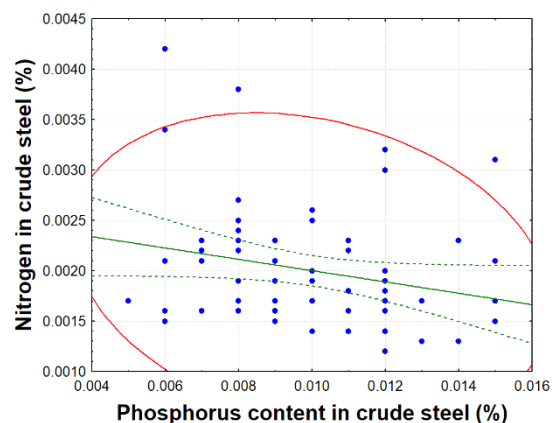

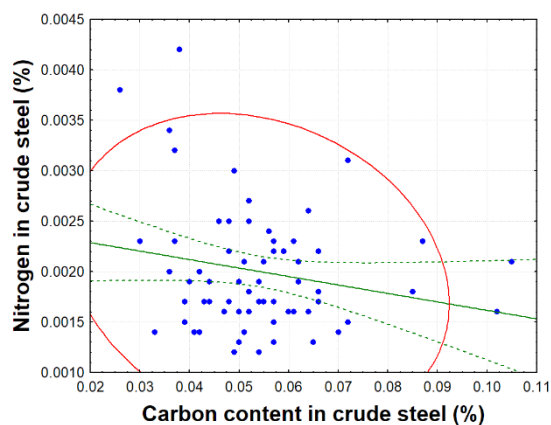**Figure 2** Relationship between the Phosphorus content in steel and the Nitrogen content in crude steel prior to tapping.

Figure 3 Relationship between the Carbon content in steel and the Nitrogen content in crude steel prior to tapping.
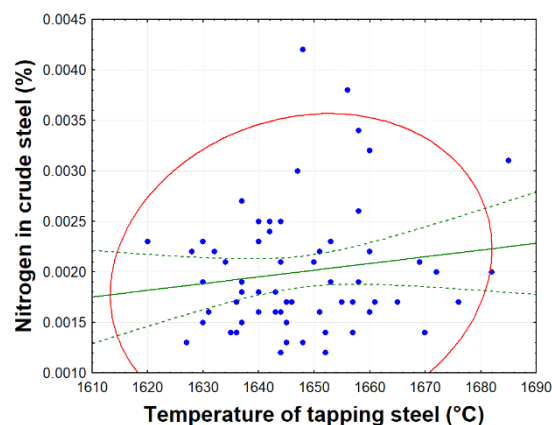

Figure 4 Relationship between the tapping temperature of steel and the Nitrogen content in crude steel prior to tapping.
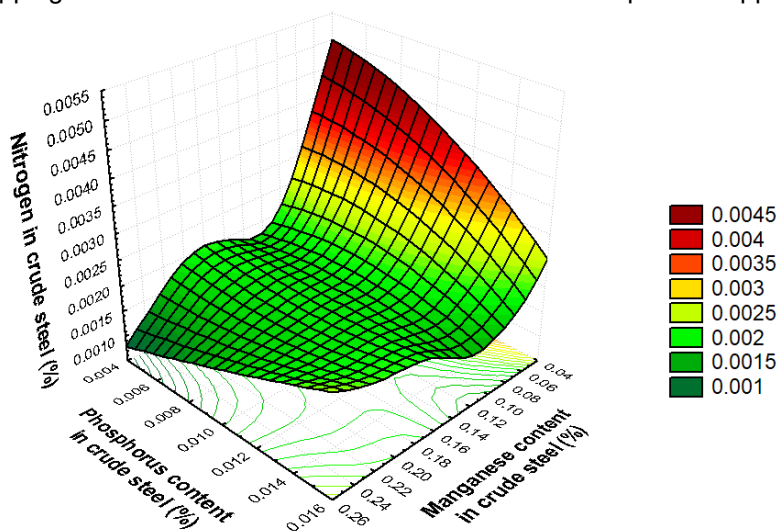

Figure 5 The impact of Phosphorous and Manganese levels in steel on nitrogen content in crude steel prior to tapping.

As shown in **Figure 6**, which represents the results of an auxiliary set of experiments, the nitrogen content in the steel increases with a higher number of reblow treatments. This is done when the chemical composition does not meet the specifications required for the target steel grade. A study was conducted on a data set of 699 reblows collected over a period of 14 months. The average nitrogen content was calculated in relation to the number of reblows performed. In heats without reblow, the nitrogen content is about 20 ppm. One reblow increases the nitrogen content to about 40 ppm, while two reblows further increase the nitrogen content to about 50 ppm in the crude steel.
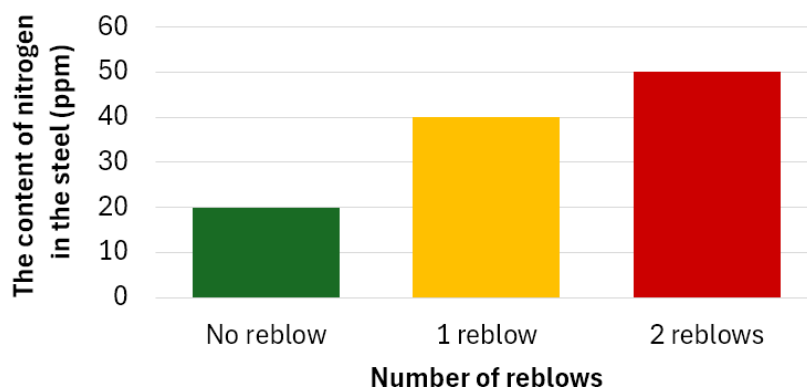

Figure 6 Nitrogen content in steel caused by number of reblows of pure-oxygen

Figure 7 presents a histogram of nitrogen activity, while **Figure 8** displays a histogram of nitrogen content in steel prior to tapping from the converter. Nitrogen activity is calculated based on the known chemical composition and activity coefficients (5), as outlined in the referenced literature [17,18].
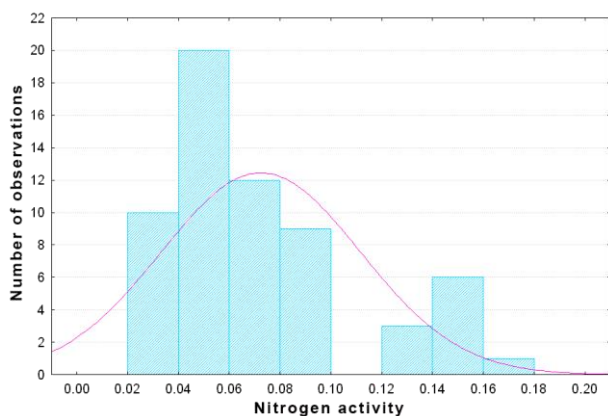

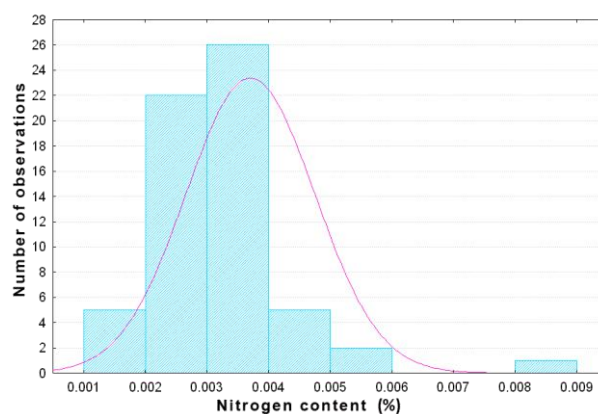**Figure 7** Histogram of nitrogen activity in crude steel prior to tapping within observed heats

Figure 8 Histogram of nitrogen content in crude steel prior to tapping within observed heats

$$a_{[N]} = f_{[N]} \cdot [N]_{steel} \tag{5}$$

where: $a_{[N]}$ - Nitrogen activity in steel

       $f_{[N]}$ - Activity coefficient of nitrogen in steel

       $[N]_{steel}$ - Dissolved nitrogen in the steel (%)

4. CONCLUSION

It is imperative that the factors that affect nitrogen content in crude steel prior to tapping from the oxygen converter are identified in order to determine the sources of nitrogen. A comprehensive understanding of the individual factors' influence is instrumental in the development and refinement of existing production processes, with the objective of reducing the nitrogen content in steel.

ACKNOWLEDGEMENT

REFERENCES

[1] FRUEHAN, R.J. Fundamentals and Practice for Producing Low Nitrogen Steels. *ISIJ International*. 1996, vol. 36, pp. 58-61. https://doi.org/10.2355/isijinternational.36.Suppl_S58

[2] SINGH, M.K., KESHARI, K.K., PRASAD, A., DAS, A. Effect of Steel Making Parameters on Nitrogen Level in Steel. In: *Processing and Characterization of Materials*. Singapore: Springer, 2021, pp. 63-73.

[3] MISRA, S., FRUEHAN, R.J. *Hydrogen and Nitrogen Control in Ladle and Casting Operations*. Pittsburgh, PA: Carnegie Mellon University, 2005. https://doi.org/10.2172/840933

[4] HERTZMAN, S., NARAGHI, R., WESSMAN, S., PETTERSSON, R., BORGGREN, U., JONSSON, J. Y., PETTERSSON, N. H., KARAMI, M. K., KOHAN-ZADE, A. Nitrogen Solubility in Alloy Systems Relevant to Stainless Steels. *Metall Mater Trans A*. 2021, vol. 52, pp. 3811-3820. https://doi.org/10.1007/s11661-021-06343-0

[5] PATRA, S., NAYAK, J., SINGHAL, L.K., PAL, S. Prediction of Nitrogen Content of Steel Melt during Stainless Steel Making Using AOD Converter. *Steel Research International*. 2016, vol. 87, pp. 1-14. https://doi.org/10.1002/srin.201600271

[6] RIIPI, J., FABRITIUS, T., HEIKKINEN, E.-P., KUPARI, P., KÄRNÄ, A. Behavior of Nitrogen During AOD Process, *ISIJ International*. 2009, vol. 49, no. 10, pp. 1468-1473. https://doi.org/10.2355/isijinternational.49.1468

[7] DERDA, W., SIWKA, J., NOWOSIELSKI, C., Controlling of the nitrogen content during EAF - technology and continuous casting of steel, *Archives of Metallurgy and Materials*. 2008, vol. 53, no. 2, pp. 523-529.

[8] ZHOU, J., ZHE, Q., ZHANG, B., PENG, Q., QIU, S., GAN, Y. Behaviors of Denitrogenation in RH-MFB, *Journal of Iron and Steel Research, International*. 2013, vol. 20, no. 7, pp. 40-44. https://doi.org/10.1016/S1006-706X(13)60124-7

[9] FRUEHAN, R. J., et. al. *The Making, Shaping and Treating of Steel, 11th Edition, Steelmaking and Refining Volume*. Pittsburgh, PA: The AISE Steel Foundation, 1998.

[10] NOMURA, K., OZTURK, B., FRUEHAN, R.J. Removal of nitrogen from steel using novel fluxes, Metallurgical Transactions B. 1991, vol. 22, no. 6, pp. 783-790. https://doi.org/10.1007/BF02651155

[11] ALLIBERT, M., GAYE, H. *Slag Atlas*. Dusseldorf: Verlag Stahleisen, 1995.

[12] TURNEY, S. *Pearson Correlation Coefficient*. [online]. 2024 [viewed: 2025-03-23]. Available from: https://www.scribbr.com/statistics/pearson-correlation-coefficient/

[13] BHANDARI, P. *Correlation Coefficient - Types, Formulas & Examples*. [online]. 2023 [viewed: 2025-03-23]. Available form: https://www.scribbr.com/statistics/correlation-coefficient/

[14] BENESTY, J., CHEN, J., HUANG, Y., COHEN, I. *Pearson Correlation Coefficient*. In: *Noise Reduction in Speech Processing*. Berlin: Springer, 2009, pp. 1-4. https://doi.org/10.1007/978-3-642-00296-0_5

[15] COHEN, J. *Statistical Power Analysis for the Behavioral Sciences*. New York: Routledge, 2013

[16] NEVIL, S. *Coefficient of Determination: How to Calculate It and Interpret the Result*. [online]. 2024 [viewed: 2025-03-23]. Available from: https://www.investopedia.com/terms/c/coefficient-of-determination.asp

[17] SIWKA, J. Equilibrium Constants and Nitrogen Activity in Liquid Metals and Iron Alloys, *ISIJ International*. 2008, vol. 48, no. 4, pp. 385-394. https://doi.org/10.2355/isijinternational.48.385

[18] DORADO, T., COEDO, A.G., FERNÁNDEZ, B.J. Chemical Analysis of Nitrogen in Steel, *Materials Science Forum*. 2002, vol. 383, pp. 131-142. https://doi.org/10.4028/www.scientific.net/MSF.383.131