PRECISE DETERMINATION OF SILICA AND SULFUR IN LIQUID PIG IRON USING INSTANT SENSOR TECHNOLOGY: BENEFITS AND ADVANTAGES OF THE PROCESS

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Abstract

In blast furnaces, the liquid pig iron filled into torpedoes undergoes desulfurization prior to the steel production process. Due to its high melting temperature, iron in its liquid state combines with sulfur to form the FeS phase. This phase has a low melting temperature, causing hot tearing during rolling. Therefore, desulfurization holds a crucial role in the steel production process. The process of reducing the sulfur content in liquid pig iron to the desired target value before it reaches the steel mill is known as the desulfurization process. In the reference facility, desulfurization is carried out in vehicles called torpedoes, which transport liquid pig iron from blast furnaces to the steel mill. For desulfurization, magnesium, lime, and metallurgical fluorspar are injected into the liquid pig iron using a blowing lance.

In the reference desulfurization facility, the sulfur content in the liquid pig iron, which averages around 1300 ppm, is targeted to be reduced to the range of 100-400 ppm. Using the blowing model present in the facility, calculated DeS agents are injected into the metal, and once the desired level is achieved, the liquid pig iron is sent to converters. After the blowing process, a sample is taken in the facility and sent for laboratory analysis before the torpedo is dispatched.

Using Heraeus Electro-Nite's patented products, Hot Metal Celox Sulphur and Hot Metal Celox Silicon sensors, the sulfur and silica levels in the liquid pig iron are rapidly determined. This aims to:

- Save time,
- Save DeS agents,
- Enable quick process control,
- Reduce laboratory costs.

In line with these objectives, measurements were conducted to monitor the process, ultimately providing significant efficiency gains to the reference facility in both process and cost aspects.

1. Introduction

1.1 Desulfurization Process

In liquid steel, sulfur precipitates at the grain boundaries in the form of sulfide inclusions, leading to defect formation during shaping, depending on the amount and type of inclusions [1]. When the Mn content in steel is very low and the S content is high, hot tearing defects occur during hot rolling due to the formation of FeS [2].

The most demanding applications of steel require reducing the sulfur content to very low levels (<0.001% S) to achieve the necessary combination of strength, ductility, formability, and weldability [3]. Low sulfur production is of great importance for steel quality. Consequently, this necessitates cost and process optimization in the desulfurization process.

Globally, the desulfurization process is carried out by injecting desulfurization agents into the liquid pig iron in ladles or torpedoes using a submerged lance. Agents such as CaO, Mg, CaC_2, and soda are commonly used for desulfurization in many steel plants worldwide.

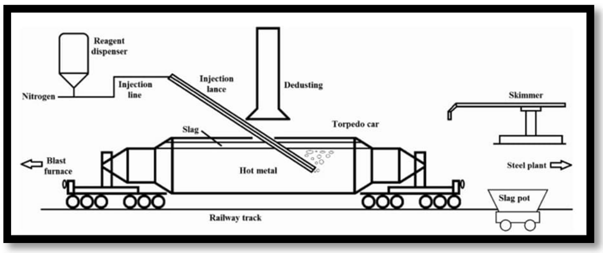


Figure 1. Desulfurization process of liquid pig iron in a torpedo [4].

The chemical reactions occurring during the desulfurization process are as shown in Equations I and II [5].

$$[S] + CaO(s) + [C] = CaS(s) + CO(g) \qquad (I)$$

$$CaO(s) + [S] + ½[Si] = CaS(s) + ½(SiO_2) \qquad (II)$$

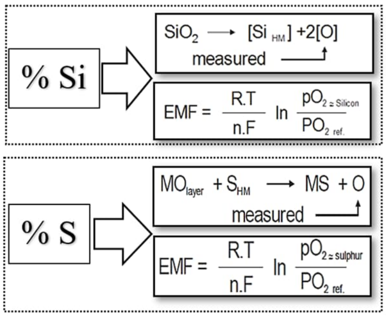
1.2 Project Motivation

The steel industry today faces various challenges, including rising costs, environmental regulations, and digitalization. Cost increases, driven by factors such as fluctuations in raw material prices, energy costs, and labor expenses, make it difficult to maintain competitive prices. Additionally, with growing environmental concerns, steel producers must comply with stricter environmental regulations, necessitating a focus on emission controls, waste management, and sustainability standards. Digitalization has triggered significant transformation in the sector, with the optimization of operational processes and faster decision-making being targeted through digital technologies such as smart manufacturing systems, data analytics, and automation. To counter these challenges and ensure sustainable growth, steel producers are taking strategic actions such as enhancing energy efficiency, investing in renewable energy sources, complying with environmental certifications, and focusing on innovation and R&D. In the desulfurization facility, which operates between the blast furnaces and the steel production process and requires high tempo and coordination, one of the primary objectives is to reduce the sulfur content in liquid pig iron to the required level as quickly and cost-effectively as possible. Due to increased analysis time and the high pace of blast furnaces, desulfurization facility operators are either forced to extend the processing time or use larger amounts of magnesium, an element with a high desulfurization capacity. The project aims to enable rapid sulfur determination independent of human intervention, thereby reducing process time and saving on desulfurization agents. The main goals are to achieve cost advantages through rapid analysis and optimal material control, and to contribute to productivity and sustainability projects.

1.3 Sensors and Measurements

- **Hot Metal Celox Silicon & Sulphur:**

Using a sensor submerged in the liquid metal, the potential voltage and temperature information in the liquid pig iron are measured. Based on measurement results, the %Si and %S values in the liquid metal are calculated using an empirical formula and displayed on the device screen. The measurement principle and method are illustrated below. The oxygen potential in the liquid metal is determined with the help of the potential voltage in the reference cell, and the %Si and %S values are determined through the following relationship.



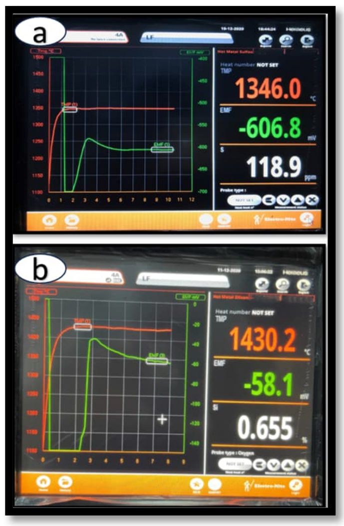


Figure 2. Example of Online Sulfur Measurement Screen (a), Example of Online Silica Measurement Screen (b).

2. Experimental Study

2.1 System Commissioning and Training

In the desulfurization process, achieving the target sulfur level requires calculating the amount of agent materials to be injected into the liquid pig iron. The primary factors in this calculation include the tonnage of the liquid pig iron, the sulfur content from the blast furnace, the target sulfur content, the silica content of the liquid pig iron, and the temperature. The tonnage of the liquid pig iron is one of the most crucial factors. In this study conducted at the reference company's desulfurization facility, the tonnage of the torpedoes coming from the blast furnace could not be accurately read; therefore, the tonnage of the liquid pig iron had to be estimated by the operators. Additionally, since the samples of the liquid pig iron were taken from the furnace's metal channel, the sulfur content in the torpedo might not accurately reflect the actual sulfur content of the liquid pig iron. Due to these factors, estimating the tonnage of the liquid pig iron and the deviations in the sulfur content values analyzed in the laboratory could lead to deviations in the targeted sulfur levels. To address these primary issues, Heraeus Electro-Nite collaborated with the reference company using the HM Celox S sensor, one of our innovative and technological solutions capable of rapid and reliable sulfur determination. The goal was to achieve the targeted sulfur level optimally. Measurements were conducted after the first phase of blowing or towards the end of the processes to determine how closely the targeted value was being approached.

In this study aimed at achieving rapid sulfur determination, measurements were taken using the HM Celox S rapid sulfur determination sensor either after the first phase of blowing or towards its end. Simultaneously, the samples were also taken with the currently used sampling probe and sent to the laboratory for analysis. The average time for the analysis results to return from the laboratory to the desulfurization facility was approximately 7 minutes. Due to the circulation of the liquid metal, torpedoes were often transferred to the steel mill before the sample results could be obtained. This situation could lead to deviations, especially in casts targeting low sulfur levels. Such deviations could result in quality discrepancies or necessitate the return of the torpedo to the desulfurization station for reprocessing, posing significant risks. By using the HM Celox S sensor, one of Heraeus Electro-Nite's innovative and technological solutions capable of rapid and reliable sulfur determination, these risks were minimized through instant measurements. Additionally, this sensor allowed simultaneous sulfur and temperature measurements. Consequently, significant savings were achieved in both temperature measurement operations and sample measurement operations for laboratory analysis.

Additionally, for the torpedoes being processed, if the desired target value is reached according to the measurement results obtained with the HM Celox S rapid sulfur determination sensor, the injection process is terminated. If the measured value is above the target, a further amount of agent material is injected into the liquid pig iron. The measurement process using the HM Celox S (rapid sulfur determination) sensor is more frequently utilized in casts where the sulfur target values of the liquid pig iron are between 50-150 ppm. Thanks to the HM Celox S rapid sulfur determination sensor, time savings, savings on DeS agent materials, rapid process control, and reduced laboratory costs are achieved.

Figure 3. Blowing process being performed on liquid pig iron in a torpedo at desulfurization facility where studies were conducted.

2.2 Data Collection and Process Monitoring

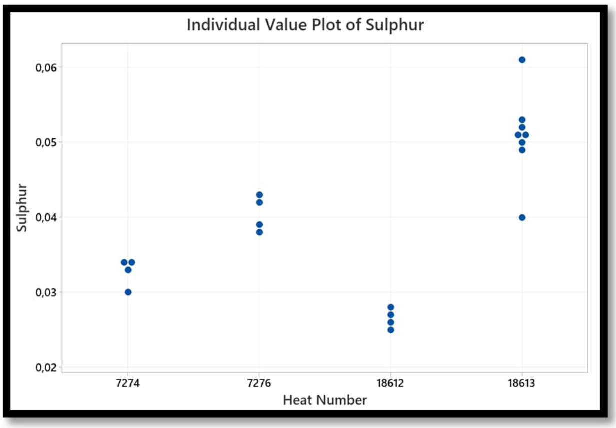
As seen in Table 1, in addition to the parameters measured by the sensor, studies were conducted to determine process parameters for dynamic sulfur measurement. The process of recording the casts performed by the facility operators into the prepared table and developing the model with the highest predictive power based on these data continued for approximately one month.

				Celox Sulphur			Spectro Results						Reagents Used		DS	
Tarih	Ölçüm No	Saat	Döküm No	Temp	EMF	S ppm	C%	P%	Mn%	Si%	S%	Ti%	Mg (Kg)	CaO (Kg)	S% Aim	Mg% of Reagent
15.12.2023	1	3:18:00 PM	123456	1351	-604,6	124,7	3,99	0,048	0,097	0,60	0,0148	0,067	20	180	0,020	
15.12.2023	1	3:21:00 PM	123457	1350	-604,0	122,3	3,88	0,049	0,098	0,58	0,0148	0,067	20	180	0,020	

Table 1: Raw Data Collection Table Before Dynamic Sulfur Measurement in the Desulfurization Process.

During data collection, the operators continued to take measurements using the sensors provided by Heraeus Electro-Nite and additionally recorded the actual and calculated sulfur amounts in the table. Throughout this process, the project teams maintained constant communication and made necessary interventions. To ensure the measurement stability of the laboratory sulfur measurement values indicated as output in the model, an MSA (Measurement Systems Analysis) study was also conducted.

According to the analysis results, the standard deviation was determined to be 15 ppm for casts targeting 100 ppm and 40 ppm for casts targeting 400 ppm. Based on these determined deviations, the prediction tolerance was established.



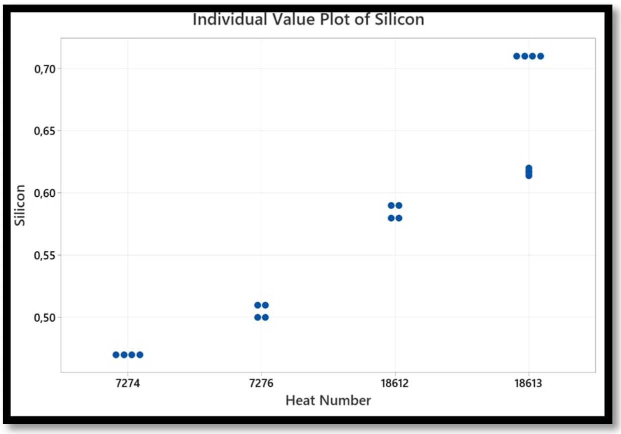


Figure 4. Single graphical representation of consecutive Sulfur and Silica measurement results

2.3 Modeling

Based on the data collected in collaboration with the reference facility staff at the desulfurization plant, the following formula was developed and controlled updates were made throughout the entire process. In all casts where measurements were taken using the HM Celox S rapid sulfur determination sensor, the following formula was obtained through regression analysis, considering HM Celox S temperature, EMF, and the reference facility laboratory (blast furnace) silica values.

<u>Model;</u>

%S = 0,14856 + 0,000050 x Temperature + 0,000327 x EMF - 0,001194 x %Si

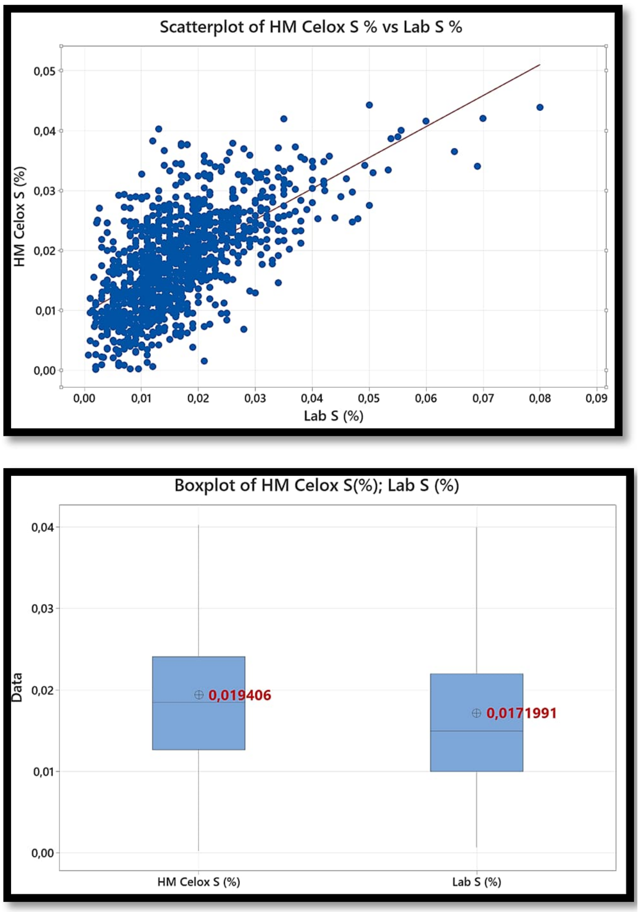


Figure 5. Scatterplot and boxplot graphs showing the sulfur values calculated using the formula derived from the HM Celox S rapid sulfur determination sensor and the laboratory sample results for the same casts.

2.4 Evaluation

In the desulfurization facility, the correlation of the sulfur values obtained from both the HM Celox S rapid and reliable sulfur determination sensor and the laboratory measurements using the standard sampling method was examined for the same casts. The HM Celox S sensor provided reliable measurements and accelerated the process. Measurements taken from each cast were recorded individually, and thorough evaluations were conducted to develop the most reliable sulfur formula.

3. Results

- Sample temperature losses during waiting were minimized, and the HM Celox S sensor allowed for real-time sulfur and temperature measurement.
- The HM Celox S sensor provided instantaneous and reliable sulfur measurement, significantly reducing torpedo processing times, which previously had an average waiting period of 7 minutes for laboratory sample results.
- In the trial torpedoes, an average savings of 0.1 kg of magnesium per ton of liquid pig iron was achieved. This resulted in an annual savings of 500,000 Euros based on calculations.
- The HM Celox S sensor not only measured sulfur values but also simultaneously measured temperature, leading to both time and cost savings.
- The practice of transferring torpedoes to the steel mill without waiting for laboratory sample results to ensure continuous production was entirely eliminated.

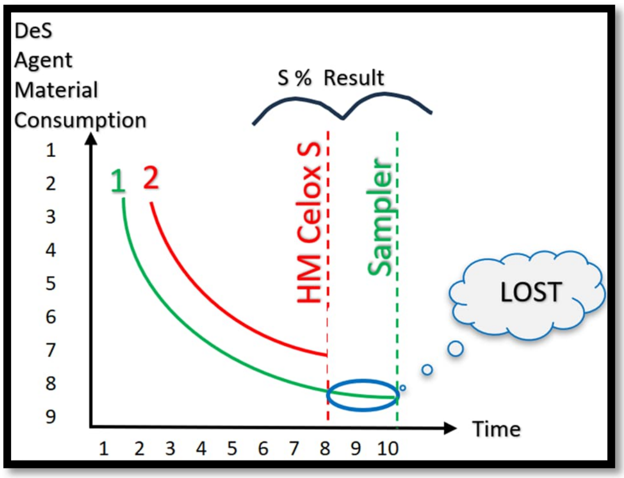


Figure 6. Time-dependent comparison graph of sulfur measurement using the HM Celox S rapid sulfur determination sensor and the standard sampling method.

4. Acknowledgement

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REFERENCES

[1] Bleck,W.(2006), Modelling of Manganese Sulphide Formation during Solidification, Part II: Correlation of Solidification and MnS Formation, Steel Research International 77(4):256-264

[2] Llewellyn, D.T.(1992), Steel: Metallurgy & Applications, Butterworth Heinemann, Oxford.

[3] www. steeluniversity.org

[4] Frank Nicolaas Hermanus Schrama, Elisabeth Maria Beunder, Bart Van den Berg, Yongxiang Yang & Rob Boom (2017) Sulphur removal in ironmaking and oxygen steelmaking, Ironmaking & Steelmaking, 44:5, 333-343.

[5] Aguiar, Felipe Nylo de et al. Hot metal desulfurization by marble waste and fluorspar. Rem: Rev. Esc. Minas, June 2012, vol.65, no.2, p.233-240. ISSN 0370-446.