Development of Synthetic Slag with Marble Waste and Calcium Aluminate Agents for Cast Iron Desulfurization

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The aim of this work was to study the use of slags to desulfurize cast iron. It was proposed to use alumina instead of fluorspar. In addition, marble waste was used instead of lime. Simulations applying Thermo-Calc® software were carried out in order to obtain the theoretical phases using thermodynamic data. Then, a comparison between theoretical data and experimental tests were performed. Cast iron was melted in induction furnace at 1550ºC. Slags composed mainly for CaO and Al_2O_3 were used to desulfurize cast iron. The results showed that the desulphurization reaction was favored when the liquid phase was increased. Furthermore, it was found that cast iron desulfurization occurs by top slag mechanism. Furthermore, the desulfurization tests showed a decrease up to 90.10% in the sulfur content to the mixture containing conventional lime and 87.25% to the mixture RMF15. The slags obtained from marble waste contained MgO, which it interfered negatively in the desulfurization yield. In addition, increasing the CaO particle diameter improved the desulfurization process. The desulphurization process more favored to particle size of 500-1000 μm.

Keywords: *Desulfurization, fluorspar, marble waste, cast iron.*

1. Introduction

Desulfurization is one of the most important process involving cast iron and steel production. Cast iron desulfurization is performed during the manufacture of ductile iron castings in order to obtain spherical graphite morphology[1,2]. Several reagents are employed to remove sulfur, such as calcium, magnesium and sodium[3]. However, the desulfurization using wire of magnesium powder is related to high operating cost[4,5].

The main sulfur removal mechanism is the transfer of sulfur from the metal to the slag phase[6]. The low solubility of sulfur at high temperatures in the iron favors the formation of sulfur-rich slags. However, it is necessary add desulfurization agents such as Ca or Mg in order to form slag, which removes sulfur from the hot metal. The Equation 1 describes the sulfur transfer from the liquid metal to the slag.

$$[S] + (0^{2-}_{slag}) \leftrightarrow (S^{2-}) + [0_{steel}] \quad (1)$$
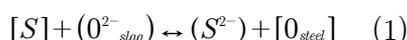
Due to the difficulty to describe the activities of the ionic elements (O^{2-} e S^{2-}), a simplified approach to this issue is to recognize that the CaO in slag is the predominant

desulfurization, as show Equation 2. Additionally, the desulfurization occurs with the formation of a stable sulfide.

$$(CaO)_{(S)} + [S] \leftrightarrow (CaS)_{(S)} + [O] \quad (2)$$
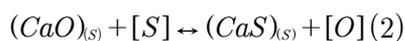
$$\Delta G^0 = 115358 - 38.66T \ (J/mol) \quad (3)$$

The effect of carbon and silicon content in steel and cast iron are also mentioned during the desulfurization tests. The Equations 4 and 6 show this relationship[7,8].

$$(CaO)_{(S)} + [S] + [C] \leftrightarrow$$
$$(CaS)_{(S)} + CO_{(g)} \quad (4)$$
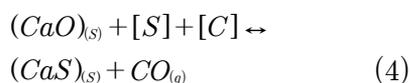
$$\Delta G^0 = 87550 - 68.50T \ (J/mol) \quad (5)$$

$$(CaO)_{(S)} + [S] + 1/2[Si] \leftrightarrow$$
$$(CaS)_{(S)} + (SiO_2)_{(S)} \quad (6)$$
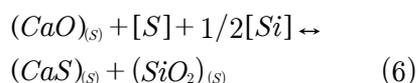
$$\Delta G^0 = 1280543 - 32.4T \ (J/mol) \quad (7)$$

Thus, the marble waste can be an alternative to be a input in the desulfurization process of hot metal, since this waste contain high percent of CaO (70%) and MgO (20%). In Brazil, approximately 468 thousand tons of marble waste

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was generated in 2015. This waste can be consumed in the Brazilian steel industry if it was used as desulfurization agents.

The current study aims to adjust the composition of synthetic slags used in the cast iron desulphurization process in order to replace the magnesium for calcium oxide or marble waste as desulfurization agent. Furthermore, this study aims to compare the results obtained through computational thermodynamic software to the experimental results.

2. Experimental

2.1. Marble waste characterization

The marble waste characterization was performed by chemical analysis via energy dispersive X-ray fluorescence (EDXRF). The X-ray diffraction test was accomplished using a Rigaku diffractometer, Miniflex 300 model, equipped with Cu Kα (λ= 1,5418Å) tube. Step scan mode was applied to obtain the data. In addition, scan range of 3-90º, step width of 0.02º and duration time of 5 seconds were used. A Netzsch thermobalance was used to performed the thermogravimetric analysis (TGA). The temperature range investigate was 25-1000ºC. It was adopted a heat rate of 10ºC min^{-1} under a flow of 50 mL min^{-1} of nitrogen. Scanning electron microscopy (SEM) assay was performed using a Philips XL-30 equipment in order to investigate the morphology of marble waste. Surface area was determined by BET (Brunauer-Emmett-Telle) through accelerated surface area and porosimetry system (ASAP 2020) equipment. A pre-treatment up to 200ºC by 24 hours was necessary to accomplish the tests. Additionally, size analyses was performed via mastersizer 2000. Such equipment uses laser diffraction technique to obtain the data.

2.2. Synthetic slags compositions

Table 1 shows the slags compositions used in the desulfurization tests.

The mixtures from CA1 to CA5 were produced using conventional lime-based slags and Al$_2$O$_3$ based slag.

The mixtures from 6 to 10 (ending with RM) were produced in order to replace the conventional lime on the slags by carbonate marble waste. The mixtures 11 and 12 (ending with CAF and RMF) were formulated with fluorspar in order to compare the results obtained with mixtures without CaF$_2$.

2.3. Desulphurization tests

The desulfurization tests were performed using a mass of 1.4 kg of solid cast iron in each experiment. The mass of solid cast iron was put into a carbon crucible (1000 mL) and enveloped with a carbon ceramic blanket to decrease the heat loss. The set (carbon crucible and carbon ceramic blanket) was inserted in an alumina crucible in the induction

Table 1. Slags compositions used in cast iron desulfurization tests.

Mixtures	Composition (wt %*)					
	Al$_2$O$_3$	CaO	MgO	SiO$_2$	Na$_2$O	CaF$_2$
CA1	20.0	65.0	0.00	0.00	15.0	0.00
CA2	25.0	65.0	0.00	0.00	10.0	0.00
CA3	30.0	60.0	0.00	0.00	10.0	0.00
CA4	25.0	60.0	0.00	0.00	15.0	0.00
CA5	15.0	75.0	0.00	0.00	10.0	0.00
RM6	15.49	50.47	18.21	4.21	11.62	0.00
RM7	19.37	50.47	18.21	4.21	7.74	0.00
RM8	23.54	47.46	17.13	3.96	7.91	0.00
RM9	19.74	47.38	17.08	3.96	11.84	0.00
RM10	11.25	56.26	20.29	4.69	7.50	0.00
CAF11	30.0	60.0	0.00	0.00	0.00	10.0
RMF12	23.68	47.37	17.08	3.95	0.00	7.89

*wt%: weight percent.

furnace, and heated up to 1550ºC. The heating was controlled at 30ºC min^{-1} from 25ºC to 1550ºC. Figure 1 sketches out a schematic diagram of the induction furnace used in the experiments.
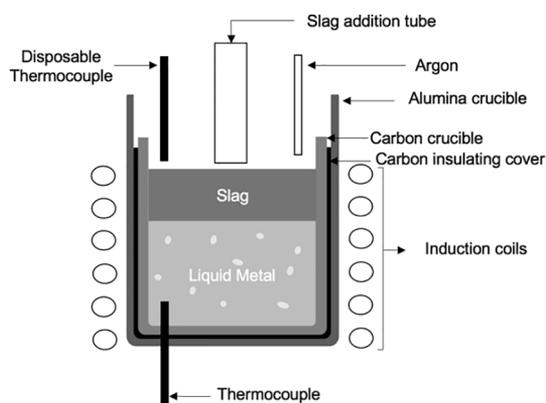
Figure 1. Schematic diagram of the induction furnace used in the experiments.

After complete melting of the cast iron, it was collected an aliquot of the liquid phase to obtain the initial content of sulfur, carbon, silicon and phosphorus (Table 2) via mass spectrometer. This step was carried out to calculate the desulphurization yield.

The addition of synthetic slag was splitted in three aliquot (containing the same mass) in order to increase the desulphurization efficient. The first aliquot was added right after the sample collected to chemical analysis. This stage was designated as time zero minute. Then, the second and third addition of synthetic slag were performed at 15 and 30 minutes, respectively.

To investigate the sulfur variation during the tests, aliquots were obtained from the bath at 5, 10, 15, 20, 25, 30, 35,

Table 2. Initial composition of cast iron used to desulphurization tests.

Mixtures	Chemical composition (wt %)				Mass (kg)
	C	Si	P	S	
CA1	3.26	1.64	0.054	0.103	
CA2	3.18	1.64	0.054	0.084	
CA3	3.20	1.61	0.050	0.090	
CA4	3.28	1.68	0.056	0.103	
CA5	3.22	1.68	0.056	0.096	
RM6	3.20	1.72	0.057	0.084	
RM7	3.16	1.72	0.053	0.084	1.4
RM8	3.24	1.69	0.052	0.082	
RM9	3.32	1.73	0.057	0.087	
RM10	3.37	1.7	0.064	0.091	
CAF11	3.25	1.71	0.064	0.101	
RMF12	3.28	1.73	0.059	0.091	

Table 3. Chemical components used on the production of synthetic slags.

Elements	Marble Waste** (wt.%)	Lime (wt. %)
SiO_2	3.43	
CaO	39.00	99.9
MgO	14.56	
LOI*	42.08	

*LOI: loss on ignition. ** Chemical composition used to determine the slags compositions in Table 1.
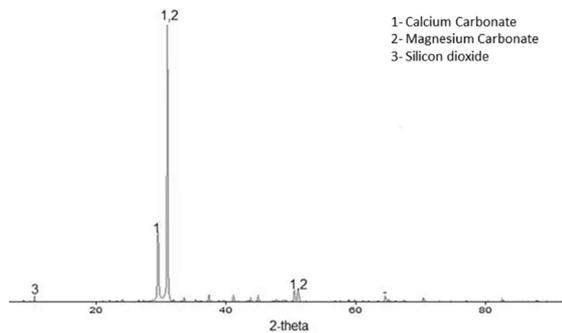
Figure 2. Marble waste X-ray diffractogram.

40 and 45 minutes. The samples obtained in each aliquots were analyzed via mass optic spectrometry to determine the content of sulfur. It is also important to mention that the bath agitation was promoted by induction furnace.

The initial and final content of sulfur were used to calculate the desulphurization yield (%η) via equation 10. Where $[\%S_i]$ and $[\%S_f]$ are the initial and final sulphur content in the bath, respectively.

$$\eta(\%) = \frac{[\%S_i] - [\%S_f]}{\%S_i} * 100 \quad (10)$$

The synthetic slags compositions presented in table 1 were also analyzed via Thermo-Calc® software in order to compare the theoretical equilibrium contents. Then, both liquid and solid fractions were also determined. The database SLAG3 was adopted to the simulated.

In addition, it was investigate the influence of lime particle size on desulfurization process. In this step, the lime was classified in three particles size (500-1000 μm, < 100 μm and < 20 μm) in order to produce the slags. It was also added 10 wt.% of fluorspar in each slag.

3. Results and Discussion

3.1. Raw material characterization

Table 3 shows the chemical analysis of marble waste and lime used to formulate the synthetic slags. The main component in the lime is CaO (99.9%), whereas marble waste contains as the mains components the CaO (39.00%) and MgO (14.56%). A loss on ignition of 42.08% was also observed. Figure 2 presents the X-ray pattern of marble waste, which shows that the marble waste is composed for calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$) and silicon oxide (SiO_2). In addition, thermogravimetric

analysis (Figure 3) of marble waste shows a mass loss of 43.81% in the temperature range of 700°C to 820°C. This fact is mentioned as the carbonates decomposing into CaO, MgO and CO_2[9-11]. Furthermore, the addition of marble waste into the cast iron at 1550°C will promote the decomposition of the carbonates to form CO_2, which it can favor the bath agitation. However, the carbonates decomposition is endothermic, which it reduces the bath temperature, disfavoring the desulfurization reaction[12].
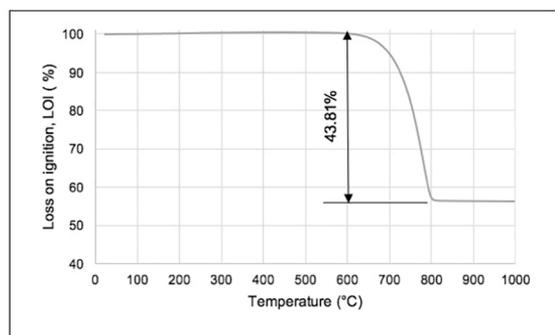
Figure 3. Marble waste thermogravimetry analysis.

Figure 4 shows images of scanning electron microscopy and EDS spectra obtained from the marble waste. It can be seen an angular morphology, coarse surface and cleavage profile. In addition, the EDS spectrum revealed that the main elements were Ca, Mg, O and Si. The results show that calcium is present in greater proportion than other elements.

Additionally, analysis of particle size indicates that marble waste presented a cumulative d50 diameter of 48μm.
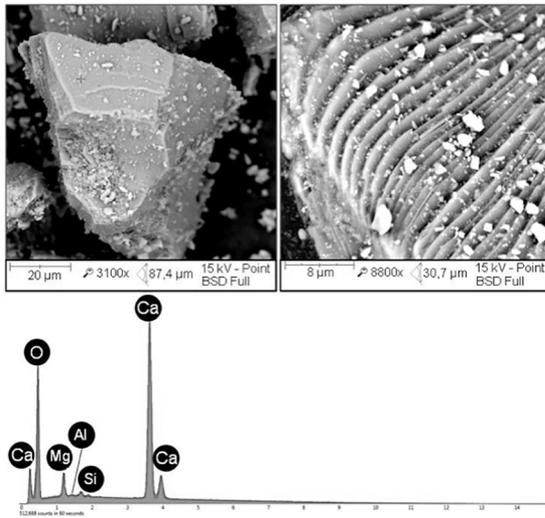
Figure 4. MEV backscattered electron images and EDS of marble waste.

The superficial area test indicates that the superficial area was 0.24m²/g. The lime size analysis shows that the d50 are about 16µm and superficial area of 1.52m²/g. Therefore, marble waste is able to substitute the calcium oxide in slags production for desulfurization of cast iron, since its chemical and physical characteristics were similar.

3.2. Desulfurization experiment

Table 4 shows the equilibrium contents in the cast iron after thermodynamics calculations via Thermo-Calc® and the desulfurization yield η(%).

The synthetics slags RM6 and RM7 (83.93% and 85.63% desulphurization yield, respectively) presented higher desulphurization yield than synthetics slags CA1 and CA2 (desulfurization yield of 82.52% and 84.64%, respectively). However, the synthetics slags CA3, CA4 and CA5 presented better desulphurization yield than the synthetics slags RM8, RM9 and RM10.

Such results indicate that addition of marble waste is a potential to the desulphurization of cast iron. However, increasing the content of marble waste in the synthetic slags decreased the desulphurization yield.

It was also noted that synthetics slags containing CaF_2 (CAF11 and RMF12) presented lower values to equilibrium sulfur ($5.17E^{-05}$ and $5.75E^{-5}$, respectively), which suggest a higher thermodynamic potential to desulfurization. However, kinetic parameter should be also considered to indicate the better synthetic slag[13,14].

Figure 5 shows the sulfur variation as a function of time for slags containing conventional lime and slags containing marble waste. In general, the slags containing conventional lime (Figure 5A) reached the final sulfur content faster than the slags containing marble waste (Figure 5B), since these slags presented higher content of MgO, which increases the percent of solid phase. It was also noted that the slags containing fluorspar (CAF11 and RMF12) reached the lesser content of sulfur (0.01%) faster than the other slags (30 and 40 minutes, respectively). The presence of fluorspar decreases the slag melting temperature and increases the liquid phase percent, which increases metal/slag interface[15].

Table 5 shows the liquid and solid phases obtained via Thermo-Calc® software from synthetics slags compositions. The thermodynamics software also indicates the composition of the solid phases formed during desulphurization process and sulfur content at equilibrium in the bath.

It was noted a linear relationship between the liquid phase and desulfurization yield, as it can be seem in Figure 6A and Figure 6B. The equations obtained were used as parameter to describe the behavior of slags CA1-CA5 (Figure 6A) and marble waste (Figure 6B) to desulfurization of cast iron by top slag.

The linear trend (R²) was 0.96 to the conventional lime-based slags (A) and 0.94 to the mixtures with addition of marble waste (B). In this case, increasing the liquid phase improves sulfur diffusion into the slag and the interface metal/slag is more effective, which favors the desulfurization[16].

Table 4. Equilibrium (wt%) obtained for Thermo-Calc® in cast iron and desulfurization yield (η(%)).

Mixture	[%S$_{eq.}$]	[%Si$_{eq.}$]	[%C$_{eq.}$]	[%Mn]	η(%)
CAF11	$5.17E^{-05}$	1.61	3.19	0.53	90.10
CA3	$2.21E^{-04}$	1.59	3.18	0.53	89.81
RMF12	$5.75E^{-05}$	1.62	3.19	0.55	87.25
RM8	$3.95E^{-04}$	1.56	3.18	0.53	87.03
CA4	$1.74E^{-04}$	1.53	3.18	0.53	86.56
RM7	$1.36E^{-04}$	1.56	3.19	0.53	85.63
RM9	$3.46E^{-04}$	1.54	3.18	0.54	85.33
CA2	$6.30E^{-05}$	1.54	3.19	0.53	84.64
RM6	$1.49E^{-04}$	1.53	3.19	0.53	83.93
CA1	$6.41E^{-05}$	1.51	3.19	0.53	82.52
CA5	$6.30E^{-05}$	1.54	3.19	0.53	79.76
RM10	$6.26E^{-05}$	1.53	3.20	0.54	79.63
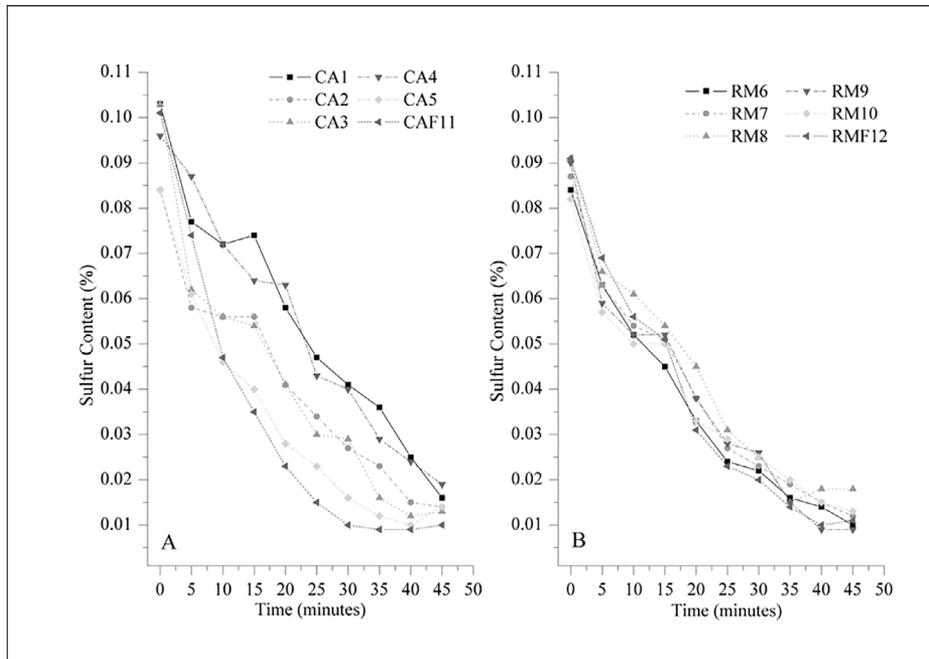
Figure 5. A- Sulfur variation as a function of time in the experiments with conventional lime. B- Sulfur variation as a function of time in the experiments with marble waste.

Table 5. Equilibrium calculations from initial mixtures of cast iron via Thermo-Calc®.

Mixtures	Liquid Phase (wt %)	Mass of the Liquid Phase (g)	Solid Phase (wt %)	Phases formed in the Solid Phase (wt %)		$[S_{eq}]_{liq}$	η(%)
				CaO	MgO		
CAF11	88.02	36.97	11.98	11.97	0	0.00057	90.10
CA3	82.74	34.75	17.26	17.26	0	0.00149	89.81
RMF12	82.39	29.99	17.61	4.14	13.47	0.00102	87.25
RM8	73.26	26.67	26.74	13.7	13.04	0.00354	87.03
CA4	75.18	31.58	24.82	24.82	0	0.00065	86.56
RM7	63.00	24.89	37.00	22.15	14.84	0.00433	85.63
RM9	67.14	24.44	32.86	19.84	13.01	0.00484	85.33
CA2	70.45	29.59	29.55	29.55	0	0.00175	84.64
RM6	56.17	22.19	43.83	28.78	15.04	0.00554	83.93
CA1	62.97	26.45	37.03	37.03	0	0.00344	82.52
CA5	46.05	19.34	53.95	53.95	0	0.00465	79.76
RM10	43.39	19.74	56.61	38.36	18.25	0.00751	79.63

Figure 7 indicates that increasing the CaO content in the liquid phase increases the desulfurization yield. For synthetic slag prepared with conventional lime was noted a linear trend (0.95) between the liquid phase and desulfurization yield. On the other hand, for slags prepared with marble waste, the linear trend was 0.659, indicating that MgO can decrease the desulfurization process.

Figure 8 shows the effect of MgO on the desulfurization reaction of the cast iron.

It can be noted in the figure 8 that increasing the MgO content in slags with marble waste decreased the desulfurization efficience from 87,25% to 79,25%. According to chemical analysis of marble waste, it was noted a higher content of MgO (14.56wt%), which can influences the percente of liquid phase in the bath, and consequently, the desulfurization efficience. Thus, figure 9 shows the influence of MgO content on the percente of liquide phase to the slags.

Increasing the content of solid MgO in the slags decreased the liquid phase, since the MgO increases the melt point of the slag. Despite the fact that carbonate decomposition content no marble waste (Table 3) improved the desulfurization by playing an important role on the sulfur transfer mechanism
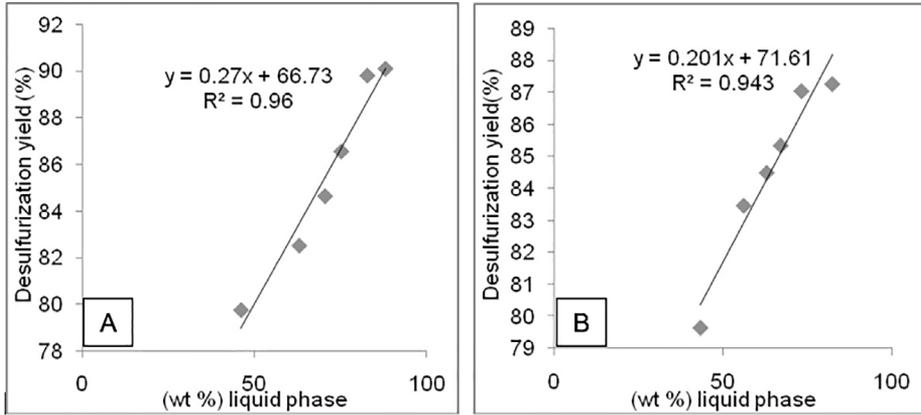
Figure 6. Relationship between liquid phase and desulfurization yield to the slags based in CaO-Al$_2$O$_3$ (A) and marble waste (B).
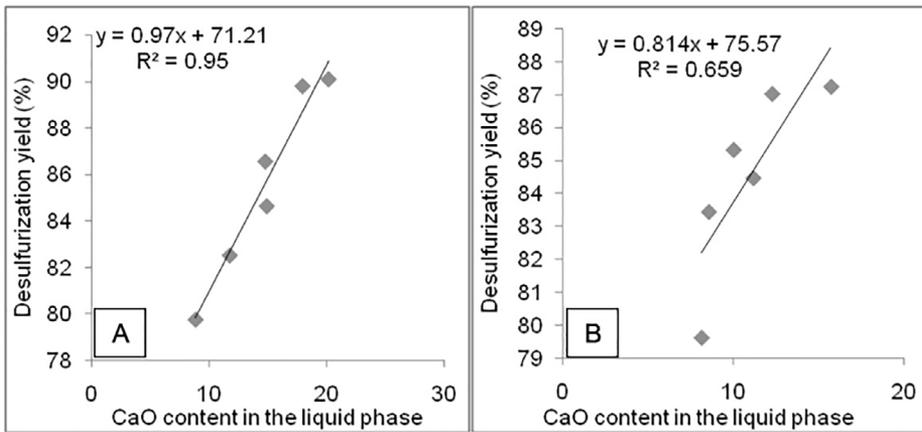
Figure 7. Relation between CaO content in the liquid phase and desulfurization yield of the slags based on conventional lime (A) and marble residue (B).
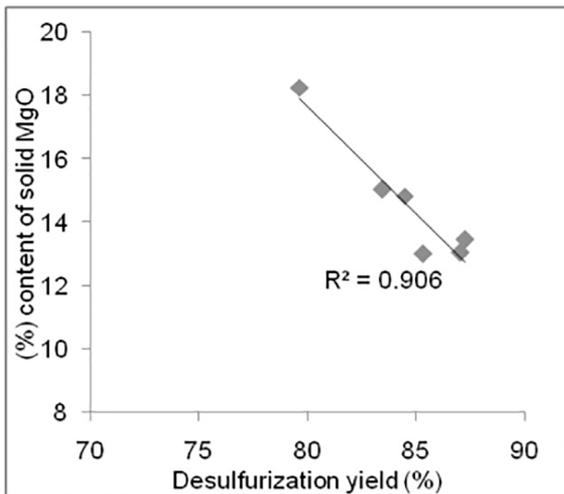
Figure 8. Relation between MgO content and desulfurization yield.
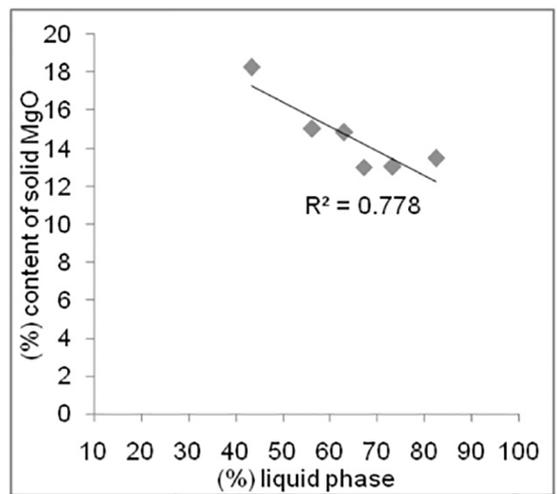
Figure 9. Graphics showing the MgO as a function of liquid phase and the desulfurization yield for all marble waste containing slags.

to the interface hot metal-slag, the presence of solid MgO acts by retarding the process.

Based on these results, the application of marble waste together with conventional lime or even substituting dolomite can be an alternative to reduce the negative effect of MgO during the desulfurization.

3.3. Tests to compare the substitution of fluorspar for Al_2O_3

The tests to compare the substitution of fluorspar for Al_2O_3 with slags containing marble waste and conventional lime indicates that the synthetic slag CAF11 presented a desulphurization yield of 90.1%, while the synthetic slag CA3 presented a desulphurization yield of 89.81%. In this way, the substitution of fluorspar for Al_2O_3 might be viable. The slags containing marble waste (RMF12 and RM8) showed desulfurization yield of 87.0%. This result suggests the marble waste as an alternative substitute to the conventional lime, since the yield is close to that yield obtained for slags with conventional lime.

3.4. Effect of particle size

Figure 10 shows the influence of particle size in the desulphurization process.

It can be noted in figure 10 that the desulfurization process more favored to particle size of 500-1000 μm. It may be contradictory, since decreasing the particle size increases the surface area. This fact can the explained by agglomeration phenomenon observed during the experiments (Figure 11).

It was observed that slags with particle size of 20μm and 100μm sintered in contact with the liquid metal, forming agglomerated particles. Slags contained particle size in the range of 0.5-1.0mm did not form agglomerated particles. This result was similar to that found by McFeaters and Fruehan[17].
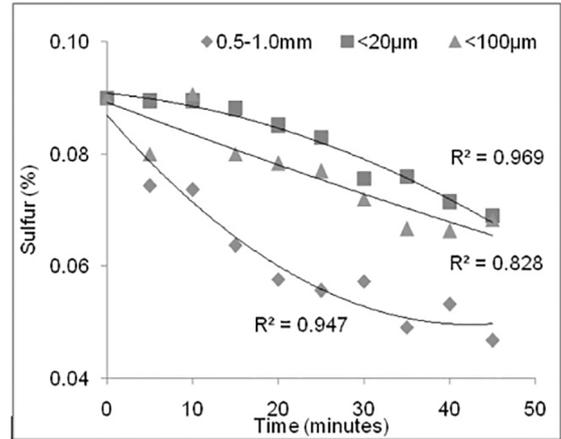
Figure 10. Content of sulfur as a function of time.

4. Conclusions

The mixtures with addition of marble waste that obtained the best desulfurization yield were RMF15 and RM8 (87.25% and 87.03%). The best results obtained from conventional lime were CAF11 and CA3 (90.10% and 89.81%). The computational thermodynamic analysis showed that the MgO present in the marble waste decreased the liquid phase fraction in the slag, once increasing liquid phase favored both sulfur mass transport into the slag and in the metal/slag interface, raising the mixtures desulfurization yield. The computational thermodynamic analysis also showed lower sulfur equilibrium for the mixtures CAF11, RMF12, CA5 and RM10, since the fluorspar increased the liquid phase fraction in the slag. Increasing the CaO particle diameter improved the desulfurization process. Particle with diameter in range of 20 to 100μm were sintered after addition on the liquid metal, decreasing the desulfurization. The substitution of fluorspar for CaO-Al_2O_3 system slags is viable. Thus, depending on the sulfur content to be reached,
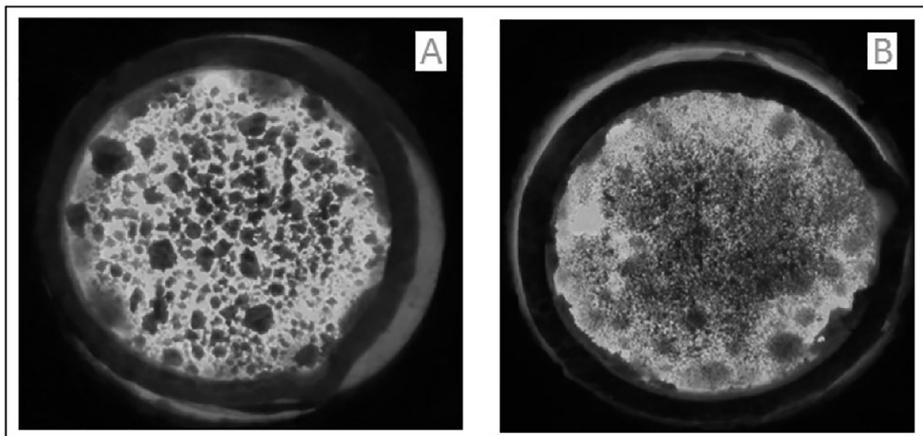
Figure 11. Image obtained after 5 minutes of desulphurization tests with lime: (A) <100 ; (B) range of 0.5 - 1.0mm.

marble waste may be a viable economic and environmental alternative to replace lime.

5. References

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