

Evaluation of recycled MgO-C bricks and dead-burned dolomite fines in setting slag foaming in the electric arc furnace

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Abstract

Production cost reduction for the Electric Arc Furnace (EAF) technology is strongly dependent on the efficiency of the electrical energy being introduced into the metal bath. Besides EAF technology, the slag foaming process is currently applied to some other equipment for steel production aiming to save energy, productivity improvements, enhance the refractory service life and inhibit steel re-oxidation. In this way, this study involved the recycling options of Crushed MgO-C spent refractories removed from the EAF without complex and costly beneficiation, with emphasis on its application as a slag conditioner, since its composition presents high MgO content. The experiments were performed in a laboratory induction furnace and the temperature was controlled at 1700°C. The initial height of the slag was recorded and foaming briquettes added into the furnace. The experiments were carried out for 30 minutes. When the foaming process was finalized, an aliquot from the slag was collected to be analyzed by chemical analysis. Then, the metal with slag was tapped into a mold. The results indicated that the best viscosity was 0.39poise. The maximum height of foam formation was observed for a binary basicity greater than 1.2. The concentration of MgO in the slag is close to the saturation point.

Keywords: electric arc furnace (EAF), slag foaming, refractory recycling, slag conditioning.

1. Introduction

The worldwide increase of steelmaking by electric arc furnaces (EAF) has impacted directly on steel production (World Steel Association, 2011). This increase has led the steel sector to search and develop a new production pattern with higher ef-

iciency at lower costs.

In this scenario, the production of steel with an electric arc furnace (EAF) process has undergone a variety of modifications in order to cope with the current market demands. According to NAKA-

HARA (1997), among these changes, the increase of the useful life of refractory materials, reduction of material costs and the increase of operational safety in the production processes are mentioned.

The refractory consumption is

directly related to the steel production. However, this relationship between the steel production and the specific refractory consumption (kg/ton steel) has been reduced by the use of new methodologies that permit an increase in the useful life of the refractory materials used in the production processes. In the last 30 years, the consumption of the refractory/steel production rate has been reduced from 20 to 10 kg/ton (NAKAHARA, 1997; FANG *et al.*, 1999; BOROVSKEJ *et al.*, 2009).

The EAF companies have interest in recycling their spent refractories, since the costs to dispose of the same are too high. This is also the case for the refractory industry, as the manufacturing process generates remaining material that needs to be disposed of. In both cases, the companies see this practice as part of its residual management, gaining a competitive advantage for business (BOROVSKY *et al.*, 2009; REICHEL *et al.*, 2008).

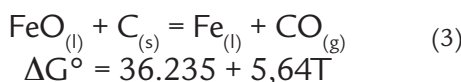
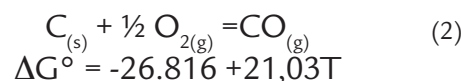
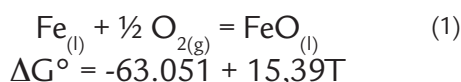
The process of recycling spent refractories has been carried out in many steel plants, as in the case of the MgO-C bricks from EAF's. This practice may be simple, but it has generally been developed on empirical grounds. Most of the applications of spent refractory material are limited due to quality, availability, consistency and transportation cost (BOROVSKY *et al.*, 2009). One application to reuse spent refractories can be as an EAF foamy slag additive to decrease the amount of fluxes and improve the foaming conditions (BENNET *et al.*, 1995; BENNET, 2000; GOODSON *et al.*, 1995; GONZALEZ, 2006).

The slag foaming process is currently applied in some equipment for steel production [i.e., electric arc furnace (EAF) and basic oxygen furnace (BOF)] aiming to save energy, improve productivity, enhance refractory service life and inhibit steel re-oxidation. In the case of EAF, the foamy slags shield the electrical arcs, preventing

radiation energy loss, eliminating arc flares, saving overall energy and extending refractory service life. Several studies showed (KWONG and BENNET, 2002; KWONG and THOMAS, 2009) that the foaming slag methodology can reduce 10-30% of the electrical consumption and 25-63% of the refractory consumption.

There are basically two requirements for foaming: (1) reactions or processes that generate small gas bubbles and, (2) suitable slag properties to keep the bubbles as stable foam (KWONG and THOMAS, 2009).

The foaming of the slag is accomplished by the direct injection of oxygen and carbon into the electric furnace baths. After that, the carbon reacts with FeO from the slag, generating CO_(g), which is mainly responsible for the foaming effect (KWONG and BENNET, 2002), generating gas bubbles that enable FeO generation in the liquid. This sequence can be seen in Equation 1, 2 and 3.



Equation (1) shows the reaction between gaseous oxygen and iron in the bath, while Equation (2) represents the reaction of the carbon injected with oxygen. Such an equation also represents the reaction of the oxygen with the carbon injected directly into the bath. Equation (3) represents the reduction of FeO by carbon in the slag.

The foaming slag has been investigated in EAFs and basic oxygen furnaces (SEDIVY and KRUMP, 2008; MORALES 1993; JIANG and FRUEHAN, 1991; JUNG and FRUEHAN, 2000). However, the correct control and optimization of the

foam generation on the slag surface are limited, since factors such as basicity, FeO concentration, surface tension, viscosity and how the suspended second phase particles in the liquid act directly in the slag foaming behavior, should be understood (PRETORIUS and CARLISLE, 1999).

Note that the factors responsible for the formation and maintenance of the foaming slag during the steel production are: the chemical composition of the slag, the process temperature, the injection and generation of gases, and also, the physical characteristics of the slag, such as its vis-

cosity and superficial tension. To reach an "optimum foaming slag" all these factors must be appropriately controlled or, in some cases, induced.

In this context, the aim of this study is to propose an improvement of the foaming slag process through the addition of a mixture of recycled refractory materials of MgO-C and dolomite sinter fines (CaO. MgO) during iron melting in the EAF, intending to reach the optimum saturation point of MgO in the slag, while inducing the formation and maintenance of a beneficial foaming slag to the process.

2. Materials and methods

2.1 Materials Characterization

The raw materials used for the formulation of mixtures of foaming briquette were the MgO-C spent refractories and dead-burned dolomite

(DBD) fines.

The raw materials were characterized by chemical analysis through energy dispersive X-ray fluorescence

spectroscopy "Philips MagiX PRO PW 2540". Table 1 shows the chemical composition of new and spent MgO-C refractories from an EAF.

	%MgO	%CaO	%SiO ₂	%Al ₂ O ₃	%FeO	%MnO	%C _{tot}
New	91.41	1.65	2.19	3.79	0.81	0.06	10.65
Spent	88.24	2.00	1.72	1.71	1.75	3.42	9.74

*C_{tot} means the total carbon

Table 1
Characterization of the new and spent MgO-C refractory.

The dead-burned dolomite (DBD) fines or dead-burned dolomite is generally used in the refractory industry for the refractory made by firing dolomite, with or without additives (Al, C and Si), at high temperature to produce dense, well-shrunk particles.

After DBD leaves the kiln, it is screened to remove the fines and under-sized particles (<8.0 mm) generated. This fine fraction is normally exposed to lower temperatures than the larger fraction, which results in material with moderate to low chemical reactivity (not fully calcined). Due

to these characteristics, this material cannot be used for the manufacture of refractory brick, creating disposal issues.

Table 2 shows the chemical composition of DBD fines from a rotary kiln process. The chemistry indicates that this material can also be applied as an MgO source.

Elements	MgO	CaO	SiO ₂	Al ₂ O ₃	FeO	C	LOI
DBD Fines	42.0	54.50	1.04	0.62	0.69	0.51	1.80

Table 2
Characterization of the DBD fines.

*LOI - Loss on ignition.

The laboratory experiment was defined in order to establish an adequate

chemical composition of the briquettes for effective foaming of carbon steel slags.

2.2 Briquette formulations

The briquettes were made by compression of the mixture by means of a press device. Six (6) formulations

were defined based on theoretical considerations and economical aspects. The briquettes were prepared in dimension

of 2.54cm and applied force of 2500psi. Table 3 shows the chemical compositions of the briquettes.

Components	B1	B2	B3	B4	B5	B6
CaO	5.70	10.01	13.57	18.25	21.46	25.78
MgO	71.68	69.20	65.70	61.79	58.98	55.75
SiO ₂	2.82	2.73	2.79	2.89	2.91	2.58
Al ₂ O ₃	1.55	1.30	1.36	1.39	1.25	1.33
Cr ₂ O ₃	0.17	0.14	0.11	0.11	0.08	0.07
Fe ₂ O ₃	17.99	16.48	16.37	15.47	15.21	14.39
MnO	0.09	0.14	0.10	0.10	0.11	0.10
Loss on Ignition at 400°C	8.76	8.05	7.17	6.57	6.14	6.33
Loss on Ignition at 1000°C	39.28	40.64	41.10	41.29	40.62	41.96

Table 3
Chemical compositions of briquettes added to each test (% wt).

The briquettes were made with a concentration of magnesium oxide of about 50%wt, via two types of raw material available with MgO: Recycled

MgO-C bricks and dead-burned dolomite fines. The metallurgical coke was added in a percentage of 41%wt. Table 4 shows the composition of the six foam briquettes in

relationship to the type of raw material: Recycled MgO-C bricks and dead-burned dolomite fines (M/D), metallurgical coke and hematite (iron scale).

Raw material	B1	B2	B3	B4	B5	B6
Recycled MgO-C bricks	45	41	36	32	27	23
dead-burned dolomite fines	5	9	14	18	23	27
Metallurgical coke	41	41	41	41	41	41
(iron scale)	9	9	9	9	9	9

Table 4
Foaming briquettes compositions to each test (% wt).

The percent of metallurgical coke and iron scale were constant in all mixtures.

The hematite (Fe₂O₃) was added to the briquette compositions to insure a briquette

density between 2-3g/cm³. In all formulations, carbon carriers (pet coke) were added.

2.3 Foaming Experiment

The experiment was performed in a laboratory induction furnace powered by a transformer 50 kVA rated power supplied by a voltage of 480V to investigate the influence of the briquettes on the height

and stability of the generated foams.

Figure 1 shows the sketch of the experimental tests. Ingots of steel (2 kg) (229x70x30 mm ± 1 mm) were put into a MgO-C crucible and sent to the furnace

Oxide	CaO	SiO ₂	Na ₂ O	F	K ₂ O	Al ₂ O ₃	FeO	MnO	MgO	P ₂ O ₅
(%wt)	28.9	15.1	0.05	4.1	0.12	2.51	43.2	4.95	5.08	0.06

After the complete melting of the load, the initial height of slag was measured with a steel wire of 1/2" inch. This step was accomplished by the slag adhesion length on a steel rod inserted in the crucible (as

shown in Figure 2). Then, 50g of briquettes with a chemical composition proposed as shown in Table 4 were added to the bath.

After addition of the briquettes, the height was measured again, as well as the

and heated at 1700°C in order to melt the iron load. The industrial slag (Table 5) was added to the liquid bath. A sample was removed in order to perform the chemical analysis of the metal and slag.

Table5

Chemical compositions of synthetic slag used in the experiments (% wt).

time of the foaming process, from the foaming initiation until the foam ceased. The experiments were carried out with a total duration time of 30 minutes, when the foaming process ceased (Figure 2).

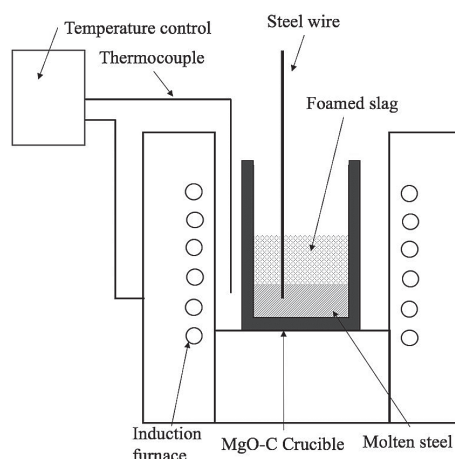


Figure 1 Sketch out of the experimental induction furnace and the apparatus to measure the slag foaming height.

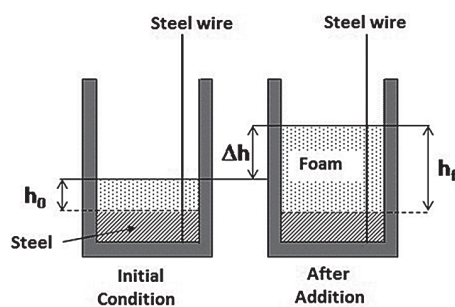


Figure 2 Schematic representation of the experiment performed for the measurement foam height (h).

The foam height slag (Δh) was calculated according Eq. 4.

$$\Delta h = h_f - h_0 \quad (4)$$

Where, h_0 is the initial foam slag (cm) and h_f is the foam height slag after briquette addition (cm).

2.4 Computational thermodynamic simulations

The Thermo-Calc software was used in order to determine the equilibrium data. The SLAG3 database was used in

this step. This software calculated Saturation MgO, liquid and solid phases. In addition, the melts database from FactSage

software was also used in order to determine final viscosity slags. The software calculates the liquid viscosity phase only.

3. Results and discussion

3.1 Slag height analysis

The experimental results of the slag foam ability translated into slag height for

the six different formulations are shown in Figure 3.

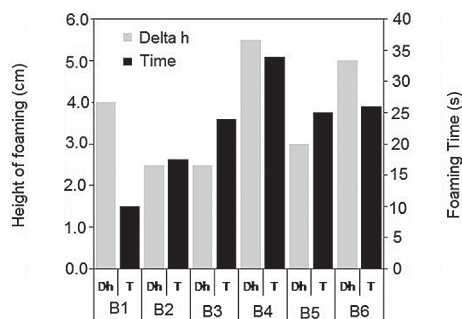


Figure 3 Differences of slag heights for the different formulations of foaming material.

The foaming behavior was different in each experimental condition. The results indicate that the highest foam ability was obtained in the B4 (5.5 cm) composition, while the lowest was observed in

formulations B2 and B3. For mixtures B4 and B6, the slag foaming began instantly when briquettes were added to the bath. In other cases (B1 and B2), the slag foaming occurred sometime after the

briquette addition. ITO and FRUEHAN (1989A, 1989B) studied slag foaming for CaO-SiO₂-FeO-MgO systems. They found foaming heights of 4-8cm in 10-15seconds for crucibles with diameters of 20-32cm.

3.2 Influence of the Slag Basicity

Table 6 shows the maximum slag height, binary and ternary basicity of the slags studied.

	Synthetic Slag	B1	B2	B3	B4	B5	B6
Binary Basicity	1.92	0.83	1.31	1.45	1.46	1.35	1.79
Ternary Basicity	1.64	0.69	1.08	1.21	1.22	1.02	1.41
slag height (cm)	-	4.0	2.55	2.5	5.5	3.0	5.0

Table 6 Slag height and final slag basicity for each formulation.

It is noted that the maximum height of foam was detected for a basicity greater than 1.2. This can be explained due to an increase of the CaO content in the slag, since a greater amount of DBD was used.

This fact increased the CaO content in the slag, which increased the surface tension and decreased the viscosity. The solid particles, such as 2CaO.SiO₂ precipitate at higher CaO, affecting foam stability.

Therefore, precipitation of the second-phase particles has a larger effect than an increase in the surface tension and a decrease in viscosity on foam stability for these slags (ITO and FRUEHAN, 1989B).

3.3 Influence of FeO

The relationship between FeO% content and the briquettes added into the bath can be seen in Figure 4.

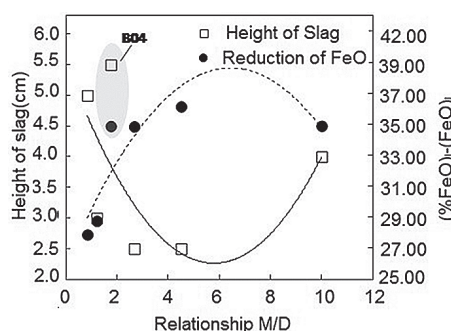


Figure 4 Relationship between the maximum slag height and the change in ((%FeO)initial synthetic slag - (%FeO) final slag) in the slag for each formulation, where M/D indicates the ratio between the amount of MgO-C spent refractory (M) and dead burned dolomite (D).

The largest reduction of FeO content in the slag was obtained for formulations containing a ratio between MgO-C spent refractory and DBD higher than 2.0. In addition, a decrease in the slag foaming was noted for a ratio between the MgO-C spent refractory and Dead Burned Dolomite of less than 2.0. This is due to the increase of the carbon con-

tent in the briquette composition using recycled bricks.

According to Equations 1, 2 and 3, the reduction of FeO in the slag occurs due to the reaction with the carbon present in the briquette composition. Equation 3 yields gaseous CO as its product, which produces an increase in the slag foaming height. Therefore, the

maximum slag height allows to conclude that it is also the maximum gaseous CO generated. In addition, the FeO strongly influences the effective viscosity and consequently, the slag foaming properties (JUNG and FRUEHAN, 2000). Increasing the FeO content increases the slag fluidity, which results in a decrease in the foaming height.

3.4 Influence on the MgO Saturation Limit in the slag

The slag with the better proper-

ties for EAF operating temperature is

a slag saturated in MgO that contains

particles in suspension. Figure 5 shows the MgO-FeO relationship to the ternary basicity of slag. In this diagram, C_2S corresponds to calcium di-silicate and MW to magnesium wüstite. The shaded area represents the ideal region

to saturate the slag with MgO and a small concentration of undissolved particles to increase the slag's viscosity. Under the saturation line, the slags present low viscosities.

PRETORIUS and CARLISLE

(1999) developed new maps to represent the saturation limits of MgO for $CaO-SiO_2-FeO-MgO-Al_2O_3$ slags as a function of MgO and FeO content at constant basicity and temperature called Isothermal Saturation Diagrams (ISD).

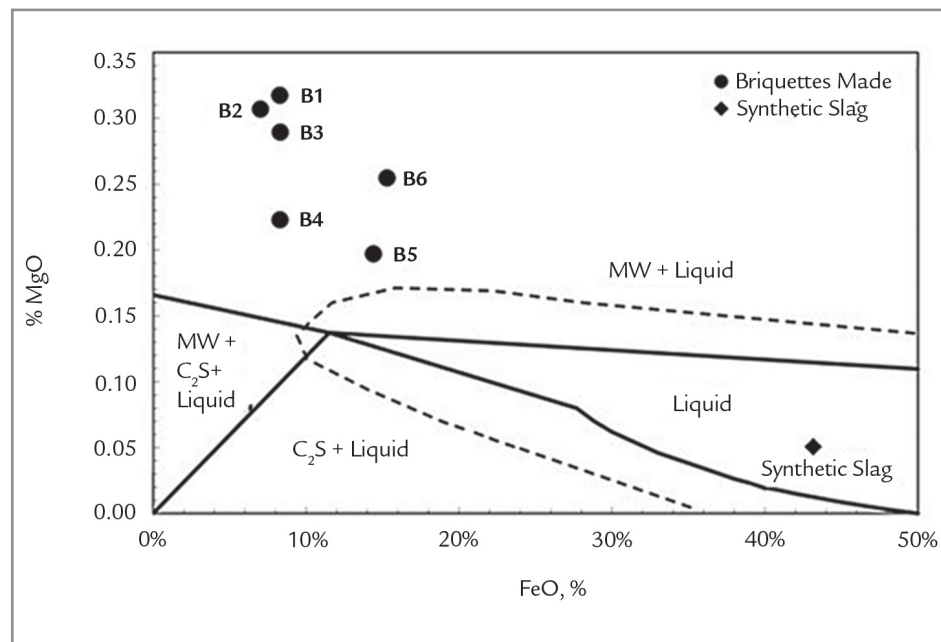


Figure 5 Relationship between the slag FeO% final levels of foaming (h) of the slag for the different formulations briquettes formers. MW = MgO.FeO. $C_2S = 2CaO.SiO_2$.

The diagram was carried out in the basicity range of 0.7-1.4 at 1700°C. The results indicate that formulations B4 and B5 are closer to the point D (dual saturation). Furthermore, the dotted lines

around the region of liquid slag suggest the best chemical composition for the slag foaming, where the foamy slag reaches its maximum. Furthermore, Figure 5 shows that the synthetic slag is localized

in the liquid phase area, which does not favor foaming. The addition of briquettes changed the liquid composition to form a second particle phase in suspension in the bath, which then favored slag foaming.

3.5 Computational thermodynamic analysis

Table 7 shows the chemical composition of the final slag after experiment of foaming slag.

Elements (%)	Synthetic Slag	B1	B2	B3	B4	B5	B6
CaO	28.89	20.45	28.97	30.47	33.37	28.31	29.55
MgO	5.08	31.78	30.73	28.97	22.31	19.73	25.49
SiO ₂	15.08	24.65	22.16	21.03	22.80	21.01	16.54
Al ₂ O ₃	2.51	5.08	4.55	4.22	4.51	6.76	4.36
FeO	43.15	8.25	7.00	8.29	8.26	14.38	15.27
MnO	4.95	9.21	5.74	6.31	8.00	9.11	7.82
TiO ₂	0.02	0.10	0.05	0.06	0.06	0.08	0.03
Cr ₂ O ₃	0.03	0.14	0.14	0.15	0.18	0.24	0.30
Na ₂ O	0.02	0.18	0.22	0.10	0.10	0.06	0.08
K ₂ O	0.12	0.06	0.07	0.02	0.06	0.07	0.02
P ₂ O ₅	0.10	0.03	0.12	0.09	0.16	0.15	0.28

Table 7 Chemical composition of slags after experiment foaming slag experiments.

The chemical compositions of Table 7 were used to calculate the equilibrium

between the liquid and solid phases contained in the final slag. The results can be seen in Table 8.

Slags	Liquid Phase (wt %)	Solid Phase (wt %) MgO	Viscosity* (poise)	(Δh cm)
B1	86.3%	13.6%	0.435	4.0
B2	84.1%	15.7%	0.417	2.5
B3	84.2%	15.6%	0.390	2.55
B4	91.7%	8.1%	0.392	5.5
B5	97.0%	2.6%	0.361	3.0
B6	84.7%	14.9%	0.314	5.0
Synthetic slag	99.1%	0.0%	0.191	-

Table 8
Equilibrium calculations from final slags.

*liquid phase.

The final slag equilibrium data showed that the highest height values (B4 and B6) were obtained which a percentage of liquid phase from 84.7 to 91.7 (wt %). In addition, the saturated MgO content in the scale should range from 8.1 to 14.9%. According to PRETORIUS and CARLISLE (1998), slags with better foaming results are obtained by the presence of a second suspended phase (Ca_2SiO_4 and/or

MgO), which is the factor with the greatest effect on slag viscosity.

It is observed that from the formulation B4 ($\Delta h_{B4} = 5.5$ cm), the calculated viscosity was 0.392 poise, this value being greater than that obtained in formulation B06, which in turn had a lower foaming level than formulation B06 ($\Delta h_{B6} = 5.0$ cm). At the same time, formulation B2 having a viscosity equal to 0.41 poise was found to

have a foaming level ($\Delta h_{B2} = 2.5$ cm) also lower than formulation B4. According to research (ZHANG and FRUEHAN, 1995; OGAWA *et al.*, 1993), this can be explained because for a slag with lower viscosity, the formed bubbles are easily eliminated and the foaming will be suppressed and even for a slag with higher viscosity, the bubbles will not be generated.

4. Conclusions

The results showed that the major component found in spent MgO-C refractories was MgO (88.24%wt). For the dead burned dolomite fines, 42%wt of MgO was found, illustrating that this material can also be applied as an MgO source. Formulations B1 and B6 had a high foaming level, 4.0 and 5.0cm respectively, but with lower foaming time, 10 and 26 seconds, respectively, when compared to

formulation B4. The maximum height of the foam was 5.5 cm with a basicity greater than 1.2. Formulations B1, B2 and B3, had the highest amount (above 35%) of recycled MgO-C bricks in the chemical composition of the briquettes increasing solid particles and the MgO saturation, contributing to raise the slag viscosity and negatively impacting the foaming level. With this data, it is possible to affirm

that the usage of recycled spent MgO-C refractories and dead burned dolomite fines as slag conditioners to saturate slags with MgO has a positive impact on the slag foaming behavior. And it is possible to apply these materials to control the performance of the foaming in an EAF operation, in order to reduce electrical energy consumption and to increase the reactor's refractory life.

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