

REPLACEMENT OF LIME WITH INDUSTRIAL WASTES IN HOT METAL DESULFURIZATION MIXTURES

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Abstract

The steel production enhancement in recent decades has increased the solid waste generation in the steel plants. Due to the increase in the environmental policies stringency, efforts have been made to give them a more appropriate destination. In this context, the internal reuse of these materials is a solution often applied by the industry to reduce production costs and to decrease slag generation. Therefore, the aim of this research is to replace calcitic lime by limestone waste and KR slag in hot metal desulfurization, which are wastes from steel production. The KR slag is the waste generated by the desulfurization process in Kambara Reactor. Experimental desulfurization tests were carried out in a resistance furnace at a temperature of 1350°C, in an inert atmosphere with constant stirring of 500 rpm. Along with the tests, simulations were carried out with FactSage 7.0 software in order to obtain the phases present in each mixture at the working temperature and compare them with the practical results. It was found that the tricalcium silicate phase ($3\text{CaO}\cdot\text{SiO}_2$) was present in mixtures with lower desulfurization efficiency, which shows its kinetic limitation. The use of limestone waste proved to be more efficient than the use of KR slag.

Keywords: Desulfurization; Limestone waste; KR slag; Solid and liquid phases

1. Introduction

According to Ahmed et al. [1], large quantities of solid wastes are annually generated in iron and steelmaking. In the last decades, efforts have been made to reintroduce these by-products as substitutes for the raw materials, in order to reduce production costs, to decrease slag generation and to give them a more appropriate destination. Usually, the residues that cannot be used internally are sold to other sectors, such as the cement industry and road construction [1, 2].

The hot metal desulfurization slag by mechanical stirring (KR slag) is an example of waste whose application feasibility has been studied in the recent years. Several authors have tested its performance when it is applied as a constituent in cement production and as a soil stabilizer for paving [3, 4, 5, 6].

According to Matsui et al. [7], KR slag recycling as part of hot metal desulfurizing mixture has been developed. However, the slag amount that can be recycled is limited due to the buildup of sulfur and the possibility of metal resulfurization. Nevertheless, recent studies have tested KR slag for this purpose.

Nakai et al. [8] developed a recycling method for desulfurization slag. A virgin flux ($\text{CaO}\cdot 5\text{wt}\%\text{CaF}_2$) was compared with KR slag for different consumptions (3 kg/t, 5 kg/t, and 10 kg/t). After 15 minutes the final sulfur content reached nearly 50 ppm, except for recycled slag whose consumption was 3 kg/t (nearly 200 ppm). Thus, the recycled slag had a 70% desulfurization capability compared with that of virgin flux. According to the authors, the slag silica content was responsible for this difference due to the formation of solid phases.

Tong et al. [9] carried out studies on KR slag. According to them, about 56 wt% of the KR slag can potentially be used as an iron-bearing raw material for steelmaking process. The non-magnetic part was characterized and tested as desulfurization flux. The main crystalline phases present were: C, $\text{Ca}(\text{OH})_2$, CaSO_4 , CaF_2 , CaCO_3 , CaS and $2\text{CaO}\cdot\text{SiO}_2$. Their results showed that the KR slag still has desulfurization ability.

Different from the aforementioned studies, Matsui et al. [7] reused previously desulfurized KR slag as a hot metal desulfurizing agent. The authors determined

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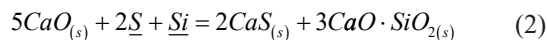
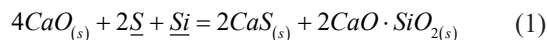
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the best temperature and oxygen potential conditions for converting CaS and CaSO₄ to CaO, in order to increase the desulfurization ability of this residue. Lime was completely replaced by KR slag, which resulted in a final sulfur content similar to the one obtained with lime utilization (25 ppm, efficiency of 90%). The desulfurization rate in the first 4 minutes was slightly higher with lime utilization. The authors concluded that it is possible to recycle KR slag as a CaO source in desulfurization.

The limestone calcination for lime production in steel mills generates a particulate by-product called limestone waste. This residue is captured by the furnaces dust filter collectors. According to Latif et al. [10], its chemical composition may vary depending on limestone type, kiln, fuel used, and also the kiln operating parameters. It usually contains a high CaO content. Studies using this residue as substitute for lime in hot metal desulfurization are still difficult to find in the literature. However, Seshadri, Silva and Silva [11] and Vuolio et al. [12] used calcium carbonate (CaCO₃) in their desulfurizing mixtures and the increase in efficiency obtained was attributed to the increase in the reaction surface generated by the limestone decomposition and CO₂ release, which promotes greater bath stirring.

The formation of solid phases around the lime particles is considered as one of the main controller mechanisms in hot metal desulfurization. Those solid products (CaS, 2CaO·SiO₂, and 3CaO·SiO₂) control the kinetic process since it hinders the sulfur mass transfer into lime [13, 14]. Equation 1 and Equation 2 show the desulfurization reaction with silicon.



Several papers demonstrated that the slags used in hot metal desulfurization process presents thermodynamic conditions to obtain lower sulfur contents, which denotes that kinetic parameters (such as phases formed, percentage of solid and liquid phases, and viscosity) may limit the desulfurization reaction. Zhang et al. [15] and Tong et al. [16] studied the hot metal desulfurization kinetics by CaO-SiO₂-Al₂O₃-Na₂O-TiO₂ and CaO-Al₂O₃-SiO₂-MgO-TiO₂-Na₂O slags, respectively. The authors indicate that the sulfur mass transfer coefficient increases as temperature increases and slag viscosity decreases. Both the melting effect and the fluidity of slag are enhanced when temperature increases, and the controlling step is the mass transfer of sulfur in slag phase.

Takahashi et al. [17] investigated the role of solid lime and liquid slag during hot metal desulfurization. The reaction rate of solid CaO was low owing to the formation of a solid interfacial layer. On the other

hand, when solid lime and liquid slag act together the desulfurization occurs by liquid slag while solid lime only supplies CaO for the liquid phase. In addition, the authors indicate that dicalcium silicate phase decreases the reaction rate since it hinders the sulfur mass transfer while tricalcium aluminate does not hinder the mass transfer and hence increases the rate. Thus, the solid phases formed around the CaO particles (CaS, 2CaO·SiO₂, 3CaO·SiO₂) hamper the mass transport of the desulfurization process, which decreases both the efficiency and desulfurization rate. Therefore, studies of desulfurizing mixtures and phase formation are fundamental to a better understanding of the desulfurization process.

According to Choi, Kim and Lee [18] the desulfurization rate is controlled by sulfur diffusion into the CaO particle (Equation 3),

$$-\frac{d[\%S]}{dt} = k' \cdot \left(\frac{A}{V_m} \right) \cdot ([\%S]_t - [\%S]_{eq}) \quad (3)$$

where A is the surface area between the CaO and the liquid metal (m²); k is the global coefficient of mass transportation (m/min); V is the hot metal volume; [%S]_t is the sulfur percentage at time t; and [%S]_{eq} is the equilibrium sulfur percentage.

Thus, the aim of this work is to propose lime partial replacement as a CaO source by residues generated in the steelmaking process: namely, limestone waste and KR slag. The mixtures' efficiency was calculated and the determination of the phases formed as well as their percentage was performed using FactSage 7.0.

2. Experimental

2.1. Raw materials chemical composition

The raw materials used in the experiments are the following: calcitic lime (C), KR slag (K), limestone waste (L), fluorspar (F), and standard flux (SF). The letters in parentheses represent the acronym for each one and will be used to name the desulfurization mixtures. The limestone waste composition is given considering all CO₂ release after calcination. This material was used without prior calcination. It is considered its calcination inside the furnace during the test. Its CaCO₃ content was 99.30%. The raw materials chemical composition is shown in Table 1.

The hot metal contained 94.6 wt% of Fe, 4.77 wt% of carbon, 0.042 wt% of sulfur, 0.29 wt% of silicon, 0.23 wt% of manganese, and 0.060 wt% of phosphorus.

2.2. Desulfurizing mixtures

The proposed mixtures were determined keeping lime as the main CaO source. In order to evaluate this raw material partial replacement, limestone waste and



KR slag were used in smaller proportions in some of them. The mixtures were designed so that the CaO mass was nearly the same. Standard flux was used as fluxing agent, always at 12wt% to fix its influence on the process. Table 2 displays the raw materials used in these mixtures, as well as their proportions.

The mixtures nomenclature follows this: raw materials initials appear accompanied by their subscript percentage.

2.3. Determination of the phases present in the mixtures

The determination of the phases present in the mixtures was carried out by FactSage 7.0 software. The databases used in the simulations were: FactPS, FToxid, and FTMisc. The Pure Solids sub-database in the FactPS database was used to determine the solid phases formed in the mixtures. The SlagH sub-database in the FToxid database was used to determine the liquid phases formed in the mixtures containing fluorspar. The SlagA sub-database was used in mixtures without fluorspar. The FTMisc database was applied to determine the equilibrium sulfur percentage using the Liquid sub-database. All simulation occurred at 1350°C and 1 atm. Table 3 displays the input data used in the thermodynamic programming.

2.4. Desulfurization tests

To carry out the practical desulfurization tests an

electric resistance furnace model MEV 1500/V, whose manufacturer is FORTELAB (Indústria de Fornos Elétricos LTDA), was used. An entrance was used to place an alumina tube for the argon injection in order to maintain the inert environment inside the furnace. Commercial argon was used at a flow rate of approximately 4 Nl/min and in none of the experiments was noticed the slag formation before the desulfurizing agents addition, which proves that the environment was inert.

Once the operating temperature reached and stabilized, which was 1350 °C, the complete hot metal melting was verified through a secondary inlet. Then the desulfurizing materials were added and to aid in the additions a stainless steel tube was used to direct the material into the MgO-C crucible. The experimental apparatus and the stirrer type used are illustrated by Figure 1 (a) and (b).

Table 2. Mixtures and the raw material proportions

Mixture	Percentage (wt%)				
	Calcitic Lime	Limestone Waste	KR Slag	Fluorspar	Standard Flux
C ₉₅ F ₅	95	-	-	5	-
C ₈₈ SF ₁₂	88	-	-	-	12
C ₈₀ L ₈ SF ₁₂	80	8	-	-	12
C ₈₂ K ₆ SF ₁₂	82	-	6	-	12
C ₇₄ L ₈ K ₆ SF ₁₂	74	8	6	-	12
C ₇₃ L ₁₅ SF ₁₂	73	15	-	-	12

Table 1 Raw materials chemical composition
*After calcination

Raw Material	Composition (wt%)													
	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	Fe ₂ O ₃	MgO	K ₂ O	FeO	MnO	Na ₂ O	S	C	P	Al
Calcitic Lime	98.84	0.67	0.05	0.00	0.08	0.21	0.00	0.00	0.00	0.00	0.08	0.00	0.06	0.00
Limestone Waste*	98.27	1.08	0.09	0.00	0.09	0.22	0.00	0.00	0.00	0.00	0.14	0.00	0.10	0.00
KR Slag	36.19	8.06	3.67	0.00	0.00	1.64	0.03	45.92	1.07	0.00	1.43	1.89	0.10	0.00
Fluorspar	3.87	12.04	5.79	72.12	4.34	0.00	1.83	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Standard Flux	3.80	26.80	22.37	0.00	0.00	1.74	3.06	0.00	0.32	26.37	0.03	0.00	0.00	15.51

Table 3. Chemical composition of the mixtures used as input data in the thermodynamic programming

Mixture	Composition (wt%)														Mass / g
	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	Fe ₂ O ₃	MgO	K ₂ O	FeO	MnO	Na ₂ O	S	C	P	Al	
C ₉₅ F ₅	15.35	0.20	0.05	0.59	0.05	0.03	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	16.31
C ₈₈ SF ₁₂	14.21	0.62	0.44	0.00	0.01	0.06	0.06	0.00	0.01	0.51	0.01	0.00	0.01	0.30	16.25
C ₈₀ L ₈ SF ₁₂	14.91	0.65	0.47	0.00	0.01	0.07	0.06	0.00	0.01	0.54	0.01	0.00	0.01	0.32	17.06
C ₈₂ K ₆ SF ₁₂	13.56	0.69	0.48	0.00	0.01	0.08	0.06	0.45	0.02	0.51	0.03	0.02	0.01	0.30	16.20
C ₇₄ L ₈ K ₆ SF ₁₂	14.21	0.73	0.50	0.00	0.01	0.08	0.06	0.47	0.02	0.54	0.03	0.02	0.01	0.32	16.99
C ₇₃ L ₁₅ SF ₁₂	15.54	0.69	0.49	0.00	0.01	0.07	0.07	0.00	0.01	0.56	0.01	0.00	0.01	0.33	17.79



The reaction time was started immediately after mixture charging (time zero). Initial samples were taken at 3, 6, 9, 12, 15, and 25 minutes after the additions and each sample weighed approximately 10 grams. Sampling was also done through the entrance located in the furnace cover center using vacuum samplers.

The stirring was carried out by means of a mechanical stirrer with a constant rotation of 500 rpm which was positioned on the top of the furnace and its rod passed through the secondary entrance after the desulfurizing mixture addition. Stirring was interrupted with each sampling and then restarted and the stop time was always the same. Finally, the sulfur content was determined by infrared analysis through samples direct combustion in a LECO model CS-444 LS.

2.5. Desulfurization efficiency

The desulfurization efficiency (Equation 4) was determined by the initial [%S_i] and final [%S_f] percentage of sulfur.

$$\eta(\%) = \frac{[\%S_i] - [\%S_f]}{[\%S_i]} \cdot 100 \quad (4)$$

3. Results and discussion

The experimental and thermodynamic results discussion was divided into the following steps: mixtures efficiency and Desulfurization Factor determination.

3.1. Mixtures efficiency

Table 4 shows the desulfurization mixtures efficiency for use of limestone waste and KR slag as substitutes for lime after 25 minutes. Figure 2 displays the sulfur variation over time for those mixtures.

The representation ([%S]/[%S_i]) in Figure 2.a) is expressed as the relationship between sulfur content for each time and initial sulfur content. This was done due to the different initial sulfur contents in each test. By making this relationship, all experiments start from the same point. In Figure 2.b) it is shown the sulfur variation considering the initial sulfur content.

From Figure 2.a) it can be seen that the lime and fluorspar mixture (C₉₅F₅) had the highest efficiency (80.70%). The mixtures containing limestone waste without addition of KR slag, (C₇₃L₁₅SF₁₂ and C₈₀L₈SF₁₂) obtained relatively high efficiency (76.00% and 75.56%). Since it is limestone, the

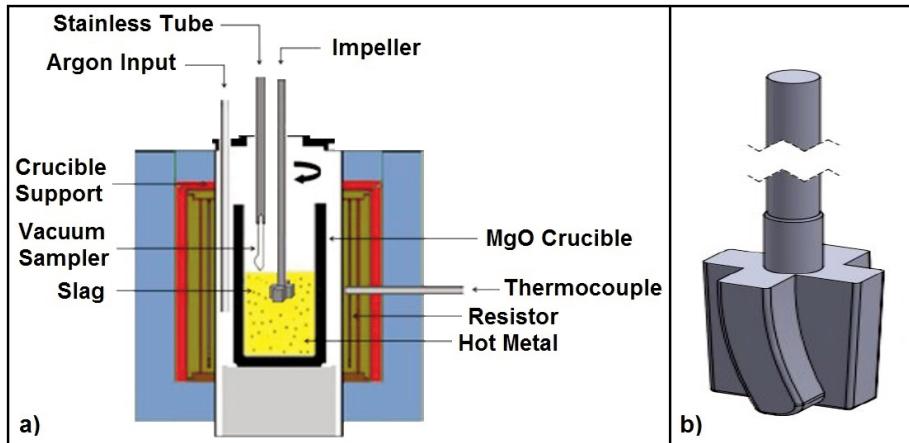


Figure 1 In a) schematic diagram of the experiments and in b) mechanical stirrer

Table 4. Sulfur content variation over time and mixtures efficiencies

Mixture	%S variation over time (min)							Efficiency (%)
	0	3	6	9	12	15	25	
C ₉₅ F ₅	0.057	0.040	0.034	0.024	0.022	0.020	0.011	80.70
C ₇₃ L ₁₅ SF ₁₂	0.050	0.043	0.037	0.030	0.028	0.023	0.012	76.00
C ₈₀ L ₈ SF ₁₂	0.045	0.036	0.033	0.027	0.023	0.020	0.011	75.56
C ₈₈ SF ₁₂	0.033	0.029	0.025	0.023	0.020	0.017	0.010	69.70
C ₈₂ K ₆ SF ₁₂	0.037	0.032	0.027	0.021	0.020	0.017	0.012	67.57
C ₇₄ L ₈ K ₆ SF ₁₂	0.043	0.032	0.027	0.024	0.024	0.022	0.015	65.12

release of gases generated by calcium carbonate calcination during the test is a possible explanation for this result. The stirring probably increased the desulfurization kinetics, as reported by Seshadri, Silva and Silva [11], and Vuolio et al. [12].

The mixtures with KR slag ($C_{82}K_6SF_{12}$ and $C_{74}L_8K_6SF_{12}$) had the lowest efficiencies probably due to the low CaO content in this residue (around 36%), the high FeO content (around 46%), and the presence of sulfur. According to Iwamasa and Fruehan [19], the increase in FeO content in the slag promotes a decrease in the desulfurization rate, since the equilibrium sulfur content increases. The oxygen potential at the metal/slag interface is greater as the FeO content increases. In this case, the driving force of the desulfurization reaction decreases. Mathematically, this is shown in Equation 3. Furthermore, the KR slag chemical analysis takes into account that the element exists in its most stable form, which in this case is CaO. However, it is likely that an amount of CaO is already converted into CaS and $3CaO \cdot SiO_2$, because it is the residue of the desulfurization process. Thus, CaO has already reacted and has the phases mentioned above formed around it. In addition, the remaining CaO probably has less reactivity than a virgin flux because it may already be sintered or hydrated. This indicates that its reuse in the mixture must be in a low proportion for

not compromising the process.

Another observation is regarding the effect of fluorspar compared to the standard flux. All mixtures, with the exception of $C_{95}F_5$, had the same amount of standard flux, that is, the same influence. Thus, 5wt% of fluorspar was more efficient than 12wt% of standard flux.

From Figure 2.b) it can be seen that in the first 9 minutes the desulfurization rate was lower for the mixtures $C_{88}SF_{12}$ and $C_{82}K_6SF_{12}$, which reached low efficiencies. Until 9 minutes, the mixture $C_{74}L_8K_6SF_{12}$ obtained high desulfurization rate, but from this moment the rate decreased probably due to kinetic factors and this mixture ended up as the worst considering efficiency. On the other hand, the remaining mixtures started with high desulfurization rates and kept this performance, reaching high efficiencies.

Table 5 shows the phases formed in mixtures after heating at 1350 °C.

It can be seen from Table 5 that the most efficient mixture ($C_{95}F_5$) was the one with greater solid CaO formation and lower solid phases that precipitate around CaO particle ($CaSand 3CaO \cdot SiO_2$). At the same time, mixtures with lower efficiencies were those with greater CaS and $3CaO \cdot SiO_2$ formation, mainly the last one. In addition, the efficiency also decreases with the decrease in solid CaO formation. McFeaters and Fruehan [13]

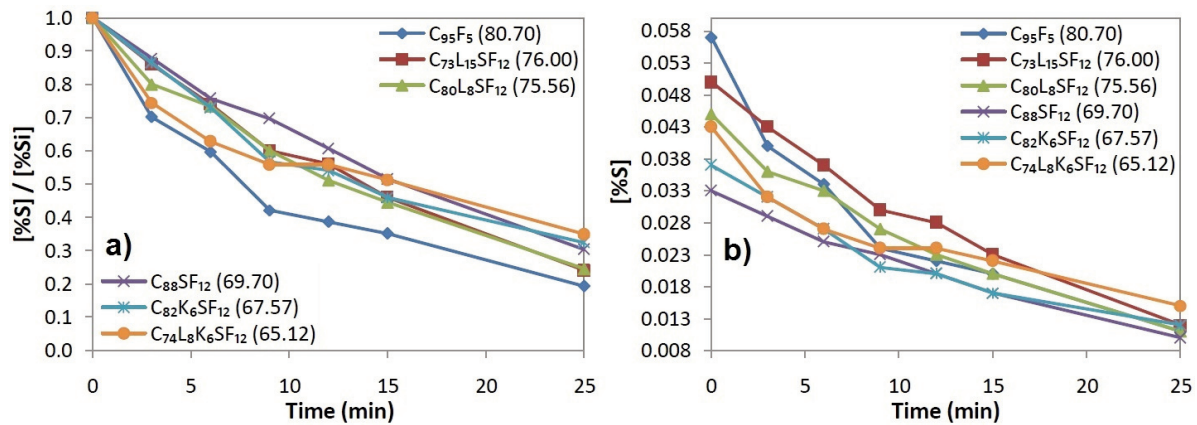


Figure 2. Sulfur variation over time. a) ($[\%S]/[\%Si]$); b) ($[\%S]$)

Table 5. Phases formed in mixtures after heating at 1350°C

Mixture	% Liq	% Sol	% Solid Phases				%Seq	Efficiency (%)
			CaO	CaS	MgO	$3CaO \cdot SiO_2$		
$C_{95}F_5$	8.60	91.40	90.99	0.10	0.19	0.00	2.16E-05	80.79
$C_{73}L_{15}SF_{12}$	14.85	85.15	74.73	0.20	0.00	7.13	2.01E-05	76.00
$C_{80}L_8SF_{12}$	15.48	84.52	77.06	0.18	0.00	7.06	1.93E-05	75.56
$C_{88}SF_{12}$	16.25	83.75	76.26	0.16	0.00	6.96	1.73E-05	69.70
$C_{82}K_6SF_{12}$	17.71	82.29	69.71	0.34	0.00	11.41	2.00E-05	67.57
$C_{74}L_8K_6SF_{12}$	17.02	82.98	69.94	0.36	0.00	11.09	2.08E-05	65.12



indicate that calcium silicates hinder the reaction kinetics by precipitating around the CaO particle and delaying sulfur diffusion. Mixtures with lower efficiencies are those that also have a higher liquid phase amount and a lower solid CaO amount. In these cases, part of the CaO particle forms the liquid slag and the solid phases, decreasing the amount available to react with sulfur. However, it is observed that the mixtures $C_{73}L_{15}SF_{12}$ and $C_{80}L_8SF_{12}$ had similar amount of $3CaO \cdot SiO_2$ and liquid phase compared to the $C_{88}SF_{12}$ mixture, which had lower efficiency. Thus, mixtures $C_{73}L_{15}SF_{12}$ and $C_{80}L_8SF_{12}$ were more efficient probably due to kinetic factors caused by the presence of limestone waste. The equilibrium sulfur content cannot be related to efficiency, which indicates that desulfurization depends mostly on factors that affect kinetics.

Based on the results, it can be stated that the most efficient mixture will be the one with the highest percentage of solid CaO and the lowest percentage of solid phases that form around the lime particles.

3.2. Influence of limestone waste addition

A direct comparison considering the influence of limestone waste on desulfurization efficiency can be taken into account if the mixtures $C_{88}SF_{12}$, $C_{80}L_8SF_{12}$ and $C_{73}L_{15}SF_{12}$ were analyzed together (0, 8 and 15% of limestone waste, respectively). Figure 3.a) shows the sulfur variation over time and Figure 3.b) shows the change in efficiency and amount of sulfur removed as the limestone waste percentage was increased.

From Figure 3.a) it is noted that the

desulfurization rate was higher for mixture $C_{73}L_{15}SF_{12}$, followed by $C_{80}L_8SF_{12}$ and $C_{88}SF_{12}$. In other words, as the limestone waste content increased the rate also increased. In the first 9 minutes, the difference between the rates was greater probably owing to the initial sulfur content. As the sulfur amount in hot metal increases, the sulfur availability for reacting with lime also increases. From 9 to 25 minutes the sulfur contents get closer and lower and hence the rates decrease and approach one another. Equation 3 shows that as the sulfur at time t decreases, the desulfurization rate decreases as well.

Figure 3.b) shows the efficiency and the amount of sulfur removed from hot metal for each mixture. It can be seen that increasing the limestone waste percentage in the mixture both the efficiency and amount of sulfur removed increased. As stated before, kinetic factors resulting from limestone decomposition may explain this behavior. From 0 to 8% of limestone waste in the mixture there was an increment of 5.86% in efficiency. On the other hand, from 8 to 15% the increase in efficiency was only 0.44%. Regarding the quantity of sulfur removed it varied from 110 ppm to 40 ppm. This fact may indicate that there is a limiting quantity of limestone waste that can replace lime, from which there is no significant increase in efficiency. However, this assumption could only be confirmed under testing, and that has not been done in this research for higher percentages of limestone waste.

Table 6 shows the phases formed in mixtures $C_{73}L_{15}SF_{12}$, $C_{80}L_8SF_{12}$ and $C_{88}SF_{12}$ after heating at 1350 °C.

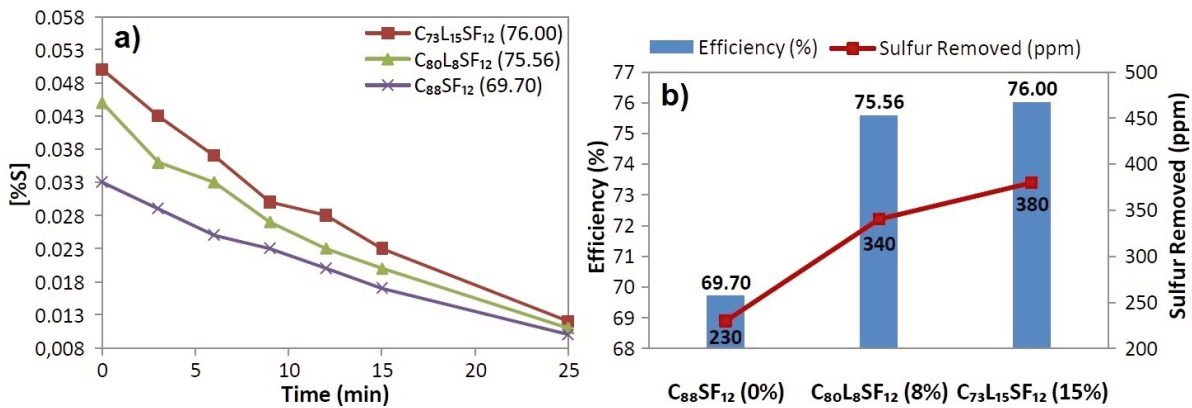


Figure 3. a) Sulfur variation over time; b) Efficiency and sulfur removed according to limestone waste amount in the mixtures

Table 6. Phases formed in mixtures $C_{73}L_{15}SF_{12}$, $C_{80}L_8SF_{12}$ and $C_{88}SF_{12}$ at 1350°C

Mixture	% Liq	% Sol	% Solid Phases				%Seq	Efficiency (%)
			CaO	CaS	MgO	$3CaO \cdot SiO_2$		
$C_{73}L_{15}SF_{12}$	14.85	85.15	74.73	0.20	0.00	7.13	2.01E-05	76.00
$C_{80}L_8SF_{12}$	15.48	84.52	77.06	0.18	0.00	7.06	1.93E-05	75.56
$C_{88}SF_{12}$	16.25	83.75	76.26	0.16	0.00	6.96	1.73E-05	69.70



Taking into account the $3\text{CaO}\cdot\text{SiO}_2$ formation, it is noted that the mixture with higher efficiency obtained greater calcium silicate formation and vice versa. However, for practical analysis the formation of that solid phase is nearly the same. The same can be said about the solid CaO and liquid phase formation. Thus, for this case these parameters cannot explain the efficiency and hence only kinetic factors such as increased reaction surface and stirring generated by limestone calcination explain the higher efficiency for mixtures containing higher limestone waste amount.

3.3. Influence of KR slag addition

Mixtures $\text{C}_{88}\text{SF}_{12}$ and $\text{C}_{82}\text{K}_6\text{SF}_{12}$ were selected for evaluating the KR slag effect on desulfurization efficiency (0 and 6% of KR slag, respectively). Figure 4.a) shows the sulfur variation over time and Figure 4.b) shows the change in efficiency and amount of sulfur removed for the mixtures.

From Figure 4.a) it is noted that the lime replacement for KR slag caused a decrease in efficiency, resulting in the opposite effect generated by limestone waste. On the other hand, it is observed that the rate of $\text{C}_{82}\text{K}_6\text{SF}_{12}$ mixture was narrowly higher than the rate of $\text{C}_{88}\text{SF}_{12}$ mixture probably due to the higher initial sulfur content of the first one.

Figure 4.b) shows that the mixture with higher efficiency removed a lower amount of sulfur from hot metal. It can be seen that both the efficiency and the amount of sulfur removed differences were small. Mixture $\text{C}_{88}\text{SF}_{12}$ had efficiency 2.13% higher than mixture $\text{C}_{82}\text{K}_6\text{SF}_{12}$, while the first had a difference of sulfur removed of only 20 ppm compared to the

second one. It shows that KR slag could replace lime partially in the cases in which sulfur requirements are not so restricted.

Table 7 shows the phases formed in mixtures $\text{C}_{88}\text{SF}_{12}$ and $\text{C}_{82}\text{K}_6\text{SF}_{12}$ after heating at 1350 °C.

It can be seen in Table 7 that the liquid phase amount is nearly the same while the solid CaO and $3\text{CaO}\cdot\text{SiO}_2$ amounts are different. Mixture $\text{C}_{88}\text{SF}_{12}$, which reached higher efficiency, formed more solid CaO: that is, there is a higher CaO availability for reacting with sulfur. At the same time, mixture $\text{C}_{82}\text{K}_6\text{SF}_{12}$ had lower efficiency and formed more tricalcium silicate and CaS, which forms on the lime particle and hence hinders the sulfur mass transfer. Besides, part of solid CaO is consumed for $3\text{CaO}\cdot\text{SiO}_2$ formation, which decreases its availability. As stated before, KR slag is a waste that has already passed for desulfurization process and then it is probable that its CaO content is transformed into CaS, $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$. So, its utilization should be restricted.

3.4. Comparison between limestone waste and KR slag

Figure 5 desulfurization rate and sulfur removed for mixtures $\text{C}_{74}\text{L}_8\text{K}_6\text{SF}_{12}$, $\text{C}_{82}\text{K}_6\text{SF}_{12}$, $\text{C}_{80}\text{L}_8\text{SF}_{12}$ and $\text{C}_{73}\text{L}_{15}\text{SF}_{12}$.

Initially, it was seen that the two mixtures containing only limestone waste reached the highest desulfurization efficiencies. On the other hand, the two mixtures containing KR slag reached the lowest ones.

Mixture $\text{C}_{74}\text{L}_8\text{K}_6\text{SF}_{12}$ contains both limestone

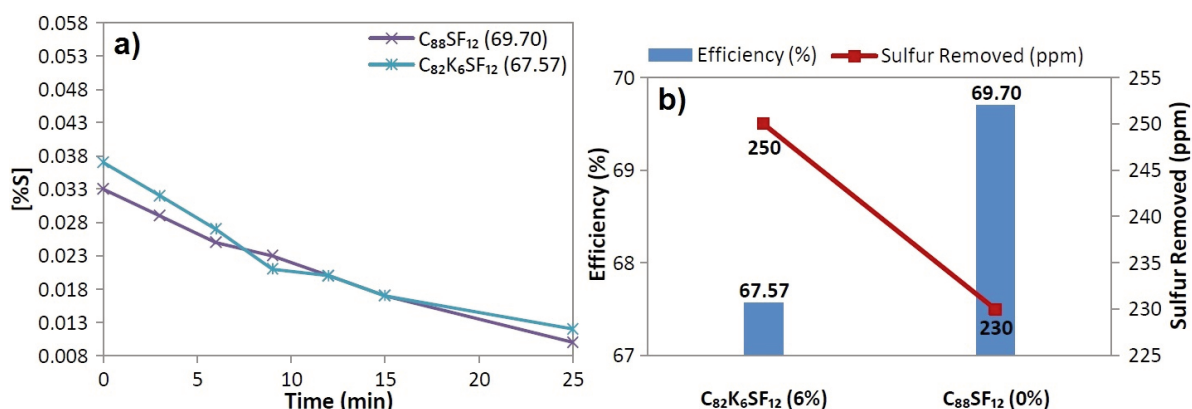


Figure 4 a) Sulfur variation over time; b) Efficiency and sulfur removed according to KR slag amount in the mixtures

Table 7. Phases formed in mixtures $\text{C}_{88}\text{SF}_{12}$ and $\text{C}_{82}\text{K}_6\text{SF}_{12}$ at 1350°C

Mixture	% Liq	% Sol	% Solid Phases				%Seq	Efficiency (%)
			CaO	CaS	MgO	$3\text{CaO}\cdot\text{SiO}_2$		
$\text{C}_{88}\text{SF}_{12}$	16.25	83.75	76.26	0.16	0.00	6.96	1.73E-05	69.70
$\text{C}_{82}\text{K}_6\text{SF}_{12}$	17.71	82.29	69.71	0.34	0.00	11.41	2.00E-05	67.57



waste and KR slag. From Figure 5, it is noted that it reached the lowest efficiency. However, it would be expected to overcome mixture $C_{82}K_6SF_{12}$ efficiency once the first one contains limestone waste. Until 6 minutes, its desulfurization rate was pretty higher than the rate of mixture $C_{82}K_6SF_{12}$ probably due to the kinetic effect of limestone waste and higher initial sulfur content; then, the $C_{74}L_8K_6SF_{12}$ rate became practically constant. It is possible that the solid phases formed mainly in this interval (between 6 and 15 minutes).

Table 8 shows the phases formed in mixtures after heating at 1350 °C.

At first, it was seen that the two mixtures containing only limestone waste (higher efficiency) formed less amount of tricalcium silicate and calcium sulfide, as well as more amount of solid CaO. On the other hand, the two mixtures containing KR slag (lower efficiency) formed more amount of solid phases that precipitate on lime particle and less solid CaO. From Table 8 it can also be seen that liquid phase, solid CaO and solid phases CaS, and $3CaO \cdot SiO_2$ amounts are nearly the same for mixtures $C_{82}K_6SF_{12}$ and $C_{74}L_8K_6SF_{12}$. However, the second was supposed to reach higher efficiency than the first one. Specific experimental conditions might have caused a limitation during the test of mixture $C_{74}L_8K_6SF_{12}$ and they could not be identified.

The following comparisons could be considered:

$C_{80}L_8SF_{12}$ and $C_{74}L_8K_6SF_{12}$: replacing 6% of

calcitic lime from the first for 6% of KR slag causes a decrease in efficiency;

$C_{80}L_8SF_{12}$ and $C_{82}K_6SF_{12}$: changing 8% of limestone waste for 6% of KR slag causes a decrease in efficiency;

$C_{80}L_8SF_{12}$ and $C_{73}L_{15}SF_{12}$: increasing limestone waste amount from 8 to 15% causes a increase in efficiency;

$C_{73}L_{15}SF_{12}$ and $C_{82}K_6SF_{12}$: changing 15% of limestone waste for 6% of KR slag causes a decrease in efficiency;

$C_{73}L_{15}SF_{12}$ and $C_{74}L_8K_6SF_{12}$: replacing 7% of limestone waste for KR slag causes a decrease in efficiency;

$C_{82}K_6SF_{12}$ and $C_{74}L_8K_6SF_{12}$: replacing 8% of calcitic lime for limestone waste when the mixture contains 6% of KR slag causes a decrease in efficiency.

Taking those comparisons into account it can be said that limestone waste is better than KR slag regarding desulfurization efficiency. However, the experimental conditions are controlled in order to keep all the tests as similar as possible. It is known that in industrial-scale the parameters such as temperature, initial sulfur content, hot metal chemical composition vary all the time and it is difficult to maintain standardization. Thus, the industrial results may not correspond to the ones obtained experimentally.

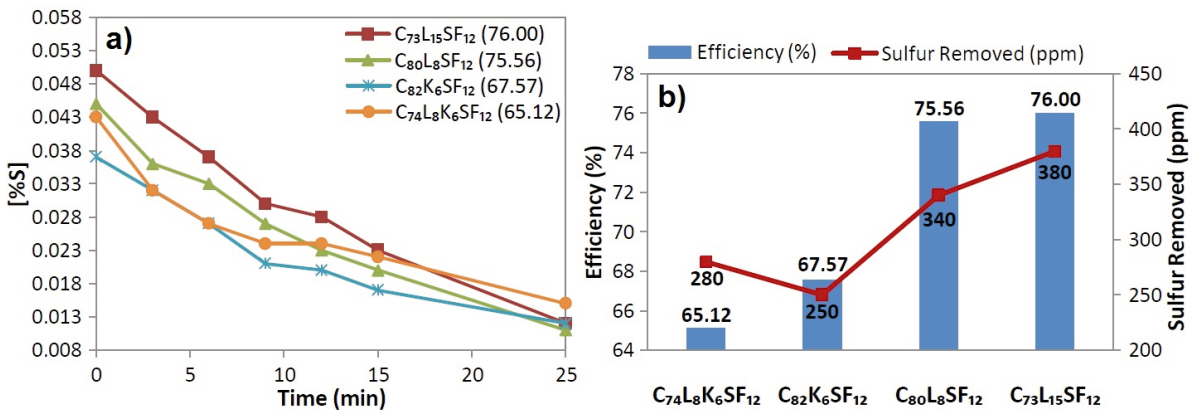


Figure 5 a) Sulfur variation over time; b) Efficiency and sulfur removed for mixtures containing limestone waste and KR slag

Table 8. Phases formed in mixtures $C_{73}L_{15}SF_{12}$, $C_{80}L_8SF_{12}$, $C_{82}K_6SF_{12}$ and $C_{74}L_8K_6SF_{12}$ after heating at 1350°C

Mixture	% Liq	% Sol	% Solid Phases				%Seq	Efficiency (%)
			CaO	CaS	MgO	$3CaO \cdot SiO_2$		
$C_{73}L_{15}SF_{12}$	14.85	85.15	74.73	0.20	0.00	7.13	2.01E-05	76.00
$C_{80}L_8SF_{12}$	15.48	84.52	77.06	0.18	0.00	7.06	1.93E-05	75.56
$C_{82}K_6SF_{12}$	17.71	82.29	69.71	0.34	0.00	11.41	2.00E-05	67.57
$C_{74}L_8K_6SF_{12}$	17.02	82.98	69.94	0.36	0.00	11.09	2.08E-05	65.12



4. Conclusion

The increase in the use of limestone waste in the mixtures favored the process efficiency, probably due to kinetic effects regarding limestone decomposition, which indicates that this residue can be used to replace part of the lime. On the other hand, the KR slag mixtures had the lowest efficiencies mainly due to tricalcium silicate and calcium sulfide formation, which indicates that it should be used in low proportions. Thus, the reuse of these residues is an alternative to reduce operating costs and a way to reduce the solid waste generation in the steelworks.

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Final approval of the version to be published: José Roberto de Oliveira.

Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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ZAMENA KREČA INDUSTRIJSKIM OTPADOM U MEŠAVINAMA ZA ODSUMPORAVANJE TEČNOG SIROVOG GVOŽDA

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Apstrakt

U poslednjih nekoliko decenija unapređenje proizvodnje čelika povećalo je stvaranje čvrstog otpada u čeličanicama. Zbog sve strožije politike zaštite životne sredine ulažu se napor da se ovom otpadu nađe primerenije odredište. U ovom kontekstu, interna reciklaža ovih materijala je rešenje koje industrija često primenjuje da bi se smanjili kako troškovi proizvodnje tako i stvaranje šljake. Iz tog razloga, cilj ovog istraživanja je da se u odsumporavanju tečnog sirovog gvožđa kalcinirani kreč zameni otpadom kreča kao i KR šljakom, a koji su otpad u proizvodnji čelika. KR šljaka je otpad koji je rezultat procesa odsumporavanja u Kambara reaktoru. Eksperimentalna ispitivanja odsumporavanja vršena su u peći na temperaturi od 1350°C, pri inertnoj atmosferi i uz stalno mešanje od 500 rpm. Zajedno sa ispitivanjima vršene su i simulacije uz softver FactSage 7.0 da bi se dobile faze prisutne u svakoj mešavini pri radnoj temperaturi i uporedile sa praktičnim rezultatima. Otkriveno je da je trikalcijum silikatna faza (3CaO·SiO₂) bila prisutna u mešavinama koje su imale nižu efikasnost odsumporavanja, što pokazuje njena kinetička ograničenja. Dokazano je da je upotreba otpada kreča efikasnija nego upotreba KR šljake.

Cljučne reči: Odsumporavanje; Otpad kreča; KR šljaka; Čvrste i tečne faze

