Researches Regarding the Air Pollution with Sulfur Dioxide (SO\textsubscript{2}) to the Steelmaking

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Abstract. The paper presents the experimental researches regarding the air pollution with sulfur dioxide (SO\textsubscript{2}) to the steelmaking in the electric arc furnace. It presents a method for determining the sulfur dioxide (SO\textsubscript{2}) concentrations from the steelmaking, the diagram variation of the sulfur dioxide (SO\textsubscript{2}) concentrations over time during specific technological stages of the steelmaking process and the potential sources that generate the sulfur dioxide (SO\textsubscript{2}) to steelmaking process in the electric arc furnaces. The air pollution during steelmaking in electric arc furnaces is manifested throughout this process, which includes the following technological stages: furnace charging, charge melting, refining, dephosphorization, desulphurization, deoxidizing, alloying and evacuation. Considering the stages of steelmaking in the electric arc furnace that have the potential to generate sulfur dioxide (SO\textsubscript{2}), it was assessed its generation evolution for the following technological stages: melting, refining, desulphurization and deoxidizing. The experimental researches were performed on two electric arc furnaces with a capacity of 10 and 30 tons. The highest concentrations of sulfur dioxide (SO\textsubscript{2}) were recorded during the desulfurization technological stage. After this stage, it has been recorded a significant reduction in sulfur dioxide (SO\textsubscript{2}) concentrations. The sulfur dioxide (SO\textsubscript{2}) concentrations from the electric arc furnace with the capacity of 30 tons are higher than those recorded in the furnace of 10 tons with 30-40%.

Introduction

One of the most important sources of SO\textsubscript{2} emissions from the ferrous metals industry includes electric arc furnaces. Sulfur in the feed materials will oxidize, to form SO\textsubscript{2}, when making steel in an EAF.

The steelmaking in the electric arc furnace belongs to the category of industrial processes with high degree of pollution because there are transferred in the air environment factors the following pollutant substances: carbon oxides, sulfur oxides, nitrogen oxides, volatile organic compounds (VOC), particulate matter, dioxins and furans [1].

Sulfur dioxide forms sulfate aerosols that are thought to have a significant effect on global and regional climate. Sulfate aerosols reflect sunlight into space and also act as condensation nuclei, which tend to make the clouds more reflective and change their lifetimes [2].

Sulfur emissions have grown rapidly and extensive researches have documented a variety of effects on the environment [3]. Sulfur dioxide is the primary cause of acid precipitation, which adversely affects natural systems, agriculture and building materials. The sulfate aerosol particles formed as a consequence of these emissions impair visibility and affect human health. Sulfur dioxide (SO\textsubscript{2}), dissolves in the water vapors from the air to form acids, and interacts with other gases and particles in the air to form particles known as sulfates and other products that can be harmful to people and their environment [4].

In the Table 1, there are presented the health effects of respiratory exposure to sulfur dioxide.
Table 1. Health effects of respiratory exposure to sulfur dioxide [5, 6, 7, 8]

| Exposure limits (ppm) | Health Effects |
|-----------------------|----------------|
| 1-5                   | Threshold for respiratory response in healthy individuals upon exercise or deep breathing |
| 3-5                   | Gas is easily noticeable. Fall in lung function at rest and increased airway resistance |
| 5                     | Increased airway resistance in healthy individuals |
| 6                     | Immediate irritation of eyes, nose and throat |
| 10                    | Worsening irritation of eyes, nose and throat |
| 10-15                 | Threshold of toxicity for prolonged exposure |
| >20                   | Paralysis or death occurs after extended exposure |
| 150                   | Maximum concentration that can be withstood for a few minutes by healthy individuals |

In Table 2 there are presented the average and maximum allowed concentrations of sulfur dioxide in the workplace atmosphere, and allowed values for this pollutant at emission.

Table 2. The Allowed Concentrations of Sulfur Dioxide (SO₂) in the Workplace Atmosphere and Allowed Values for this Pollutant at Emission [9, 10, 11]

| Pollutant                  | Allowed Average Concentration (AAC) [mg/ Nm³] (8 hours) | Allowed Maximum Concentration (AMC) [mg/Nm³] (15 minutes) | Emissions Limit Value (ELV) [mg/Nm³] | Alert threshold (AT) | Intervention threshold (IT) |
|---------------------------|--------------------------------------------------------|----------------------------------------------------------|--------------------------------------|----------------------|-----------------------------|
| Sulphur dioxide (SO₂)     | 5                                                      | 10                                                       | 24.5                                 | 35                   | 35                          |

The purpose of the paper constitutes the assessment of air pollution with sulfur dioxide (SO₂) to the steelmaking in the electric arc furnace.

Potential Sources that Generate the Sulfur Dioxide (SO₂) to Steelmaking

The sources with sulfur dioxide generating potential in the electric arc steelmaking are [12]:

- the metallic charge;
- additions of auxiliary materials;
- first fusion pig iron (0.05 – 0.07 % S);
- electric arc furnace atmosphere, when using fuels containing sulfur.

The sulfur may derive from some impurities of the charge and from the electrodes. The sulfur from the charge in the form of metal sulfides <MeS> can undergo the reaction:

\[
<\text{MeS}> + 2\{\text{O}_2\} = <\text{MeSO}_4>. \\
\]

\[
2<\text{MeSO}_4> \rightarrow 2<\text{MeO}> + 2\{\text{SO}_2\} + \{\text{O}_2\}. \\
\]

The reactions of sulfur dioxide and sulfur trioxide formation are [12]:

\[
[S] + 2 [O] = \{\text{SO}_2\}. \\
\]

\[
[S] + 3 [O] = \{\text{SO}_3\}. \\
\]
SO₂ + ½ O₂ ↔ SO₃.  

(5)

[FeS] + 2 [O] → {SO₂} + [Fe].  

(6)

[FeS] + 3 [O] → {SO₃} + [Fe].  

(7)

[FeS · MnS] = 2 {SO₂} + [Fe] + [Mn].  

(8)

Sulfur can be usually found in the iron ore the form of pyrite (FeS₂) or pirotin (FeS). When entering the ore in the furnace it takes place is a process of dissociation and oxidation of iron sulfides [1, 12]. Pyrite dissociates easily at 600°C and p=1atm. according to this reaction:

2FeS₂ =2 FeS + S₂.  

(9)

then the pirotin oxides according to this reaction:

3/5(FeS) + {O₂} = 1/5 (Fe₃O₄) + 3/5 {SO₂}.  

(10)

It can take place also this reaction:

(FeS) + 10 (Fe₂O₃) = 7(Fe₃O₄) + {SO₂}.  

(11)

The presence of sulfur dioxide in the furnace atmosphere is a potential source of sulfuring and oxidation of metal bath.
The sulfuring and oxidation of metal bath in the presence of {SO₂} take place according to this reaction:

2{SO₂} = {S₂} + 2{O₂}.  

(12)

Materials and Method
The experimental researches were carried out on two electric arc furnaces with alkaline lining, having a capacity of 10 tons and 30 tons. The type of steel produced in both furnaces was low alloyed steel.
The sulfur dioxide (SO₂) concentrations were determined in the front of charging door of the two furnaces, and at height of about 15 [m] from electric arc furnaces (on the existing bridge of the electric steelworks). The measurement of sulfur dioxide (SO₂) was performed using a Maxilyzer computer for burned gases automated analysis.
Considering the stages of steelmaking in the electric arc furnace that have the potential to generate sulfur dioxide (SO₂), it was assessed its generation evolution for the following technological stages: melting, refining, desulfurization and deoxidizing. The measurement of sulfur dioxide concentration (SO₂) was performed every 20 minutes, during the technological stages mentioned above.
The results obtained from experimental researches were compared with the intervention threshold for sulfur dioxide (SO₂) specified in the reference [9].

Results and Discussions
In the Figure 1 and in the Figure 2 there are presented the concentrations of sulfur dioxide (SO₂) and maximum sulfur dioxide (SO₂ max) recorded during technological stages specific to the steelmaking process in the electric arc furnaces with a capacity of 10 tons, respectively 30 tons. The measurements were made in the front of in the electric arc furnace (at the charging door).

Figure 1 shows that the values recorded for sulfur dioxide (SO₂) and maximum sulfur dioxide (SO₂ max) falls below the intervention threshold. The highest value recorded for sulfur dioxide (SO₂) was during the desulfurization stage (6 ppm), and for the maximum sulfur dioxide (SO₂ max) was (8 ppm).
Fig. 1. The sulfur dioxide (SO$_2$) and maximum sulfur dioxide (SO$_2$ max) concentrations variations in the electric arc furnace having the capacity 10 [t]
Fig. 2. The sulfur dioxide (SO$_2$) and maximum sulfur dioxide (SO$_2$ max) concentrations variations in the electric arc furnace having the capacity 30 [t]

Figure 2 shows that the values recorded for sulfur dioxide (SO$_2$) and maximum sulfur dioxide (SO$_2$ max) falls below the intervention threshold. The highest value recorded for sulfur dioxide (SO$_2$) was during the desulfurization (9 ppm) and for the maximum sulfur dioxide (SO$_2$ max) was (13 ppm).

Figure 3 presents a comparative analysis between the concentrations of sulfur dioxide (SO$_2$) recorded during the technological stages of steelmaking in the electric arc furnaces with a capacity of 10 tons and 30 tons respectively. The measurements were made at the charging door level of the two electric arc furnaces.
Fig. 3. The sulfur dioxide (SO$_2$) concentrations variations, recorded at the charging door level of the electric arc furnaces having the capacity of 10 [t] and 30[t] respectively.

Figure 3 shows that the values recorded for sulfur dioxide (SO$_2$) falls below the intervention threshold for both development aggregates. The highest value recorded for sulfur dioxide (SO$_2$) was during the desulphurization. For the electric arc furnace with a capacity of 10 tons, the highest concentration recorded was (6 ppm) and for the 30 tons furnace it was (9 ppm).

Figure 4 presents a comparative analysis between maximum concentrations of sulfur dioxide (SO$_2$ max) recorded during the technological stages of steelmaking in the electric arc furnaces with a capacity of 10 tons and 30 tons respectively. The measurements were made at the charging door level of the two electric arc furnaces.
Fig. 4. The maximum sulfur dioxide (SO$_2$ max) concentrations variations, recorded at the charging door level of the electric arc furnaces having the capacity of 10 [t] and 30 [t] respectively.

Figure 4 shows that the values recorded for the maximum sulfur dioxide (SO$_2$ max) falls below the intervention threshold for both development aggregates. The highest value recorded for the maximum sulfur dioxide (SO$_2$ max) was during the desulfurization. For the electric arc furnace with a capacity of 10 tons, the highest concentration recorded was (8 ppm) and for the 30 tons furnace it was (13 ppm).

Figure 5 and Figure 6 present the results recorded on the changes in concentrations of sulfur dioxide (SO$_2$) and sulfur dioxide maximum (SO$_2$ max) during technological stages specific to the steelmaking process in the electric arc furnaces with a capacity of 10 tons and 30 tons. The determinations were made at a height of about 15 m from the electric arc furnace (on the existing bridge of the electric steelworks).
Fig. 5 shows that the values recorded for sulfur dioxide \((\text{SO}_2)\) and maximum sulfur dioxide \((\text{SO}_2\text{ max})\) generally fall under below the intervention threshold. There is a single measurement greater than the intervention threshold, respectively (14 ppm). The highest value recorded for sulfur dioxide \((\text{SO}_2)\) was during the desulfurization (12 ppm) and for the maximum sulfur dioxide \((\text{SO}_2\text{ max})\) was (14 ppm).
Figure 6 shows that the values recorded for sulfur dioxide (SO$_2$) and maximum sulfur dioxide (SO$_2$ max) exceed the intervention threshold. The highest value recorded for sulfur dioxide (SO$_2$) was during the desulfurization (14 ppm) and for the maximum sulfur dioxide (SO$_2$ max) it was (18 ppm). In this case there is an exceeding of intervention threshold for sulfur dioxide (SO$_2$) by 1.04 times and for the maximum sulfur dioxide (SO$_2$ max) recorded by 1.34 times.

Figure 7 presents a comparative analysis between the concentrations of sulfur dioxide (SO$_2$) recorded during the technological stages of steelmaking in the electric arc furnaces with a capacity of 10 t and 30 t respectively. The determinations were made in electric steel mill at a height of about 15 [m] from electric arc furnaces.
Fig. 7. The sulfur dioxide (SO\textsubscript{2}) concentrations variations recorded at a height of about 15 [m] from the electric arc furnace having the capacity of 10 [t] and 30[t] respectively.

From Figure 7 shows that the values recorded for sulfur dioxide (SO\textsubscript{2}) exceed only once the intervention threshold. The highest values recorded for sulfur dioxide were during the desulfurization (14 ppm) for the electric arc furnace with a capacity of 30 tons and (12 ppm) for electric furnace with a capacity of 10 tons. In this case, the intervention threshold for sulfur dioxide (SO\textsubscript{2}) was exceeded by 1.04 times at the 30 tons furnace. After that, there was a significant reduction in sulfur dioxide concentrations recorded, due to the completion of the desulfurization period of the metal bath.

Figure 8 presents a comparative analysis between maximum concentrations of sulfur dioxide (SO\textsubscript{2} max) recorded during technological stages of steelmaking in the electric arc furnaces with a capacity of 10 tons and 30 tons respectively. The measurements were made at a height of about 15 [m] from electric arc furnaces.
Fig. 8. The sulfur maximum dioxide (SO\textsubscript{2} max) concentrations variations recorded at a height of about 15 [m] from the electric arc furnace having the capacity of 10 [t] and 30[t] respectively

From Figure 8 shows that the values recorded for the maximum sulfur dioxide (SO\textsubscript{2} max) exceed the threshold of intervention for both development aggregates. The highest values recorded for maximum sulfur dioxide (SO\textsubscript{2} max) were during the desulfurization, respectively (18 ppm) for electric furnace with a capacity of 30 t and (14 ppm) for electric furnace with a capacity of 10 tons. In this case there is an exceeding of intervention threshold value by 1.34 times for the 30 tons furnace and by 1.04 times at 10 tons furnace. After that, there was a significant reduction in maximum sulfur dioxide concentrations (SO\textsubscript{2} max) recorded, due to the completion of the desulfurization period of the metal bath.

**Conclusions**

The sulfur dioxide (SO\textsubscript{2}) has a negative impact on the environment in general and particularly on the quality of the air environmental factor, being responsible for generating acid rain. The negative impact of sulfur dioxide (SO\textsubscript{2}) manifests itself on the steel works and on the population. The highest concentrations of sulfur dioxide were determined during the desulfurization period. It was formed from the sulfur contained in raw materials, such as coal, oil and metal-containing ores. After this technological stage, it was recorded a significant reduction in the concentrations of sulfur dioxide (SO\textsubscript{2}).
The sulfur dioxide (SO\textsubscript{2}) concentrations recorded at the electric arc furnace having the capacity of 30 [t] are higher than those recorded in the furnace having the capacity of 10 [t] with 30-40%. The sulfur dioxide (SO\textsubscript{2}) concentrations recorded at a height of about 15 [m] above the two electric arc furnaces are higher compared to those recorded at their charging door. The level of air pollution with sulfur dioxide, during steelmaking in electric arc furnaces is influenced by the sulfur content of the charge components. The pollution prevention and control techniques to reduce the air pollution with sulfur dioxide (SO\textsubscript{2}) to the steelmaking includes the following: the selection feedstocks and scrap with low sulfur content; the usage of fuel with low sulfur content, such as natural gas; the usage of wet scrubbing systems before dry scrubbers as part of collecting and dedusting system; emissions control technologies such as sorbent injection and flue gas desulfurization (methods may include wet or dry processes).

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