Hot metal desulfurization by marble waste and fluorspar

Dessulfuração de ferro gusa utilizando resíduo de mármore e fluorita

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, because 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 2.2x10^{-17} atm, which will produce a low $\mu_{S^2}$, thus favoring the desulfurization in...
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 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 0.1nm.

The thermodynamic capacity that a slag presents to remove sulfur from 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.

\[
C_s = \left( \frac{\%S}{P_{O2} / P_{S2}} \right)^{1/2}
\]  

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 that allows the calculation of that sulfide capacity \( \left(C_s^\prime\right) \) is shown in the Equation 4:

\[
C_s^\prime = \left( \frac{\%S}{\%FeO} \right) \left( \frac{h_0}{f_S} \right)
\]

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 7, which are valid for \( \Lambda \).\( <0,8 \) e \( \Lambda \).\( \geq0,8 \), respectively:

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

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

Then, by using these thermodynamic equations, it is possible to find the equilibrium sulfur content and the partition of sulfur between slag and metal \( L_s = \frac{\%S}{\%S eq} \).

The rate of the desulfurization is dependent on a diffusion process and it can be described by the Equation 8 (Ghosh, 2001; Turkdogan, 1996).

\[
\frac{-dS}{dt} = k (\%S - \%S_{eq})
\]

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- XPERT).

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

<table>
<thead>
<tr>
<th>Additions</th>
<th>%CaO</th>
<th>%MgO</th>
<th>%SiO₂</th>
<th>%CaF₂</th>
<th>CO₂</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) CaO pure</td>
<td>7.22g</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.22g</td>
</tr>
<tr>
<td>2) CaO + CaF₂</td>
<td>6.64g</td>
<td>-</td>
<td>-</td>
<td>0.58g</td>
<td>-</td>
<td>-</td>
<td>7.22g</td>
</tr>
<tr>
<td>4) Waste</td>
<td>7.22g</td>
<td>2.61g</td>
<td>0.60g</td>
<td>-</td>
<td>7.64g</td>
<td>0.07g</td>
<td>18.14g</td>
</tr>
<tr>
<td>5) Waste + CaF₂</td>
<td>6.64g</td>
<td>2.40g</td>
<td>0.56g</td>
<td>0.58g</td>
<td>7.03g</td>
<td>0.06g</td>
<td>17.27g</td>
</tr>
</tbody>
</table>

Table 1
Additions used in this study.

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 +CaF₂ 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.

3. Results and discussion

Characterization of the used materials

The chemical compositions of the marble waste was CaCO₃ = 70.5%; MgCO₃ = 24.8%; SiO₂ = 3.3%; others = 0.4%; and the hot-metal C=5%; Si= 0.27%; Mn= 0.38%; P= 0.065%; S= 0.025%. Considering that occurs the
carbonates decomposition, the following composition of waste is produced: CaO=72.7%; MgO=21.0%; SiO₂= 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 unnecessary with the use of the waste.

The lime and fluorspar showed purity over 99.9%. The medium size of the waste particles was of approximately 69 µm, presenting a heterogeneous size distribution, where almost 43% of the particles have size by 38 µm. Lime showed 89% of the particle size less than 69 µm and the remaining less than 75µm. 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.

**Experiments**

The results of all experiments are shown in Table 2. This table presents the initial and final contents for each experiment, the ones that were used to calculate the desulfurization degree (ηₕ) of each experiment.

<table>
<thead>
<tr>
<th>%S Initial</th>
<th>%S Final</th>
<th>Reagent</th>
<th>Reagent type</th>
<th>Agitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>0.023</td>
<td>7.22g</td>
<td>CaO (C)</td>
<td>1200rpm</td>
</tr>
<tr>
<td>0.026</td>
<td>0.014</td>
<td>7.22g</td>
<td>CaO + CaF₂ (CF)</td>
<td>1200rpm</td>
</tr>
<tr>
<td>0.030</td>
<td>0.025</td>
<td>18.14g</td>
<td>waste (R)</td>
<td>1200rpm</td>
</tr>
<tr>
<td>0.029</td>
<td>0.015</td>
<td>17.27g</td>
<td>waste + CaF₂ (RF)</td>
<td>1200rpm</td>
</tr>
<tr>
<td>0.027</td>
<td>0.006</td>
<td>17.27g</td>
<td>waste + CaF₂ RF(1800)</td>
<td>1800rpm</td>
</tr>
</tbody>
</table>

Equation 9 shows the ηₕ calculation formula and Figure 22(A) shows the variation of these parameter in the experiments.

$$\eta_h = \frac{([%S]_i - [%S]_f) \times 100}{[%S]_i}$$  (9)

The variation of sulfur content in the different treatment intervals is shown in 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), ηₕ 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 CaCO₃ 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 CaF₂, 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 CaF₂ are converted in CaS in the absence of CaF₂, 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 (Cₛ=1.062) that is smaller than CaO (Cₛ=1.143). A decrease in Cₛ increases the sulfur content equilibrium, decreasing (-dS/dt) according to Equation (8) and, consequently ηₕ.

Besides, in the case of the addition of pure waste, the presence of SiO₂, 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 S²⁻ and delay the desulfurization.
**Additions of CaO+CaF₂ and Waste+CaF₂**

Based on the Figure 2, it is possible to observe that CaO+CaF₂ and waste+CaF₂ presented better results than the additions of pure CaO or waste, given that the addition of waste+CaF₂ obtained greater ηₚ.

These results were achieved because the addition of CaF₂ 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 CaF₂ reduces the mixture fusion point CaO+CaF₂, 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, CaF₂ 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+CaF₂ mixture can be attributed to the existence of SiO₂ in the waste in 3.3% content, that together with CaF₂, at the temperature employed, act attempting to increase the amount of the liquid phase, avoiding the precipitation of tricalcium silicate (Ca₃SiO₅). 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 CaF₂ at 1450°C form 20% of liquid phase, which is enough to avoid the precipitation of tricalcium silicate (Ca₃SiO₅). 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 (ΔG) reaction is negative.

**Influence of the increased stirring in hot metal desulfurization**

The additional experiment with 1800rpm and the waste+CaF₂ 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 ηₚ 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 ηₚ = 77.78%.

**Calculation of Sulfide Capacity**

As already mentioned, to compare the effect of the different mixtures/slags in desulfurization, Cₛ 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 mixtures. Knowing the values of Cₛ and using the Equation 11, it is possible to calculate the sulfur partitions of equilibrium (Lₛₑ) 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.

**Equilibrium Sulfur Capacity**

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In the Figure 3, the basicity of each mixture used in this study is too presented in Figure 3.

**Calculation of Sulfide Capacity**

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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 desulfurization, 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 (Lₛₑ) and practical sulfur partition (Lₛₚₑ) from Table 3, it is possible to see that (Lₛₑ) 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.
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 CaF₂, 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+CaF₂ and Waste+CaF₂ achieved greater degrees of desulfurization (46.15% CaO+CaF₂ and 48.28% waste +CaF₂), because with the addition of CaF₂, CaS solid layer formation does not occur.

• The largest desulfurization degree obtained with the waste+CaF₂ mixture in relation to CaO+CaF₂ can be attributed to the existence of SiO₂ in the waste in 3.3% content, that together with CaF₂, 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 prevail over the thermodynamic conditions.

• Finally, this study suggests that marble waste in mixture with CaF₂, gathers interesting characteristics from both the thermodynamic as well as kinetic aspect to its use in the process of hot metal desulfurization. Different mixtures/slags in desulfurization, C, is used. However, to calculate this, it is necessary to know the optic basicity (A) 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

%St = sulfur percentage of the metal in time t.
%S_eq = equilibrium percentage of sulfur of the metal.
k = the reaction rate constant (s⁻¹).
C = Lime.
CF = Lime + Fluorspar.
R = Waste.
RF = Waste + Fluorspar
%S₀ = initial sulfur content in the hot metal.
(%S)₀ = initial sulfur content in the slag.

6. Acknowledgment

The authors thank CAPES.

7. References

