

INFLUENCE OF SLAG COMPOSITION ON THE DESULPHURIZATION PROCESS IN THE LADLE FURNACE*

Janacely Demonier Kill¹
Patrick Queiroz dos Anjos²
VÍctor dos Santos Dagostini³
Felipe Fardin Grillo⁴
José Roberto de Oliveira⁵

Abstract

The market has a growing demand for steels with increasingly low sulfur levels. In order to reach these levels, it is necessary that the secondary refining, increasingly improve its desulfurization processes. Motivated by this situation, the present work aims to evaluate the process parameters and the properties of steel desulphurizing slags, determining their influence on the desulphurization efficiency in the ladle furnace. 12 compositions were selected with desulfurizing slag from the CaO-CaC₂-CaF₂ system. The equilibrium conditions were simulated using the composition of mixtures and steel in the computational thermodynamics software FactSage® and Thermo-Calc®. Was concluded that slags containing higher percentages of liquid phase have greater desulfurization efficiency. Another point observed was the decrease in the desulfurization efficiency with the increase in the viscosity of the system. Equations have been suggested to predict slag efficiency.

Keywords: Desulfurization; Secondary refining; Computational thermodynamics.

- 1 *Production Engineer, Supervisor of Secondary Refining at Simec, Simec, Cariacica, ES, Brazil*
- 2 *Metallurgical Engineering Student at Federal Institute of Espírito Santo, Vitória, ES, Brasil*
- 3 *Metallurgical Engineering Student at Federal Institute of Espírito Santo, Vitória, ES, Brasil*
- 4 *Dr. Metallurgical and Materials Engineering. Professor at Federal Institute of Espírito Santo, Vitória, ES, Brasil.*

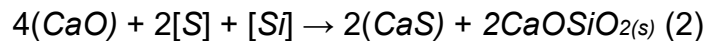
- 5 *Dr. Metallurgical and Materials Engineering, Professor at Post-Graduation Program in Metallurgical and Materials Engineering at Federal Institute of Espirito Santo, Vitória, ES, Brasil.*

1 INTRODUCTION

The desulfurization reaction is based on the transport of sulfur dissolved in the liquid metal to the slag, mainly through diffusion. Desulphurization can be carried out if the slag composition is capable of absorbing sulfur. Slag containing calcium aluminate ($\text{CaO}\cdot\text{Al}_2\text{O}_3$) or fluorite-based slag ($\text{CaO}\cdot\text{CaF}_2$ or $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaF}_2$) have a much greater desulphurizing power than slag with silicate ($\text{CaO}\cdot\text{SiO}_2$) (RIZZO, 2006). Normally, calcium is added to react with sulfur, either directly injected or as a component of the slag, and the most common and cheapest reagent for sulfur removal is lime, CaO . According to Grillo [1], for desulfurization to occur, a stable sulfide must be formed. Therefore, the reaction can be represented according to Equation (1).



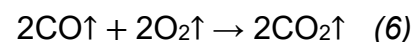
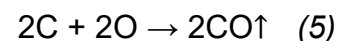
According to Mcfeaters and Fruehan [2], with the use of CaO as a desulfurizing agent in fusions that have the presence of silicon in the steel, in addition to sulfur, the reaction occurs according to Equation (2).



In addition to lime, calcium carbide is also employed as a solid desulfurization agent, as presented in Equation (3):



Motta et al. [3] also say that, similarly, calcium carbide used as a deoxidizing agent will have a desulfurizing effect. This is because carbide deoxidation reactions increase the CaO activity in the slag, as seen in Equation (4), and reduce the oxygen potential in the system as shown in Equations (4), (5) and (6).



According to Pretorius and Oltmann [4] kinetic study is important to predict the speed of reactions as well as their mechanisms. The metal-slag reaction is relatively fast, that is, the rate at which sulfur is transferred from the metal to the metal-slag interface is the limiting one. Choi et al. [5] evaluated the sulfur mass transfer rates in the metal, slag and metal-slag interface and proposed the model presented by Equation (7).

$$\frac{-d[\%S]}{dt} = \frac{k \cdot A}{V} ([\%S] - [\%S_{eq}]) \quad (7)$$

k is the sulfur mass transfer coefficient; A is the interfacial area (m^2); V is the metal volume (m^3); $[\%S]$ and $[\%S_{eq}]$ are the mass percentages of sulfur in the metal at time t and equilibrium, respectively.

The term $\frac{k.A}{V}$ can be replaced by the rate constant of the desulfurization reaction K . Thus, the desulfurization rate is given by Equation (8).

$$\frac{-d[\%S]}{dt} = K \cdot ([\%S] - [\%S_{eq}]) \quad (8)$$

Pezzin [6] says that the kinetic constant determines how quickly the sulfur content in the metal decreases or is transferred from the metal to the slag. The higher the kinetic constant, the faster the sulfur removal. Grillo [1] studied the replacement of lime by marble residues in synthetic desulfurizing slag and presented the relationship between the desulfurization efficiency and certain values of velocity constants (K), and the correlation is shown in Figure 1.

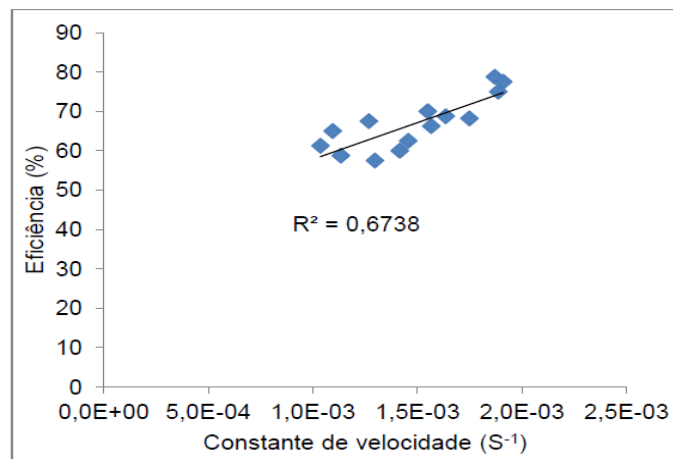


Figure 1. Correlation between values of velocity constants (K) with desulfurization efficiency.

1.1 Influence of solid and liquid phases

The studies by Grillo [1] showed that the percentage of liquid and solid phase is directly related to the desulfurization efficiency. The relationship of the percentage of liquid phase with the desulfurization efficiency obtained in the experiments with steel by Grillo [1] is shown in Figure 2.

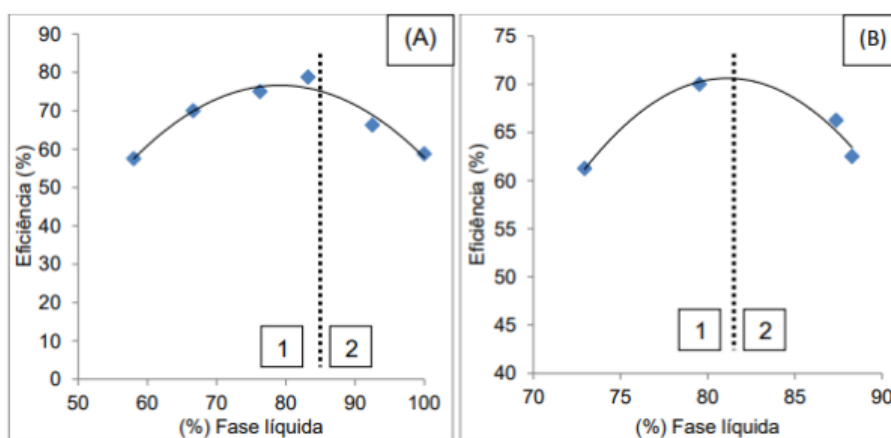


Figure 2. Relationship between the liquid phase fraction and the desulfurizing efficiency of the mixtures formulated based on conventional lime (A) and with marble residue (B).

In region 1, in both cases, it is observed that the increase in the percentage of liquid phase contributed to increase the desulfurizing efficiency. On the other hand,

in region 2, the percentage of liquid phase is still increasing, however, a decrease in desulphurizing efficiency is observed. Thus, the author concluded that the transport of sulfur mass at the metal-slag interface is favored by the increase in the liquid phase to a certain extent.

1.2 Viscosity

According to Mills [7] Viscosity is a measure of the ability of a layer of molecules to move over an adjacent layer of molecules. Viscosity decreases with increasing temperature and for liquid slag the relationship between viscosity and temperature can be represented by the classical Arrhenius relationship presented in Equation (9).

$$\mu = \mu_0 \exp\left(-\frac{E}{RT}\right) \quad (9)$$

μ = Viscosity (Pa·s) ; μ_0 = Arrhenius constant (Pa·s); E = Activation energy (J/mol); R = Gas constant ($J \cdot mol^{-1} K^{-1}$); T = temperature (K).

Slag viscosity, as already mentioned, is influenced by temperature and chemical composition. Hence, for a given stage of the operation, a slag with an appropriate composition at its temperature is sought to obtain an ideal viscosity [6]. In order to have an adequate slag it is important that there is a balance between the oxides that form the slag. Refractory oxides: CaO and MgO and fluxing oxides: SiO₂, Al₂O₃ and CaF₂.

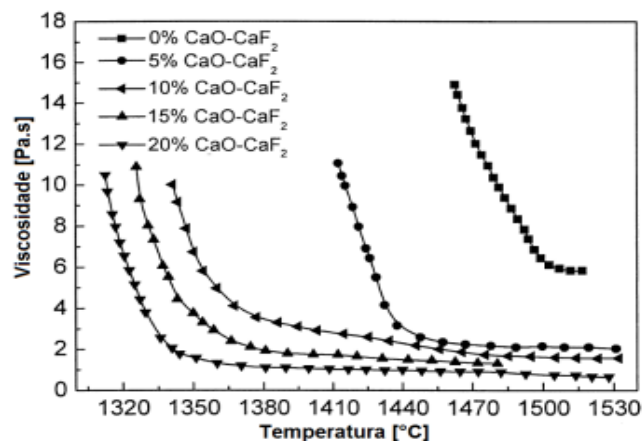


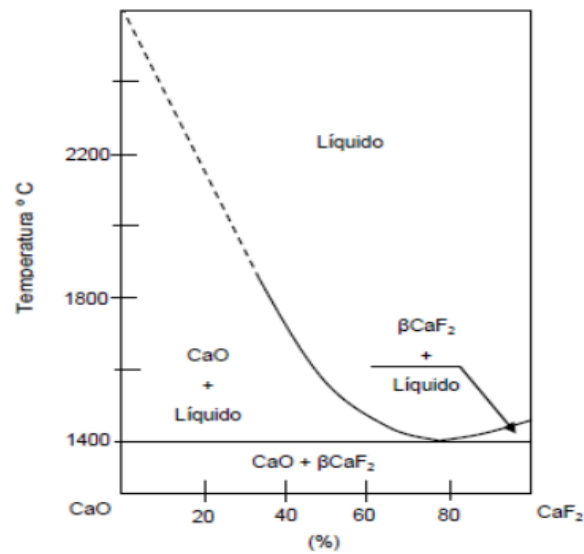
Figure 3. Effect of CaO-CaF₂ on ladle slag viscosity.

An excess of refractory oxides can increase the slag viscosity so that it has an excess of solids, impairing the incorporation of non-metallic inclusions. An excess of fluxing oxides can cause an attack on the steel ladle refractory by reducing the slag viscosity.

1.4 Fluorite

Fluorite is a slag flux that reduces its viscosity and promotes rapid dissolution of CaO. However, the use of fluorite has been avoided due to its corrosive attack on all types of refractory, both in the converter and in the ladle. In addition, there are strong fluorine acid emissions that corrode pipes and gas collection equipment (MILLER et al., 1998).

In Figure 4, the CaO-CaF₂ diagram is shown, where the influence of fluorite in lowering the melting point of this torque is highlighted. Note that the percentage of fluorite can vary approximately up to 50% of the mixture with CaO, forming a 100% liquid phase at steel processing temperatures (FACUNDES, 2019).



Fonte: (Kirmse, 2006).

Figure 4. CaO-CaF₂ Binary Diagram..

1.5 Influence of the passing slag of the electric arc furnace on the desulphurization efficiency

One of the main factors to be evaluated for the formation of a suitable slag for the desulphurization process in the ladle furnace is the amount of slag passed in the casting of the Electric Arc Furnace (EAF) steel and the level of oxidation of this slag. The passage of EAF slag means having a slag with a high content of unstable oxides such as FeO and MnO. This slag is harmful to steel refining, as one of the slag functions is to absorb impurities present in the steel in the form of inclusions. It is generally recommended that these total oxides present in ladle slag be less than 2%. The effect of the presence of these oxides is shown in Figure 5.

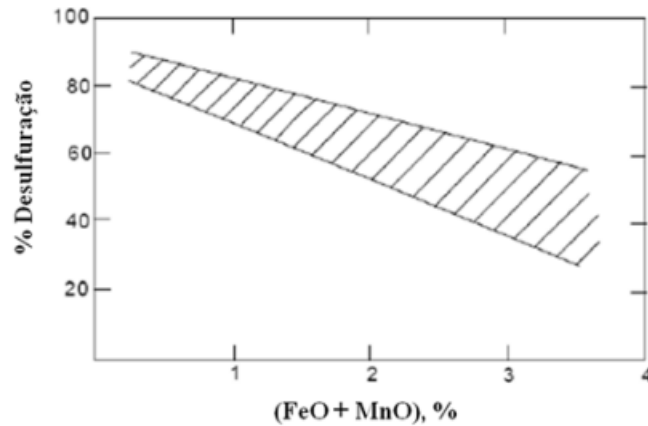


Figure 5. Effect of %FeO + %MnO present in the slag on steel desulphurization.

Ribeiro [8] evaluated the oxidation state of the slag, verifying the reduction in the desulfurization rate in runs treated in the ladle furnace, with an expressive presence of FeT (total iron) and MnO in the slag. During the desulfurization process with the elements and/or oxides mentioned above, the final sulfur percentage of the metal is affected by the oxygen content of the steel. Therefore, it is noted that a high degree of oxidation of the metallic bath coming from the EAF constitutes a great barrier to the desulphurization of steel. Therefore, to increase the desulfurization efficiency, a strong deoxidation is necessary.

2 MATERIALS AND METHODS

2.1 Selection of Steels

Twelve steels were selected from the company's database, with the choice of S20 and S20IT steels (Table 1):

Table 1. Chemical compositions of steels

Nº	T* (°C)	Steel	Chemical composition of steels (% by mass)										
			C	Mn	Si	P	S	Cu	Cr	Ni	Sn	Mo	out.*
1	1584	S20	0,20	0,55	0,16	0,025	0,015	0,29	0,11	0,09	0,043	0,018	0,099
2	1610	S20	0,23	0,57	0,14	0,025	0,020	0,28	0,10	0,07	0,017	0,013	0,068
3	1540	S20	0,20	0,55	0,19	0,018	0,021	0,30	0,09	0,01	0,016	0,019	0,081
4	1617	S20IT	0,21	0,57	0,16	0,025	0,022	0,35	0,09	0,13	0,020	0,033	0,102
5	1600	S20	0,19	0,59	0,16	0,019	0,022	0,35	0,11	0,15	0,019	0,033	0,090
6	1565	S20	0,19	0,56	0,14	0,015	0,021	0,28	0,07	0,07	0,017	0,018	0,070
7	1617	S20IT	0,21	0,55	0,14	0,030	0,019	0,28	0,11	0,08	0,017	0,010	0,063
8	1578	S20	0,21	0,57	0,16	0,017	0,020	0,29	0,09	0,09	0,017	0,030	0,086
9	1630	S20	0,21	0,56	0,14	0,025	0,017	0,29	0,09	0,09	0,023	0,016	0,077
10	1594	S20IT	0,22	0,57	0,15	0,024	0,021	0,34	0,10	0,09	0,021	0,016	0,076
11	1626	S20	0,18	0,57	0,15	0,027	0,022	0,29	0,09	0,07	0,019	0,011	0,066
12	1609	S20IT	0,21	0,55	0,15	0,026	0,019	0,33	0,09	0,08	0,021	0,013	0,077

* T = temperature, out. = other chemical elements

2.2 Desulfurizing slag

In the desulfurization process, 12 different desulfurizing slags were used in order to establish an efficient desulfurization (Table 2).

Table 2. Chemical compositions of desulfurizing slag

Nº	m* (kg)	CaC ₂ (kg)	Chemical composition of slag (% by mass)									
			CaO	MgO	SiO ₂	Al ₂ O ₃	MnO	Cr ₂ O ₃	P ₂ O ₅	FeO	CaF ₂	
1	3438,39	100	45,65	7,39	15,45	7,45	5,27	1,13	0,119	10,72	4,75	
2	3820,44	120	43,44	8,55	26,15	6,07	5,62	0,28	0,11	7,09	2,67	
3	3820,44	120	45,63	12,43	19,66	5,44	6,51	0,53	0,30	6,56	2,94	
4	3820,44	120	46,94	7,55	22,71	4,13	8,68	0,41	0,14	6,81	2,63	
5	3820,44	160	42,71	13,22	23,52	4,10	6,38	0,90	0,12	5,47	3,58	
6	4584,53	160	45,52	8,88	28,38	3,28	6,99	0,28	0,09	5,05	1,51	
7	4584,53	160	57,96	12,67	18,48	5,23	1,26	0,17	0,00	1,28	2,95	
8	4584,53	160	41,29	9,32	28,53	4,36	8,64	0,53	0,08	5,01	2,24	
9	4584,53	160	45,74	7,69	16,89	7,91	5,74	1,35	0,32	11,37	2,98	
10	4584,53	200	44,25	7,91	23,66	3,99	9,87	0,48	0,17	7,49	2,17	
11	4584,53	280	37,17	7,56	19,22	6,49	8,46	0,70	0,28	18,37	1,76	
12	4584,53	200	50,44	6,84	21,51	4,03	7,55	0,34	0,16	6,26	2,87	

* m = mass

2.3 Determination of the influence of slag properties on desulfurization efficiency

For the treatment of data using computational thermodynamics, the software FactSage® 8.0, and the Thermo-Calc® 2021-b were used, where simulations were performed that determined the phases formed in the initial slag, liquid and solid phase fraction, viscosity and CaO activity. The software license belonging to the Federal Institute of Education of Espírito Santo — PROPEMM, Campus Vitória. In FactSage® 8.0 the databases that were used are FToxid and FactPS, with the sub-database SlagA. In Thermo-Calc® 2021-b the TCOX10 database was used. The initial thermodynamic treatment of the slag consisted of simulating the heating of each one of them to the process temperature. The parameters obtained were the CaO activity, the liquid and solids fraction and the liquid viscosity of the slag. These results were also correlated with the efficiency of the process in order to validate and obtain an empirical model to predict the effect of the chemical composition of the slag on the desulfurization of the steel.

3 RESULTS AND DISCUSSION

Through the results obtained by the chemical analysis of the steel and using Equation 11, the desulfurization efficiency (η) of the runs was calculated, as shown in Table 3.

$$\eta(\%) = \frac{[S]_0 - [S]_f}{[S]_0} \cdot 100 \quad (10)$$

Table 3. Desulfurization efficiency (η) of the desulfurization process

Nº	%sulfur in steel		η (%)
	S ₀	S _f	
1	0,041	0,015	63,41
2	0,043	0,020	53,49
3	0,040	0,021	47,50
4	0,043	0,022	48,84
5	0,049	0,022	55,10
6	0,042	0,021	50,00
7	0,050	0,019	62,00
8	0,041	0,020	51,22
9	0,039	0,017	56,41
10	0,045	0,021	53,33
11	0,039	0,022	43,59
12	0,044	0,019	56,82

It can be seen from Table 3 that the desulfurization process efficiencies are low, with the most efficient desulphurizing slag (1 and 7) reaching respectively 63.41 and 62.00%. This is due to the fact that the steel produced does not need a high rate of desulphurization, thus allowing it to adapt to its targeted chemical composition range with reduced sulfur removal.

3.1 Simulations of the properties of desulfurizing mixtures

Simulations were carried out with the software FactSage® and Thermo-Calc® of the equilibrium conditions for the desulphurizing mixtures, with or without the addition of CaC₂, in order to verify some variables in the desulphurization process of the ladle furnace.

Table 4 and Table 5 show some properties of the desulfurizing mixtures, calculated with the FactSage® and Thermo-Calc® software, with the percentage values of the liquid and solid phases formed, the CaO activity, liquid and corrected viscosity, in addition to of the carbide mass added to the desulfurizing mixture, when applicable. The slags were divided into groups taking into account their respective weights.

Table 4. Properties of desulfurizing mixtures simulated via Thermo-Calc® (group 1) and FactSage® (group 2), with the addition of CaC₂.

Group	Nº	CaC ₂ (kg)	a _{CaO}	Liquid phase (%)	Solid phase (%)	μ^* (Pa·s)	μ_c^* (Pa·s)
1	1	100	0,12	79,86	20,14	0,050	0,111
	2	120	0,04	77,29	22,71	0,061	0,152
	3	120	0,12	47,15	52,85	0,070	1,593
	4	120	0,13	57,60	42,40	0,047	0,393

	5	160	0,07	51,32	48,68	0,056	0,814
	6	160	0,26	96,00	4,00	0,063	0,072
	7	160	0,17	96,84	3,16	0,060	0,067
	8	160	0,59	94,79	5,21	0,033	0,040
2	9	160	0,22	94,74	5,26	0,031	0,037
	10	200	0,40	95,11	4,89	0,043	0,051
	11	280	0,93	94,08	5,92	0,039	0,048
	12	200	1	68,84	31,36	0,051	0,202

* μ = viscosity, μ_c = corrected viscosity

Table 5. Properties of desulfurizing mixtures simulated via Thermo-Calc® (group 1) and FactSage® (group 2), without the addition of CaC₂.

Group	Nº	a _{CaO}	Liquid phase (%)	Solid phase (%)	μ^* (Pa·s)	μ_c^* (Pa·s)
	1	0,62	100	0	0,038	0,038
	2	0,11	100	0	0,051	0,051
1	3	0,47	89,43	10,57	0,054	0,079
	4	0,34	100	0	0,039	0,039
	5	0,31	96,21	3,79	0,046	0,053
	6	0,26	99,22	0,78	0,063	0,065
	7	1	70,89	29,11	0,049	0,171
	8	0,17	1	0	0,060	0,060
2	9	0,59	98,65	1,35	0,033	0,035
	10	0,40	98,90	1,10	0,043	0,045
	11	0,22	1	0	0,031	0,031
	12	0,93	97,74	2,26	0,038	0,041

* μ = viscosity, μ_c = corrected viscosity

The corrected viscosity is calculated by Equation (11).

$$\mu_c = \mu(1-1,35F_{\text{solids}})^{-2,5} \quad (11)$$

where μ_c is the corrected viscosity, μ is the viscosity of the liquid in the slag and F_{solids} is the mass fraction of solids in the slag. As the desulfurization process is complex, it should not be mathematically modeled only by one variable, being necessary a multivariate analysis of the desulfurization process.

3.2 Efficiency prediction

According to the studies carried out, attempts were made to generate mathematical relationships that took into account easily obtainable parameters in order to estimate the efficiency that will be obtained with a given slag composition and property. The analysis was initially performed taking into account the slag mass. Thus, they were separated into 2 groups, as shown in Table 4 and 5.

The parameters of interest listed in Table 4 and 5 were related to efficiency, looking for the lowest level of dispersion and the highest degree of correlation R².

Based on this correlation, a Desulfurization Factor (F_{DeS}) was generated for each slag group.

$$F_{DeS} = k_1 a_{CaO} + k_2 F_{liq} + k_3 \mu_c \quad (12)$$

where F_{DeS} is the desulfurization factor; a_{CaO} is the activity of CaO in the slag; k_1 the constant relative to the CaO activity; k_2 the constant related to the fraction of liquid in the slag F_{liq} ; μ_c the corrected viscosity of the slag and k_3 the constant relative to the corrected viscosity of the slag.

The constants vary according to the mass of each group. Thus, 4 graphs were generated, with and without the addition of CaC_2 , to correlate the degree of correlation R^2 to demonstrate the prediction of each equation, with each respective constant.

Figure 6 shows the correlation between F_{DeS} for group 1 of slag with addition of CaC_2 with the efficiency of the desulfurization process.

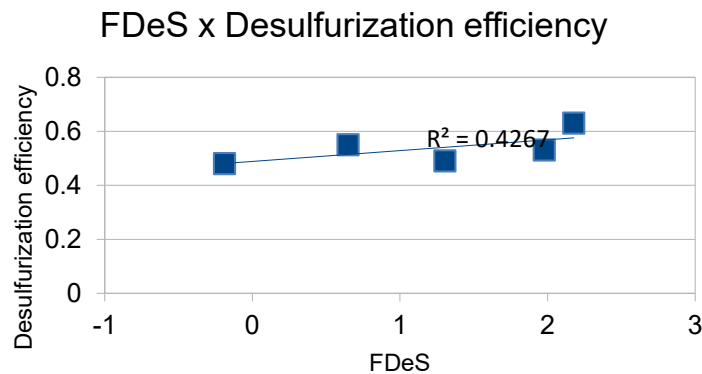


Figure 6. Correlation between F_{DeS} and desulfurization efficiency of slag group 1 with the addition of CaC_2 .

Figure 7 shows the correlation between F_{DeS} for group 2 of slag, with the addition of CaC_2 , with the efficiency of the desulfurization process.

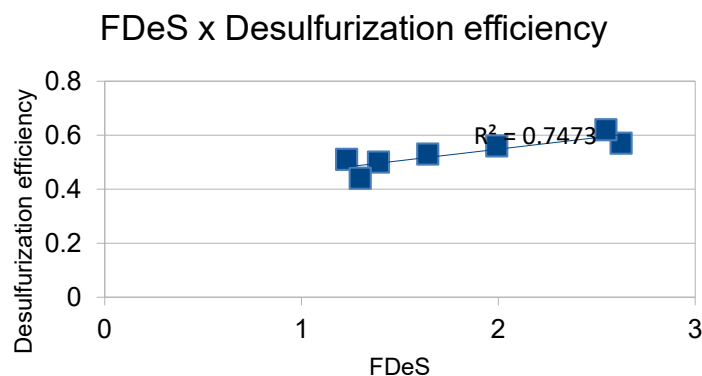


Figure 7. Correlation between F_{DeS} and desulfurization efficiency, of slag group 2, with the addition of CaC_2 .

Figure 8 shows the correlation between F_{DeS} for group 1 of slag, without the addition of CaC_2 , with the efficiency of the desulfurization process.

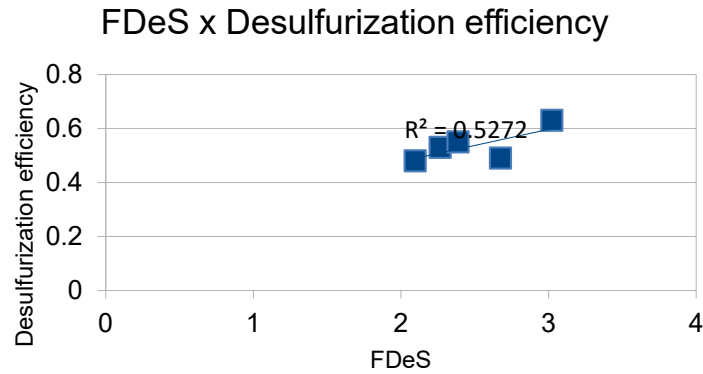


Figure 8. Correlation between F_{DeS} and desulfurization efficiency, of slag group 1, without the addition of CaC_2 .

Figure 9 shows the correlation between F_{DeS} for group 2 of slag, without the addition of CaC_2 , with the efficiency of the desulfurization process.

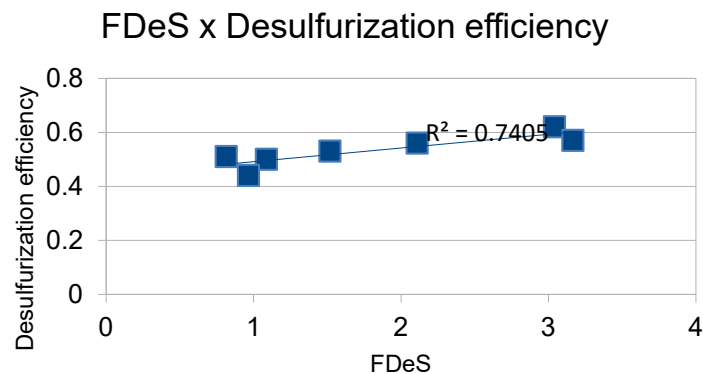


Figure 9. Correlation between F_{DeS} and desulfurization efficiency, of slag group 2, without the addition of CaC_2 .

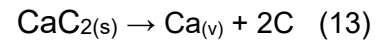
The prevailing desulfurization factor constants for slag group 1 and 2 are shown in Table 6. It is possible to denote that the process is complex, since the correlation varies according to the slag mass in the desulfurization process, the activity of the CaO in the system, corrected viscosity and liquid fraction of the slag.

Table 6. F_{DeS} constants for each slag group

Group	F_{DeS}		
	k_1	k_2	k_3
1	1,1	2,7	-11,1
2	15	19	-1

According to the results, it is clear that the use of CaC_2 in this case did not cause significant changes. How calcium carbide is added to the bath makes a difference in the results. In this work, CaC_2 was added from above, which causes the volatilization of calcium resulting from decomposition, as shown in Equation (13), when in contact with the top slag, thus, at most a deoxidation of the slag would occur. When CaC_2 is added inside the bath or during pouring, a better result is expected during the desulfurization process due to the reaction of calcium with sulfur from the

bath, as shown in Equation (4), removing sulfur from the liquid metal and forming CaS in the slag.



4 CONCLUSION

- The addition of CaC₂ from above, in the top slag, did not cause significant variation during the desulphurization process;
- Mathematical modeling provides an efficient analysis from experimental data;
- The constants of the equation that governs the desulphurization of selected steels vary according to the mass of the desulphurizing slag;
- It is not simple to determine a desulfurization factor when there are many variations in parameters during the process.

REFERENCES

1. GRILLO, F. F. Estudo da Substituição da Fluorita por Alumina ou Sodalita e de Cal por Resíduo de Mármore em Escórias Sintéticas Dessulfurantes. USP. São Paulo, SP. 2015.
2. MCFEATERS, L. B.; FRUEHAN, R. J. Desulfurization of Bath Smelter Metal. Metallurgical Transactions B, v. 24B, p. 441-447, June 1993.
3. MOTTA, L. S. et al. A Evolução do Emprego de Carbureto de Cálcio No Refino Secundário das Siderúrgicas Brasileiras. 45º Seminário Internacional de Aciaria. Porto Alegre, RS: ABM. 2014.
4. PRETORIUS, E. Slags and the relationship with the refractory life and steel production. Santos: LWB Refractories, 2002.
5. CHOI, J.; KIM, D.; LEE, H. Reaction Kinetics of Desulfurization of Molten Pig Iron Using CaO–SiO₂–Al₂O₃–Na₂O Slag Systems. ISIJ International, v. 41, p. 216-224, 2001.
6. PEZZIN, R. DE O. Influência das fases sólidas e líquidas na dessulfuração de aço no refino secundário por escória de topo. 2017.
7. MILLS, K. C.; SRIDHAR, S. Viscosities of ironmaking and steelmaking slags. Ironmaking and Steelmaking, v. 38, n. 6 p. 911-915 2007.
8. RIBEIRO, D.B. ASSOCIAÇÃO BRASILEIRA DE METALURGIA E MATERIAIS. REFINO SECUNDÁRIO DOS AÇOS. CURSOS ABM, SÃO PAULO, P. 168 – 201, 2013.