Optimization of the Ferronickel Production Process through Improving Desulfurization Effectiveness

Izet Ibrahimi a, Nurten Deva a*, Sabri Mehmeti a

a Faculty of Geosciences; University of Mitrovica “Isa Boletini” Ushin Kovacica, 40000 Mitrovicë, Kosovo.

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Abstract

Desulphurization of Ferronickel in the converters with oxygen is the most complex part of the technological process in the Drenas foundry. Sulphur in the ferronickel melting is mostly in the form of FeS, with a melting temperature of 1195°C, and it has tendency to dissolve indefinitely in liquid iron. Our objective is to determine the sulphur removal coefficient, as a key indicator of the desulphurization efficiency in the converter, by measuring the activity and concentration of sulphur and other elements in liquid Fe and melting. Determination of this coefficient is done according to the analytical method, while comparing the current process parameters with those of the new desulfurization methods, other indicators of the refining process are determined. The refining process and the effective conduct of the study depend on the XRD analysis database of metal and slag, and as well of the technological refining process analysis data. Research has shown that desulfurization efficiency is a function of the sulphur removal coefficient, respectively; metal composition, slag, oxygen activity, CaO/SiO₂ ratio, sulphide capacity, fluidity, surface pressure, etc.). In addition to this coefficient, other indicators of refining process optimization are defined.

Keywords: Ferronickel; Slag; Sulphur Portion Coefficient; Desulphurization; Sulphide Capacity; Refined Ferronickel.

1. Introduction

The pyrometallurgical obtaining of ferronickel from oxide-laterite ores, regardless of the degree of technical-technological excellence even in the newer processes, has many unresolved technical and technological problems, first of all the process of refining ferronickel in the converter is followed by low efficiency due to the lack of desulphurization outside the furnace as well as the low desulphurization dynamics in the converter. During pyrometallurgical processing the converter is one of the most important aggregates to produce and to refine ferronickel. The oxygen blowing process is necessary to decrease the sulphur, phosphorus, carbon, silicon and the iron content in the FeNi metal to the requested levels [1].

During the production of ferronickel in the electric furnace, in addition to iron and nickel, and other metals such as cobalt, manganese, chromium, sulphur, copper, silicon, phosphorus, carbon, etc., pass to the alloy, which adversely affects the properties of it and their removing presents additional difficulties, adversely affecting the process economy.

Since ferronickel, is used for the production of various steels must contain a minimum amount of sulphur below 0.04% [2, 3], then it is necessary to make the deepest desulphurisation, whether through out-furnace desulphurisation, before that the metal passes to the converter or during process of refining in the converter. With technological advancements, the requirement for minimum sulphur content in steels has reached up to 0.02%, while for special

* Corresponding author: nurten.deva@umib.net
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steels up to 0.005%. Under the current operating conditions at the Foundry of NewCo Ferronickel in Drenas, such quality parameters of refined ferronickel are almost inaccessible. Refining, and especially sulphur removal phase as it is not being applied between the desulphurization phase out-furnace, but all the sulphur removal takes place in converter, followed by a slow process and with a high consumption of materials and energy resources [4, 5].

Sulphur in the components of charge is pyrite, metallic and organic origin. This third form is likely to have the greatest negative impact, since it is thermodynamically more stable and is expected to burn to the melting zone [6]. In the electric furnace ferronickel, sulphur is most commonly present in the form of FeS, as iron constitutes the largest proportion of molten ferronickel. During oxygen blowing in the converter, one part of the sulphur is removed with slag and the other part with gas. Removal of ferrous sulphur is possible with the help of oxidizing slag [4]. The quality of the refined ferronickel, the effectiveness of desulphurization and the stability of the technological parameters are directly related to the sulphur separation coefficient, the physico-chemical properties of the metal as well as the fluidity, optimal basicity and sulphide capacity of the slag [6, 7].

The main purpose of this study is to provide solutions that would improve the effectiveness of desulphurization, by reducing the duration time of the metal in the converter, which would directly affect the optimization of refining process in the converter and generally to decrease the production costs of ferronickel at the "Ferronickel Foundry" in Drenas [8].

2. Research Methodology

This study is based on chemical analyzes of raw materials, electric furnace of ferronickel, chemical composition of metal and slag according refining stages, gases, smelter and other technological materials. Based on these data and process operational indicators, we have determined the sulphur separation coefficient as a key determinant of desulphurization effectiveness. Also are determined the other performance indicators of the production process at the "Ferronickel Foundry" in Drenas, according to the comparative method. Comparison of outputs, process parameters, and production practices, are based on review the production period November 1997 and January 2009. Whereas the effectiveness of desulphurization according to these operating parameters is compared with theoretical parameters, assuming the development of off-furnace desulphurization, where magnesium would be used as a desulphurizer Stirling [9].

Evaluation of desulphurization efficiency and measurement of process indicators are supported by chemical- technological analysis of furnace metal and slag, metal and slag of converters, chemical and granulometric composition of CaCO₃ as and content and amount other technological materials, which are used during the production process in the "Ferronickel Foundry" [10].

This study program will follow the standard research diagram are shown in Figure 1. Important indicators of the experimental part are given in the load ratio see table 1. The charge of the refining process on the oxygen converter at the Ferronickel Foundry in Drenas is designed depending on the chemical composition of the metal. An important indicator in the determination of process parameters is the composition of Si and C in the furnace metal (EF). For our case study, we converted 1.5 t of unrefined scrap and 1.5 t of refined scrap into the converter.

The scrap is used for thermal balancing and for improving the chemical environment in the process reaction area. During the first phase (the burning process of Si and C) due to the high Si coefficient on the metal, the phase lasted 16 min, and the whole process would take place in an acidic environment with high heat release. For the thermal and chemical balancing of the process, the amount and frequency of CaCO₃ dosing will be increased. After this phase the chemical analysis of the metal is carried out, on the basis of which the second stage of the process is designed - refining under the basic environment. At this stage it is projected: the addition of CaO₂ (kg / min), the flow of O₂, (m³ / h), the position of the spear towards the metal bath and the best possible removal of the process slag. During the third phase besides the one mentioned above, other added additions in charge are calculated. Since at this stage high effects of refractory material damage on the converter appear, the amount of MgO (90%) refractory brick powder mixed with CaCO₃ in 1: 2 ratios and the amount of refined metal scrap will be added, which would help enrich the metal with Ni in FeNi. For successful conduct of research program besides samples for chemical analysis of metal we have also analyzed 3 samples for chemical analysis of slag. The refined metal has been subjected to the deoxidation process. For the development of this intermediate process, Fe-Si and Al have been used as a means of deoxidation.

Furthermore, the study relates to the experimental research, which used the results of XRD analysis by the NewCo “Ferronickel” laboratory in Drenas, the values of the operating indicators in the converters unit, but also descriptive data and comparative models from good practices of refining processes.
Figure 1. Flowchart for the research methodology

Table 1. New Co Ferronikeli complex L.L.C Convertors – Charging Report

<table>
<thead>
<tr>
<th>Serial No. of charge; (C=0844)</th>
<th>No. of convertor.1</th>
<th>Lance: 1</th>
<th>Ladle for metal (Temp. of refractory = 700-800 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oxygen indication (m³)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. of ladle.; 18/4</td>
</tr>
<tr>
<td>O₂ Flow (m³/h)</td>
<td>H₂O Flow (m³/h) -51.2</td>
<td>Converctor charge: 18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Departure time; t[^{i}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dead weight; 2 t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Arrival time; t[^{i}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Net weight; 23 t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Preheating time: 800 °C</td>
</tr>
<tr>
<td>P (bar) – 12.</td>
<td></td>
<td></td>
<td>No. of charge; 18</td>
</tr>
<tr>
<td>(Flow O₂ (m₃/min):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Phase 1 and 2 = 30 m₃/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Phase 3,4,5 = 25 m₃/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Phase 6,7 = 30 m₃/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Phase 8, 9 = 35 m₃/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (bar) – 10.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>½(H₂O) = 16 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase</th>
<th>Time (from/to)</th>
<th>Duration (min)</th>
<th>O₂ – consumption (m₃)</th>
<th>Lance position</th>
<th>Scrap before charge (tNi(t))</th>
<th>CaCO₃</th>
<th>(MgO + CaCO₃ = 2:1) (kg)</th>
<th>Temp. by phase (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1^{st} 1^{st}</td>
<td>10</td>
<td>302</td>
<td>1.3</td>
<td>1.5 (t) from EF</td>
<td>460</td>
<td>120</td>
<td>1629</td>
</tr>
<tr>
<td>2</td>
<td>1^{st} 2^{nd}</td>
<td>6 (Analysis)</td>
<td>204</td>
<td>1.2</td>
<td></td>
<td>600</td>
<td>100</td>
<td>1565</td>
</tr>
<tr>
<td>3</td>
<td>2^{nd} 2^{nd}</td>
<td>6</td>
<td>208</td>
<td>1.1</td>
<td>Scrap during charge 1.5 (t)</td>
<td>880</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>2^{nd} 2^{nd}</td>
<td>6 (Analysis)</td>
<td>218</td>
<td>1.2</td>
<td></td>
<td>950</td>
<td>60</td>
<td>1565</td>
</tr>
<tr>
<td>5</td>
<td>2^{nd} 2^{nd}</td>
<td>6</td>
<td>204</td>
<td>1.1</td>
<td></td>
<td>700</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2^{nd} 2^{nd}</td>
<td>6</td>
<td>198</td>
<td>1.1</td>
<td></td>
<td>600</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>7</td>
<td>2^{nd} 3^{rd}</td>
<td>6</td>
<td>213</td>
<td>1.1</td>
<td></td>
<td>850</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3^{rd} 3^{rd}</td>
<td>5</td>
<td>201</td>
<td>1.1</td>
<td></td>
<td>700</td>
<td>1572</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3^{rd} 3^{rd}</td>
<td>2</td>
<td>70</td>
<td>1.1</td>
<td></td>
<td>-</td>
<td>1568</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3^{rd} 3^{rd}</td>
<td>3</td>
<td>110</td>
<td></td>
<td></td>
<td>-</td>
<td>1630</td>
<td></td>
</tr>
</tbody>
</table>

Total  = 55 min 1942 3 (t) 5740
In order to compare the heat balance with the chemical composition of the metal from the electric furnace and to determine the duration of the process phases, have been measured in advance: the temperature and residence time of the metal in ladle from the start of the electric furnace up to the spill to the converter, the amount of metal spilled into the converter and scrap added before the start of the first phase. After chemical analysis of charge were evaluated; elongation period of silicon oxidation, decarburization and removal efficiency of other impurities from metal, consumables of refractory material, oxygen flow (Nm$^3$/min), spear height (m) above metal melting, temperature (°C) afterwards at which stage of the process, the chemical composition of the metal and coating after the first, second and third phases, the composition and amount of scrap and other additives. After chemical analysis of the charge have been determined the ratios; CaO/SiO$_2$, time required for oxidation of silicon, carbon and other impurities, oxygen flow (Nm$^3$/min), the spear position (m) above and temperature (°C) for every each phase of process.

Ferronickel of electric furnace of "Ferronickel Foundry" in Drenas, is followed by various impurities, such as: silicon, chromium, copper, carbon, sulfur, phosphorus, phosphorus, cobalt, etc. Sulphur, of all the impurities, has the greatest negative impact on ferronickel properties, when is used for the production of steel, and its removal proceed slowly and is followed by high energy costs.

### Table 2. Chemical analysis of Fe-Ni

<table>
<thead>
<tr>
<th>Samples</th>
<th>As</th>
<th>Fe</th>
<th>Si</th>
<th>Cr</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample from EF</td>
<td>0.03</td>
<td>72.52</td>
<td>2.68</td>
<td>0.76</td>
<td>0.60</td>
<td>0.07</td>
<td>1.62</td>
<td>11.22</td>
<td>0.74</td>
<td>0.03</td>
<td>1629</td>
</tr>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.67</td>
<td>15.63</td>
<td></td>
<td>1565</td>
</tr>
<tr>
<td>Sample 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.44</td>
<td>17.61</td>
<td></td>
<td>1568</td>
</tr>
</tbody>
</table>

### Table 3. Chemical analysis of slag

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>FeO</th>
<th>Cr$_2$O$_3$</th>
<th>Ni</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>23.26</td>
<td>18.40</td>
<td>36.18</td>
<td>2.86</td>
<td>0.19</td>
<td>10.10</td>
<td>0.93</td>
</tr>
<tr>
<td>Sample 2</td>
<td>23.37</td>
<td>17.42</td>
<td>34.81</td>
<td>2.94</td>
<td>0.21</td>
<td>9.79</td>
<td>0.93</td>
</tr>
<tr>
<td>Sample 3</td>
<td>19.91</td>
<td>15.14</td>
<td>45.95</td>
<td>1.00</td>
<td>0.25</td>
<td>11.60</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Ferronickel of electric furnace of "Ferronickel Foundry" in Drenas, is followed by various impurities, such as: silicon, chromium, copper, carbon, sulfur, phosphorus, phosphorus, cobalt, etc. Sulphur, of all the impurities, has the greatest negative impact on ferronickel properties, when is used for the production of steel, and its removal proceed slowly and is followed by high energy costs.

### 3. Desulphurization of Ferronickel

Ferronickel of electric furnace of "Ferronickel Foundry" in Drenas, is followed by various impurities, such as: silicon, chromium, copper, carbon, sulfur, phosphorus, phosphorus, cobalt, etc. Sulphur, of all the impurities, has the greatest negative impact on ferronickel properties, when is used for the production of steel, and its removal proceed slowly and is followed by high energy costs. Thus, this phase of the refining process is quite complex, which is usually preceded by desulfurization in the ladle for metal or in the case of new technologies in electric furnace for desulphurization, where used different reagents and then continued in LD converters during the oxygen refining process [7]. The refining process in LD-oxygen converters consists of removing impurities from molten metal, relying on their different affinity to oxygen. Most of the impurities are removed between gases or process slag. Sulphur and phosphorus in ferronickel pass through the ore, reducer and fuel. Sulphur, which is organically bound to the charge components, part of it is expected to pass through the gases during the pre-reduction process, part pass through the electric furnace, where during the melting process approximately 50% is expected to pass through the gas and and the remainder pass into metal and slag [4, 11].

From the GIBSS energy calculations, is confirmed the solubility of (S) to (Fe), as a result of which the molecule of (FeS) is formed. The formation reaction of (FeS) is followed by large heat release effects [4, Steeluniversity.org Basic 2006 [12]. However, during blowing to the surface of the metal, a reaction may occur between the (S) and the (O2) oxygen from the gases, which resulting in the formation of SO$_2$ or SO$_3$ which leave with gases. The gas created is absorbed by the ventilator and it is likely that there will be no reversible reaction, NewCo Ferronickel [5].

The dynamics of removal of harmful impurities, depending on their concentration in ferronickel and oxygen flow (Nm$^3$/min). Reaction of sulphur metal with oxygen, under refining conditions in converter, is not possible [4, 13], no matter that Gipss' free energy for this reaction is identical to Equation 1:

$$G_0 = 1340 + 12.8T$$  (1)
The transition of sulfur from metal to slag has been the subject of many researchers. According to data from the Соколов (1982) research [14], the isotope of S\(^{35}\) and Fe\(^{59}\) are the first to transition from metal to slag and enable reactions in the metal-slag system. Such a process in the metal-slag system, during refining in metallurgical reactors, is enabled by the presence of basic oxides (MeO) and formation of (MeS) according to the basic reactions (2, 3 and 19):

\[
(S) + (O^2-) = (S^2-) + (O) \tag{2}
\]

\[
(FeS) + (S) = (FeS) \tag{3}
\]

After those, metal sulphide dissolved in metal can react with the calcium and nickel oxides in slag, according to reactions 4 and 5:

\[
(FeS) + (CaO) = (CaS) + (FeO) \tag{4}
\]

\[
3(NiO) + 3[FeS] + O_2 = (Ni_3S_2) + 3(FeO) + SO_2 \tag{5}
\]

\[
(FeS) = (FeS) \tag{6}
\]

Whereas:

- (CaO), (FeO), (CaS) dhe (MeS) are components dispersed in slag and
- (S) and (O) are components dispersed in metal.

Theoretically, reaction 4 and 6 begin to develop prior to the process of refining the converter, but reaction 6 may continue to develop during the blowing with oxygen. During oxygen blowing conditions should be created for the change of the standard isobaric potential for the oxidation reactions of Fe and FeS to occur. Sulphur activity in iron is determined on the basis of concentrations of (S) and other elements involved in ferronickel melting Branković et al., 1980 [15]. The desulphurizing capacity, which is determined by the sulfur separation coefficient, is depend on the oxygen activity participating in the reaction, the metal composition, the sulfur to metal concentration, the reactivity of the limestone used as defroster, process temperature, partial pressure of oxygen and sulphur in gaseous phase in equilibrium with slag, chemical-physical composition of the slag and above all by; viscosity, surface tension, ratio between oxides of SiO\(_2\), CaO, MgO, FeO, as well as other technological parameters that would stimulate the interactive process in system metal-slag.

\[
(S) + (MeO) + Fe_{\text{liquid}} = (MeS) + (FeO) \tag{7}
\]

Desulphurization mechanism is believed to consist of transfer of ionic iron pairs from metal to slag (reciprocally) according to the scheme:

\[
(S) + Fe_{\text{aq.}} \leftrightarrow S^{2-} + Fe^{2+} \tag{8}
\]

Equilibrium constant of reaction is usually described by equation:

\[
K_S = \frac{a_s(CaS) \cdot a_s(FeO)}{a_s(S)^2 \cdot a_s(CaO)} \tag{9}
\]

To increase the desulphurization rate, operating regime temperatures must be maintained at optimum values (optimum values considered slightly above the melting temperature level of electrical furnace ferronickel), but maintaining at optimum ratio (CaO)+(MgO)/SiO\(_2\) parameters. In acidic slurries the rate of ferronickel desulphurization is almost negligible. According to B.P. Onshine, the desulphurization rate in the acidic medium reaches a maximum value of up to 15%, shown in Figure 2 [4].

Slag desulphurization capacity towards the metallic phase may be expressed as the slag sulphide capacity:

\[
C_S = \frac{(S)}{[S]} = f\left[\frac{CaO}{SiO_2}, T, \frac{1}{FeO}\right] \tag{10}
\]

Slag’s compounds with high iron content will decrease the sulfur activity. Increasing the amount of FeO (above the concentration limit of 18% FeO), will adversely affect the desulphurization effectiveness of molten ferronickel. Equation 10 shows that the following conditions must be met for successful desulphurization:

- That sulfur has this strong bond, in the form of (mes),
- That chemical component (mes) to have good solubility in slag,
- That the desulphurizing ability of meo is high,
- That the left side of the reaction 10 to shows good dispersive capabilities of S, from metal to slag, and
The ratio \( \frac{S}{S} \) to be linearly dependent on ratio \( \frac{[CaO]}{[SiO_2]} \).

Figure 2. Dependence of transition of:
(a) sulfur on slag from basicity of slag and
(b) concentration of total Fe

In the case of oxygen bowling on the surface of the molten ferronickel, will be suitable conditions are created to oxidize the sulfur together with the iron, whereby the isobaric-isothermal reaction potential Equation 11 changes at temperature 1600 °C, \( \Delta G_0 = -134000 \) J/mol. Thus it is possible that this reaction is thermodynamically dependent on partial pressure of oxygen on molten metal and transfer / passage conditions of this mass of sulfur in surface melting slag [10].

\[
S + O_2 = SO_2 \tag{11}
\]

Slag desulphurization capacity against the gaseous or metallic phase may be expressed as the slag sulphide capacity [13]:

- System slag – gas:

\[
\frac{1}{2}O_2 + \frac{1}{2}S_2 = \frac{1}{2}O_2 \tag{12}
\]

\[
C_s = \left(\%S^{2-}\right) \cdot \left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2} = K_0 \cdot a_{O_2^{2-}}/f_{S^{2-}} \tag{13}
\]

- System metal-slag:

\[
S + (O^2) = (S^2) + (O) \tag{14}
\]

\[
C'_s = \left(\%S^{2-}\right) \cdot \frac{a_{[O^2]}^{[S^{2-}]} a_{[S]}^{[O^2]}}{a_{[S]}^{[O^2]} a_{[S]}^{[S^{2-}]} = K_0 \frac{a_{O_2^{2-}}}{f_{S^{2-}}} \tag{15}
\]

Sulphur partition between slag and metal may be expressed using the sulphur partition coefficient \( L_s \):

\[
L_s = \frac{\%S}{\%S^{2-}} = K_0 \frac{a_{O_2^{2-}} f_{[S]}^{[O_2]} a_{[S]}^{[O_2]} a_{[S]}^{[S^{2-}}}{a_{[S]}^{[O_2]} f_{S^{2-}}} \tag{16}
\]

Where:

- \( a(O) \), \( a(S) \) - oxygen and sulphur activity in molten metal,
- \( a_{O_2^{2-}}, a_{S^{2-}} \) - oxygen and sulphur ions activity in slag,
- \( \%S^{2-} \) - sulphur weight % in slag,
- \( p_{O_2}, p_{S_2} \) - partial pressure of oxygen and sulphur in gaseous phase in equilibrium with slag,
- \( K_0 \) - reactions equilibrium constant,
- \( f_{[S]}, f_{S^{2-}} \) - Henry’s activity coefficient of sulphur in metal and slag [7].

It is possible to determine \( L_s \) from known thermodynamic data of oxygen and sulphur dissolution in molten iron using CS. Sulphur partition coefficient (LS) is not only the function of slag composition, but depends also on the oxygen activity in metal, i.e. also on the metallic phase composition [13]. The value of the sulfur partition coefficient
in case of ferronickel slag usually increases with the increase in CaO activity, which represents the precise size of the basic slag and in the case of a decrease in oxygen activity. The sulfur equilibrium in metal-slag system is also highly dependent on the level of metal oxidation. The relationship between [S] in this system is expressed as; \( S \approx 4 \text{(O)} \), Stirling [9].

The higher the oxidation of the metal (O), the higher the residual sulfur concentration in the metal (S). To this dependence on desulfurizing mechanism, some metallurgist have given a different interpretation, according to which there is a sulfur volume-oxygen between metal and slag of oxidizing smelter, which oxidizes metal according to the scheme; \( S + \text{O}_2^{2-} \rightarrow S^{2-} + \text{(O)} \), [4]. According to this equation the separation coefficient of sulfur will be;

\[
L_s = K_s \left( \frac{[\text{O}_2]}{[\text{O}]} \right)
\]  

The relatively high desulfurization rate (up to 40%) of the converter bath can be explained by a two-phase process, involving the slag and a phase of the oxidizing gas by reaction;

\[
(S) + (CaO) + Fe\text{slag} \rightarrow (CaS) + (FeO)
\]  

\[
(CaS) + \text{O}_2 \rightarrow (CaO) + \text{SO}_2
\]

When sulfur is separated from slag, its equilibrium is shifted to slag-metal system, which contributes to the further partition of sulfur from the metal to slag, i.e. deepens desulfurization. This fact derives from the high activity of sulfur in the case of low oxidation. The development of reactions however is actually conditioned by the effectiveness of the removal of the slag after desulfurization. This process is essentially similar to diffusive oxidation of steel baths.

4. Results and Discussion

Based on the average chemical composition shown in Table 4, it is observed that the electric furnace metal from "Ferronickel Foundry" in Drenas in its composition, besides the high Si concentrations, the other impurity with high concentration is also S, which presents difficulties in the process of desulfurization.

At electric furnace ferronickel, sulfur is most commonly present in form of FeS, as it accounts for most of this melting [4, 16]. Sulfur activity in liquid iron is determined based on the concentrations of [S] and other elements involved in ferronickel melting. So the chemical composition of the ferronickel melting of the electric furnace is what determines the bond between sulfur and the liquid iron. Slag desulfurization capacity (Cs) depends on the chemical composition of the slag, that is, the ratio \((\text{CaO}) + (\text{MgO})/\text{SiO}_2\) as well as the process temperature. Increasing the amount of FeO in the slag, in the first and second phase of blowing with \(\text{O}_2\), positively affects the partition of sulfur from the molten ferronickel, but this can only be up to the concentration of 18% FeO.

| Table 4. Average of chemical composition of ferronickel |
|---------------------------------|---------|-------|-------|-------|-------|-------|-------|-------|
| As                | Fe      | Si    | Cr    | C     | P     | S     | Ni    | Co    | Cu    |
| 0.03              | 72.5-84 | 2.7-4.0 | 0.25-0.76 | 0.3-0.6 | 0.07-0.2 | 0.7-2.0 | 11.22-17 | 0.5-0.74 | 0.03-0.05 |

Figure 3. Dependence activity of coefficient S on the concentration of the constituent elements of ferronickel
Further increase of (FeO) in slag shows negative effects on desulphurization. The desulphurization rate increases if the process takes place only slightly above the melting temperature of the ferronickel. In the first refining period the removal rate of S is not large shown in Figure 3, so there are large oscillations with respect to the increase in S in the slag. In this case, for a volume unit of oxygen, three times as much gas is formed and about twice as much heat is released, compared to the last refining stage [4, 13]. All reactions of the first phase of refining are followed by high heat release at this phase, to reduce the temperature and soften the acidic medium, it is necessary to use a large amount of limestone.

Although chemical composition of metals gained from electric furnace shown in Table 5, for comparative period November 1997 and January 2019, does not present any major change, as observed from Figure 2 and Table 4, quality of refined ferronickel and the average effectiveness indicators, desulphurization has a high difference in their selves.

Table 5. Comparison of average converter efficiency indicators for November 1997 and January 2019

<table>
<thead>
<tr>
<th>Nr. of charge</th>
<th>Resource costs</th>
<th>Metal from electric furnace and refined</th>
<th>Analysis of molten ferronickel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaCO₃ (kg)</td>
<td>O₂ (Nm³)</td>
<td>Ground magnesite-bricks and CaCO₃rap. 2:1 (kg)</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td>---------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>1719</td>
<td>6620</td>
<td>1043</td>
<td>-</td>
</tr>
<tr>
<td>C-0831</td>
<td>5380</td>
<td>1855</td>
<td>360</td>
</tr>
<tr>
<td>1722</td>
<td>8550</td>
<td>1214</td>
<td>-</td>
</tr>
<tr>
<td>C-0833</td>
<td>6480</td>
<td>2101</td>
<td>670</td>
</tr>
<tr>
<td>1724</td>
<td>7650</td>
<td>1169</td>
<td>-</td>
</tr>
<tr>
<td>C-0835</td>
<td>6940</td>
<td>1743</td>
<td>840</td>
</tr>
<tr>
<td>1726</td>
<td>9010</td>
<td>1414</td>
<td>-</td>
</tr>
<tr>
<td>C-8441</td>
<td>5740</td>
<td>1942</td>
<td>600</td>
</tr>
</tbody>
</table>
According to the process indicators, at the first refining phase, the desulphurization was very low, while at the second phase when the composition of FeO in the slag it's about 18% FeO, then conditions are created favorable conditions for desulfurization. Slag of second phase are characterized by low percentage of silicon oxide while high percentage of CaO and FeO, shown in Figure 6. Theoretically, if desulphurization was carried out of furnace using desulphurizer Mg, Na₂CO₃, synthetic slag or any similar desulphurizer the desulphurization rate during this intermediate phase would have to be 40-60% [S], removed from the electric furnace of ferronickel [3, 4]. Such desulfurization practices would stimulate the relationship between the LS coefficient and the no. 2-/(O) ratio, favoring the formation of basic slag’s. In cases where favorable kinetic conditions are created it is possible to provide additional desulfurization of the molten bath as the result of the metal-slag reactions. During additional desulfurization an LS partition coefficient of 50 to 150 can be obtained Michalek, 2014 [10].

According to current parameters, virtually this mid-phase is eliminated, and all desulfurization is carried out on the converter. This practice has resulted in high deviation of the sulfur partition coefficient from the metal between charge 1721 and C-0835, as well as the assumed coefficient of separation assumed to be developed according to theoretical parameters shown in Figure 7 [7, 8]. The theoretical parameters of the partition constant were calculated assuming magnesium desulfurization outside the furnace.

Figure 5. Reaction rates for oxidation reaction in BOS [5]
The equilibrium state between the metal and slag would be reached quickly, that is, the desulphurization time would be shortened, and action of reactive components between them would be at a high level if desulphurization would take place outside the furnace, but above it, is necessary to precisely determine the boundary between the liquid and solid temperature molten ferronickel, the partial oxygen pressure, presence of ferrous oxides in slag and degree of slag basicity [17].
5. Conclusion

Considering the desulfurization of electric furnace ferronickel, which is produced at the “Ferronickel Foundry” in Drenas, it is very important to discuss in the future the quality of Kosovo's lignite, which is used as a reducer. Such lignite qualities have, as a consequence, created carbon-poor and highly sulphur-rich metal. The effectiveness of desulfurization, optimization and economic effects process will be achieved through new desulfurization practice application outside of furnace that would utilize desulfurizers, such as; Mg, CaO, synthetic slag, or even mixture of Na₂CO₃ and FeSO₄, etc. Practically in recent times the removal rate of sulphur from the furnace ferronickel has been completely developed in the converter, by this process flaw, refined metal has been followed with concentration up to 0.45% S, production capacity level has dropped in parameters minimum utilization, normative costs of energy resources and raw materials and all other circumstances to economize the production process have been unfavorable. From the data of this study, it has been concluded that in addition to the application of mid-phase desulfurization outside the furnace, which is, in fact, the main component of the effectiveness of the ferronickel refining process, it is also important maintaining of optimum composition parameters and extended sulphide capacity, metal composition (especially the drop in optimum values for Si and C), operating temperature, granulometric composition and proper melting reactivity, as well as maintaining the optimum operating parameters.

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7. Conflicts of Interest

The authors declare no conflict of interest.

8. References


