EVALUATION OF CAST IRON DESULFURIZATION WITH SYNTHETIC SLAGS*

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Abstract

The aim of this work was to study the use of slags to desulfurization of cast iron. It was proposed to use alumina instead fluorspar. In addition, marble waste was used instead lime. Simulations applying Thermo-Calc software were performed in order to obtain the theoretical phases thermodynamic data. Then, a comparison between theoretical data and experimental tests were performed. The cast iron was melting in induction furnace at 1550°C. Slags composed mainly for CaO and Al_2O_3 were used to cast iron desulphurization. It was observed that increasing liquid phase, the desulphurization reaction was favored. Besides, it was found that cast iron desulfurization occurs by top slag mechanism.

Keywords: Desulfurization; Fluorspar; Marble waste; Cast iron.

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1 INTRODUCTION

According to Roskill, the China produced around 75% of primary magnesium in the world in 2012. The sum of Russia and USA production was about 16%. Other important countries are Israel, Kazakhstan, Brazil, Serbia and Ukraine(1).

One of the most important process involving cast iron and steel production is desulfurization. Desulfurization of cast iron is practiced in manufacture of ductile iron castings in order to obtain spherical graphite morphology. Ductile iron is used in applications where high fracture toughness is required. Several reagents are employed to remove sulfur, such as: calcium, magnesium and sodium(2). The desulfurization cast iron using magnesium powder wire is related to high operating cost(3).

The goal of this paper is to substitute metallic magnesium for calcium oxide or marble waste as desulfurization agent.

2 MATERIALS AND PROCEDURE

2.1 Composition of the synthetic slags

Table 1 shows the composition of the slags used in the experiments

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

Mixtures	Composition (wt %)						Mass (grams)			
	Al_2O_3	CaO	MgO	SiO_2	Na_2O	CaF_2	CaO	Al_2O_3	Total	Calcined waste
CICA1	20.0	65.0	0.00	0.00	15.0	0.00	27.3	8.4	42	0
CICA2	25.0	65.0	0.00	0.00	10.0	0.00	27.3	10.5	42	0
CICA3	30.0	60.0	0.00	0.00	10.0	0.00	25.2	12.6	42	0
CICA4	25.0	60.0	0.00	0.00	15.0	0.00	25.2	10.5	42	0
CICA5	15.0	75.0	0.00	0.00	10.0	0.00	31.5	6.3	42	0
CIRM6	15.49	50.47	18.21	4.21	11.62	0.00	27.3	8.4	83.2	39.5
CIRM7	19.37	50.47	18.21	4.21	7.74	0.00	27.2	10.5	83.2	39.5
CIRM8	23.54	47.46	17.13	3.96	7.91	0.00	25.2	12.6	80.0	36.5
CIRM9	19.74	47.38	17.08	3.96	11.84	0.00	25.2	10.5	80.0	36.5
CIRM10	11.25	56.26	20.29	4.69	7.50	0.00	31.5	6.3	89.4	45.6
CICAF11	30.0	60.0	0.00	0.00	0.00	10.0	25.2	12.6	42	0
CIRMF12	23.68	47.37	17.08	3.95	0.00	7.89	25.2	12.6	80.0	36.5

The mixtures from 1 to 5 (ending with CA) were formulated in conventional lime-based and Al_2O_3. The mixtures from 6 to 10 (ending with RM) have been made in order to replace the conventional lime for carbonate contained in marble waste. The same CaO/Al_2O_3 ratio was maintained in all of those mixtures. 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. It was used 30kg of slag per ton of cast iron.

The experiments were also carried out to evaluate the lime particle size influence on desulfurization process. Table 2 shows the lime particle size used on desulphurization essays. Table 3 shows the initial composition of the cast iron used in the tests.

Table 2. Lime particle size used for cast iron desulfurization.

Experiment	Particle size
CaO-1	0.5-1.0mm
CaO-2	100 μm
CaO-3	20 μm

Table 3. Initial composition of the cast iron.

Mixtures	Chemical composition (wt %)				Mass (kg)
	C	Si	P	S	
CICA1	3.26	1.64	0.054	0.103	1.4
CICA2	3.18	1.64	0.054	0.084	
CICA3	3.20	1.61	0.050	0.090	
CICA4	3.28	1.68	0.056	0.103	
CICA5	3.22	1.68	0.056	0.096	
CIRM6	3.20	1.72	0.057	0.084	
CIRM7	3.16	1.72	0.053	0.084	
CIRM8	3.24	1.69	0.052	0.082	
CIRM9	3.32	1.73	0.057	0.087	
CIRM10	3.37	1.7	0.064	0.091	
CICAF11	3.25	1.71	0.064	0.101	
CIRMF12	3.28	1.73	0.059	0.091	

2.2 Experimental apparatus used and experimental procedures

The experiments were performed in the Metallurgical Technology laboratory of Duisburg-Essen University. Figure 1 shows the experimental apparatus used.

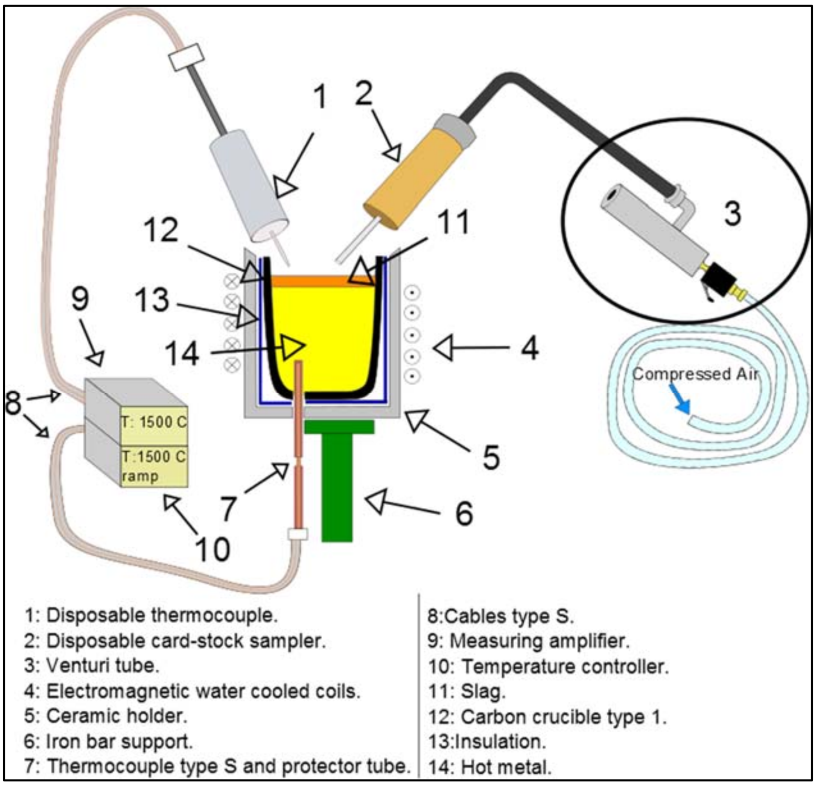

Figure 1. Apparatus used in desulphurization experiments(4).

A mass of 1.4kg of cast iron was placed into a carbon crucible. This crucible was enveloped with a carbon ceramic blanket to avoid heat losses and, then, inserted in an alumina crucible. Agitation was promoted by the induction furnace. After reaches 1550°C, it was collected a sample to perform the metal chemical analysis. Samples were obtained each 5 minutes. The full experimental time was set up in 45 minutes. The slag was added in 3 times (0, 15 and 30 minutes). After the end of the experiments, the samples were analyzed for mass optic spectrometry. Thermocalc® software was used in order to compare the theoretical equilibrium contents and both liquid and solid fractions with the values obtained in experimental tests. The database used in the software was the "SLAG3".

3 RESULTS AND DISCUSSION

Figure 2 shows the sulfur variation versus time for: (A) – slags containing conventional lime; (B) – slags containing marble waste. Table 4 shows the equilibrium contents in the cast iron after thermodynamics calculations via Thermo-Calc® and the desulfurization yield η(%).

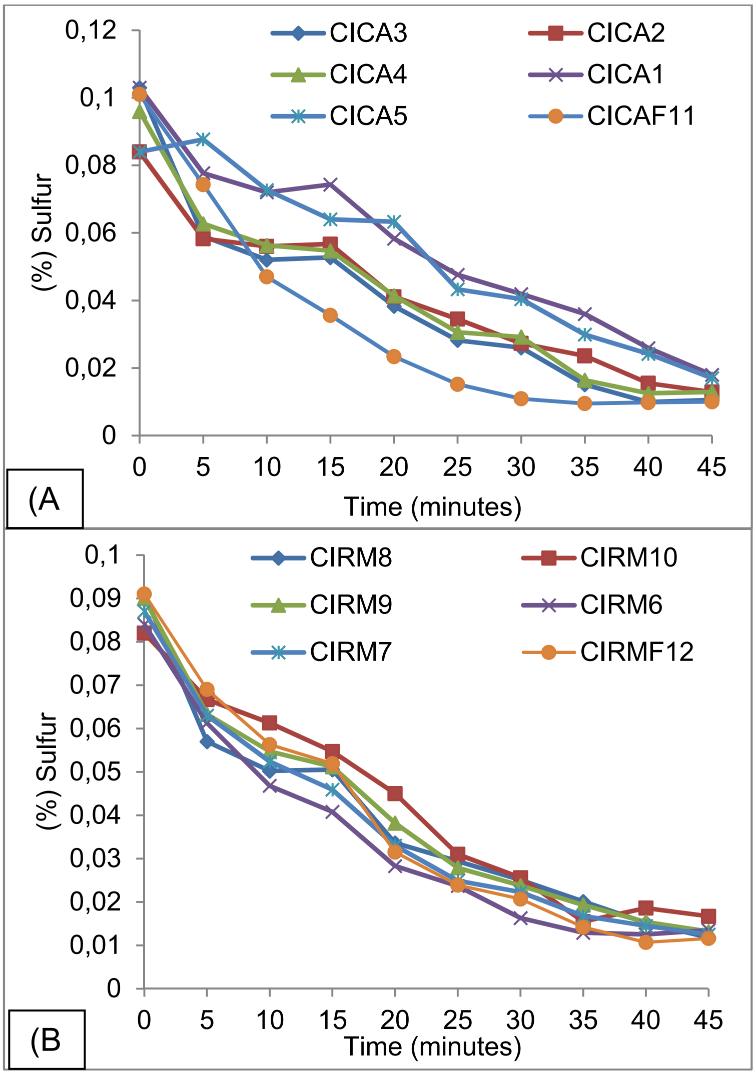

Figure 2. Sulfur variation versus time (A - conventional lime; B - marble waste).

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

Mistura	[%$S_{eq.}$]	[%$Si_{eq.}$]	[%$C_{eq.}$]	[%Mn]	η(%)
CICAF11	5.17E-05	1.61	3.19	0.53	90.10
CICA3	2.21E-04	1.59	3.18	0.53	89.81
CIRMF12	5.75E-05	1.62	3.19	0.55	87.25
CIRM8	3.95E-04	1.56	3.18	0.53	87.03
CICA4	1.74E-04	1.53	3.18	0.53	86.56
CIRM7	1.36E-04	1.56	3.19	0.53	85.63
CIRM9	3.46E-04	1.54	3.18	0.54	85.33
CICA2	6.30E-05	1.54	3.19	0.53	84.64
CIRM6	1.49E-04	1.53	3.19	0.53	83.93
CICA1	6.41E-05	1.51	3.19	0.53	82.52
CICA5	6.30E-05	1.54	3.19	0.53	79.76
CIRM10	6.26E-05	1.53	3.20	0.54	79.63

The experiments CIRM6 and CIRM7, which used marble waste were better desulfurizer (83.93% and 85.63%, respectively) when compared with experiments using conventional lime CICA1 and CICA2 (desulfurization yield of 82.52% and 84.64%, respectively). In the experiments CICA3, CICA4 and CICA5, conventional lime showed better results than the experiments with marble waste addition (CIRM8, CIRM9 and CIRM10).

The mixtures with lower equilibrium sulfur values were those with CaF_2 in the composition (CICAF11 and CIRMF12). Then, the mixtures contained higher percentages of CaO in the compositions (CICA5 and CIRM10). The higher thermodynamic potential to desulfurization do not mean higher desulfurization yield, since kinetic factors should be considered(5,6). Table 5 shows both liquid and solid phases contained in the initial mixtures, phases formed in the solid and the equilibrium sulfur content when only the liquid phase is considered in the desulfurization [S_{eq}]$_{liq}$.

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

Mixtures	Liquid Phase (wt %)	Mass of the Liquid Phase (grams)	Solid Phase (wt %)	Phases formed in the Solid Phase (wt %)		[S_{eq}]$_{liq}$	η(%)
				CaO	MgO		
CICAF11	88.02	36.97	11.98	11.97	0	0.00057	90.10
CICA3	82.74	34.75	17.26	17.26	0	0.00149	89.81
CIRMF12	82.39	29.99	17.61	4.14	13.47	0.00102	87.25
CIRM8	73.26	26.67	26.74	13.7	13.04	0.00354	87.03
CICA4	75.18	31.58	24.82	24.82	0	0.00065	86.56
CIRM7	63.00	24.89	37.00	22.15	14.84	0.00433	85.63
CIRM9	67.14	24.44	32.86	19.84	13.01	0.00484	85.33
CICA2	70.45	29.59	29.55	29.55	0	0.00175	84.64
CIRM6	56.17	22.19	43.83	28.78	15.04	0.00554	83.93
CICA1	62.97	26.45	37.03	37.03	0	0.00344	82.52
CICA5	46.05	19.34	53.95	53.95	0	0.00465	79.76
CIRM10	43.39	19.74	56.61	38.36	18.25	0.00751	79.63

It was noted a linear relationship between the liquid phase and desulfurization yield, as it can be seem in figure 3. The equations obtained were used as parameter to describe the behavior of slags based in CaO-Al_2O_3 and marble waste to desulfurization of cast iron by top slag.

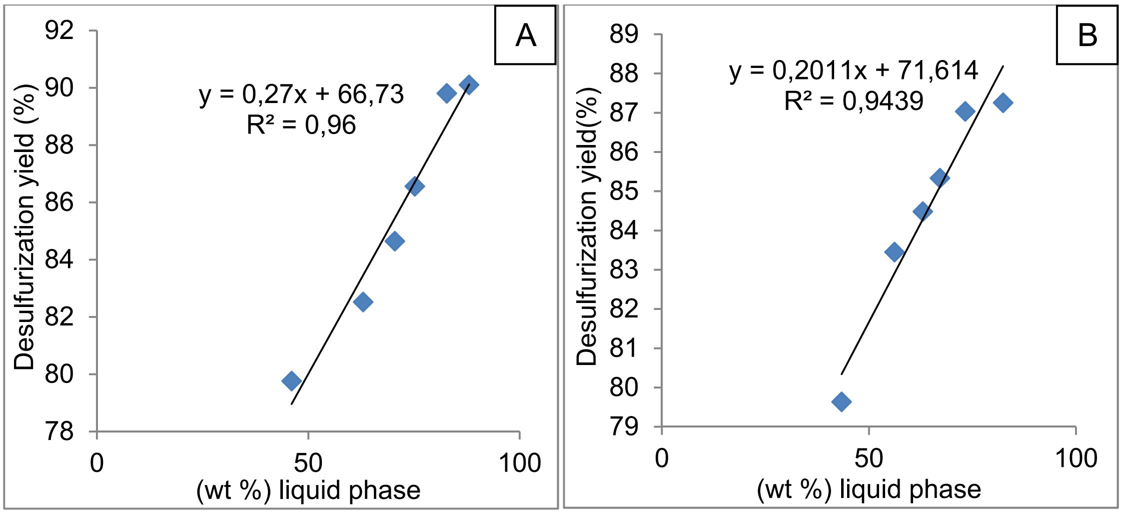

Figure 3. Relationship between liquid phase and desulfurization yield.

The linear correlation coefficient (R^2) was 0.96 to the conventional lime-based slags (Figure 3A) and 0.94 to the mixtures with addition of marble waste (Figure 3B). In this case, increasing the liquid phase, the mass transport of sulfur into the slag and in the interface metal/slag is more effective, favoring the desulfurization(7). Increasing the liquid phase increase the free CaO content to react. Figure 4 shows the relation between the CaO content in liquid phase against the desulfurization yield.

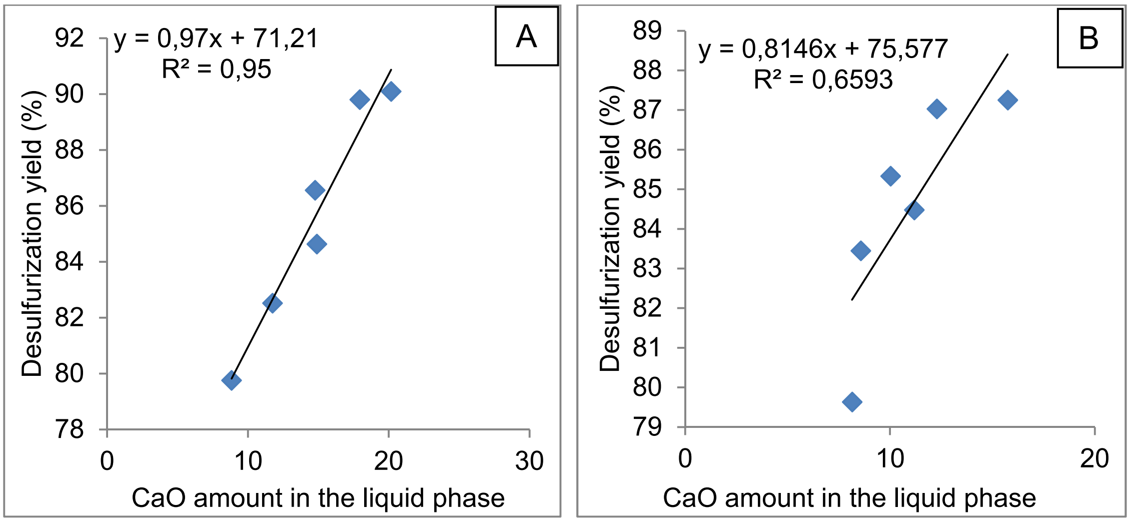

Figure 4. Relation between CaO amount in the liquid phase and desulfurization yield of the slags based on conventional lime (A) and marble residue (B).

For the mixtures prepared with conventional lime, the results show that the amount of CaO in the liquid phase has correlation with the desulfurization yield ($R^2=0.95$). On the other hand, for the mixtures carried out with marble waste, it wasn't observed the same linear behavior. Thereby, it was assumed that concentration of solid MgO in the marble waste may interfere negatively in the desulfurization. From Table 5, it can be noted that increasing the solid MgO decreasing both liquid phase and efficiency. Even the carbonates decomposition has favored the desulfurization, the solid MgO decreases the process.

In order to compare the substitution of fluorspar for Al_2O_3, slags containing marble waste and conventional lime with the same CaO mass were studied. Comparing the desulfurization yield obtained by slags containing conventional lime (CICAF11 and

CICA3), it was noted values of 90.1% and 89.81%, respectively. In this way, the substitution of fluorspar for Al_2O_3 might be viable. The slags with marble waste (CIRMF12 and CIRM8) showed desulfurization yield of 87.0%. This result places the marble waste as an alternative substitute to the conventional lime, since the efficiency is close to that efficiency obtained for slags with conventional lime.
Figure 5 shows the influence of particle size in the process.

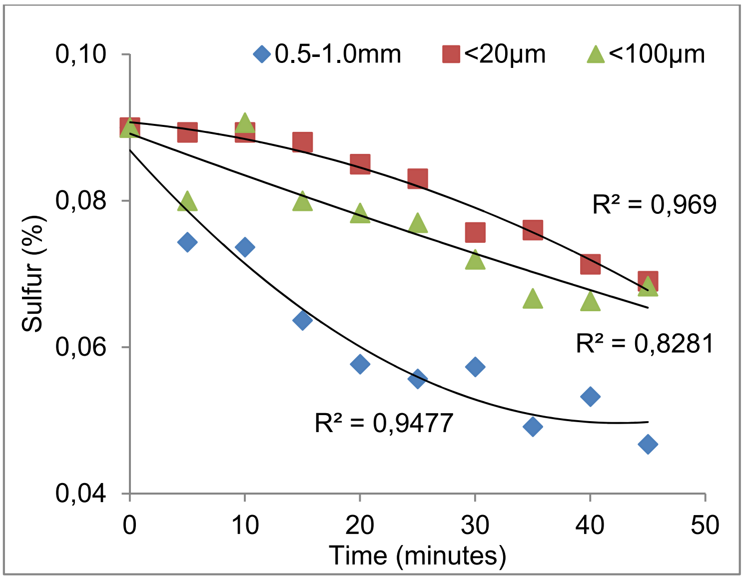

Figure 5. Amount of sulfur versus time.

It can be noted in figure 5 that increasing the CaO particle size favors the desulfurization process. It may be contradictory, since decreasing the particle size increase the surface area. However, it was observed that slags with particle size of 20µm and 100µm were sintered after addition on the metal. This result was similar to that found for McFEATERS and FRUEHAN(8). Figure 6 shows agglomeration phenomenon observed during the experiments.

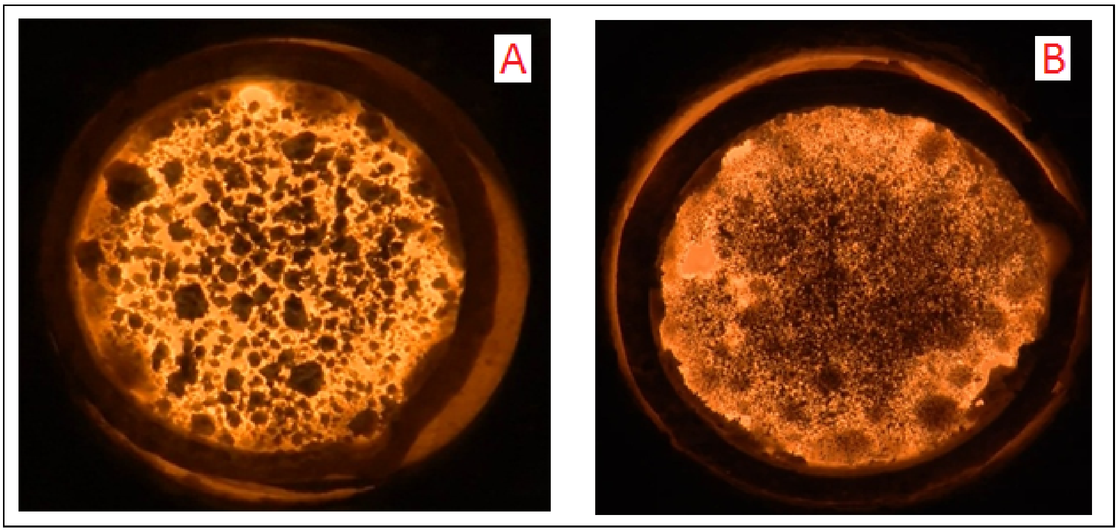

Figure 6. Picture taken at 5 minutes of analysis with lime: (A) <100 presenting particle agglomeration; (B) between 0.5 – 1.0mm, showing that the process of agglomeration doesn’t occur.

4 CONCLUSION

The mixtures with addition of marble waste that obtained the best desulfurization yield were: CIRMF15 e CIRM8 (87.25% and 87.03%). The best results obtained from conventional lime were: CICAF11 and CICA3 (90.10% and 89.81%). The computational thermodynamic analysis showed lower sulfur equilibrium to the mixtures CICAF11, CIRMF12, CICA5 and CIRM10. The MgO concentration in slags containing marble waste interfered negatively in the desulfurization yield, decreasing both liquid phase fraction and efficiency. Increasing the liquid phase favored both sulfur mass transport into the slag and in the metal/slag interface, raising the mixtures desulfurization yield. Increasing the CaO particle diameter improved the desulfurization process. Particle with diameter in range of 20 to 100µm were sintered after addition on the metal, harming the desulfurization. The substitution of fluorspar for CaO-Al2O3 system slags is a viable alternative as well the substitution of conventional lime for marble waste.

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