

## Hot metal desulfurization by marble waste and fluorspar

### *Dessulfuração de ferro gusa utilizando resíduo de mármore e fluorita*

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### **Resumo**

O objetivo desse trabalho é apresentar uma análise dinâmica da utilização de misturas à base de resíduo de mármore na dessulfuração de ferro-gusa. Na realização do trabalho, foram utilizados: resíduo de mármore, fluorita, cal e ferro-gusa. Foram elaboradas quatro diferentes misturas, que foram adicionadas em um banho de ferro-gusa a 1450°C com composição conhecida. A quantidade de cada material foi calculada a partir de suas análises químicas e comparadas com uma mistura utilizada na indústria. Todas as quatro misturas foram utilizadas em experimentos com agitação promovida por um agitador mecânico. Amostras do banho foram retiradas através de amostradores a vácuo nos tempos de 5, 10, 15, 20 e 30 minutos e analisadas para verificar a variação de enxofre no banho com o tempo. Os resultados obtidos com as adições foram analisados segundo parâmetros termodinâmicos, sendo verificada a possibilidade de utilização do resíduo como agente dessulfurante.

**Palavras-chave:** Resíduo de mármore, fluorita, dessulfuração de ferro-gusa.

### **Abstract**

*The objective of this paper is to present an analysis of the use of residual marble mixtures in the pig iron desulfurization process. The study involved the use of: marble waste, fluorspar, lime, and hot metal. Four mixtures were made and added to a liquid hot metal - with known chemical composition - at a temperature of 1450°C. The mass of each element was calculated from its chemical analysis and compared with an industrial mixture. All of the four mixtures used in the experiments were stirred by a mechanical stirrer. Samples were collected by vacuum sampling for times of 5, 10, 15, 20, and 30 minutes, and analysis was performed to check sulfur variation in the bath with time. The results were analyzed and they verified that it was possible to use marble waste as a desulfurizer.*

**Keywords:** Marble waste, fluospar, hot metal desulfurization.

### **1. Introduction**

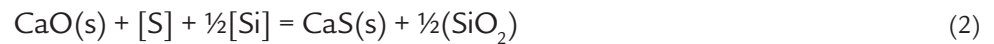
To obtain the sulfur content in the acceptable steel limits, treatment technologies of the liquid hot metal have been developed to remove sulfur before the primary refining step, due to the thermodynamic conditions. The desulfurization is favored at this point of the process, be-

cause the hot metal has elements dissolved in the metal that increase the activity of the sulfur, besides a low potential of oxygen ( $\mu_{O_2}$ ). The partial pressure of oxygen corresponding to the pre-treatment is about  $2.2 \times 10^{-17}$  atm, which will produce a low  $\mu_{O_2}$ , thus favoring the desulfurization in

this step of the metallurgical process.

In the liquid hot metal, the desulfur-

ization reaction through the lime (CaO) can occur according to the Equation 1 or Equa-



In both cases the sulfur equilibrium content 1450°C is less than 0.0004% (Deo, 1992). Yet, due to a kinetic limitation of the process, this content is not reached. An important factor that affects the desulfurization kinetics by the CaO is

its particle size. According to Shevchenko et al., (1984), for a better efficiency, the diameter of the particles of CaO should not be larger than 0.1mm.

The thermodynamic capacity that a slag presents to remove sulfur from

$$C_s = (\%S)(P_{O_2} / P_{S_2})^{1/2} \quad (3)$$

However, the  $C_s$  parameter is based on a reaction of gas-slag equilibrium and due to the difficulty of finding the partial

pressures of oxygen and sulfur, the equilibrium reaction between metal and slag is used to determine  $C_s$ . The equation

$$C_s' = \{(\%S) / [ \%S ]\} (h_o / f_s) \quad (4)$$

The term  $C_s$  is called “modified sulfide capacity”, by Ghosh (2001), and

“sulfur capacity”, by Hollapa (1984). The relationship between  $C_s$  and  $C_s'$  is

$$C_s' = C_s e^{(3.76-3176/T)} \quad (5)$$

Another way to calculate the sulfide capacity is through its relationship with

the optic basicity ( $\Lambda$ ). Young et al. (1992) presented it through the Equations 6 and

$$\log C_s = -13.913 + 42.84\Lambda - 23.82\Lambda^2 - (11710/T) - 0.02223(\%SiO_2) - 0.02275(\%Al_2O_3) \quad (6)$$

$$\log C_s = -0.6261 + 0.4808\Lambda + 0.7197\Lambda^2 + (1697/T) - (2587\Lambda/T) + 0.0005144(\%FeO) \quad (7)$$

Then, by using these thermodynamic equations, it is possible to find the equilibrium sulfur content and the

partition of sulfur between slag and metal ( $L_s = (\%S)/[\%S]$ ).

The rate of the desulfurization is de-

$$-dS/dt = k (\%S_t - \%S_{eq}) \quad (8)$$

The best desulfurization process known occurs through the stirring of the desulfurizer mixture with the bath. In this process, as a result of strong stirring, a CaO based mixture attains desulfurization rates of up to 90% in a treatment time of 10 to 15 minutes (Nylo & Oliveira, 2011).

Researches have been performed to increase the efficiency of the stirring, as in the study done by Wu et al. (2008). Also, Takahashi & Iguchi (2006), studied methods to reduce the mixture time, by employing a cylinder immersed in an eccentric position to the bath, obtaining good results. Chushao and Xin (1992),

showed that the desulfurization increases with the increase of CaF<sub>2</sub> in mixture with the CaO in the strip from 0 to 10%.

Ohya et al. (1977) showed that when 15% of each particle of CaO is converted in CaS, the desulfurizer power of this reagent is practically annulled. This is because the CaS layer is solid, reducing the rate of the sulfur diffusion at industrially insignificant levels. However, with the addition of CaF<sub>2</sub>, this layer becomes liquid, favoring the desulfurization.

Niedringhaus & Fruehan (1998), in their experiments, show that the formation of liquid phase is critical for effective desulfurization.

tion 2, depending on the content of Silicon in the liquid metal (Turkdogan, 1996).

the liquid metal is the sulfide capacity ( $C_s$ ). The sulfide capacity can be used to compare the characteristics of different slags in the desulfurization (Anderson et al., 2000). It can be evaluated using Equation 3.

that allows the calculation of that sulfide capacity ( $C_s'$ ) is shown in the Equation 4:

presented in the Equation 5.

7, which are valid for  $\Lambda < 0,8$  e  $\Lambda \geq 0,8$ , respectively:

pendent on a diffusion process and it can be described by the Equation 8 (Ghosh, 2001; Turkdogan, 1996).

Finally, due to the high content of CaO (70%), and MgO (20%), found in the marble waste, there is potential for its use as desulfurizer agent of hot metal. In Brazil in 2010, approximately 468 thousand tons of marble waste was generated. Considering that the production of steel in the same period was 30 million tons and that the desulfurizer consumptions around 10kg per ton of steel, approximately 70% of this waste could be consumed in the Brazilian steel industry if it was used as desulfurizer. Then, the objective of this study is to evaluate the technical viability of the use of this waste in the process of hot metal desulfurization.

## 2. Materials and methods

For the development of the present study, firstly, the materials were acquired,

the marble waste was characterized, the mixtures were prepared, and, finally, the

experiments were done. The acquired materials for the accomplishment of the

experiments were as follows: marble waste, fluorspar, lime, and hot metal. The waste was homogenized through a rotary mixer (Marconi-R 300), where it stayed for 4 hours and was directed for particle size laser analysis, chemical analysis by X-ray fluorescence spectrometer (PANalytical - Axios Advanced), and mineralogical analysis by X-ray diffraction (PHILIPS- X'PERT).

After characterizing the waste, the mixtures were prepared. The definition of the CaO mass to be used in the experiments was made based in the data of the

KR of ArcelorMittal Tubarão (AMT) operation. That mass was defined as the average specific consumption value for desulfurization that was equal to 9.62 kg/ton, or 0.962% of the mass of the hot metal. With this consumption of CaO, an average sulfur removal of 92% was reached.

In this study, the experiments consisted of 4 types of additions, and the results are presented in Table 1. It is important to clarify that, even with these different additions, the amount of CaO was always proportional to the hot metal mass.

Also, with data supplied by AMT, when  $\text{CaF}_2$  was used together with the CaO, the proportion of these materials was 92% of CaO and 8% of  $\text{CaF}_2$ . Then, in the experiments, 750g of hot metal mass were used, and the above considerations were made in the calculation of the desulfurizer agent amount. The materials used in this study were added in the powder form. The generation of  $\text{CO}_2$ , due to decomposition of carbonates presents in the waste, can increase the agitation of the bath, and favor the reaction of desulfurization.

Table 1  
Additions used in this study.

Aditions	%CaO	%MgO	%SiO <sub>2</sub>	%CaF <sub>2</sub>	CO <sub>2</sub>	Others	Total
1) CaO pure	7.22g	-	-	-	-	-	7.22g
2) CaO + CaF <sub>2</sub>	6.64g	-	-	0.58g	-	-	7.22g
4) waste	7.22g	2.61g	0.60g	-	7.64g	0.07g	18.14g
5) waste + CaF <sub>2</sub>	6.64g	2.40g	0.56g	0.58g	7.03g	0.06g	17.27g

After the waste characterization and preparation of the mixtures, the experiments were carried out. In these experiments, the hot metal was carried in graphite crucibles of high purity and the heating took place in a resistance furnace, (MAITEC - FEE 1700/V), shown in Figure 1.

The argon injection was made with the purpose of leaving the inert ambience inside of the furnace; commercial argon was used in the flow rate of 6 Nl/min.

Once the work temperature of 1450°C was reached, the complete fusion of the hot metal was verified and, soon afterwards, the desulfurizer materials were added. The reaction time was counted immediately after the loading. Samples were taken before the additions and at intervals of 5, 10, 15, 20 and 30 minutes after the additions.

In each one of the experiments the stirring of the bath was made by a mechanical stirrer positioned on top of

the furnace. The stirrer's rotation speed was fixed at 1200rpm which was the minimum rotation required for the formation of the bath vortex. Besides the experiments with 1200rpm, an experiment with 1800rpm rotation was made with the addition of Waste +  $\text{CaF}_2$  mixture. Once the experiments were completed, the variation of sulfur content in the metal was determined through chemical analysis by infrared direct combustion in a LECO, CS-444 LS model.

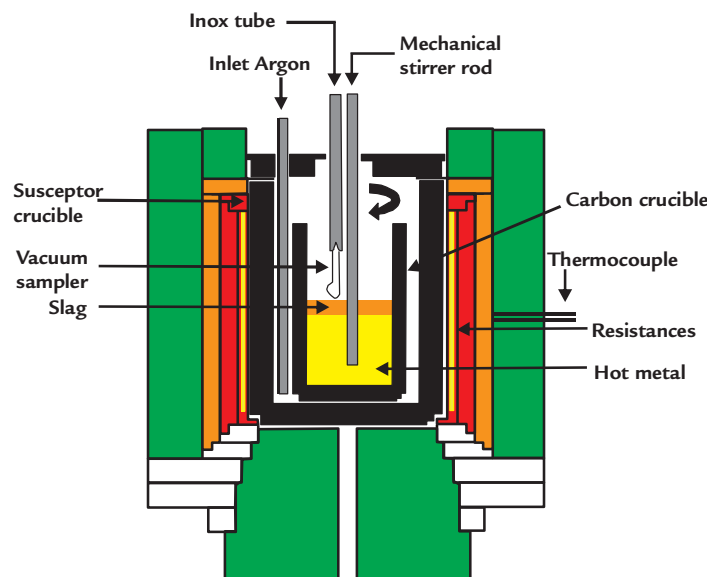


Figure 1  
Employed experimental apparatus.

### 3. Results and discussion

#### Characterization of the used materials

The chemical compositions of the marble waste was  $\text{CaCO}_3 = 70.5\%$ ;

$\text{MgCO}_3 = 24.8\%$ ;  $\text{SiO}_2 = 3.3\%$ ; others 0.27%; Mn = 0.38%; P = 0.065%; S = 0.4%; and the hot-metal C = 5%; Si = 0.025%. Considering that occurs the

carbonates decomposition, the following composition of waste is produced: CaO=72.7%; MgO=21.0%; SiO<sub>2</sub>= 6.1%. Besides 70% CaO, the waste also presents about 25% MgO content, which is usually added to the slag to reduce the wear and tear of the pot refractory, being unneces-

## Experiments

The results of all experiments are shown in Table 2. This table presents the

%S Initial	%S Final	Reagent	Reagent type	Agitation
0.030	0.023	7.22g	CaO (C)	1200rpm
0.026	0.014	7.22g	CaO + CaF <sub>2</sub> (CF)	1200rpm
0.030	0.025	18.14g	waste (R)	1200rpm
0.029	0.015	17.27g	waste + CaF <sub>2</sub> (RF)	1200rpm
0.027	0.006	17.27g	waste + CaF <sub>2</sub> RF(1800)	1800rpm

Equation 9 shows the  $\eta_s$  calculation

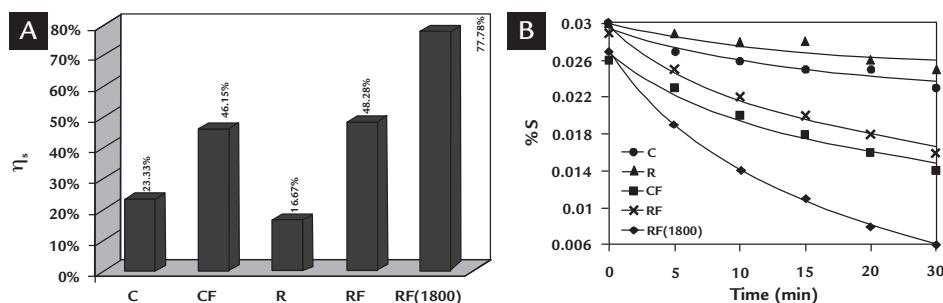
initial and final contents for each experiment, the ones that were used to calculate

formula and Figure 22(A) shows the varia-

$$\eta_s = \{([\%S]_i - [\%S]_t) \cdot 100\} / [\%S]_i \quad (9)$$

The variation of sulfur content in the

different treatment intervals is shown in



showed 89% of the particle size less than 69  $\mu\text{m}$  and the remaining less than 75  $\mu\text{m}$ . Then the waste and the lime satisfies the condition quoted by Shevchenko et al., (1984), which states that the best diameter for the CaO injection is not greater than 0.1mm.

the desulfurization degree ( $\eta_s$ ) of each experiment.

Table 2  
Results of the experiments.

tion of these parameter in the experiments.

the Figure 2(B).

## Additions of pure waste and pure CaO

Analyzing Figure 2, we can observe that the worst results were obtained with the additions of pure waste or pure CaO. The Figure 2(B) presents the variation of sulfur content according to time and %S, 2(A),  $\eta_s$  in each one of the experiments.

The worst results of the waste in relation to CaO might have occurred because the transport of the sulfur mass from the metal till CaO particle - which is favored by the stirring provoked by the CaCO<sub>3</sub> calcination and by the mechanical stirring - was not the controlling step of the desulfurization reaction.

This fact agrees with the statements of Ohya et al. (1977) and Niedringhaus and Fruehan (1988), that state that in the absence of CaF<sub>2</sub>, the controlling step is not the transport of metal sulfur mass to the interface

with the CaO, but the transport of the sulfur mass through the layer of solid CaS that is formed around the CaO particles. These results indicate that this layer did not suffer changes with the action provoked by the decomposition of the carbonates present in the waste and mechanical stirring.

Also according to Ohya et al. (1977), when 15% of each particle of CaO are converted in CaS in the absence of CaF<sub>2</sub>, the desulfurizer power of CaO is practically annulled, giving the presented results. In this case, it was the interaction of three factors. Firstly, with the waste addition in the place of the CaO, there was a larger temperature reduction caused by the decomposition of the carbonates and also by the greater mass of waste in relation to the CaO. The temperature fall was 25°C with waste addition and

10°C with CaO addition. Even with the temperature recovering quickly (5 and 2.5 minutes, respectively), there was a decrease in the desulfurization percentage, because a decrease in the temperature is harmful to the reaction in question.

Another reason for this result is the sulfide capacity of the waste ( $C_s=1.062$ ) that is smaller than CaO ( $C_s=1.143$ ). A decrease in  $C_s$  increases the sulfur content equilibrium, decreasing  $(-dS/dt)$  according to Equation (8) and, consequently  $\eta_s$ .

Besides, in the case of the addition of pure waste, the presence of SiO<sub>2</sub>, might have lead to the formation of some calcium-silicate, that according to Mitsuo et al. (1982), has low sulfur solubility and high fusion point, that obstruct the transfer of the ions S<sup>2+</sup> and delay the desulfurization.

## Additions of CaO+CaF<sub>2</sub> and Waste+CaF<sub>2</sub>

Based on the Figure 2, it is possible to observe that CaO+CaF<sub>2</sub> and waste+CaF<sub>2</sub> presented better results than the additions of pure CaO or waste, given that the addition of waste+CaF<sub>2</sub> obtains greater  $\eta_s$ .

These results were achieved because the addition of CaF<sub>2</sub> did not permit the formation of solid layer of CaS, which occurred when it was added pure CaO or pure waste. This fact favored the desulfurization reaction, leading to a better result (Ohya et al., 1977; Niedringhaus & Fruehan, 1988).

The CaF<sub>2</sub> reduces the mixture fusion point CaO+CaF<sub>2</sub>, which produces a greater amount of liquid phase and,

consequently, the mass transport is facilitated, favoring the desulfurization. Besides reducing the point of the mixture fusion, CaF<sub>2</sub> also reduces the viscosity of the formed slag and also there is no formation of a possible calcium-silicate that would delay the desulfurization process.

The superior result of the waste+CaF<sub>2</sub> mixture can be attributed to the existence of SiO<sub>2</sub> in the waste in 3.3% content, that together with CaF<sub>2</sub>, at the temperature employed, act attempting to increase the amount of the liquid phase, avoiding the precipitation of tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>). This process facilitates the transfer of CaS mass,

formed in the slag, favoring the desulfurization, in agreement with Niedringhaus and Fruehan (1988). These authors show through calculations that 5% of CaF<sub>2</sub> at 1450°C form 20% of liquid phase, which is enough to avoid the precipitation of tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>). This composite forms a solid shell around the CaO particle, or precipitates the solid state in slag, harming the desulfurization.

These results indicate that in the desulfurization, the influence of the mass transport is preponderant to the influence of the thermodynamics conditions, obviously, respecting the limit in which Gibbs Free Energy ( $\Delta G$ ) reaction is negative.

## Influence of the increased stirring in hot metal desulfurization

The additional experiment with 1800rpm and the waste+CaF<sub>2</sub> mixture was done with the intention of evaluating the influence of the stirring increment in the hot metal desulfurization. Figure 2 (B) presents the sulfur content variation for the

experiment with 1800rpm together with the result for the same mixture with 1200rpm stirring. Figure 2 (A) shows  $\eta_s$  reached in these experiments.

Comparing the results, it is possible to see that the stirring of the bath has a strong influence on the

desulfurization. Then, the experiment with a 1800rpm rotation, by a greater transport of the reagents to the reaction interfaces and removal of the generated products, leads to an increase of 29.5% in the desulfurization in relation to the experiment with  $\eta_s = 77.78\%$ .

## Calculation of Sulfide Capacity

As already mentioned, to compare the effect of the different mixtures/slugs in desulfurization,  $C_s$  is used. However, to calculate this, it is neces-

sary to know the optic basicity ( $\Lambda$ ) of each mixture; the ones which can be found in Equation 10, together with the chemical analysis of the marble waste

$$\Lambda_{\text{mixture}} = \sum(n_i \cdot x_i \cdot \Lambda_{\text{oxide}}) / \sum(n_i \cdot x_i) \quad (10)$$

By the analysis of this table, it is noticed that due to the great amount of CaO in each mixture, which has  $\Lambda_{\text{CaO}} = 1$ , the basicities show values close to this oxide basicity, between 0.872 and 1.005. Due to these values, it can be considered that the mixtures are also basic, and according to Ghosh (2001), these slags provide a greater diffusion capacity of its constituents in themselves. As the desulfurization depends on a diffusion process, these slags

are favorable to this process.

The relationship between  $C_s$  and  $\Lambda$  for mixtures/slugs with  $\Lambda \geq 0.8$  is described by Equation 5 (Young et al., 1992). As in this study all the mixtures showed  $\Lambda \geq 0.8$ , this equation was used to calculate  $C_s$  of each mixture; the results are also presented in Figure 3.

The Figure 3 shows larger  $C_s$  of the C ( $C_s = 1.143$ ) and R ( $C_s = 1.062$ ) than CF ( $C_s = 1.074$ ) and RF ( $C_s = 1.038$ )

showed in the Figure 3. The basicity of each mixture used in this study is too presented in Figure 3.

mixtures. Knowing the values of  $C_s$  and using the Equation 11, it is possible to calculate the sulfur partitions of equilibrium ( $L_{SE}$ ) which is another way to show the desulfurization efficiency. However, in order to use this equation, it is necessary to define the oxygen activity. Considering hot metal with 10 ppm of oxygen (0.001%), it is possible to reach the results shown in Figure 3.

$$\log L_s = \log (\%S)/[ \%S ] = - (935/T) + 1.375 + \log C_s + \log f_s - \log h_o \quad (11)$$

Based on the results of the Figure 3, it is possible to observe that for equilibrium sulfur partition, the values for C and R are greater than for CF and RF, respectively. However, due to kinetic limitations these mixtures did not obtain the best results, as shown in the Figure 3. These results corroborate with what has been said earlier: that in the desulfuriza-

tion, the influence of the mass transport is preponderant to the influence of the thermodynamics conditions. It is also important to note that when processing a waste, the mixtures with the marble waste obtained a sufficiently close partition to those achieved with mixtures of lime base, which is used industrially.

Comparing the equilibrium sulfur

partitions ( $L_{SE}$ ) and practical sulfur partition ( $L_{SP}$ ), where  $L_{SP} = \{(\%S)/[\%S]\}_{\text{final}}$ , as shown in Table 3, it is possible to see that ( $L_{SE}$ ) was higher, therefore the desulfurization was more efficient, in the experiments that had better mass transport of sulfur in the slag, which proves the preponderance of the mass transport influence on the desulfurization process.



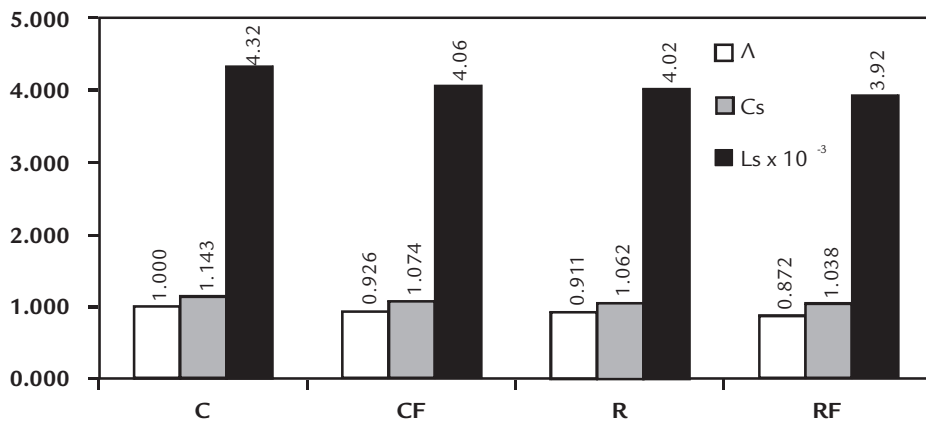


Figure 3  
Optic basicity, sulfur capacities and equilibrium sulfur partition of the mixtures.

Mixture	L <sub>SP</sub>	L <sub>SE</sub>	Agitation
C	31.6	4321	1200rpm
CF	89.0	4060	1200rpm
R	14.3	4017	1200rpm
RF	68.4	3924	1200rpm
RF	256.3	3924	1800rpm

Table 3  
Sulfur partition of the mixtures used in the experiments.

## 4. Conclusions

As already mentioned, to compare the effect of the desulfurization from the experiments carried out, the following conclusions can be reached:

- The additions of CaO and pure waste presented the worst degrees of desulfurization of this study, being pure Waste worse than pure CaO. This occurred because in the absence of CaF<sub>2</sub>, the controlling step is not sulfur mass transport of the metal to the interface with the CaO, but the sulfur mass transport through the solid CaS layer that is formed around CaO particles.
- The additions of CaO+CaF<sub>2</sub> and Waste+CaF<sub>2</sub> achieved greater degrees of desulfurization (46.15% CaO+CaF<sub>2</sub> e 48.28% waste +CaF<sub>2</sub>), because with the addition of CaF<sub>2</sub>, CaS solid layer formation does not occur.
- The largest desulfurization degree obtained with the waste+CaF<sub>2</sub> mixture in relation to CaO+CaF<sub>2</sub> can be attributed to the existence of SiO<sub>2</sub> in the waste in 3.3% content, that together with CaF<sub>2</sub>, act attempting to increase the amount of liquid phase, increasing CaS dissolution.
- An increase of 50% in the stirrer's rotation (from 1200 to 1800rpm) provoked an increase of 29.5% in the desulfurization (from 48.28% to 77.78%), with the 1800rpm experiment showing the best result of this study.
- In the desulfurization the kinetic

conditions prevails over the thermodynamics conditions.

- Finally, this study suggests that marble waste in mixture with CaF<sub>2</sub>, gathers interesting characteristics from both the thermodynamic as well as kinetic aspect to its use in the process of hot metal desulfurization. Different mixtures/slugs in desulfurization, C<sub>s</sub> is used. However, to calculate this, it is necessary to know the optic basicity (Λ) of each mixture; the ones which can be found in Equation 10, together with the chemical analysis of the marble waste showed in the Figure 3. The basicity of each mixture used in this study is too presented in Figure 3.

## 5. Symbols

%S<sub>t</sub> = sulfur percentage of the metal in time t.  
 %S<sub>eq</sub> = equilibrium percentage of sulfur of the metal.  
 k = the reaction rate constant (s<sup>-1</sup>).

C = Lime.  
 CF = Lime + Fluorspar.  
 R = Waste.  
 RF = Waste + Fluorspar

%S<sub>0</sub> = initial sulfur content in the hot metal.  
 (%S)<sub>0</sub> = initial sulfur content in the slag.

## 6. Acknowledgment

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## 7. References

- ANDERSON, M., JÖNSSON, P., HALLBERG, M. Optimisation of ladle slag composition by application of sulphide capacity model. *Ironmaking and Steelmaking*, v. 27, n. 4, p. 286-293, 2000.
- CHUSHAO, X., XIN, T. The kinetics of desulfurization of hot metal by CaO-CaF<sub>2</sub> based fluxes. *ISIJ International*, v. 32, n. 10, p. 1081-1083, 1992.

- DEO, B., BOOM, R. *Fundamentals of steelmaking metallurgy*. Prentice Hall International, 1993. cap. 2, p. 60-62. 300p.
- GHOSH, A. *Secondary steelmaking: principles and applications*. Boca Raton: CRC Press LLC, 2001. 307p.
- HOLLAPA, L. E. K. Review of ladle metallurgy. *Scandinavian Journal of Metallurgy*, n.9, p.261-269, 1984.
- MITSUO, T., SHOJI, T., HATTA, Y., ONO, H., MORI, H., KAI, T. Improvement of desulfurization by addition of aluminum to hot metal in the lime injection process. *Transactions of the Japan Institute of Metals*, v. 23, n. 12, p. 768-779, 1982.
- NIEDRINGHAUS, J. C.; FRUEHAN, R. J. Reaction mechanism for the CaO-Al and CaO-CaF<sub>2</sub> desulfurization of carbon-saturated iron. *Metallurgical Transactions B*, v.19B, p. 261-268, 1988.
- NYLO, F., OLIVEIRA, J. R. Utilização de caulim e resíduo de mármore na dessulfuração de ferro-gusa. *Tecnol. Metal. Mater. Miner.*, v. 8, n. 1, p. 37-43, 2011.
- OHYA, T., KODAMA, F., MATSUNAGA, H., MOTOYOSHI, M., HIGASHIGUCHI, M. Desulfurization of hot metal with burnt lime. *Steelmaking Proceedings*, v.60, p.345-55, 1977.
- YOUNG, R., DUFFY, J., HASSAL, G., XU, Z. Use of optical basicity concept for determining phosphorus and sulphur slag-metal partitions. *Ironmaking and Steelmaking*, v. 19, n. 3, p. 201-219, 1992.
- SHEVCHENKO, A., KIYASHKO, A., MAL'KOV, A. Influence of particle size of lime on effectiveness of pig iron desulphurization. *Steel in the USSR*, v. 14, n. 3, p. 116-117, 1984.
- TAKAHASHI, Y., IGUCHI, M. Correlation of flow establishment time for uniform dispersion of fine particles in a bath with an immersion cylinder. *ISIJ International*, v. 48, n. 8, p. 1143-1148, 2006.
- TURKDOGAN, E. *Fundamentals of steelmaking*. London: The Institute of Materials, 1996. cap 9, p. 275. 331p.
- WU, W., WU, W., HU, Y., LIU, L., DING, Y. Physical simulation of new desulphurization technology using pulsed and rotary stirring-injection. *Journal of Iron and Steel Research*, International, v.15, n. 1, p. 15-18, 2008.

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