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## Analysis of pig iron desulfurization with mixtures from the CaO-Fluorspar and CaO-Sodalite system with the use of computational thermodynamics

*Análise de dessulfuração de ferro-gusa com misturas do CaO-Fluorita e CaO-Sodalita com o uso de termodinâmica computacional*

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### Resumo

Esse trabalho tem como objetivo o uso da termodinâmica computacional no estudo de dessulfuração de ferro-gusa com misturas de CaO-Fluorita e CaO-Sodalita. As experiências foram realizadas com a adição de diferentes misturas a partir desses sistemas em ferro-gusa a uma temperatura de 1,400°C. Os resultados do teste foram analisados e comparados com os obtidos pelo programa de termodinâmica computacional THERMOCALC. Através deste software, foi calculado o teor de equilíbrio de enxofre do metal, as fases sólidas presentes e a quantidade de líquido em cada uma das misturas dessulfurantes utilizadas no processo na temperatura de 1,400°C. A termodinâmica computacional provou ser uma ferramenta eficaz para estimar a capacidade de dessulfuração das misturas.

**Palavras-chave:** Pré-tratamento de ferro-gusa, dessulfuração e termodinâmica computacional.

### Abstract

*This work aims at the use of computational thermodynamics in the study of desulfurization of pig iron through CaO-Fluorspar and CaO-Sodalite mixtures. Experiments were performed with the addition of different mixtures from these systems in molten pig iron at a temperature of 1,400°C. The test results were analyzed and compared with those obtained by the computational thermodynamics software program THERMOCALC. Through this software, were calculated the equilibrium sulfur content in the metal, solid phases, and the amount of liquid in each desulfurizing mixture used in the process at a temperature of 1,400°C. The computational thermodynamics proved to be an effective tool in predicting the desulfurization capacity of the mixtures.*

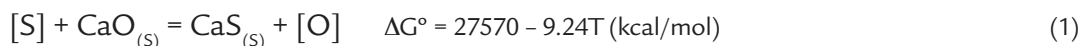
**Keywords:** Pretreatment of pig iron, desulfurization, computational thermodynamics.

## 1. Introduction

Normally the desulfurization of pig iron is made using mixtures containing CaO and fluorspar. However, the fluorspar can cause contamination of the water used

for Fluoride. Therefore this work uses mixtures with CaO and sodalite, with the aim to verify its efficiency for a possible substitution of fluorspar.

The desulfurization reaction of pig iron can occur according to the reaction (1) (Anderson et al., 2000).



Depending on the carbon and silicon content in the pig iron and  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the slag, there may be also formation

of carbon monoxide (CO) and tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ), respectively according to the following reactions (2) and (5)

respectively (Niedringhaus & Fruehan, 1988).



To evaluate the efficiency of sulfur removal from the metal by a given desulfurizing mixture, normally are used the parameters: optical basicity ( $\Lambda$ ), sulfide capacity (Cs), sulfur partition coefficient (Ls) and equilibrium sulfur content.

Sosinsky and Sommerville (1986) determined optical basicity values for a few elements that are typically used in desulfurizing mixtures agents, namely:  $\text{CaO} = 1$ ;  $\text{MgO} = 0.78$ ;  $\text{CaF}_2 = 0.37$ ;  $\text{SiO}_2 = 0.48$ ;  $\text{Al}_2\text{O}_3 = 0.61$ ;  $\text{P}_2\text{O}_5 = 0.40$ ;  $\text{Na}_2\text{O} = 1.15$ . Young (1991) defined sulfide capacity as the slag's capacity to absorb sulfur, establishing relationships between Cs and optical basicity.

The sulfur partition coefficient (Ls) is a parameter that expresses the relationship between sulfur concentration in slag ( $\%S_{\text{eq.}}$ ) and the metal bath ( $\%S_{\text{eq.}}$ ) through

the thermodynamic equilibrium (Turkdogan, 1996).

The equilibrium sulfur concentration [ $\%S_{\text{eq.}}$ ] in pig iron can be obtained from a mass balance in the system.

However, besides the models mentioned, there are others in literature (Yoshinori et al., 2009). All these models sometimes show different results, which are not always consistent with those found in practice. In addition, these models do not provide information on viscosity, amount of liquids and solids, and phases present in the mixtures.

The computational thermodynamics presents itself as a tool which determines the desulfurizing mixtures that show better thermodynamic conditions and allows for the calculation of viscosity, melting temperature, amount of liquid and solid

phases, and phases present in the mixtures at a given temperature. Through these parameters, as well as thermodynamic knowledge, we may have data that give us a position to conclude which mixture has better kinetics, allowing for a more complete analysis than that performed by the classical thermodynamic parameters.

Therefore, this work aimed at studying pig iron desulfurization by using desulfurizing mixtures of CaO-Fluorspar (CF) and CaO-Sodalite (CS) systems and by using computational thermodynamics software with the aim of determining the equilibrium sulfur concentration, melting point, and phases present in the mixture.

The thermodynamic data obtained from the software *THERMOCALC* TCW v.5, whose database used it was Slag3.

## 2. Materials and methods

### Experimental procedure

First, were carried out pig iron desulfurization experiments using desulfurizing mixtures of CaO-Fluorspar (CF) and CaO-Sodalite (CS) systems.

Table 1 shows the initial chemical

composition and the mass of the mixtures used.

Table 2, in turn, shows the initial chemical composition and mass of the pig iron used in each experiment.

The chemical composition in both cases was determined by X-ray fluorescence, using a device PHILIPS, model Axios Advanced analytical.

Mixtures	Chemical Composition (%)					Mixture mass (g)
	CaO	Na <sub>2</sub> O	CaF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	
CF5	92.5	-	4.59	0.42	2.49	9.25
CF10	87.43	-	9.16	0.61	2.80	9.28
CS5	92.95	0.65	-	1.50	4.90	9.21
CS10	88.38	1.30	-	2.70	7.62	9.19

CF5 (CaO + 5%CaF<sub>2</sub>); CF10 (CaO + 10%CaF<sub>2</sub>); CS5 (CaO + 5%Sodalite);CS10 (CaO + 10%Sodalite).

Table 1  
Initial chemical composition and mass of the mixtures used in the experiments.

Table 2  
Initial chemical composition  
and mass of the pig iron used.

Mixture	%Si	%Mn	%P	%S	%C	Pig iron Mass (g)
CF5	0.5	0.2	0.12	0.028	4.5	1000
CF10	0.5	0.2	0.12	0.031	4.5	1000
CS5	0.5	0.2	0.12	0.036	4.5	1000
CS10	0.5	0.2	0.12	0.028	4.5	1000

The mass of the mixture used was determined based on industrial data.

Initially, the solid pig iron was charged in MgO-C crucibles and in the electrical resistance oven MAITEC, model 1700-FEE/ at 1400°C. Further, argon gas was injected onto the pig iron with a flow rate of 10Nl/min to inert the environment and prevent oxidation of the metal.

After melting the pig iron, a sample

of the metal was removed and, then, the desulfurizing mixture went to the metal bath through a stainless steel tube. After adding the mixture, samples were taken at 10, 15, 20 and 30 minutes. The samples were taken using glass vacuum samplers. Figure 1 shows a schematic drawing of the experimental setup used. It was made only one test for each mixture.

The mechanical stirrer used is

equipped with a 4-vane impeller to simulate desulfurization in a KR reactor. The mechanical rotation was 400 rpm, because in this rotation the vortex formed in the bath presented similar format compared to the vortex formed in industrial processes.

Finally, final sulfur concentration was determined through the samples taken by chemical analysis by direct infrared combustion in a LECO.

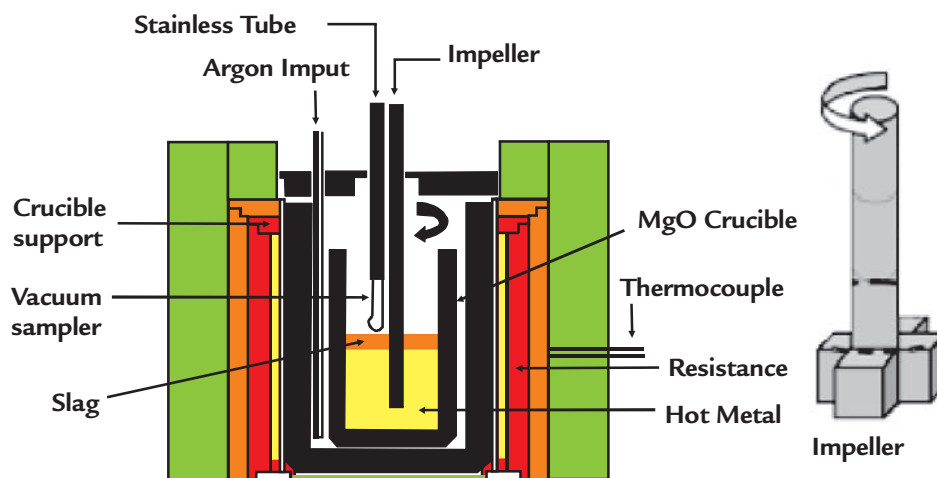


Figure 1  
Schematic diagram of the experiments.

### Computational thermodynamics simulations

Through the chemical compositions of the desulfurizing mixtures and pig iron present in Tables 1 and 2, thermodynamic

simulations were performed using the software *THERMOCALC V.5* to identify the equilibrium sulfur concentration

in the metal, phases present, and amount of liquid present in the mixture at 1400°C.

### 3. Results and discussion

Figure 2 shows the efficiency of desulfurization obtained by conducting

experimental tests at the Pyrometallurgy Laboratory. Desulfurization yield ( $\eta$ ) was

$$\eta = \frac{[\%S_i] - [\%S_f]}{[\%S_i]} \times 100 \quad (6)$$

where:

$[\%S_i]$  = initial sulfur concentration.

$[\%S_f]$  = final sulfur concentration.

It is observed that desulfurizing mixtures of the CaO-Fluorspar (CF5 and CF10) system had higher desulfurization yields, with 96.43% and 97.08%, respectively. However, the addition of twice the amount of fluorspar in the CF10 mixture did not show much influence on the yield, with an increase of only 0.65%. Mixtures of the CaO-Sodalite (CS5 and CS10) system show a lower yield than

that obtained by CF5 and CF10 mixtures, with 94.22% and 74.58% yield, respectively. This might have occurred due to the amount of liquid phase present in the mixtures and the formation of solid compounds such as tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ) and/or tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) (Niedringhaus & Fruehan, 1988), which are not taken into account by the thermodynamic parameters.

Therefore, the use of thermodynamic software can enable better desulfurizing capacity analysis of the mixtures, allowing

calculated from Equation 6.

for more accurate evaluation of what is the best desulfurizing mixture to be used in an industrial process. Through computational thermodynamics, we can determine the equilibrium sulfur concentration and the percentage of liquid phase and solid phases formed in the mixture. This information allows for a more accurate analysis of the desulfurizing capacity of these mixtures.

Table 3 shows the equilibrium sulfur concentration values in metal and sulfur partition coefficient calculated using the software *THERMOCALC*.

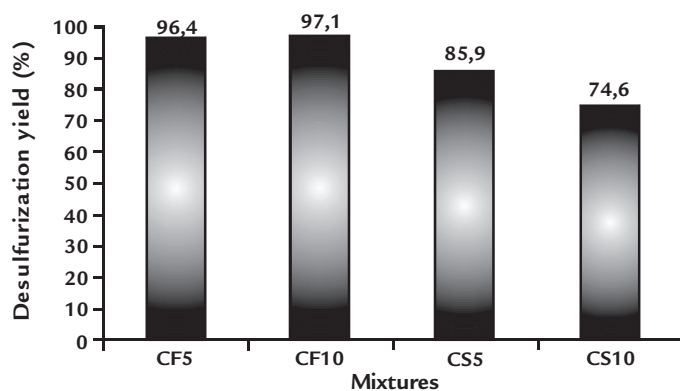


Figure 2

Desulfurization yield obtained in the experimental Mixtures (%S<sub>f</sub>: CF5 = 0.00099; CF10 = 0.00093; CS5 = 0.00278; CS10 = 0.00718).

Mixture	%S <sub>eq.</sub>	Ls
CF5	$1.54 \cdot 10^{-5}$	$2.76 \cdot 10^5$
CF10	$1.50 \cdot 10^{-5}$	$2.97 \cdot 10^5$
CS5	$1.57 \cdot 10^{-5}$	$2.15 \cdot 10^5$
CS10	$1.62 \cdot 10^{-5}$	$1.74 \cdot 10^5$

Table 3

Equilibrium final sulfur concentration and sulfur partition coefficient obtained through the software THERMOCAL.

Using data obtained from computational thermodynamics, it is possible to notice that the mixtures with higher desulfurizing efficiency are CF10, CF5, CS5, and CS10, respectively, as shown in Figure 2.

In addition to the thermodynamic parameters, there is other data on a desulfurizing mixture that can help in the analysis of its efficiency. This data is mainly the percentage of the liquid and solid phases in the slag, formation of the compounds tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ) and tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) and the concentration of free CaO in the slag.

It can be argued that the best desulfurizing mixture is one that is presented when added to the bath:

1. Higher percentage of liquid phase and, consequently, a lower percentage of the solid phase.
2. Less formation of compound tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ).
3. Less formation of compound tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ).

#### 4. Conclusions

Based on the data obtained in this study, it can be concluded that:

- Desulfurizing mixtures of the CaO-CaF<sub>2</sub> system, CF5 and CF10, showed higher desulfurizing yield, with 96.43% and 97.08% yields, respectively.
- The addition of twice the amount of fluorspar in the CF10 mixture did not show much influence on the desulfurization efficiency, with an increase of only 0.65% in the yield.
- Mixtures of the CaO-Sodalite system,

4. Higher concentration of CaO in the slag.

This is because a larger percentage of the liquid phase helps dissolve the formed CaS, preventing the formation of a solid layer around the CaO particle, impeding the transfer of the S mass in the metal until the CaO particle. The solid compounds  $3\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  also form around the CaO particle and in the same way the CaS impedes the transfer of the S mass to the CaO particle.

The graphs (generated by software THERMOCALC) presented in Figure 3 show the percentages of the stages mentioned in the different experiments with temperature, and Table 4 shows the percentage of these phases at a temperature of 1,400°C.

Based on the analysis of Table 4 and Figure 3, it can be observed that the mixtures that met parameters 1 to 4 are those that showed greater desulfurization capacity.

By comparing with the CF5 mixture with CF10, it is observed that the latter

CS5 and CS10, have lower yield than that obtained by the CF5 and CF10 mixtures, with 94.22% and 74.58% yield, respectively.

- The mixtures that had better efficiency were those that showed the highest liquid phase percentage, lower solid percentage, lower formation of compound tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ) and tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ), and a higher percentage of CaO.

had a better performance as it showed a greater percentage of the liquid phase and there was no formation of  $3\text{CaO} \cdot \text{SiO}_2$ . The comparison between the CS5 and CS10 mixtures shows that the former had a better desulfurization yield, even with a lower liquid phase percentage, since it showed lower formation  $3\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and higher concentration of CaO in the slag.

By comparing the mixtures of the CaO-Fluorspar system with the CaO-Sodalite system, it is noted that those with a higher liquid phase amount and lower solid phase amount ( $3\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) had higher desulfurization efficiency. As said previously, the solid compounds  $3\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  form around the CaO particle and impedes the transfer of the S mass to the CaO particle. Finally, by comparing all mixtures, the most efficient was the CF10 mixture, which had a higher liquid phase percentage, with lower formation of  $3\text{CaO} \cdot \text{SiO}_2$  and none of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and 81.28% free CaO.

- The classic thermodynamic parameters can sometimes lead to erroneous conclusions on the desulfurization efficiency of different mixtures. Due to their capacity to perform calculations and determine percentages of the different phases formed, computational thermodynamics allows for a better evaluation of desulfurization efficiency of these mixtures in industrial processes.

Figure 3  
Heating graphs of the  
desulfurizing mixture obtained  
from THERMOCALC:

A) CF5.  
B) CF10.  
C) CS5).  
D) CS10.

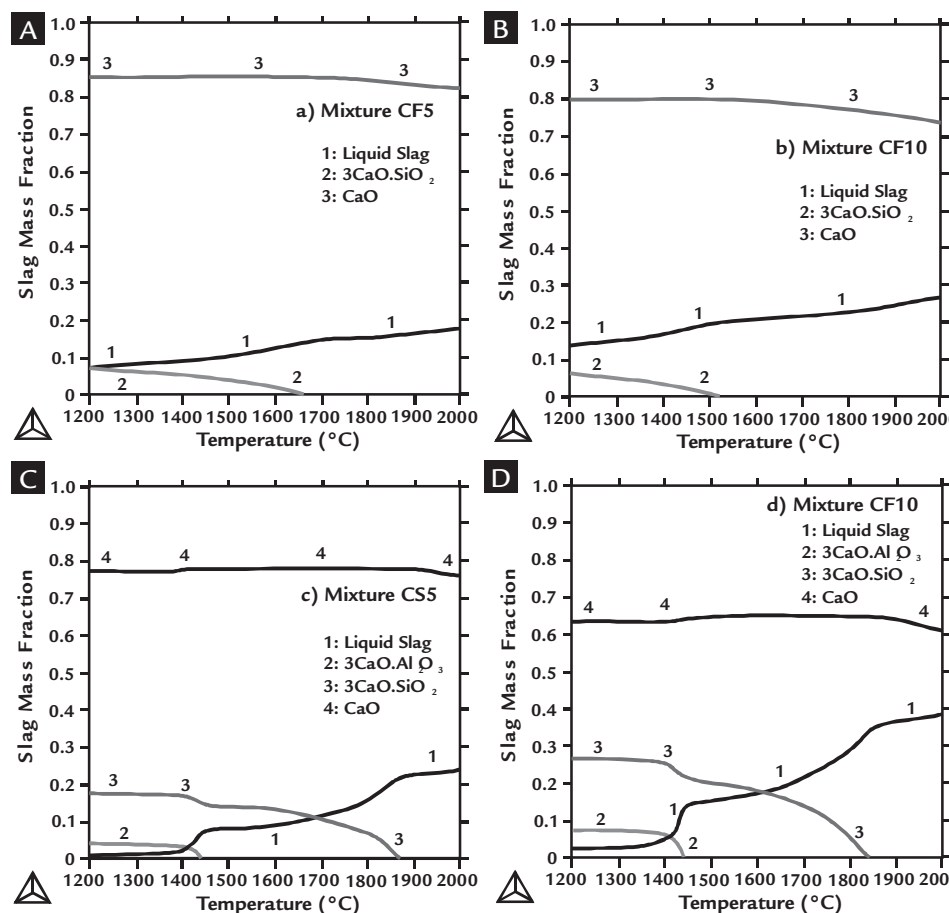


Table 4  
Percentage of phases formed in different  
experiments at the temperature of  
1,400°C, calculated based on Figure 3.

Mixture	$\eta$ (%)	% Liquid	% $3\text{CaO.SiO}_2$	% CaO	% $3\text{CaO.Al}_2\text{O}_3$
CF10	97.08	18.72	-	81.28	-
CF5	96.43	9.15	5.72	85.12	-
CS5	92.00	2.38	16.20	77.95	3.46
CS10	74.58	4.75	24.11	65.00	6.12

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