Original Article

Analysis of the influence of the solid and liquid phases on steel desulfurization with slags from the CaO–Al₂O₃ systems using computational thermodynamics

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Abstract

Normally, CaO is used in steel desulfurization in slags from the systems: CaO–CaF₂, CaO–Al₂O₃, and CaO–SiO₂. Among these, the CaO–CaF₂ slags are more efficient. This paper uses computational thermodynamics to study the influence of solid and liquid phases in the efficiency of desulfurizing slags in the CaO–Al₂O₃ system. Desulfurizing slags were prepared to produce steels with sulfur levels below 20 ppm. Simulations using computational thermodynamics were made to determine the properties of the slags at 1600 °C. The experimental tests were carried out in an induction furnace at 1600 °C. The experimental results showed that slags from CaO–Al₂O₃ system can be as efficient as slags from CaO–CaF₂ system, reaching final sulfur contents lower than 10 ppm. The conclusion was that slags containing higher quantities of liquid phase are more efficient. However, the presence of some amount of solid CaO is necessary to keep the liquid phase of slag always saturated in CaO and its activity equal to unity. A Steel Desulfurization Factor was proposed as an easy way to estimate the desulfurization efficiency.

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1. Introduction

The research on high-efficiency and low-cost production technology of the low sulfur and ultra-low sulfur steel has become a focus recently aiming to improve the product profit and to increase products market competitiveness [1]. Sulfur is an
impurity in the steelmaking industry that causes many problems. It is known to contribute hydrogen-induced cracking [2,3], to deteriorate hot ductility [4,5], and increase solidification cracking susceptibility during welding processes [6].

About 90% of the metal produced in the iron blast furnace is desulfurized before it is sent to be processed in a steelmaking furnace because, in general, desulfurizing hot metal is more economical than desulfurizing steel [7]. However, to achieve the present demands for the sulfur contents in steel and reach values below 0.01% a deeper desulfurization process during secondary steelmaking is necessary [8]. Desulfurization by treatment with synthetic slag (in this work, the term slags refers to the amount of solid and liquid phase formed over the liquid metal after adding the desulfurizing mixture) on top of molten steel is being practiced [8].

When CaO is used as desulfurizer, the desulfurization reaction may be represented in accordance with Eq. (1) [9,10].

\[
\langle \text{CaO} \rangle + \langle \text{S} \rangle \rightarrow \langle \text{CaS} \rangle + \langle \text{O} \rangle; \Delta G^\text{″} = 114300 - 32.5T[J/mol]
\]  

(1)

where \( < > \) means that the compound is solid; \( [ ] \) means that the compound is dissolved in the steel.

According to Kor and Glaes [11], in the presence of dissolved aluminum in steel, the desulfurization reaction is represented by Eq. (2).

\[
\frac{2}{3}\langle \text{Al} \rangle + \langle \text{S} \rangle + \langle \text{CaO} \rangle \rightarrow \langle \text{CaS} \rangle + \frac{1}{3}\langle \text{Al}_2\text{O}_3 \rangle; \Delta G^\text{″} = -319343 + 111.3T[J/mol]
\]  

(2)

where \( ( ) \) means that the compound is dissolved in the liquid slag.

The desulfurization with the use of synthetic liquid top slag in secondary steelmaking is based on the passage of sulfur dissolved in the liquid steel to the slag. It is possible to desulfurize in the ladle a totally Al-killed steel using slags based on CaO to sulfur levels lower than 20 ppm [12].

Aluminum is usually added to promote steel deoxidization. The sulfur partition ratio or sulfur distribution \((L_S)\) decreases with the increase of the activity of the oxygen dissolved in the steel [13]. The sulfur partition ratio measures the sulfur distribution between the slag and the metal [14]. Xu et al. [15] used the relation presented in Eq. (3) in their work to calculate the sulfur partition of their experiments.

\[
L_S = \left(\frac{\langle \text{S} \rangle_f}{\langle \text{S} \rangle_t}\right) = \frac{m_m(\langle \text{S} \rangle_0 - \langle \text{S} \rangle_f)}{m_s \langle \text{S} \rangle_t}
\]  

(3)

where \( \langle \text{S} \rangle_f \) is the final sulfur mass percentage in the slag; \( \langle \text{S} \rangle_t \) is the final percentage of sulfur in steel; \( \langle \text{S} \rangle_0 \) is the initial percentage of sulfur in steel; \( m_m \) is the mass of metal (kg); \( m_s \) is the mass of slag (kg).

The relationship between the mass of alumina and the mass of lime in the slag has an influence on the sulfur partition ratio and on the sulfide capacity \((C_S)\) [13]. The sulfide capacity is defined as the thermodynamic ability of a liquid slag to remove sulfur from steel and can be used to compare the desulfurization characteristics of different slags [16].

According to Fincham and Richardson [16] the sulfide capacity is given by Eq. (4).

\[
C_S = \left(\frac{\langle \text{S} \rangle}{\langle \text{O} \rangle}\right)^{1/2} = \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}}\right)^{1/2}
\]  

(4)

where \( p_{\text{O}_2} \) is the oxygen partial pressure; \( p_{\text{S}_2} \) is the sulfur partial pressure.

Ghosh [8] compare values of sulfide capacity from typical slag systems of interest in secondary steelmaking at 1600 °C: CaO–CaF₂, CaO–Al₂O₃, CaO–Al₂O₃–CaF₂, and CaO–SiO₂. The author shows, for CaO–Al₂O₃ system, that varying the molar fractions of CaO and Al₂O₃, it is possible to achieve the same values of sulfide capacity of slags from CaO–CaF₂ system [8]. Fluxes par has been used very sparingly because of its very corrosive attack of all types of refractories and also the formation of strong acids by the fluorides, which could become an environmental issue [17].

Empirical models were created to calculate the sulfide capacity as a function of the optical basicity \((\Lambda)\), which is a function of the slag composition. Sosinsky and Sommerville [18] developed an empirical equation to calculate the sulfide capacities of an oxide slag of virtually any composition at any temperature between 1400 and 1700 °C. Their model is shown in Eq. (5).

\[
\log C_S = \frac{22690 - 54640.1}{T} + 43.6\Lambda - 25.2
\]  

(5)

where \( T \) is the temperature in Kelvin; \( \Lambda \) is the optical basicity which is calculated according to Eq. (6).

\[
\Lambda = \sum X_i \Lambda_i
\]  

(6)

where \( \Lambda_i \) is the optical basicity of the oxide \( i \); \( X_i \) is given by Eq. (7).

\[
X_i = \frac{N_i \cdot n_{O_i}}{\sum N_i \cdot n_{O_i}}
\]  

(7)

where \( N_i \) is the molar fraction of the oxide \( i \); \( n_{O_i} \) is the number of oxygen atoms in the oxide \( i \) molecule.

The optical basicity concept can only be applied to steelmaking slags if these are completely liquid [19]. Thus, the model of Sosinsky and Sommerville [18] is valid only for liquid slags or for the liquid phase of a multi-phase slag. Using their relation to a whole multi-phase slag (not only to the liquid phase) can generate erroneous interpretations.

Grillo [20] performed different experiments of steel desulfurization with slags containing CaO, Al₂O₃, Fe₂O₃, MgO, MnO, SiO₂, and CaF₂. His work showed that the fraction of liquid and solid phases has a direct relationship with desulfurization efficiency. The author concluded that increasing the amount of liquid phase favored sulfur mass transport in the slag/metal interface and, moreover, increased the rate constant, \( K \). Desulfurization rate can be written as in Eq. (8) [21].

\[
\frac{d\langle \text{S} \rangle}{dt} = k' \left( \frac{A}{V_m} \right) \left( \langle \text{S} \rangle - \langle \text{S} \rangle_{eq} \right)
\]  

(8)
where: [\%S] is the mass percentage of sulfur in steel; [\%S]_eq is the mass percentage of equilibrium sulfur; k’ is the overall coefficient of sulfur mass transport; A is the slag/metal interface area; V_m is the volume of steel. 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 or kinetic constant.

Some authors, such as Lindström and Sichen [22], have shown in their works (specially in hot metal desulfurization) that a layer of CaS is formed over solid CaO particles, causing desulfurization. However, the experiments of Lindström and Sichen [22] used a mechanical stirrer which dragged the CaO particles into the bulk of the hot metal.

Takahashi et al. [23] evaluated the influence of solid CaO and liquid slag on hot metal desulfurization using an induction furnace. They found that the desulfurization rate is quite slow when solid lime is immersed into the hot metal without liquid slag. Therefore, in the experiments using solid CaO and liquid slag, the authors said that the mass transfer of sulfur from the liquid slag to the solid CaO does not occur. The authors also stated that solid CaO does not play a direct role in the desulfurization reaction which is solely dependent on the liquid slag.

Xu et al. [15] studied the steel desulfurization behavior and mechanism of CaO-saturated slags used in an induction furnace. Similarly as Takahashi et al. [23] and Xu et al. [15] have found that only the slag liquid phase participates in the desulfurization reaction. However, the authors said that slags with a small amount of solid CaO can optimize desulfurization efficiency.

In different studies using these types of slags, the ones with CaO–CaF2 are always more efficient than the systems CaO–Al2O3–SiO2 and CaO–Al2O3–SiO2 [15,20,24].

Berger et al. [25] studied the influence of different slags from the system CaO–Al2O3–CaF2, with the same amount of liquid phase and different viscosities, on desulfurization efficiency. The authors concluded that efficiency is higher for lower viscosities.

Phase diagrams are crucial to understanding the correlation between composition and the material properties [26]. However, the number of combinations of elements, images or data tables to create all the diagrams needed in an industrial operation, for example, are prohibitively large, especially for more complex diagrams [26,27]. The calculation of phase diagram method (CALPHAD or computational thermodynamics) was developed based on knowledge of thermodynamics [26]. In the CALPHAD method the Gibbs energy of each phase is described as a function of composition, temperature and pressure for calculating phase equilibria [27]. ThermoCalc® and FactSage® are among the most well-known commercially available calculation software packages [26]. Therefore, computational thermodynamics can greatly improve process development and is an important tool for steelmaking process design, although only equilibrium states can be calculated, deviations from the equilibrium could estimate kinetics problems [28]. Thus, computational thermodynamics became a tool to evaluate a large number of steelmaking problems since the requirements for cleanliness, strict adherence to narrow composition ranges, and pressure for more efficiency and economy increased [28].

| Table 1 – Composition of the desulfurizing slags. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Slag            | CaO (mass%)     | Al2O3 (mass%)   | CaF2 (mass%)    | SiO2 (mass%)    |
| D70             | 72.4            | 27.6            | 0               | 0               |
| D75             | 70.4            | 29.6            | 0               | 0               |
| D85             | 66.5            | 33.5            | 0               | 0               |
| D90             | 64              | 36              | 0               | 0               |
| D95             | 62.6            | 37.4            | 0               | 0               |
| D100            | 60.7            | 39.3            | 0               | 0               |
| D25F            | 80.74           | 0.5             | 18.25           | 0.51            |

Thus, the objective of this study was to evaluate the effect of liquid and solid phases amounts of a top slag from the CaO–Al2O3 system on steel desulfurization efficiency. In addition, this work compared the efficiency of slags from CaO–Al2O3 system with the efficiency of a slag from CaO–CaF2 system.

2. Materials and methods

The aluminum killed steel used in the experiments was provided by the ArcelorMittal Tubarão. It came from the tip of a slab cast in the company’s continuous casting. Its chemical composition, also provided by the company is 0.718% C, 0.073% Si, 0.71% Mn, 0.013% P, 0.0031–0.007% S, 0.0073% Al, 0.039% Nb, 0.0029% Ca, 0.0003% O (soluble), and balance Fe.

2.1. Determination of slags composition

First, the amount of liquid phase desired at 1600 °C was chosen for the slags (70%, 75%, 85%, 90%, 95% and 100%). Then, many simulations varying the CaO/Al2O3 mass ratio were made using ThermoCalc® software (Version: TCWS5; Database: SLAG3) until the compositions which produce the desired amounts of liquid and solid phases at 1600 °C were found. A slag from the CaO–CaF2 system was developed in order to compare the efficiency of a slag containing fluor spar with the efficiency of slags from the CaO–Al2O3 system. Table 1 shows the chemical composition of the desulfurizing slags used.

The number in the identification of each slag refers to the fraction of liquid phase shown by the slag at 1600 °C. The slag containing fluor spar followed the same pattern, adding an F, referring to Fluorspar.

2.2. Experimental tests

The experiments were carried out in a 25 kW induction furnace. Initially, 1 kg of steel was added to a crucible made of MgO-C which was then inserted in a silico-aluminous protection crucible positioned inside the induction furnace. The protection crucible had a cover with three holes – a central hole through which the samples were taken from the bath and the slag additions were carried out; two smaller holes, through which a thermocouple and an alumina tube for argon injection at a flow rate of 5 Nl/min in order to maintain the atmosphere inert, were introduced. The argon injection started at the same time as the heating of the furnace and remained throughout the test. The thermocouple was inserted in the bath after the
steel merge, to measure the temperature. The bath stirring was ensured by induction.

After reaching the working temperature (1600 °C), an initial sample was taken. Then, the desulfurizing slag was added in the proportion of 10 g of slag for 1000 g of steel (10 kg/t) and the experiment running time started. The steel samples were taken at the times of 4, 6, 8, 15, and 20 min to determine the variation of the sulfur content as a function of time. The desulfurization efficiency was calculated using Eq. (9).

\[ \eta = \frac{[S]_0 - [S]_f}{[S]_0} \times 100 \]  

(9)

where \( \eta \) is the percentage desulfurization efficiency; \([S]_0\) is the initial percentage of sulfur in the steel; \([S]_f\) is the final percentage of sulfur in the steel.

Fig. 1 shows the layout of the equipment during the experiments.

2.3. Classical thermodynamic analysis

The sulfide capacity and the optical basicity are parameters that essentially refer to a liquid slag. Then, the calculations carried out used the composition of the liquid phase of the slags. The calculations were made through Eqs. (5)–(7).

2.4. Computational thermodynamics simulations

The slag properties and the metal-slag equilibrium (using the initial sulfur, \( S_i \), as the sulfur content), both at 1600 °C, were calculated using ThermoCalc® software.

The viscosities of the slags at 1600 °C were obtained with FactSage® software. However, the viscosity calculated by FactSage® does not consider the solid phase. Thus, the viscosity of each slag was corrected using Eq. (10) [29], since it considers the solid phase fraction in the slag.

\[ \mu_e = \mu_L (1 - 1.35 \times X_{\text{sol}})^{-5/2} \]  

(10)

where: \( \mu_e \) is the effective viscosity of the slag; \( \mu_L \) is the viscosity of the slag’s liquid phase (calculated by FactSage®); \( X_{\text{sol}} \) is the solid phase fraction.

### 3. Results and discussion

#### 3.1. Experimental results

Table 2 shows the values of initial and final sulfur, as well as the equilibrium sulfur content calculated with ThermoCalc®, and the desulfurization efficiency of each experimental test. Table 2 shows that slags D25F, D95, D90, D85, and D75 achieved the goal of reducing the steel sulfur content to below 20 ppm. However, the test using slag D75 already had initial sulfur of 23.5 ppm which contributed to this slag reaching a final sulfur value below 20 ppm. Table 2 also shows that the slag with the lowest equilibrium sulfur value will not necessarily be the most efficient. This indicates the dependence of other parameters (metal/slag interface, stirring, and slag viscosity, among others), kinetics in general, as limiting factors of the desulfurization process.

Fig. 2 shows the percentage variation of sulfur as a function of the experimental time (where: \([S]_0\) is the percentage of sulfur content measured at the time of sampling; \([S]_0\) is the percentage of initial sulfur in the experiment). It can be assessed from Fig. 2 that most of desulfurization (approximately two thirds), occurs before 10 min of experiment, for all the experiments. Moreover, it can be observed that the less efficient desulfurizing slags were the slag with 100% of liquid phase (D100) and the two slags with the highest solid phase percentages (D70 and D75).

Even though oxygen plays an important role in desulfurization thermodynamics, as seen in Eq. (11) [8], its influence was not taken into consideration in this work.

### Table 2 – Initial sulfur \( (S_i) \), final sulfur \( (S_f) \), equilibrium sulfur \( (S_{eq}) \) and efficiency \( (\eta) \) of the experimental tests.

<table>
<thead>
<tr>
<th>Slag</th>
<th>( S_i ) (%)</th>
<th>( S_f ) (%)</th>
<th>( [S]_{eq} ) (%)</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D25F</td>
<td>2.54 × 10⁻³</td>
<td>3.1 × 10⁻⁴</td>
<td>1.9 × 10⁻⁶</td>
<td>87.80</td>
</tr>
<tr>
<td>D95</td>
<td>3 × 10⁻³</td>
<td>5 × 10⁻⁴</td>
<td>1.099 × 10⁻⁴</td>
<td>83.33</td>
</tr>
<tr>
<td>D90</td>
<td>2.8 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>1.068 × 10⁻⁴</td>
<td>78.57</td>
</tr>
<tr>
<td>D85</td>
<td>4.7 × 10⁻⁴</td>
<td>1.6 × 10⁻³</td>
<td>1.916 × 10⁻⁴</td>
<td>65.96</td>
</tr>
<tr>
<td>D100</td>
<td>6 × 10⁻³</td>
<td>3.7 × 10⁻¹</td>
<td>2.638 × 10⁻⁴</td>
<td>38.33</td>
</tr>
<tr>
<td>D75</td>
<td>2.35 × 10⁻³</td>
<td>1.63 × 10⁻⁴</td>
<td>1.099 × 10⁻⁴</td>
<td>30.64</td>
</tr>
<tr>
<td>D70</td>
<td>6.38 × 10⁻³</td>
<td>4.7 × 10⁻³</td>
<td>3.119 × 10⁻⁴</td>
<td>26.33</td>
</tr>
</tbody>
</table>

**Fig. 2 – Sulfur content percentage as a function of time.**
where:

\[
L_S = \left( \frac{f_S}{h_0} \right) \cdot C_S \cdot e^{(3.76 - 0.02t)}
\]  
(11)

where: \( f_S \) is Henry's sulfur activity coefficient; \( h_0 \) is Henry's oxygen activity.

Since the steel used was already aluminum-killed and the experiments had a controlled atmosphere, it was assumed that the oxygen content remained constant.

### 3.2. Influence of the slag’s composition

Table 3 shows the properties of the desulfurizing slags calculated with ThermoCalc® software.

It was observed that, as expected, with the exception of D25F, all slags have the same composition of liquid phase, the same activities of lime and alumina, and only CaO as solid phase. The CaO activity of all slags is equal to 1. Fig. 3 shows a CaO–Al_{2}O_{3} binary diagram that helps explain why this happens.

All slags are within the field “liquid slag + solid CaO”. The slags are represented in Fig. 3 as red dots (D70, D75, D85, D90, D95, and D100, from left to the right). The slag D100 is located at the edge of the field, which explains why it is 100% liquid and, yet, has a CaO activity equal to 1. Therefore, according to thermodynamics, slags within this field at the same temperature will have the same liquid phase composition. The variation in the CaO and Al_{2}O_{3} mass percentages will only entail variations in the solid fraction of CaO formed because the liquid phase within this field is always saturated in CaO, as thermodynamics mandates.

### 3.3. Influence of the liquid and solid phase amounts

Fig. 4a shows the influence of liquid phase percentage on the desulfurization efficiency of slags CaO–Al_{2}O_{3}-based used in the tests.

An increase in efficiency is observed as the percentage of the liquid phase of the slag increases, up to a limit (95%, in this study). This behavior is due to the fact that only the liquid phase participates in the desulfurization reaction [15,23]. Thus, the presence of the solid phase decreases the metal/slag interface area, which is represented by the constant A in Eq. (8). Therefore, the presence of the solid phase impairs desulfurization kinetics. Slags D70 and D75, which have the smallest liquid content, highlight this situation, showing much lower efficiency values than slags D85, D90 and D95. However, it may be observed that slag D100, which has 100% of liquid phase at 1600 °C, was more efficient only in relation to slags D70 and D75. This can be explained by the fact that this slag is completely liquid, but has CaO activity equal to 1. This means that it is about to precipitate solid CaO. Theoretically, this would be the best situation for the desulfurization, with the best possible thermodynamic condition (lime activity equal to 1) and the best kinetic condition possible (without the presence of the solid phase). However, when the desulfurization reaction starts, the sulfur dissolved in the steel reacts with the CaO from the slag, forming CaS. This causes the CaO activity to decrease with the progress of the reaction, consequently impairing thermodynamics. Therefore, it can be said that a small amount of solid lime is required to keep the liquid phase of the slag saturated in CaO and with its activity always equal to 1. This contributes to keeping the percentage of equilibrium sulfur as low as possible and, consequently, the term \([\% S] - [\% S]_{eq}\) from Eq. (8) as high as possible which increases the desulfurization rate.

Thus, it can be said that a fully liquid slag will probably never be the most efficient. It also can be seen in Fig. 4b that the correlation with the efficiency is higher when slag D100 is not used (R^2 = 0.9718).

Similar behavior is observed in the works of Matsuzawa and Harada [24], Grillo [20] and, Xu et al. [15], and are shown in Fig. 5.

It can be observed that all authors have found the same behavior where there is an increase in the desulfurization efficiency with the increase of the liquid phase, up to a certain limit. However, the behavior peculiarities of each line are due to the experimental conditions used such as: type of furnace,
Fig. 4 – (a) Influence of liquid phase percentage on desulfurization efficiency; (b) influence of liquid phase percentage on desulfurization efficiency without slag D100.

Fig. 5 – Comparison of efficiency as a function of the percentage of liquid phase.

<table>
<thead>
<tr>
<th>Slag</th>
<th>Liquid phase viscosity (poise)</th>
<th>Effective viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D70</td>
<td>0.726</td>
<td>2.659</td>
</tr>
<tr>
<td>D75</td>
<td>0.726</td>
<td>2.032</td>
</tr>
<tr>
<td>D85</td>
<td>0.726</td>
<td>1.278</td>
</tr>
<tr>
<td>D90</td>
<td>0.726</td>
<td>1.043</td>
</tr>
<tr>
<td>D95</td>
<td>0.726</td>
<td>0.865</td>
</tr>
<tr>
<td>D100</td>
<td>0.726</td>
<td>0.726</td>
</tr>
<tr>
<td>D25F</td>
<td>0.175</td>
<td>*</td>
</tr>
</tbody>
</table>

* Eq. (10) only works for values of $X_{CaO}$ lower than 0.741.

3.4. Classical thermodynamic analysis

The optical basicity and the sulfide capacity, which are dependent on the composition, presented the same values for all the slags also. The optical basicity and the sulfide capacity values are, respectively, 0.7934 and 0.023. This means that the liquid phase of all slags has the same thermodynamic ability to remove sulfur from steel. Then, the differences in the desulfurizing efficiencies from each other slags are due to the amounts of liquid and solid phases presented by them, as previously discussed.

3.5. Influence of viscosity

The increase in viscosity affects the desulfurization kinetics since it hinders sulfur mass transport in the slag, i.e., it decreases the sulfur mass transport coefficient, represented by $k'$ in Eq. (8) [8].

Table 4 shows the viscosity calculated with FactSage® software and Eq. (10).

Table 4 shows that the slag D25F is the only one with different viscosity of the liquid phase, and this helps to explain its greater efficiency. Even this slag having only 25.72% of liquid phase at 1600 °C, the fluidizing action of the fluorspar makes the solid CaO dissolve quickly to the slag liquid phase, keeping it always saturated in CaO and with its activity equal to 1. Furthermore, the lower liquid phase viscosity (0.175 P) facilitates the sulfur mass transport in it.

Fig. 6a shows the relationship between the effective viscosity and desulfurization efficiency.

It can be observed that the increase in the effective viscosity of the slags was accompanied by a decrease in efficiency, caused by the kinetic loss of the decrease of the kinetic constant. However, slag D100, which is completely liquid and has the lowest effective viscosity (0.726 P) showed low efficiency. This is explained by the fact mentioned in Section 3.3, that, when the desulfurization reaction begins, the sulfur dissolved in the steel reacts with the CaO of the slag forming CaS, which decreases the CaO activity in the slag. It can be observed in Fig. 6b that, when slag D100 is not used, the correlation ($R^2$) of the effective viscosity with desulfurization efficiency is equal to 0.9848.

Slag's viscosity can influence on desulfurization rate because of its influence on lime dissolution to the liquid phase and because of its influence on the mass transfer of reactants and products in the slag. A low viscosity (in terms of solid phase, which means effective viscosity) causes a faster CaO dissolution into the slag [30,31]. As stated in Section 3.3, lime's dissolution is important to keep the liquid phase of the slag always saturated in CaO. The mass transfer of reactants and products in the slag depends on both liquid and solid phases. In other words, the mass transfer depends on the slag's effective viscosity. Then, an increase in the effective
viscosity would decrease the overall coefficient of sulfur mass transport \((k')\) from Eq. (8).

### 3.6. Efficiency prediction

As observed in Fig. 4b and Fig. 6b, the correlation of liquid phase percentage and of effective viscosity with desulfurization efficiency is higher than 0.9 for slags with solid CaO and without CaF\(_2\). This is due to the fact that, in this study, these slags have the same liquid phase composition and the CaO activity equal to 1, therefore their efficiency is a function of the liquid phase percentage and of the viscosity.

This occurs because of the more the percentage of liquid phase, the higher the value of \(A\) in Eq. (8), and, the lower the viscosity, the higher the value of \(k'\) in Eq. (8) and the solid CaO dissolution.

Based on these properties, a new parameter was created to measure the efficiency of desulfurizing slags from CaO–Al\(_2\)O\(_3\) system that have some amount of solid CaO. It was called Steel Desulfurization Factor \((SF_{\text{Des}})\) which is calculated according to Eq. (12).

\[
SF_{\text{Des}} = \%L - \mu
\]  

where \(SF_{\text{Des}}\) is the Steel Desulfurization Factor; \(\%L\) is the liquid phase percentage; \(\mu\) is the viscosity (of the liquid phase or effective, depending on each case).

Fig. 7 shows the relation of \(SF_{\text{Des}}\) (calculated using the effective viscosity) with desulfurization efficiency and Fig. 7b shows the relation of \(SF_{\text{Des}}\) (calculated using the liquid phase viscosity) with desulfurization efficiency.

It can be seen in Fig. 7a and b that the correlations \((R^2)\) of the steel desulfurization factor (without slag D100) with efficiency are high. Since the correlation of the factor calculated using the liquid phase viscosity was higher, the equation of the trend line of the graph in Fig. 7b, shown below in Eq. (13), was used to predict the efficiency of the desulfurizing slags.

Fig. 7c shows the results of predicted efficiency versus the actual efficiency measured in the experiments. It can be seen that the line equation of the graph is very close to the perfect agreement (which would be a straight line with the equation: \(y = x\); represented by the dashed line in Fig. 7b), where the predicted efficiency would be equal to the actual efficiency obtained.

\[
PE = -0.0205(SF_{\text{Des}})^2 + 5.8898(SF_{\text{Des}}) - 287.03
\]  

where \(PE\) is the predicted efficiency; \(SF_{\text{Des}}\) is the steel desulfurization factor (calculated using the liquid phase viscosity).

It can be observed that the steel desulfurization factor is a good way to estimate the desulfurization efficiency, where, the higher the factor, the higher the efficiency. Although, the factor works for slags from CaO–Al\(_2\)O\(_3\) system that presents some amount of solid CaO.
4. **Conclusions**

The results obtained in the present study allow the following conclusions:

- Slags from the CaO–Al₂O₃ system can be as efficient as slags from the system CaO–CaF₂, and can reach values of final sulfur content less than 10 ppm with a slag-to-metal ratio of 10 kg/ton. Thus, the use of fluor spar could be avoided, meaning less corrosion problems on refractory and less environmental problems;
- Slags containing higher percentages of liquid phase have higher desulfurization efficiency. However, the presence of some amount of solid lime is crucial to keep the liquid slag always saturated with CaO and its activity equal to 1. Therefore, there is an optimal point between the amount of liquid and solid phases to maximize desulfurization (95% of liquid phase for this work). Thus, a 100% liquid slag will probably never be the most efficient;
- The steel desulfurization factor can be used to estimate the desulfurization efficiency of a slag from the CaO–Al₂O₃ system that presents some solid CaO.

**Conflicts of interest**

The authors declare no conflicts of interest.

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