Original Article

Analysis of the influence of adding CaF₂ and Na₂O to steel desulfurizing mixtures using computational thermodynamics

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ABSTRACT

Steel desulfurization mixtures of the CaO-Al₂O₃ system are the most industrially used. These mixtures require an amount of solid CaO to keep them always saturated in CaO. The aim of this paper is to study the influence of adding CaF₂ and Na₂O on the desulfurization efficiency of CaO-Al₂O₃ system mixtures. Desulfurizing steel mixtures capable of producing steels with sulfur content of less than 0.0020% were formulated. Desulfurizing mixtures based on CaO-Al₂O₃-flux were prepared with fluxes CaF₂ and Na₂O. All mixtures presented 95% of liquid phase and 5% of solid CaO, which, according to the literature, are the most efficient slags of this system. The equilibrium conditions were simulated using the composition of the mixtures and the steel by means of computational thermodynamic software. In these simulations, the activities of the slag components, the percentage of solids and liquids, the slag viscosity, and the equilibrium sulfur content were determined. The experimental tests were carried out in an induction furnace at 1600 °C. In addition, data on sulfide capacity (Cₗ), sulfur partition (Lₙ) and optical basicity (λ) of the initial mixtures, were calculated. The results of the simulations show that all mixtures have thermodynamic potential to reach the target of sulfur content set for this work. The mixtures with CaF₂ proved to be the most efficient. However, it is possible to obtain sulfur contents of 0.0020% using mixtures without CaF₂.

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1. Introduction

Sulfur, with rare exceptions, is an undesirable element in steel because it causes loss of mechanical properties necessary for the various applications of steel. One of the deleterious effects of sulfur on steel is the hot brittleness, which, for example, impairs the hot rolling process. Thus, the development of steel desulfurization techniques begins to determine the progress of the production of certain types of steel with specific applications [1,2].

Concentrations of the order of 20 ppm or less can be obtained in the secondary refining using a slag of the CaO-Al2O3 and CaO-Al2O3-CaF2 system [3,4].

Steel desulfurization usually occurs by top slag through the diffusion mechanism. When slags containing CaO is used in the process without silicon and aluminum, the desulfurization reaction can be represented according to Eq. 1 (ANDERSON et al.) [5].

\[
(CaO) + [S] = (CaS)_{(s)} + [O] \quad (1)
\]

\[\Delta G_i = 115358 - 38, 66 T [\text{J/mol}]\]

In the presence of silicon and aluminum, the desulfurization occurs according Eq. 2 and 3.

\[4(CaO) + 2[S] + [Si] = 2(CaS)_{(s)} + (Ca2SiO4)_{(s)} \quad (2)\]

\[\Delta G_2 = -492444 + 156.7 T [\text{J/mol}]\]

\[\frac{2}{3}[Al] + [S] + (CaO) \rightarrow (CaS) + \frac{1}{3}(Al_2O_3)\]

\[\Delta G_3 = -319343 + 111, 3T [\text{J/mol}]\]

According to the ionic theory, the sulfur is in the slag in the form of the \text{S}^{2-}\ ion, in some competition with the \text{O}^{2-}\ ions, although oxygen is more likely to pick up electrons than sulfur. The desulfurization reaction can then be written according to Eq. 4.

\[S + O^{2-} \rightarrow S^{2-} + O \quad (4)\]

If oxygen potential is controlled by Si, the desulfurization occurs according to Eq. 5 and if oxygen potential is controlled by aluminum, the desulfurization occurs according to Equation 6 [6].

\[[Si] + [S] + (O^{2-}) = (S^{2-}) + (SiO_2) \quad (5)\]

\[[Al] + [S] + (O^{2-}) \rightarrow (S^{2-}) + (Al_2O_3) \quad (6)\]

According to Kor and Glaws in order to obtain a sulfur content of less than 0.0020% in steel, a calcium aluminate slag is required to previously perform a deoxidation with aluminum [7].

The liquid phase of the slag is the one that participates in the desulfurization reaction. Solid CaO present in the slag is necessary to maintain the liquid phase always saturated with CaO, which guarantees a CaO activity in the liquid phase always equal to 1 [8,9].

Putan et al. studied the influence of viscosity on steel desulfurization. According to the authors, an increase in the viscosity of the slag from 1.5 to 4.5 Poise leads a decrease of 30% in the interaction of the steel-slag interface, which impaired the desulfurization [10].

Simeonov et al. studied effects of CaF2, MgO and SiO2 addition on sulphide capacities of the CaO-Al2O3 slag. The authors concluded that, the substitution of CaO by CaF2 reduced the sulphur equilibrium distribution, while replacement of SiO2 by CaF2 slightly raised the sulphur equilibrium distribution at 1500 °C [11].

Ohta et al. studied the influence of CaF2 on CaO-Al2O3-CaF2 slag. The results show that increasing CaF2 content in desulfurizing slag increased sulphide capacity and sulfur partition coefficient [12].

Matsuzawa and Harada analyzed the mass transport coefficient for the slags of the CaO-CaF2 and CaO-Al2O3 systems. The authors concluded that, to some extent, the mass transfer coefficient in the slag increases with the increase of the liquid phase in both slags. However, after approximately 80% of the liquid phase, the total mass transfer coefficient of the slag decreases. This result suggests that the solid phase of CaO affects the sulfur mass transfer, but its presence is important to obtain a higher global transfer coefficient [13].

The de-S rate occurs according to Eq. 7 [14].

\[- \frac{d [\% S]}{dt} = k' \left( \frac{A}{V_m} \right) [\% S] - [\% S]_e \quad (7)\]

where: [\% S] is sulfur concentration at time t; [\% Seq] is the mass percentage of equilibrium sulfur; k' is the overall coefficient of sulfur mass transport; A is the effective interfacial area; \( V_m \) is the steel volume. Due to the difficulty of determining the parameters A and k', the expression k'(A/V_m) is usually replaced by K, which is the rate constant.

Therefore, an increase in the mass transfer coefficient is expected to increase the desulfurization rate.

Fluorspar is a slag flux that reduces viscosity and promotes a fast dissolution of CaO. However, the use of fluorspar is avoided due to its corrosive attack on refractory surfaces in the converter and in the steel ladle. In addition, there are emissions of strong fluorine acids that corrode piping and gas collection equipment [15].

According to Moraes et al., computational thermodynamics helps modeling and optimizing processes, simulating new processes, as well as developing new alloys. Computational thermodynamics software has been used in the evaluation of phenomena that occur in the metal-slag and metal-inclusions interfaces during the refining process of the steels, in addition to obtaining important properties for the refining processes [16].

The aim of this paper was to study the influence of CaF2 and Na2O fluxes on the desulfurization efficiency of the CaO-Al2O3 system in the production of steels with less than 0.0020% sulfur content. The possibility of the replacing CaF2 by Na2O and also of producing these steels without the use of CaF2 will be verified.
2. Materials and methods

2.1. Experimental tests

The experiments were carried out in the 25-kW induction furnace. First, 1 kg of steel was added to an MgO-C refractory crucible, which, in turn, was inserted into the silica-alumina protection crucible positioned inside the induction furnace. The protecting crucible had a three-hole cover—one in the center, through which sample withdrawals and addition of mixtures were made; and two smaller ones, through which the thermocouple and the alumina tube for argon injection were introduced. The oxygen content controlled by the argon injection in a flow rate of 5 NL/min to provide an inert atmosphere and started at the same time as the heating of the furnace and remained throughout the test. Fig. 1 shows the equipment layout in the steel desulfurization tests.

Once the steel melted, a thermocouple was inserted into the bath to gauge the temperature. The bath stirring was ensured by induction. Once the working temperature was confirmed (1600 °C), the initial sample was withdrawn.

Subsequently, the desulfurizing mixture was added at the rate of 10 g to 1000 g of steel (10 kg/t of steel). Steel samples were taken at 4, 6, 8, 15, and 20 min to determine the sulfur content with the reaction time.

The desulfurization efficiency was calculated by means of Eq. (8):

\[ \eta (\%) = \frac{[S]_{\text{initial}} - [S]_{\text{final}}}{[S]_{\text{initial}}} \times 100 \]  

where: \( \eta (\%) \) is the desulfurization efficiency; \([S]_{\text{initial}}\) is the initial percentage of sulfur in the steel; \([S]_{\text{final}}\) is the final percentage of sulfur in the steel.

2.2. Materials and determination of the mixtures

The aluminum killed steel used in the experiments was provided by the ArcelorMittal Tubarão. It came from the tip of a slag cast in the company’s continuous casting. Its chemical composition, also provided by the company is 0.718 % C, 0.073 % Si, 0.71 % Mm, 0.013 % P, 0.0031-0.007 % S, 0.0273 % Al, 0.039 % Nb, 0.0029 % Ca, 0.0003 % O, and balance Fe.

CaO, Al\(_2\)O\(_3\) and Na\(_2\)O were chemically pure reagents. CaF\(_2\) was provided by Tecnosulfur and the chemical composition, also provided by the company is 3.7% CaO, 2.55% SiO\(_2\), 2.48% Al\(_2\)O\(_3\) and 91.27% CaF\(_2\).

The selection of the mixtures and conditions used in this work was based on the study of Pezzin [17], where the slag with 95% of liquid phase and 62.6% of CaO and 37.4% of Al\(_2\)O\(_3\) showed better desulfurization efficiency (83.88%). This work aimed at evaluating the effect of viscosity on desulfurization, as well as investigating the efficacy of the fluxes used for this slag with 95% liquid phase. The working temperature used was 1600 °C; thus, it remained at the same temperature.

All mixtures were prepared to have approximately 95% of liquid phase (simulation with ThermoCalc 5.0 software), by determining the desired amount of fluxes (CaF\(_2\) or Na\(_2\)O) and varying the amount of CaO and Al\(_2\)O\(_3\) until the thermodynamic simulation indicated a result of 95% of liquid phase. The composition of the mixtures is shown in Table 1.

Regarding the nomenclature of the mixtures, C was used for presence of CaO, A for presence of Al\(_2\)O\(_3\) and NF/F/N, being N\(^2\) for flux content, F for presence of CaF\(_2\), and N for presence of Na\(_2\)O.

2.3. Computational thermodynamic simulations

The equilibrium of the desulfurizing mixtures with the steel composition used in the experiments was calculated. The equilibrium simulations between the mixture and the steel were performed using the ThermoCalc 5.0 software; the database used for the calculations was the SLAG3 Database. The viscosity of the liquid phase of the added desulfurizing mixtures was calculated using the FactSage 7.6® software. Eq. 9 [18] must be used for correction, since it considers the fraction of the solid phase of the mixture, and with the data of the liquid phase viscosity the effective viscosity of the mixture can be calculated.

\[ \eta_e = \eta \times (1 - 1.35 \times X_{\text{sol}})^{-\frac{1}{2}} \]  

where: \( \eta_e \) = Effective viscosity of the mixture; \( \eta \) = Viscosity of liquid slag and \( X_{\text{sol}} \) = Fraction of the solid phase.

3. Results and discussion

3.1. Experimental results

Table 2 shows the initial and final sulfur contents and the efficiency of the mixtures used, and Fig. 2 shows the variation of the S content in the steel over time.

When analyzing Table 2, it was initially observed that the most efficient mixtures were those with fluor spar and the least efficient were those with Na\(_2\)O in their composition.

It was observed that the CA mixture showed satisfactory results, with final sulfur content in the steel equal to 0.0005%, a slag indicated for the desulfurization process.

From Table 2 and Fig. 2 it can be observed that the mixtures with fluor spar and the CA mixture showed higher efficiency, with CA6F being the most efficient (94.12%). This result is in accordance with the one found by Grillo [8], where the most efficient slag had fluor spar in its composition. However, care should be taken with the amount of fluor spar added since in excess, it can cause a greater wear of the equipment’s refractory lining, besides being harmful to the environment.

Furthermore, Fig. 2 also shows that the initial composition of the steel is an important factor in the reaction rate. As previously mentioned, the most efficient mixture was CA6F. However, as the initial sulfur content was not the same in all experiments, this mixture was not the one with the highest reaction rate (Eq. 7), as shown in Fig. 2. The CA6F mixture had a faster decrease in sulfur content: from 0.0071% of S to 0.0009% in 20 min (variation of 0.0062%). However, the CA6F mixture, which had the lowest initial sulfur content of 0.0017%, reached 0.0001% in 20 min (variation of 0.0007%). The reaction tends to occur faster for mixtures with higher initial sulfur contents, since there is more sulfur available for the reaction, according
to the Eq. 7. If the initial sulfur content in the CA8F mixture were the same as that of the CA6F mixture, the reaction rate would probably be as fast as that of CA6F.

For mixtures with Na2O, it was observed that the increase of this compound in the chemical composition of the mixture decreased the efficiency of desulfurization, since the CA mixture obtained efficiency of 83.33%, while the less efficient mixture was the one with higher Na2O content in its composition (CA6N, 31.58%).

Fig. 2 also shows that the most efficient mixtures (CA and CA2N) had a higher reaction rate, according to the Eq. 7, that is, the slope of the straight line from 0 to 4 min is higher for these mixtures, which leads to a decrease in sulfur in the first four minutes. The CA mixture went from 0.003 to 0.0012 (60% efficiency) and the CA2N mixture from 0.007 to 0.004 (42.86% efficiency), while the CA6N mixture from 0.0057 to 0.0055 (3.51% efficiency) and the CA4N from 0.0023 to 0.0017 (26.09% efficiency). In this case, a higher reaction rate led to higher desulfurization efficiency, but this does not always occur, as previously shown with the mixtures CA8F and CA6F.

3.2. Evaluation of the computational results for steel desulfurizing mixtures

3.2.1. Analysis of the process by determining the phases present in the slag

The equilibrium conditions for the desulfurization mixtures at 1600 °C without the presence of steel were simulated using the software Thermocalc to verify the phases present in the mixtures at the working temperature. The mixtures with Na2O and CaF2 were designed to obtain approximately 95% of liquid, as mentioned above. Table 3 shows the results obtained only for the equilibrium of the mixtures at 1600 °C with the Thermocalc software while Fig. 3 shows the % of liquid phase x efficiency.

Table 3 shows that the liquid/solid phase content is not associated with the efficiency of the desulfurization reaction, as for the same amount of liquid/solid phase, different

Table 1 – Composition of the desulfurizing mixtures. Source: Adapted from Grillo [8].

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Mixture</th>
<th>CaO (%)</th>
<th>Al2O3 (%)</th>
<th>CaF2 (%)</th>
<th>Na2O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CA</td>
<td>62.6</td>
<td>37.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>CA8F</td>
<td>59</td>
<td>33</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>CA6F</td>
<td>59.9</td>
<td>34.1</td>
<td>6</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>CA4F</td>
<td>60.8</td>
<td>35.2</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>CA2F</td>
<td>61.7</td>
<td>36.3</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>CA6N</td>
<td>58.4</td>
<td>35.6</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>CA4N</td>
<td>59.7</td>
<td>36.3</td>
<td>–</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>CA2N</td>
<td>61.1</td>
<td>36.9</td>
<td>–</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2 – Initial and final sulfur contents and the efficiency of the mixtures used.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mixture</th>
<th>Sinitial</th>
<th>Sfinal</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>CA8F</td>
<td>0.0017</td>
<td>0.0001</td>
<td>94.12</td>
</tr>
<tr>
<td>3</td>
<td>CA6F</td>
<td>0.0071</td>
<td>0.0009</td>
<td>87.32</td>
</tr>
<tr>
<td>4</td>
<td>CA4F</td>
<td>0.0064</td>
<td>0.0009</td>
<td>85.85</td>
</tr>
<tr>
<td>1</td>
<td>CA</td>
<td>0.003</td>
<td>0.0005</td>
<td>83.33</td>
</tr>
<tr>
<td>5</td>
<td>CA2F</td>
<td>0.0065</td>
<td>0.0012</td>
<td>81.54</td>
</tr>
<tr>
<td>8</td>
<td>CA2N</td>
<td>0.007</td>
<td>0.0002</td>
<td>71.43</td>
</tr>
<tr>
<td>7</td>
<td>CA4N</td>
<td>0.0023</td>
<td>0.0012</td>
<td>47.83</td>
</tr>
<tr>
<td>6</td>
<td>CA6N</td>
<td>0.0057</td>
<td>0.0039</td>
<td>31.58</td>
</tr>
</tbody>
</table>
efficiency values were obtained. A liquid phase content of 94.92% was obtained for the C6N4 mixture with an efficiency of 31.6%, while for the CAF mixture a liquid phase content of 95.15% was obtained for the desulfurization efficiency of the order of 94.1%. Therefore, the efficiency of the desulfurization process cannot be predicted only by defining the amount of liquid phase; other parameters should be considered, such as the properties of the liquid phase formed. Besides, in these mixtures, CaO was identified only in the solid phase.

It was observed that the addition of the fluxes decreased the viscosity of the liquid phase. The increase in the fluxes led to a lower viscosity of the liquid phase.

However, the result obtained for the mixtures with Na2O was opposite to the result expected for fluorspar, since the increase in Na2O decreased the efficiency of desulfurization instead of increasing it.

For a better understanding of the results, the influence of CaF2 and Na2O will be analyzed separately below.

### 3.2.2. Influence of CaF2 addition to CaO-Al2O3 slags

Based on the results shown in Tables 2 and 3, the values of equilibrium sulfur were correlated with desulfurization efficiency, as well as with initial sulfur and final sulfur. These correlations are shown in Fig. 3. Fig. 4 shows the correlation between the chemical composition and the desulfurization efficiency, the if it is an empirical proposal. The equations are linear for the first case and polynomial for the second, and are proposed empirically.

Fig. 3 (A) shows that the correlation between efficiency and equilibrium sulfur is low; however, a trend could be observed whereby the higher the equilibrium sulfur, the lower is the desulfurization efficiency. As the efficiency and rate of desulfurization depend on factors other than equilibrium sulfur, a lower equilibrium sulfur content does not imply a more efficient mixture. In addition, Fig. 3 (B) shows that the mixture added to a steel with lower initial sulfur content achieves a lower equilibrium sulfur content; similarly, a mixture with lower final sulfur attempts to reach a lower equilibrium sulfur (Fig. 3 (C)). As the composition of the steel influences the equilibrium sulfur, the correlation between the equilibrium sulfur and the efficiency becomes lower, since the composition of the steel varied in the different experiments.

When analyzing Fig. 4, it was observed that for the same amount of liquid, the same amount of solid CaO formed, and CaO activity equal to 1, increased CaO and Al2O3 in the composition of the mixtures decreases efficiency, since the increase of CaF2 in the mixtures increases desulfurization efficiency. This occurred because for the content of CaF2 to increase (8, 6, 4 and 2%) it was necessary to decrease CaO and Al2O3 contents, and the increase in CaF2 content decreases the corrected viscosity, leading to higher efficiency as viscosity is directly related to desulfurization efficiency. Less viscous slag increases k (mass transfer coefficient) favoring the transfer of sulfur from the metal to the slag. This behavior is demonstrated in Fig. 5, the equations are linear and are proposed empirically.

Fig. 5 shows that the increase in CaF2 decreased the corrected viscosity and, as previously explained, it was necessary

### Table 3 - Phases formed in the desulfurizing mixtures using ThermoCalc at 1600°C.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>CaO (g)</th>
<th>Solid (%)</th>
<th>Liquid Slag (%)</th>
<th>Liquid (%)</th>
<th>Visc. of the liquid phase (poise)</th>
<th>S_eq (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA8F</td>
<td>0.48</td>
<td>4.85</td>
<td>57.23</td>
<td>34.89</td>
<td>0.21</td>
<td>7.67</td>
<td>95.15</td>
</tr>
<tr>
<td>CA6F</td>
<td>0.49</td>
<td>4.87</td>
<td>58.08</td>
<td>36</td>
<td>0.16</td>
<td>3.76</td>
<td>95.13</td>
</tr>
<tr>
<td>CA4F</td>
<td>0.49</td>
<td>4.93</td>
<td>58.93</td>
<td>37.13</td>
<td>0.11</td>
<td>3.84</td>
<td>95.07</td>
</tr>
<tr>
<td>CA</td>
<td>0.51</td>
<td>5.07</td>
<td>60.6</td>
<td>39.4</td>
<td></td>
<td>94.93</td>
<td>94.99</td>
</tr>
<tr>
<td>CA2F</td>
<td>0.5</td>
<td>4.98</td>
<td>59.77</td>
<td>38.26</td>
<td>0.21</td>
<td>1.93</td>
<td>95.02</td>
</tr>
<tr>
<td>CA2N</td>
<td>0.51</td>
<td>5.1</td>
<td>59.01</td>
<td>38.88</td>
<td></td>
<td>94.9</td>
<td>94.98</td>
</tr>
<tr>
<td>CA4N</td>
<td>0.5</td>
<td>5.02</td>
<td>57.57</td>
<td>38.22</td>
<td>0.21</td>
<td>4.21</td>
<td>94.98</td>
</tr>
<tr>
<td>CA6N</td>
<td>0.51</td>
<td>5.08</td>
<td>56.17</td>
<td>37.5</td>
<td>0.21</td>
<td>6.32</td>
<td>94.92</td>
</tr>
</tbody>
</table>

### Fig. 3 - Influence of (A) equilibrium sulfur on desulfurization efficiency and of (B) initial sulfur and (C) final sulfur on equilibrium sulfur.
to decrease the amount of CaO and Al₂O₃ to increase the amount of CaF₂; thus, CaO and Al₂O₃ behavior was opposite to that of CaF₂.

Putan et al. state in their work that the viscosity of the synthetic slag is important when it comes to chemical processes that occur during the treatment of molten steel, having a significant influence in the slag emulsion capacity. An increase in the viscosity of the slag from 1.5 to 4.5 Poise leads to a 30% decrease in the steel-slag interaction surface. Therefore, less viscous slags tend to be more efficient, as shown in Fig. 6(d), which shows the correlation between the corrected viscosity and the desulfurization efficiency [9]. Fig. 5(d) shows that by reducing the viscosity in the mixtures with the same amount of solid phase, the efficiency increased, as stated by Putan et al. [10], Ko and Park [19], and Kim and Sohn [20].

3.2.3. Influence of Na₂O addition to CaO-Al₂O₃ slags

According to the equilibrium simulation between the metal and the slag, it was observed that the Na₂O did not remain in the slag, having almost all of it been reduced to the gaseous form, Na(g) (99.03%) and Na₂(g) (0.07%). This decrease in Na₂O was probably caused by the Al and Si contents de acordo com as Eq. (10) and (11).

That’s because in the equilibrium simulations conducted, when adding Na₂O there was a decrease in Si and Al contents in the steel, as well as formation of SiO₂, and increase in Al₂O₃ in the liquid slag. There was no 3Na₂O(s) in the slag

\[ 3\text{Na}_2\text{O(g)} + 2\text{Al} = \text{Al}_2\text{O}_3(g) + 6\text{Na}_2(g) \]  
(10)

\[ 2\text{Na}_2\text{O(g)} + \text{Si} = \text{SiO}_2(g) + 4\text{Na}_2(g) \]  
(11)

Iwai and Kunisada added the mixture by the immersion method, and although Na₂O reduces to Na₂(g) and Na(g), the gas reacts with the sulfur present in the steel, releasing NaS(g). On the other hand, Kim et al. and Li et al. added the pre-fused mixture, which may have contributed to the Na₂O remaining in the mixture [21–23].

This difference in the present study occurred because of the method used for adding the mixtures, since in the experiments part of this work, the different reagents were mixed and added to the bath still in powder form, facilitating the release of Na(g) and Na₂(g).

Therefore, a mass balance was made considering the decrease in Na₂O, and the new chemical composition of the mixtures is shown in Table 4.

For better visualization and discussion, the results were divided into groups according to the different mixtures used, and from this point onwards, mixtures with Na₂O will always be those that consider the decrease in Na₂O.

Based on the results shown in Tables 2 and 3, the values of equilibrium sulfur were correlated with the desulfurization efficiency, as well as the initial sulfur and final sulfur. These correlations are shown in Fig. 6, the equations are linear and are proposed empirically.

Fig. 6 shows that the correlation between efficiency and equilibrium sulfur is low; however, a trend could be observed whereby the higher the equilibrium sulfur, the lower is the desulfurization efficiency, since, as mentioned earlier, a lower equilibrium sulfur content does not imply a more efficient mixture. In addition, Figs. 6 (B) and (C) also show a trend whereby the higher the initial and final sulfur contents, the higher is the equilibrium sulfur content. Thus, there was a lower correlation between equilibrium sulfur and efficiency, because the steel composition varied in the different experiments.

It was observed that the composition of the liquid phase was the same for all mixtures, because they are within the
same field in the binary diagram CaO-Al₂O₃ at a constant temperature and, thus, the composition of the liquid does not change. However, the amount of liquid phase formed, since the amount of solid CaO increased with the increase in CaO content in the composition of the mixtures, according to Table 4. Given that the composition of the liquid phase was the same, the viscosity of the liquid phase was also repeated. The desulfurization efficiency was correlated with the amount of solid CaO formed, and the result is shown in Fig. 7 (A); Fig. 7 (B) shows the correlation between the corrected viscosity and the desulfurization efficiency, the equations are linear and are proposed empirically.

Fig. 7 (A) shows that the increase in CaO(%) increased the desulfurization efficiency. This is probably because the mixture with a higher amount of CaO(%) was able to guarantee its supply during the whole experiment, thus having CaO activity equal to 1, ensuring improved conditions for desulfurization, as stated by Xu et al. [8]. It was also observed that the mixture with a value of CaO(%) closer to 5%, presented higher levels of efficiency.

Fig. 7 (B) shows that the corrected viscosity increased with the desulfurization efficiency, since the increase in solid CaO increased the corrected viscosity and the desulfurization efficiency.

Table 4 – New composition of the mixtures considering loss of Na₂O, liquid and solid slag of mixtures CA6N*, CA4N* and CA2N*.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Initial composition</th>
<th>Liquid slag</th>
<th>CaO(%)</th>
<th>Visc. of liquid phase</th>
<th>Corrected visc.</th>
<th>%S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>Al₂O₃</td>
<td>CaO</td>
<td>Al₂O₃</td>
<td>%Liq</td>
<td></td>
</tr>
<tr>
<td>CA6N*</td>
<td>62.13</td>
<td>37.87</td>
<td>60.6</td>
<td>39.4</td>
<td>96.12%</td>
<td>3.88</td>
</tr>
<tr>
<td>CA4N*</td>
<td>62.19</td>
<td>37.81</td>
<td>60.6</td>
<td>39.4</td>
<td>95.97%</td>
<td>4.03</td>
</tr>
<tr>
<td>CA2N*</td>
<td>62.35</td>
<td>37.65</td>
<td>60.6</td>
<td>39.4</td>
<td>95.57%</td>
<td>4.43</td>
</tr>
</tbody>
</table>

4. Conclusion

Considering the conditions used in this work, the following can be concluded:

- The CA (CaO-Al₂O₃ system) mixture achieves a final sulfur of approximately 0.0005% without the use of fluxes (CaF₂ and Na₂O).
- Mixtures with CaF₂ in their composition improved the desulfurization process. Increasing the amount of CaF₂ (8, 6 and 4%) in the mixture increased efficiency, with final sulfur contents of 0.0001%, 0.0009% and 0.0009%, respectively.
- The mixtures with CaO-Al₂O₃-Na₂O were the most ineffective due to the form the reagents were mixed and added to the bath, leading to a decrease in Na₂O and volatilization of Na(%)..

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References


