

## Elaboration of synthetic slags containing marble waste and aluminum oxide used in steel desulfurization process

Felipe F. Grillo<sup>a,✉</sup>, Jorge L. Coleti<sup>b</sup>, Eduardo Junca<sup>c</sup>, Victor B. Telles<sup>c</sup>, José R. de Oliveira<sup>a</sup>,  
Tiago E.A. Frizon<sup>d</sup>, Denise C.R. Espinosa<sup>b</sup>

<sup>a</sup>Federal Institute of Espírito Santo, 1729 Vitoria Avenue, Vitória, ES, 29040-780, Brazil

<sup>b</sup>Polytechnic School of the University of São Paulo, 1080 Prof. Luciano Gualberto Avenue, São Paulo, SP, 05508-010, Brazil

<sup>c</sup>University of the Extreme South of Santa Catarina, 1105 Universitária Avenue, Criciúma, SC, 88806-000, Brazil

<sup>d</sup>Federal University of Santa Catarina, University campus Reitor João David Ferreira Lima Trindade, Florianópolis, SC, 88040-900, Brazil

(✉Corresponding author: [felipefarding@gmail.com](mailto:felipefarding@gmail.com))

Submitted: 21 April 2020; Accepted: 4 August 2020; Available On-line: 15 October 2020

**ABSTRACT:** The aim of this paper is to investigate the desulphurization process of steel using synthetic slags containing marble waste and aluminum oxide. The tests were performed using a SAE 1020 steel containing 80 ppm of sulfur. The temperature was 1600 °C under an argon flow of 1NL/minute. Each desulfurization test lasted 30 minutes long. Aliquots of steel were removed from the bath every 5 min. Then, each aliquot was characterized by LECO CS240 infrared spectrometer to determine the sulfur content. The results indicated a desulphurization yield up to 78.7 wt% and 70.0 wt% for slags containing aluminum oxide and marble waste, respectively. It was also concluded that the fraction of liquid phase had influence on the desulfurization yield. The maximum desulfurization yield was reached with 83.2 wt% and 82.0 wt% of liquid phase for slags containing aluminum oxide and marble waste, respectively. In addition, in slags containing lime, the maximum desulfurization yield was reached with 85.0 wt% of liquid phase. The tests also demonstrate that in desulfurization processes is necessary containing solid CaO phase in the synthetic slag composition to reach the maximum desulfurization yield. Therefore, the use of aluminum oxide instead fluorspar is an interesting alternate for desulfurization of steel, as well as the replacement of lime for marble waste.

**KEYWORDS:** Aluminum oxide; Desulfurization; Marble waste

**Citation/Citar como:** Grillo, F.F.; Coleti, J.L.; Junca, E.; Telles, V.B.; de Oliveira, J.R.; Frizon, T.E.A.; Espinosa, D.C.R. (2020). "Elaboration of synthetic slags containing marble waste and aluminum oxide used in steel desulfurization process". *Rev. Metal.* 56(3): e174. <https://doi.org/10.3989/revmetalm.174>

**RESUMEN:** *Elaboración de escorias sintéticas con residuos de mármol y óxido de aluminio utilizados en el proceso de desulfuración de acero.* El objetivo de este trabajo es investigar el proceso de desulfuración del acero utilizando escorias sintéticas que contienen residuos de mármol y óxido de aluminio. Las pruebas se realizaron usando un acero SAE 1020 que contenía 80 ppm de azufre. La temperatura fue 1600 °C bajo un flujo de argón de 1NL/minute. Cada prueba de desulfuración duró 30 min. Se retiraron muestras de acero del baño cada 5 min. Posteriormente, cada muestra se caracterizó en un espectrómetro infrarrojo LECO CS240 para determinar el contenido de azufre. Los resultados indicaron un rendimiento de desulfuración de 78,7% y 70% en peso para escorias que contienen óxido de aluminio y residuos de mármol, respectivamente. Con estos resultados fue posible concluir que la fracción de la fase líquida influye en el rendimiento de desulfuración. El rendimiento máximo de desulfuración se alcanzó con 83,2% y 82,0% en peso de la fase líquida para escorias que contenían óxido de aluminio y residuos de mármol, respectivamente. Además, en las escorias que contienen cal, el rendimiento máximo de desulfuración se alcanzó con 85,0% en peso de la fase líquida. Las pruebas también demostraron que en los procesos de desulfuración es necesario contener una fase sólida de CaO en la composición de escoria sintética para alcanzar el rendimiento máximo de desulfuración. Por lo tanto, el uso de óxido de aluminio en lugar de fluorita es una alternativa interesante para la desulfuración del acero, así como el reemplazo de la cal por los residuos de mármol.

**PALABRAS CLAVE:** Desulfuración; Residuos de mármol; Óxido de aluminio

**ORCID ID:** Felipe F. Grillo (<https://orcid.org/0000-0002-0224-9075>); Jorge L. Coleti (<https://orcid.org/0000-0003-1748-5991>); Eduardo Junca (<https://orcid.org/0000-0002-7068-2583>); Victor B. Telles (<https://orcid.org/0000-0003-0277-8513>); José R. de Oliveira (<https://orcid.org/0000-0003-3785-2306>); Tiago E.A. Frizon (<https://orcid.org/0000-0003-3803-3556>); Denise C.R. Espinosa (<https://orcid.org/0000-0003-2359-9485>)

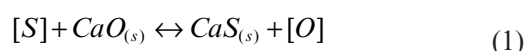
**Copyright:** © 2020 CSIC. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International (CC BY 4.0) License.

## 1. INTRODUCTION

Due to the increasing demand for steels containing lower sulfur content (up to 10 ppm), the steelmakers companies have been adopting a better control of the production process, as well as an optimization of chemical adjustment in synthetic slags in order to obtain steels with better mechanical behaviors (Holappa, 1982; Taguchi *et al.*, 2003; Nita *et al.*, 2010; Xu *et al.*, 2016).

The desulfurization process in ladle furnace and Kanbara reactor are used widely (Emi, 2015; Alba *et al.*, 2015; Tong *et al.*, 2016; Ma *et al.*, 2017). The main inputs used in those processes are the calcium oxide (CaO), calcium carbide (CaC<sub>2</sub>) and magnesium (Mg), where they can be used singly or added in mixtures containing calcium fluoride (fluorspar – CaF<sub>2</sub>) and sodium oxide (Na<sub>2</sub>O).

The desulfurization reaction Eq. (1) occurs due to the preference in the formation of sulfides instead oxide. Besides, the mechanism of the desulfurization reaction is based on the mass transport of sulfur from the liquid metal to the calcium oxide particles in the slag. Thus, the reaction can be improved by increasing the metal/slag agitation system or using basic slag with low oxygen potential (Rosenqvist, 1988).



$$\Delta G^0 = 27570 - 9.70 * T \text{ (Kcal / mol)} \quad (2)$$

In addition, the slags used in the desulfurization process were composed by liquid and solid fractions, where each fraction variation controls the slag viscosity. Furthermore, slags with concentration of CaO above 60% trends to contain solid phase, which it may limit the desulfurization process. An alternative is the use of fluorspar, since this material increases the proportion of liquid phase in the slags,

which it is necessary to improve the desulfurization process. However, the use of fluorspar takes a serious environmental problem. The steelmaking companies have been looked for new materials to replace fluorspar, such as CaO-Al<sub>2</sub>O<sub>3</sub> slag system (Shimizu *et al.*, 2001; Pretorius, 2002; Coleti *et al.*, 2015). Besides, the companies have also financed studies to use wastes instead the inputs mentioned previously. In this way, the marble waste may be an alternative to the desulfurization process, since its composition is mainly CaO, MgO and SiO<sub>2</sub>. Some works have mentioned this waste to produce synthetic slag for desulfurization process as a practicable route (Grillo *et al.*, 2017; Coleti *et al.*, 2017).

The computational thermodynamic is an important tool in order to investigate the behavior of slags in the desulfurization process. This tool indicates the percent of liquid and solid phases in a certain temperature and condition of desulfurization, which it allows to determine the content of CaO that participate of the desulfurization process. Thus, the aim of this paper is to produce a synthetic slag in order to replace both fluorspar and lime by aluminum oxide and marble waste in desulfurization process of steel. Additionally, the results obtained from computational thermodynamic are compared with the experimental tests.

## 2. MATERIALS AND METHODS

### 2.1. Slags formulation

The chemical analyzes of the raw materials (Table 1) were carried out in order to formulate the compositions of synthetic slags. This characterization step was performed by X-ray fluorescence.

The synthetic slags were elaborated in order to investigate the use of marble waste instead lime in desulfurization process. In addition, it was also determinate the relationship between the fraction of liquid phase with the percentage of CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO. Then, the influence of viscosity on

TABLE 1. Chemical characterization of raw materials used to prepare the synthetic slags

Compounds wt%	Lime	Magnesium oxide	Aluminum oxide	Fluorspar	Marble waste
CaO	92.9	0.8	-	-	39.8
MgO	0.5	94.0	-	-	14.4
Al <sub>2</sub> O <sub>3</sub>	0.4	1.0	98.4	-	-
CaF <sub>2</sub>	-	-	-	98.6	-
Fe <sub>2</sub> O <sub>3</sub>	0.4	2.0	-	-	-
SiO <sub>2</sub>	1.5	1.0	-	-	3.3
MnO	-	1.2	-	-	-
PF	4.2	-	-	-	42.1
Other	-	-	1.6	1.4	0.4

TABLE 2. Composition and liquid phase percent for each mixture in the desulfurization process of steel

Synthetic slag	Components (wt%)						Liquid phase
	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>	MnO+Fe <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	
CA1	20.1	72.3	6.0	1.2	0.5	0.0	58.0
CA2	23.1	69.1	6.0	1.2	0.4	0.0	66.6
CA3	26.8	65.5	6.0	1.2	0.4	0.0	76.3
CA4	29.5	62.9	5.9	1.1	0.4	0.0	83.2
CA5	33.2	59.3	5.9	1.1	0.4	0.0	92.5
CA6	36.8	55.8	5.9	0.9	0.4	0.0	100.0
CF	19.5	65.6	6.0	1.2	0.4	7.0	72.9
RA1	21.8	54.1	19.6	4.5	0.0	0.0	79.5
RA2	24.4	52.3	18.1	4.4	0.0	0.0	87.4
RA3	29.6	50.1	17.8	4.2	0.0	0.0	88.3
RA4	28.9	49.2	17.5	4.1	0.0	0.0	97.0
CRA	21.8	54.2	19.4	4.5	0.0	0.0	77.7
RF	20.3	50.3	18.2	4.2	0.0	7.0	72.9
CRF	20.3	50.4	18.2	4.2	0.0	7.0	77.7

the desulfurization process was also investigated. Table 2 shows the chemical composition for each synthetic slag obtained via mass balance. The content of liquid phase was simulated by Thermo-Calc software at 1600 °C.

The synthetic slags CA1-CA6 (containing lime and aluminum oxide) were performed in order to investigate the influence of liquid phase on the desulfurization process. The synthetic slags RA1 to RA4 were formulated to investigate the use of marble waste instead of lime. In these slags, the content of CaO was kept equal to the slags CA3-CA6, respectively. The Al<sub>2</sub>O<sub>3</sub> was added in the slags composition in order to react with CaO (from lime or marble waste) to form the calcium aluminate phase. It was also investigated the use of calcined marble waste on the desulfurization process. In this step, the marble waste was calcined at 1000 °C before add it in the synthetic slag. The content of CaO was the same of that used in the synthetic slag RA1. This synthetic slag was called CRA.

## 2.2. Experimental

In each test of desulfurization was used 1000 g of SAE 1020 steel containing 80 ppm of sulfur. The sample of steel was put into a MgO-C crucible and sent it to a vertical furnace. Then, it was purged argon into the furnace to avoid the steel oxidation, once the furnace was heated up to 1600 °C. When the steel was melted, the synthetic slag was added on the bath. At the same time, the impeller was turned on at 200 rpm for the bath homogenization. Figure 1 show the experimental apparatus used in the desulfurization process.

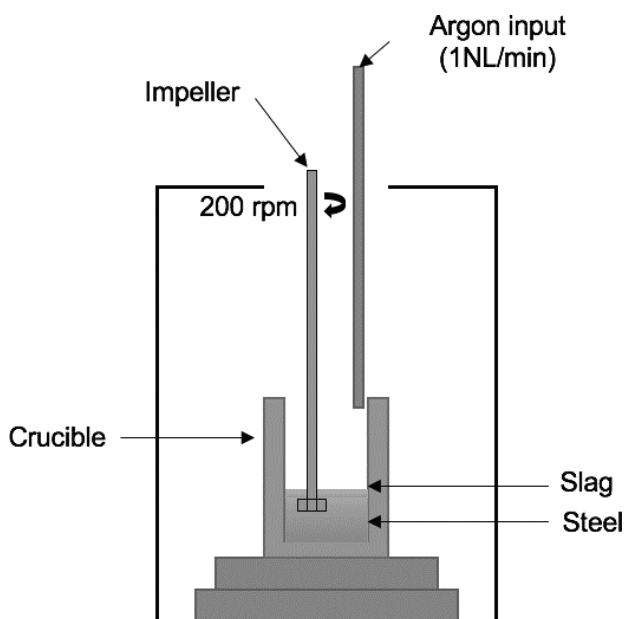


FIGURE 1. Experimental apparatus used in the desulfurization process of steel.

Aliquots of liquid steel were obtained from the bath at 0, 5, 10, 15, 20 and 30 min to determine the sulfur content via LECO CS240 infrared spectrometer.

In addition, Thermo-calc software (database SLAG3) was used to determine the fraction of liquid and solid phases, the solid phases formed, content of equilibrium sulfur and CaO activity for all synthetic slags at 1600 °C.

### 2.3. Desulfurization yield

The desulfurization yield was calculated via Eq. (3):

$$\eta(\%) = \frac{([\%S_i] - [\%S_f])}{[\%S_i]} * 100 \quad (3)$$

where  $\eta(\%)$  is the desulfurization yield;  $[\%S_i]$  is the initial sulfur content and  $[\%S_f]$  is the final sulfur content.

## 3. RESULTS AND DISCUSSION

### 3.1. Influence of marble waste

Figure 2 shows the desulfurization tests with slags containing  $Al_2O_3$  and conventional lime. The desulfurization for slags containing  $Al_2O_3$  and marble waste is shown in Fig. 3.

In all tests, the desulfurization reaction occurred in 10 min. After this time, the sulfur content kept constant. Such results suggest that the synthetic slags can be used in steelmaking companies with that perform the desulfurization process between basic oxygen furnace and transfer ladle, since the running time is around 10 min.

The lesser sulfur content (0.0017 wt%) was obtained for the synthetic slag CA4 (containing conventional lime), while the synthetic slag RA2 (containing marble waste) reached a sulfur content of 0.0024 wt%.

Two effects can explain this behavior. First, the presence of MgO from marble waste increased the melting temperature of the slags (Wilson and Mclean, 1980). Thus, the formation of liquid phase

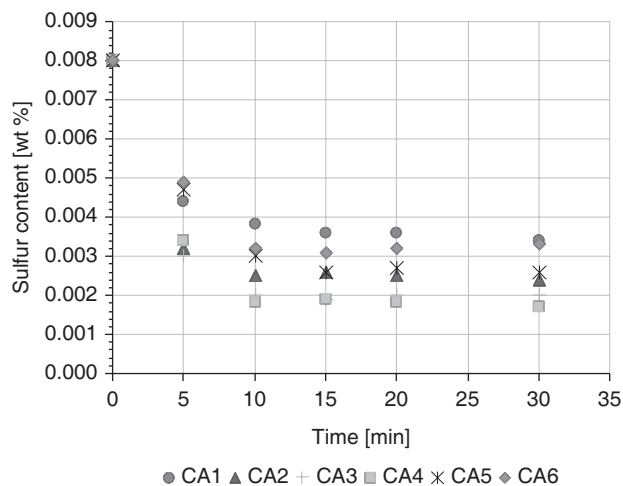


FIGURE 2. Influence of aluminum oxide and lime under desulfurization process.

was lesser for synthetic slags produced with marble waste. Second effect is due the decomposition of carbonates. Figure 4 shows the results obtained when calcined marble waste was used as an input in synthetic slag.

The synthetic slags with marble waste (RA1 and RF) showed a desulfurization yield of 61.1 wt% and 60.0 wt%. The synthetic slags CRF (containing fluor-spar and calcined marble waste) and CRA (containing calcined marble waste) showed a desulfurization yield of 68.2 and 65.0 wt%, respectively. It is clear that the use of calcined marble waste increased the desulfurization process. This behavior is due the carbonates decomposition, as it can be demonstrated in equations 4 and 6 (Caceres and Attiogbe, 1997). These equations indicate that desulfurization is an

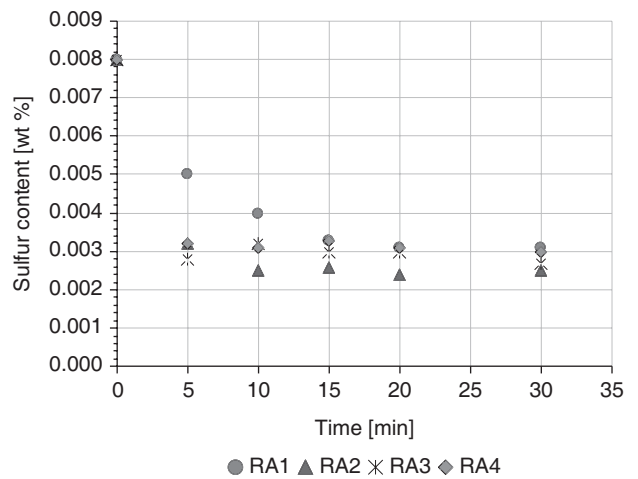


FIGURE 3. Influence of aluminum oxide and marble waste under desulfurization process.

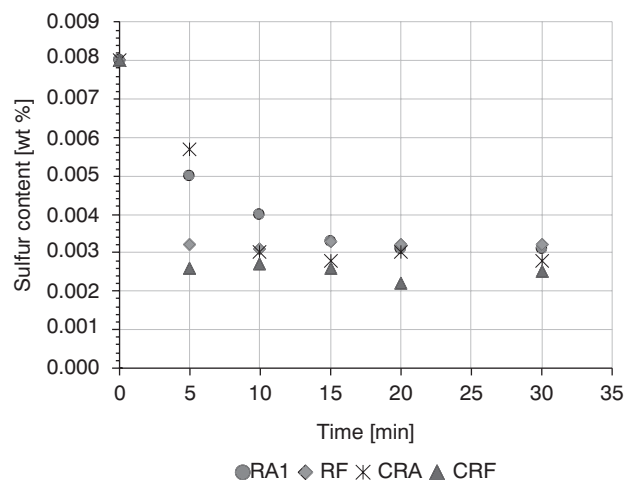
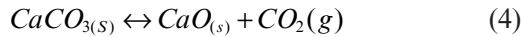
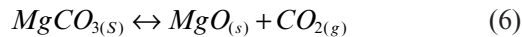


FIGURE 4. Influence of calcined marble waste on the desulfurization process.

endothermic reaction. Therefore, a decrease of the bath temperature trend to harm the desulfurization yield.



$$\Delta G^0 = 41769 - 36.19T \text{ (cal)} \quad (5)$$



$$\Delta G^0 = 27237 - 39.72T \text{ (cal)} \quad (7)$$

### 3.2. Influence of liquid phase

Table 3 shows the relationship between the desulfurization yield and liquid phase. Figure 5 shows that the replacement of lime for marble waste in the synthetic slags did not presented a significant change in the percentage of liquid phase.

The use of marble waste increased the amount of liquid phase, since the marble waste contain  $\text{SiO}_2$  in its composition, which it supports the formation of liquid phase at 1600 °C (Wilson and Mclean, 1980). In addition, synthetic slags with higher percentage of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (consequently a lesser percentage of CaO) also suggested a lesser melting temperature,

which implies in higher percent of liquid phase. Such facts have effect on the desulfurization process, as it can be seen in Fig. 6.

It was noted an increase on the desulfurization yield up to 85.0wt% of liquid phase (in the synthetic slags with lime). In synthetic slags containing marble waste, it was observed an increase of desulfurization yield up to 82.0 wt% of liquid phase. Similar result was found by Xu *et al.* (2016) using a vacuum-induction furnace (Fig. 7). The authors obtained the maximum desulfurization yield with a slag containing around 87.0 wt% of liquid phase. Thus, regardless of the desulfurization process and raw materials, a slag with 100% of liquid phase is not the ideal for desulfurization process of steel.

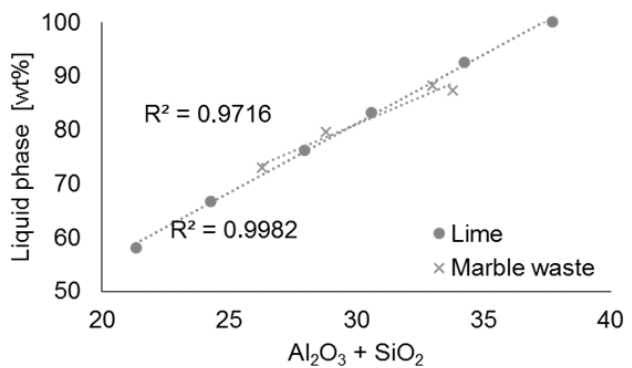


FIGURE 5. Influence of  $\text{Al}_2\text{O}_3 + \text{SiO}_2$  content on the liquid phase in slags containing lime and marble waste.

TABLE 3. Composition of solid and liquid phases, initial and final CaO activities used in the desulfurization tests

Synthetic slag	Liquid phase [wt%]	Solid phase [wt%]		Final Activity CaO	Initial Activity CaO	$\eta$ [%]
		CaO	%MgO			
CA1	58.0	39.8	2.1	1.0	1.0	57.5
CA2	66.6	31.9	1.5	1.0	1.0	68.7
CA3	76.3	23.0	0.8	1.0	1.0	75.0
CA4	83.2	16.6	0.2	1.0	1.0	78.7
CA5	92.5	7.5	0.0	1.0	1.0	67.5
CA6	100.0	0.0	0.0	1.0	1.0	58.7
RA1	72.9	12.1	15.0	1.0	1.0	61.2
RA2	79.5	6.7	13.8	1.0	1.0	70.0
RA3	87.4	0.2	12.4	0.96	1.0	66.2
RA4	88.3	0.0	11.7	0.85	0.89	62.5
CF	97.0	3.0	0.0	1.0	1.0	77.5
RF	77.7	8.4	22.3	1.0	1.0	60.0
CRA	72.9	12.1	15.0	1.0	1.0	65.0
CRF	77.7	8.4	22.3	1.0	1.0	68.2

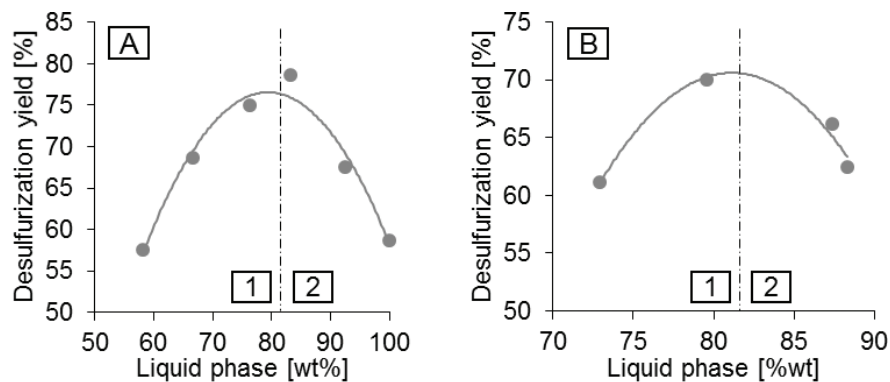


FIGURE 6. Relation between liquid phase and desulfurization yield: A) Synthetic slag with lime, and B) Synthetic slag containing marble waste.

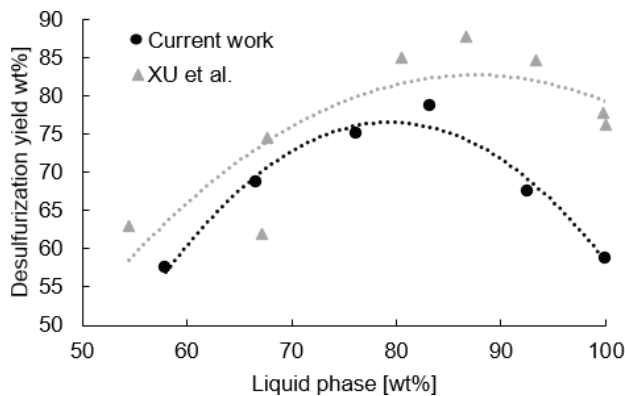


FIGURE 7. Comparison of desulfurization yield against percentage of liquid phase obtained by Xu *et al.* (2016) and the results obtained in this work.

### 3.3. Influence of liquid phase

Figure 8 shows the influence of initial content of CaO in the slag composition and the percentage of solid CaO on desulfurization yield.

In slags containing lime, the content of initial CaO up to 64 wt% and a percentage of solid CaO was up to 17.0 wt% increased the desulfurization yield. In slags containing marble waste, the content of initial CaO was 51.0 wt%, while the solid CaO was up to 5.0 wt%. Therefore, there is a saturation limit of CaO solid for processes controlled by top slag and liquid phase mechanisms. The same affirmation can't be made for processes controlled by top slag mechanism. In this case, increasing the liquid phase also increases the desulfurization yield (Pretorius, 2002). Thus, the presence of solid phase as well as the activity of solid CaO equal 1 are necessary to increase the desulfurization yield in process controlled by top slag and solid phase mechanisms.

According to Xu *et al.* (2016), the slags containing solid CaO presented higher desulfurization yield. They also concluded that the capacity for

remove sulfur from the steel is more dependent of liquid CaO than solid CaO. Besides, the authors mention that CaO-CaF<sub>2</sub> slags system have a better behavior than CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub>-SiO<sub>2</sub> slags system in the desulfurization.

### 3.4. Influence of CaF<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>

Figure 9 shows the results for synthetic slags elaborated with marble waste (RA1 and RF) and lime (CA3 and CF) containing CaF<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

In synthetic slags containing lime were obtained a content of sulfur around 0.002 wt%, while for synthetic slags with marble waste was reached a content of sulfur around 0.003 wt%, indicating that synthetic slags containing lime can reached lesser content of sulfur.

For the same raw material (lime or marble waste), the replacement of fluorspar by Al<sub>2</sub>O<sub>3</sub> didn't change the final content of sulfur. The fluorspar is added to decreases the melting temperature of slags, and consequently, it decreases the percentage of solid Ca. Thus, the presence of fluorspar decreased the percentage of CaO solid (as it was shown in Table 3), which it harmed the desulfurization process.

### 3.5. Influence of viscosity

Figures 10 and 11 show the effect of viscosity on the desulfurization yield in synthetic slags with lime and marble waste, respectively. The maximum desulfurization yield for slags containing lime was reached with 16.6 wt% of solid CaO and an effective viscosity of 1.1 poise. The synthetic slags containing marble waste reached the maximum desulfurization yield of 6.7 wt% with 1.3 poise of effective viscosity. The presence of solid phase increased the slag viscosity, which can impaired the interaction between steel and slag (Putan *et al.*, 2013). However, the presence of solid CaO up to a certain limit is beneficial to the desulfurization process, as it was discussed previously.

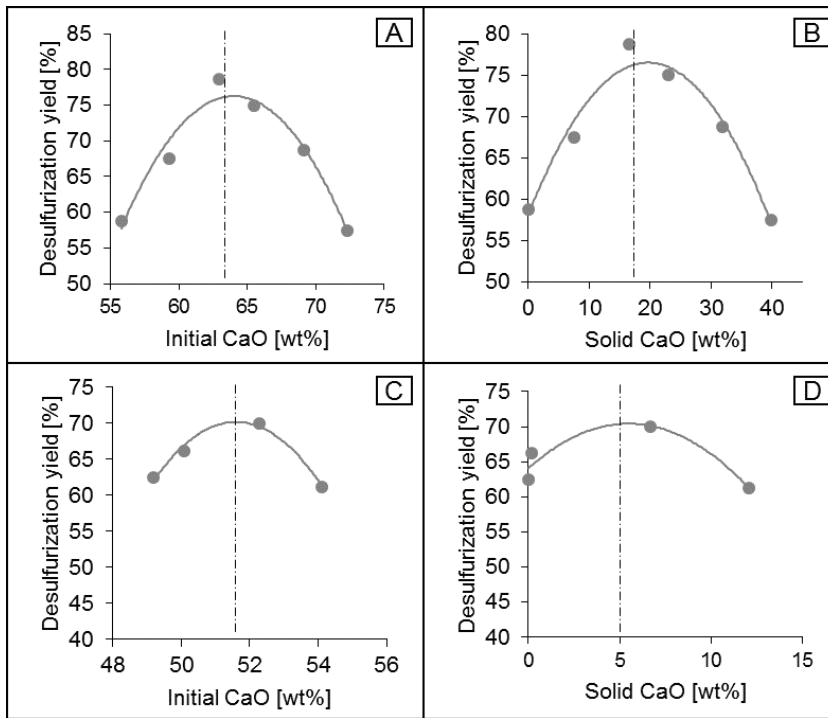


FIGURE 8. Relation of initial CaO and Solid CaO percentage obtained via Thermo-calc software: A) and B) Lime; C and D) marble waste.

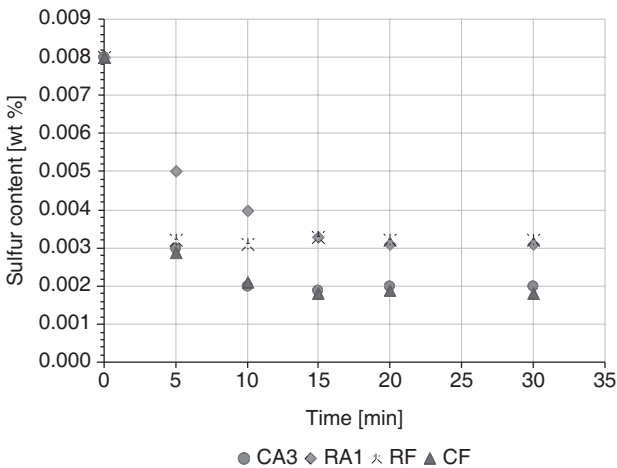


FIGURE 9. Effect of fluorspar in slags containing lime and marble waste.

#### 4. CONCLUSIONS

The results indicated that the use of marble waste in synthetic slags in the desulfurization process of steel is an alternative when the final content of sulfur is around 0.003 wt%. For this application, some parameters should be controlled to favors the reaction. The synthetic slag contained 82.0 wt% of liquid phase with 51.0 wt% of CaO. Besides, the synthetic slag contained 5 wt% of solid CaO. An alternative to increase the desulfurization yield is to use

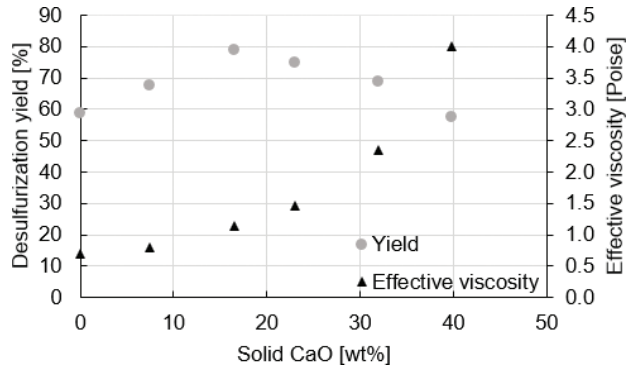


FIGURE 10. Effect of viscosity on the desulfurization yield in synthetic slag with lime.

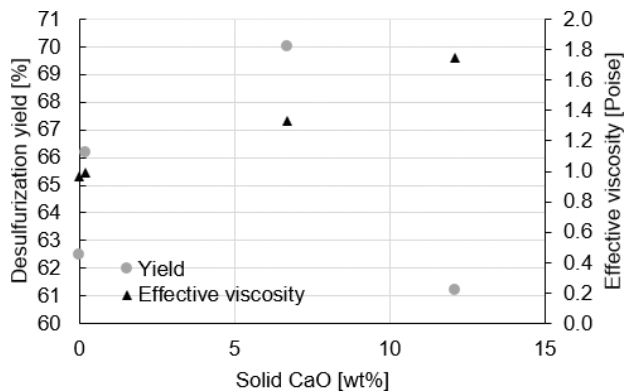


FIGURE 11. Effect of viscosity on the desulfurization yield in synthetic slag with marble waste.

calcined marble waste. The study showed that this practice decreased the sulfur content to 0.0025 wt%. In addition, the replacement of fluorspar by  $\text{Al}_2\text{O}_3$  indicated to be an alternative for the desulfurization process, since the desulfurization tests using fluorspar and  $\text{Al}_2\text{O}_3$  reached the same values of final sulfur.

## ACKNOWLEDGMENTS

The authors are grateful to the Coordination for the Improvement of Higher Education Personnel (CAPES) and São Paulo Research Foundation (FAPESP).

## REFERENCES

- Alba, M., Jung, S.H., Kim, M.S., Seol, J.Y., Yi, S.J., Kang, Y.B. (2015). Desulfurization of Liquid Steel by Passing Steel Droplets through a Slag Layer. *ISIJ Int.* 55 (8), 1581–1590. <https://doi.org/10.2355/isijinternational.ISIJINT-2015-120>.
- Caceres, P.G., Attiogbe, E.K. (1997). Thermal decomposition of dolomite and the extraction of its constituents. *Miner. Eng.* 10 (10), 1165–1176. [https://doi.org/10.1016/S0892-6875\(97\)00101-5](https://doi.org/10.1016/S0892-6875(97)00101-5).
- Coleti, J.L., Grillo, F.F., Silva, F.L., Oliveira, J.R., Espinosa, D.C.R., Tenório, J.A.S. (2015). Uso do resíduo de mármore e aluminato de cálcio em escórias sintéticas dessulfurantes de aço. *Tecnol. Metal. Mater. Min.* 12 (3), 188–194. <https://doi.org/10.4322/2176-1523.0793>.
- Coleti, J.L., Grillo, F.F., Tenório, J.A.S. (2017). Marble waste recycling and its application in the steel desulphurization process. International Conference on Solid Waste Technology and Management, Philadelphia, pp. 649–656.
- Emi, T. (2015). Steelmaking Technology for the Last 100 Years: Toward Highly Efficient Mass Production Systems for High Quality Steels. *ISIJ Int.* 55 (1), 36–66. <https://doi.org/10.2355/isijinternational.55.36>.
- Grillo, F.F., Coleti, J.L., Oliveira, J.R., Junca, E., Deike, R., Espinosa, D.C.R. (2017). Development of synthetic slag with marble waste and calcium aluminate agents for cast iron desulfurization. *Mater. Res.* 20 (5), 1230–1237. <https://doi.org/10.1590/1980-5373-mr-2016-0834>.
- Holappa, L. (1982). Ladle injection metallurgy. *International Metals Reviews* 27 (2), 53–76.
- Ma, W., Li, H., Cui, Y., Chen, B., Liu, G., Ji, J. (2017). Optimization of Desulphurization Process using Lance Injection in Molten Iron. *ISIJ Int.* 57 (2), 214–219. <https://doi.org/10.2355/isijinternational.ISIJINT-2016-167>.
- Nita, O.S., Butnariu, I., Constantin, N. (2010). The efficiency at industrial scale of a thermodynamic model for desulfurization of aluminium killed steels using slags in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ . *Rev. Metal.* 46 (1), 5–14. <https://doi.org/10.3989/revmetalm.0849>.
- Pretorius, E. (2002). *Slags and the Relationship with Refractory Life and Steel Production*. LWB Refractories.
- Putan, A., Putan, V., Heput, T., Socalici, A. (2013). Steel treatment with calcium-aluminate synthetic slag and addition of titanium oxide. *Rev. Metal.* 49 (1), 31–44. <https://doi.org/10.3989/revmetalm.1210>.
- Rosenqvist, T. (1988). *Principles of extractive metallurgy*. McGraw-Hill, 2<sup>nd</sup> Ed., EE.UU.
- Shimizu, K., Suzuki, T., Jimbo, I., Cramb, A.W. (2001). An Investigation on the Vaporization of Fluorides from Slag Melts. *Iron and Steelmaker* 28 (7), 87–93.
- Taguchi, K., Nakazato, H.O., Nakai, D., Usui, T., Marukawa, K. (2003). Deoxidation and Desulfurization Equilibria of Liquid Iron by Calcium. *ISIJ Int.* 43 (11), 1705–1709. <https://doi.org/10.2355/isijinternational.43.1705>.
- Tong, Z., Ma, G., Cai, X., Xue, Z., Wang, W., Zhang, X. (2016). Characterization and valorization of Kanbara reactor desulfurization waste slag of hot metal pretreatment. *Waste Biomass Valori.* 7 (1), 1–8. <https://doi.org/10.1007/s12649-015-9429-5>.
- Wilson, W.G., Mclean, A. (1980). *Desulfurization of Iron and steel and sulfide shape control*. Iron & Steel Society – AIME, Warrendale, EE.UU. pp. 3–11.
- Xu, J.F., Huang, F.X., Wang, X.H. (2016). Desulfurization Behavior and Mechanism of CaO-saturated. Slag. *J. Iron. Steel Res. Int.* 23 (8), 784–791. [https://doi.org/10.1016/S1006-706X\(16\)30121-2](https://doi.org/10.1016/S1006-706X(16)30121-2).