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Chapter

Treatments and Recycling of Metallurgical Slags

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Abstract

Steelmaking plants continuously strive to reduce the environmental load in the steelmaking process, resulting in the recycling of energy, water, and other byproducts. In this chapter, techniques for the treatment and recycling of metallurgical slags are described. Metallurgical slags are considered secondary raw materials and are used or added during the process to improve steelmaking practice. Steelmaking slag added into ladle slags makes it possible to minimize slag line wear. BOF-converter slags are also applied in buildup, foaming, or slag splashing practices carried out to prolong the lifespan of refractory lining. Also, EAF slags are commonly used to avoid refractory wear and decrease energy consumption. It is known that cement concrete is one of the most common building materials. Blast furnace crystallized slags are used in cement production, in different percentages. In this sense, understanding the properties of slags is a prerequisite to apply them in different functions. This chapter deals with the measurement and modeling of thermochemical properties of slags, thermophysical properties, and interproperty correlations. Different experimental tests applied in slag characterization are also detailed.

Keywords: slag, recycling, steelmaking, refractory wear, slag properties

1. Introduction

In modern steel plants, the emphasis is placed simultaneously on quantity and quality. Energy consumption per ton of steel production is often considered a benchmark of operational efficiency. Steel production necessarily involves production of millions of tons of slag as well as waste gases containing harmful constituents such as carbon dioxide, dioxin, and furans. Safe disposal of slag and elimination of atmospheric pollution by waste gases are now a matter of serious concern in all steel producing countries. Developed countries are now laying tremendous emphasis on: (a) reduction in energy consumption per ton of steel produced and (b) sustainable environmental management. The most recent thrust is on more integrated green manufacturing and more intensive waste recycling for sustainable development. Efforts are on for economic use of all types of steel plant wastes, such as slag, dust, and flue gases [1]. Slag in ironmaking and steelmaking processes has several metallurgical functions such as preventing contamination by atmosphere, providing thermal insulation, and removing impurities in the liquid metal. Slag as a mixture of oxide has specific properties of melting behavior, viscosity, and surface tension, among others [2]. Optimal slag properties require: low thermal conductivity for

better thermal insulation, low diffusion coefficients to inhibit unwanted pickup from the atmosphere, and high absorption capacity for nonmetallic inclusion removal. Physicochemical properties of slag and molten metal directly affect the surface and interfacial properties in refining process of molten metal [2].

Slag is of great relevance in metallurgy processes for steel quality; however, during long years, it was considered an important waste together with the accumulation of refractories after use. This forces us to look for alternative uses to minimize the impact on the environment. A new concept considers to use the waste of one industry as a resource in another industry. One of the main applications that can be given to the slag is as recycled aggregate in the formulation of concrete or abrasive material applications. Nowadays, it is possible to consider the slag as a possible raw material for ceramics, road buildup, or cement production. The mentioned uses include an exhaustive control of the content of Ba, Cd, Cr, Mo, Ni, Pb, V, and Zn, in order to avoid contamination or air pollution. The content of sulfates or sulfides is also controlled to avoid the SO_2 emissions. To avoid volumetric instability of the cement material, MgO content is determined.

The addition of blast furnace slag into cement avoids a part of limestone and coal extraction and makes it possible to diminish the CO_2 emissions that cause environment pollution. It is important to have in mind that blast furnace slags present particular hydraulic properties. They are produced at high temperatures, and under fast-cooling rates, the structure obtained is amorphous. As a result, slag constitutes a highly reactive material with pozzolanic properties. On the contrary, at low-cooling rate, a crystalline structure with a considerable hardness is produced. In this case, slag constitutes a good raw material for cement production and also contributes with Fe addition to the clinker. A great part of the steel produced in the world is obtained through electric arc furnace (EAF), the process involves the use of scrap metal and reduces the CO_2 emissions. EAF slags present great possibilities of recycling, similar to those of BOF slags.

Slags recycling in cement production, road buildup, or other applications (that involve soil contact) are subjected to important environmental requirements. The material must not present reactions or composition changes greater than 1% in a period of 100 years.

One of the biggest challenges for metallurgists is to recycle the slag directly in the steelmaking processes. The operation temperatures and aggressive conditions promote a rapid wear of the refractories of BOF converters and EAF furnaces. Modern LD converters are lined with MgO-C refractories. The presence of carbon controls slag penetration and chemical attack. The capacity of graphite to reduce wear is based upon its large wetting angle for oxide melts. Slags can penetrate the bricks only when the graphite is burnt away near the hot face owing to diffusion of oxygen in between flows during a campaign [1].

In BOF converters, different operation practices using slags as protection media are used to prolong the lifespan of lining refractory:

- Slag coating or buildup, which protects the bottom part of the converter

- Slag foaming, which protects the refractories below the trunnion line

- Slag splashing, which protects the bottom, the middle, and the upper parts of the refractory lining.

In the three cases, the slags require good physical properties (viscosity and surface tension) to achieve good protection results and an adequate slag adherence to MgO-C bricks. In the slag splashing technology, a portion of slag is retained in the

vessel after tapping. Slag with low FeO and high MgO is desirable. The practice is carried out with nitrogen injection through a lance at different heights. In this case, some plants require special equipment installation.

Slag foaming is also applied in EAF to prevent the heat loss and to decrease the refractory wear. To improve the performance of these industrial practices and their applications, it is necessary to deeply understand the fundamental phenomena so as to determine slag's characteristics and physical properties required at process conditions.

Another type of slag that is produced in considerable quantity (ton/year) by the steelmaking industry is ladle slag. Because ladle slag is a premelted flux, when it is recycled in the steelmaking process, it is easy to be remelted. This type of slag has good physical properties, high inclusion absorptivity, and high sulfide capacity. Choi et al. [3] described two possible methods to recycle ladle slag: (a) by pouring molten ladle slag to another ladle, at time (taking advantage of the heat) and (b) by making a ladle slag ingot. The latter option mentioned is complex because of the unstable method used for making ingots. Ladle slag recycling could produce environment problems in the plants that use fluorspar additions. HF emissions generated increased F concentrations in the plant water and exhaust gas. However, it is relevant to highlight that ladle slag reuse promotes dephosphorization reaction at BOF and can substitute expensive steelmaking agents, and besides, the process can be more ecofriendly.

To summarize, slag recycling requires the availability of detailed and precise information on their behavior, physical properties, and structural characteristics. This chapter is focused on the chemical composition, structural characteristics, thermal and physical properties, and behavior (at high temperature) of different slags used to protect refractories in BOF and EAF as recycling possibilities.

2. BOF slags recycling practices

Longer lifespans of BOF lining and greater availability result in a reduction of costs per ton of liquid steel. Different steel plants, depending on their lay out, process conditions, and operation, have developed and implemented various techniques for protecting MgO-C refractory lining: brick patching, gunning, manual splashing, chemical splashing, slag coating, slag foaming, and slag splashing [1, 4]. In this chapter, two main slag practices are described: slag coating and slag foaming considering experimental data and theoretical information.

2.1 BOF slags applied in slag coating practice

The application of MgO saturated coating slags helps to reduce the impact of the BOF operation on the refractory lining. These slags form a protective layer on the bottom of BOF MgO-C bricks improving the lifespan of the lining. Slag fluidity and the physics and chemistry of the refractory-slag interaction are relevant to the design of these coating slags. The blowing practice, the end of blow temperature, the ratio of solid-to-liquid phases in the slag, its morphology, its particle size, and chemistry are determining factors for the required properties. Slag-refractory adherence mechanisms are analyzed, and measurements of slag fluidity at high temperature and other physical properties obtained by thermodynamic simulation (up to 1700°C) are informed. Slags of appropriate characteristics allow lining recovery, reducing corrosion damage, oxidation, and erosion of the refractory, as well as the impact of the charge, without altering the metallurgical function of the BOF. Slags used for this purpose need to be optimized and characterized [4].

Slag behavior at process temperatures depends on slag chemistry, melting behavior, viscosity, surface tension, fluidity, FeO content, and MgO saturation. In addition, solid and liquid phases of the slag (at practice temperatures) in the system have relevant influence on the adherence behavior. All these factors lead to/foster the achievement of a good slag layer on the surface of MgO-C bricks.

Experimental tests of physical properties as viscosity and surface tension of multicomponent systems at high temperatures (higher than 1500°C) are difficult to carry out due to the complexity of the process and the amount of time involved. The presence of impurities and possible reactions between the crucible material and the slag produces a transportation problem in the interface that can reduce the values of the properties and can occasionally modify wettability. These factors induce the development of mathematical models and thermodynamic simulation applications to predict the viscosity of a system as a function of slag chemistry [5–8]. The Urbain theoretical model is being one of those more used for the steel-making slags [5], being the Urbain model one of the most widely used for industrial slags. The model estimates the viscosity of liquid silicates and alumino-silicates in function of chemical composition and describes temperature dependence of viscosity through the Weymann expression, Eq. (1):

$$\eta = AT \exp \left(10^3 \, B/T\right) \tag{1}$$

where η is the viscosity in poise; T is the absolute temperature in K; and A and B are the parameters that depend on slag chemical composition (A is expressed in poise K^{-1} and B in K), Eq. (2).

$$-\ln A = 0.2693B + 11.6725 \tag{2}$$

The Urbain model [5] classified the oxides into three groups:

- Glass formers: $X_G = X_{SiO_2} + X_{P_2O_5}$

- Modifiers: $X_M = X_{CaO} + X_{MgO} + X_{Na_2O} + X_{K_2O} + 3X_{CaF_2} + X_{FeO} + X_{MnO} + 2X_{TiO_2} + 2X_{ZrO_2}$

- Anfoters: $X_A = X_{Al_2O_3} + X_{Fe_2O_3} + X_{B_2O_3}$

In this chapter, viscosity values of end-of-blow slags were estimated taking into account the Urbain model and applying the viscosity module for melts of FactSage 7.2 software [6]. It is important to mention that during the last year, large thermodynamic databases of multicomponent oxide systems have been developed, and parameters have been optimized in order to reproduce all reliable experimental data within experimental errors. The information obtained through FactSage 7.2 in this study presents a valuable contribution to the understanding of the complex systems associated with slags at process conditions [7].

The industrial end-of-blow slags selected for this study were divided into five groups with different FeO contents: A (18 < FeO < 22), B (22 < FeO < 25), C (25 < FeO < 30), D (FeO>30) and E (FeO<18). Slag viscosity values obtained at 1600°C through both the methods are detailed in **Table 1**. In **Figure 1**, a comparison of the viscosity values obtained for slags A, B, C, D, and E shows that slags of the E group, with FeO content lower than 18 %wt. and a binary index (BI) 2.88, present the highest viscosities. In **Figure 2**, it is possible to evaluate the impact of slag FeO content on the viscosity evolution.

Slag	SiO$_2$ (%)	CaO (%)	FeO (%)	MgO (%)	MnO (%)	Al$_2$O$_3$ (%)	P$_2$O$_5$ (%)	S (%)	η_{FS} (poise)	η_{Urbain} (poise)
Group A (18 < FeO < 22)										
1	15.9	44.3	19.6	10.2	6.3	0.8	2.8	0.06	0.25	0.78
2	15.4	47.0	18.7	8.4	5.9	1.5	2.7	0.08	0.26	0.80
3	14.8	45.3	21.6	8.4	6.3	1.0	2.4	0.06	0.24	0.75
4	15.3	45.7	20.7	7.6	6.2	1.9	2.5	0.08	0.25	0.81
5	15.3	45.1	21.0	7.6	6.4	2.1	2.5	0.07	0.25	0.83
Group B (22 < FeO < 25)										
6	14.2	44.1	22.5	8.8	6.3	1.4	2.4	0.07	0.23	0.75
7	14.7	43.9	22.5	7.9	6.4	1.4	2.7	0.07	0.23	0.77
8	14.0	44.3	24.4	7.5	5.8	1.6	2.5	0.08	0.23	0.75
9	15.3	43.8	23.7	7.2	6.2	1.6	2.5	0.08	0.23	0.80
10	14.4	44.2	24.1	7.2	6.1	0.9	2.6	0.07	0.22	0.74
Group C (25 < FeO < 30)										
11	13.2	44.6	25.6	7.5	5.6	1.2	2.3	0.08	0.21	0.70
12	13.8	43.7	26.3	6.9	5.5	1.2	2.1	0.09	0.22	0.73
13	12.1	44.3	25.8	7.9	5.7	1.6	2.2	0.08	0.21	0.68
14	13.9	44.0	25.3	6.9	6.2	1.2	2.5	0.07	0.22	0.73
15	13.4	43.7	26.0	6.9	5.9	1.6	2.3	0.08	0.21	0.73
Group D (FeO > 30)										
16	12.7	39.7	32.1	7.6	5.8	0.8	2.2	0.08	0.18	0.67
17	10.5	32.1	39.9	8.5	6.0	0.8	1.8	0.07	0.15	0.59
18	10.5	42.3	31.4	6.5	5.6	1.2	1.9	0.09	0.18	0.60
19	12.0	40.0	32.5	6.4	5.6	0.9	2.0	0.08	0.17	0.65
20	11.5	39.9	33.6	6.7	5.3	0.7	1.8	0.07	0.17	0.62
Group E (FeO < 18)										
21	18.5	45.2	16.7	7.8	6.8	1.0	3.1	0.06	0.29	0.90
22	13.0	48.2	16.4	9.8	6.0	1.7	2.8	0.09	0.26	0.72
23	18.2	49.9	14.1	6.8	5.6	1.6	3.3	0.09	0.31	0.91
24	17.9	49.0	15.3	6.8	5.9	1.8	3.0	0.10	0.30	0.92
25	17.7	49.1	16.1	6.4	5.8	1.7	2.9	0.10	0.30	0.90

Table 1.
End of blow slag chemistry.

A slag sample with FeO ≈ 18, MgO ≈ 11, CaO ≈ 43, Al$_2$O$_3$ ≈ 1.6, and SiO$_2$ ≈ 17% wt. was characterized by different experimental tests. The melting behavior was determined by hot-stage microscopy (HSM). The critical temperatures obtained are $T_{initial}$ = 1398°C, $T_{softening}$ = 1408°C, $T_{hemisphere}$ = 1412°C, and $T_{fluidity}$ = 1419°C. At 1600°C, the average of the contact angle measured was $\theta_{average}$ = 33°. Also, a good adherence behavior on MgO-C samples was obtained by means of dipping tests. Viscosity values estimated by the Urbain model and FactSage 7.2 at 1600°C for the slag were η_{FSage} = 0.29 poise/η_{Urbain} = 0.90 poise. The solid and liquid phases predicted (at 1600°C) by the Equilib module of the software are 92.25 g of a liquid
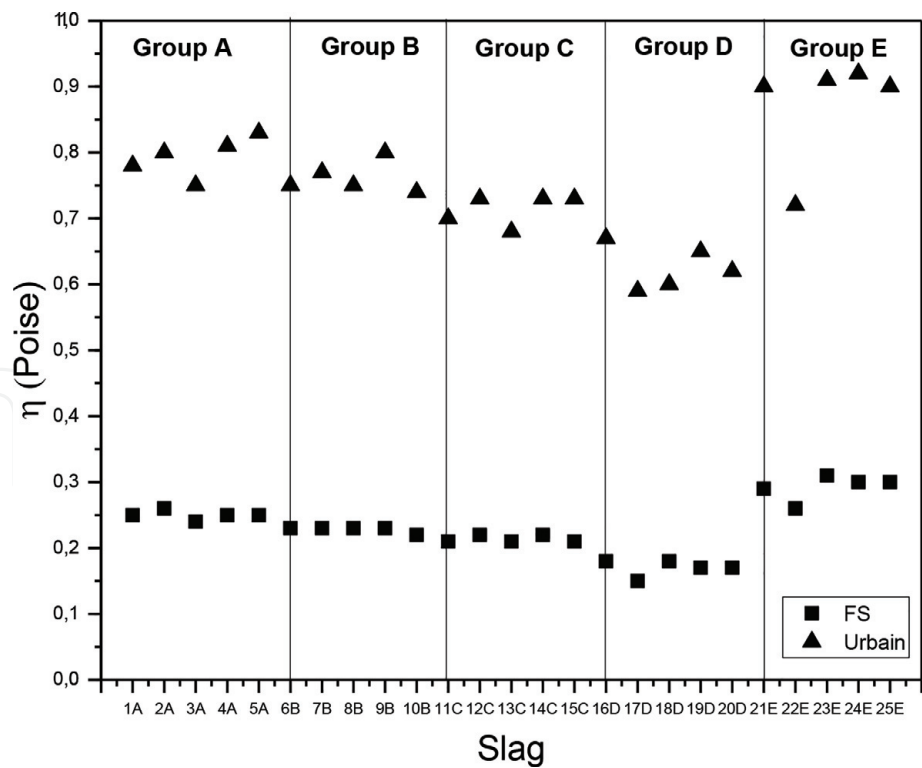
Figure 1.
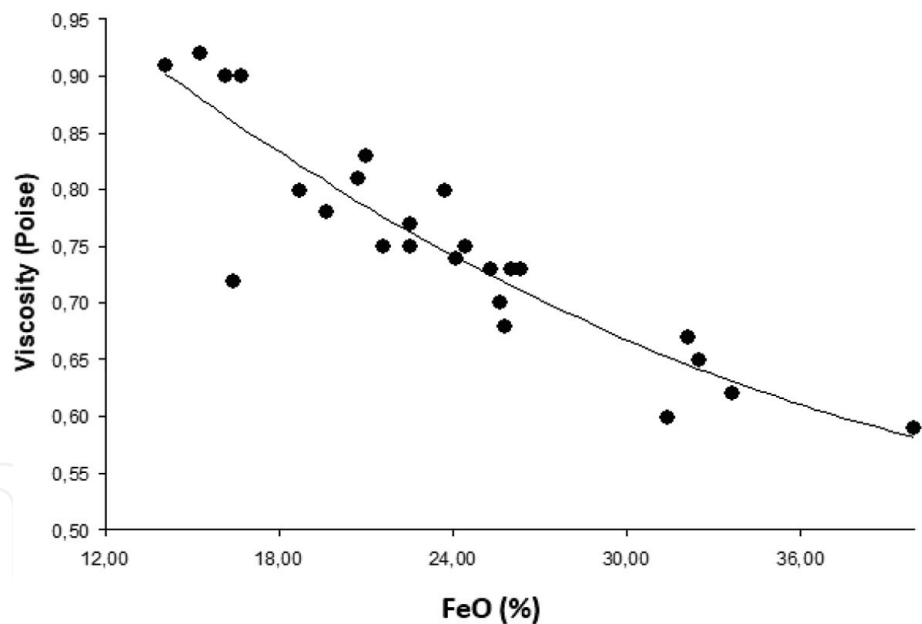*Comparison of viscosity values of slags for groups A, B, C, D, and E with different FeO content.*

Figure 2.
Influence of iron oxide content on viscosity at 1600°C.

phase L_1 with a chemical composition: 4.70% MgO, 17.4% FeO, 6.47% MnO, 18.42% SiO_2, 44.87% CaO, 2.16% Al_2O_3, 0.98% Fe_2O_3, 3.21% $Ca_3(PO_4)_2$, 0.40% $Mg_3(PO_4)_2$, and 1.12% $Fe_3(PO_4)_2$ and two solid phases: 6.4 g of MgO and 0.33 g of Fe (bcc).
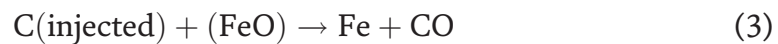
For slags with FeO ≈ 25.8%wt, MgO ≈ 7%wt., CaO ≈ 44%wt., Al_2O_3 ≈ 1%wt., and SiO_2 ≈ 14%wt., the liquid phase L_1 increases up to 97 g, and the chemical composition is as follows: 4.33% MgO, 24.2% FeO, 6.16% MnO, 14.45% SiO_2, 43.8% CaO, 1.03% Al_2O_3, 1.23% Fe_2O_3, 2.82% $Ca_3(PO_4)_2$, 0.33% $Mg_3(PO_4)_2$, and 1.40% $Fe_3(PO_4)_2$. The solid phases include 2.66 g of MgO and 0.44 g of Fe (bcc).

On the basis of the information obtained, it is possible to conclude that slags with 18% FeO at 1600°C present the adequate quantity and chemical composition

of liquid phase (L_1), promoting optimum viscosity and contact angle values that favor the adherence of slag on MgO-C bricks on the bottom of the converter. However, slags with higher FeO content promote the increase of the liquid phase proportion (L_1) with chemical composition changes that produce disadvantages regarding wettability. Slags with the chemical and physical properties mentioned are applied in BOF slag coating practice in the industry with good results increasing the lifespan of the lining and protecting the bottom of the converter.

2.2 BOF slags used in foaming practice

Slag foaming constitutes another alternative to use the converter slags to protect MgO-C bricks below the trunnion line [8, 10]. It is important to take into account that in order to enhance the performance of this industrial practice, it is necessary to understand deeply the associated fundamental phenomena. Along the steel conversion process, the oxygen blown is mostly combined with elements dissolved in the melt. The reaction products are oxides, which are finally incorporated into the slag. If a carbonaceous material is added after blow, C reacts with FeO and generates CO, Eq. (3), causing slag foaming.

$$C(injected) + (FeO) \rightarrow Fe + CO \qquad (3)$$

CO for foaming is also produced by decarburization of the metal given by Eq. (4):

$$C(in\ metal) + \tfrac{1}{2}\,O_2 \rightarrow CO \qquad (4)$$

Gas bubbles in the slag foam could be small or large. The size of the bubbles determines the foam behavior. Foam with small bubbles is dense avoiding the risk of slopping and promoting good slag adherence to the refractory surface. On the contrary, large bubbles like soap generate unstable foam and the likelihood of slopping. Two types of foams can be distinguished: (i) foams initially formed by spherical bubbles that are separated by thick films of liquid and (ii) polyhedral foams in which the bubbles are deformed because of drainage of the liquid film [9–12]. Drainage phenomena decrease the thickness of the liquid separating film to values lower than 1 μm.

As it is known, converter slags are an extremely complex mix of oxides that determine the slag physical properties such as viscosity, density, surface tension, and others. Therefore, accurate viscosity values are essential for the optimization and improvement of metallurgical processes. Experimental measurements have difficulties associated with the high temperature needed (or the high melting point of some slags). Consequently, an alternative is the application of theoretical models to estimate the viscosity and surface tension, as a function of temperature, on the basis of slag chemical compositions [13, 14].

As it was already mentioned, viscosity is considerably affected by FeO content. If the FeO increases in the slag, the viscosity decreases and causes foam bubbles to drain more rapidly, resulting in foam decay. Hence, there is a critical FeO content below which foaming increases and above which the foam is less stable. Surface tension consists in a physical property that depends principally on the surface and not on the bulk. This is affected by the concentration of surfactants and the chemical activity of the surface active component, which determines the surface active concentration in the surface layer [15]. Both properties (viscosity and surface tension) are necessary to estimate the foaming index Σ and to increase the knowledge about this practice. Different expressions have been proposed for

foaming index Σ. In this study, Eq. (5) detailed by Fruehan and Matsura [16], is considered:

$$\Sigma = 115 \frac{\mu^{1/2}}{\sigma^{0.2}\rho D_B^{0.9}} \qquad (5)$$

where D_B, μ, ρ, and σ are the foam bubble diameter, slag viscosity, slag density, and slag surface tension, respectively.

Another point of interest is the foam life time, because it can vary greatly depending on the surfactant compounds present. Transient foams last for a few seconds, while stable foams have prolonged shelf life [12]. In this chapter, results of 16 BOF slags characterized for foaming practice are informed. Slag viscosity and surface tension were determined by theoretical models in order to establish the foaming index applying Eq. (5). The Urbain model [5] and Zaharia, Sahajwalla and Khanna model [17] were used to determine viscosity and surface tension, respectively. The results were completed with information about the thermal behavior of the slags obtained by hot-stage microscopy (HSM). Also, based on the slag chemical compositions, the isothermal solubility diagram (ISD) was applied in order to predict a good foaming behavior and capability of refractory protection.

Another contribution of this work is the information concerning different carbonaceous materials used to foam BOF slags. Three materials were studied considering physicochemical properties and structural aspects. The results were correlated with the information of the slag characterization.

Table 2 details the chemical composition of the BOF slags selected for the study in order to improve the foaming process. Based on the slag chemical composition, the binary basicity index (IB2) and ternary basicity index (IB3) are calculated to predict foamability of the slags applying ISD (see **Table 3**). The values of IB2

Slag	% SiO_2	%CaO	% Al_2O_3	%MgO	%FeO	%MnO	%P_2O_5	%S
1	13.96	42.60	3.04	12.39	22.18	5.96	1.70	0.11
2	13.55	42.97	2.89	8.58	23.56	5.31	1.79	0.09
3	12.31	42.45	2.60	8.28	25.79	7.76	1.76	0.10
4	13.12	46.10	2.26	8.95	21.46	7.06	1.86	0.09
5	16.20	42.41	1.63	10.83	20.71	6.64	1.87	0.07
6	18.09	42.02	2.79	10.08	19.99	6.79	1.71	0.08
7	12.74	41.13	2.25	10.96	26.40	5.79	1.61	0.06
8	17.23	44.32	3.13	9.43	19.15	5.47	2.08	0.09
9	16.74	44.02	2.34	8.66	20.47	7.73	2.04	0.11
10	13.84	40.95	2.14	7.99	25.65	8.33	1.81	0.09
11	12.21	38.19	2.62	7.20	29.55	7.68	1.77	0.09
12	14.47	40.16	1.99	8.26	28.34	5.79	1.60	0.07
13	13.03	39.23	2.67	8.32	26.22	9.96	1.66	0.10
14	14.91	42.47	2.46	9.52	24.05	5.41	1.78	0.09
15	19.68	44.61	3.86	9.47	17.20	5.28	1.96	0.09
16	17.15	45.13	2.57	8.07	19.95	6.67	1.92	0.09

Table 2.
Chemical composition of foaming slags.

Slag	IB2	IB3	η (1550°C) (Poise)	γ (1550°C) (mN/m)	$\Sigma D_b = 0.015$ m	$\Sigma D_b = 0.005$ m
1	3.05	2.51	1.14	665	4.97	14.97
2	3.17	2.62	1.17	648	5.17	15.57
3	3.45	2.85	1.04	646	4.88	14.72
4	3.51	3.00	1.06	642	4.96	14.96
5	2.62	2.38	1.20	638	5.32	16.02
6	2.32	2.01	1.41	630	5.84	17.58
7	3.23	2.74	1.03	625	5.03	15.15
8	2.57	2.18	1.40	630	5.82	17.52
9	2.63	2.31	1.29	621	5.66	17.06
10	2.96	2.56	1.12	625	5.24	15.79
11	3.13	2.57	1.07	623	5.14	15.49
12	2.78	2.44	1.14	619	5.34	16.09
13	3.01	2.50	1.10	627	5.18	15.59
14	2.85	2.45	1.19	616	5.48	16.52
15	2.27	1.90	1.61	617	6.37	19.18
16	2.63	2.29	1.34	618	5.80	17.47

Table 3.
Basicity index, viscosity, surface tension and foaming index values.

Figure 3.
ISD (%MgO-%FeO) for three ternary basicity index ranges.

indicate that the slags are saturated in MgO and are compatible with refractory lining. All the slags were classified into three ternary basicity index (IB3) ranges: 1.9 > IB3 > 2.29, 2.29 > IB3 > 2.74, and 2.74 > IB3 > 3 and then placed in ISD (%MgO-%FeO).

As it is known, a creamy slag is the optimum condition to obtain the good foamability described by Pretorious [18]. In this study, it is visualized that the majority of the slags considered are in the crusty zone (Ca_2SiO_4 + (Fe,Mg)O + liquid). Only four slags (E1, E10, E11, and E14) with IB3 ∼ 2.5 are near the creamy zone ((Fe,Mg)O + liquid; see **Figure 3**). Nevertheless, when ISD includes the % MnO, the same four slags (E1, E10, E11 and E14) are moved toward the right
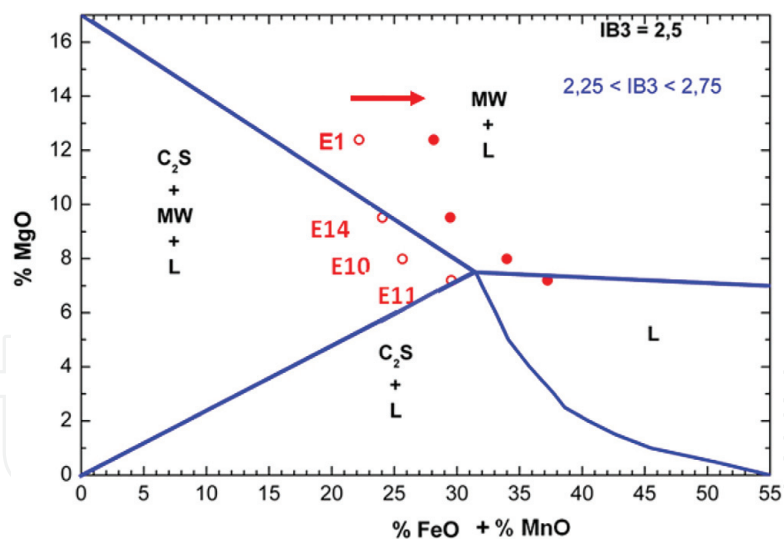
Figure 4.
ISD (%MgO-FeO + %MnO) for IB3 = 2.5.

showing the MnO effect (**Figure 4**). MgO content in the slags mentioned is between 7.2 and 12.4%.

Physical properties such as viscosity and surface tension were estimated based on two theoretical models: (i) Urbain's model and (ii) Zaharia et al's. model, respectively, in order to predict the foaming index (Σ) at 1550°C (see **Table 2**). Two different diameters (D_B) of bubbles were considered in the Σ calculus: 0.015 m and 0.005 m. The results obtained are also detailed in **Table 3**. For slags (E1, E10, E11, and E14) with good foamability properties, the viscosity (η) values are between 1.07 and 1.19 poise and the surface tension between 616 and 665 mN/m, at 1550°C. The results are in agreement with Pretorious [18], who suggests low or medium values of surface tension in the slag for good foaming behavior. At 1550°C, the predicted average foaming index values for two bubble diameters (D_B = 0.015 m and D_B = 0.005 m) are 5.2 and 15.7, respectively. The content of %FeO in these four slags is between 22 and 30% and of %MnO between 5.4 and 8.3%. This information represents a good starting point to optimize the BOF foaming industrial practice. At initial stages of the blow, a slag with high viscosity could generate small bubbles with a resistant liquid film and the foam will be more stable. The correlation between IB3 and Σ shows that the foaming index decreases (slightly) as the basicity index increases (**Figure 5**).

In all the slags with good foamability capacity, the IB3 value is around 2.5. It was observed that when the bubbles present a D_B = 0.005 mm (small size), MnO content (for MnO < 8%) results in random foaming index values compared to the effect of FeO content. The highest foaming index Σ was obtained for slag E15 with 19.68% SiO_2, 17.20% FeO, 9.47% MgO, and 5.28% MnO. FeO content in the slag constitutes a variable that enables to control slag foaming. The study shows the sensibility of viscosity and surface tension, regarding FeO and MnO contents. Also, the higher the viscosity the higher the foaming index.

Slag samples, obtained pre (B_f) and post (A_f) foaming practice, were character-ized. The melting behavior was determined by hot-stage microscopy (HSM). **Figure 6** shows the average critical temperatures: softening temperature (T_s), hemisphere temperature (T_h), and fluidity temperature (T_f) of the samples.

It is worth noting that critical temperatures in slag samples increase after the foaming practice. These results indicate a dynamic evolution of the slag chemical composition during the practice. Average critical temperatures range for B_f (before
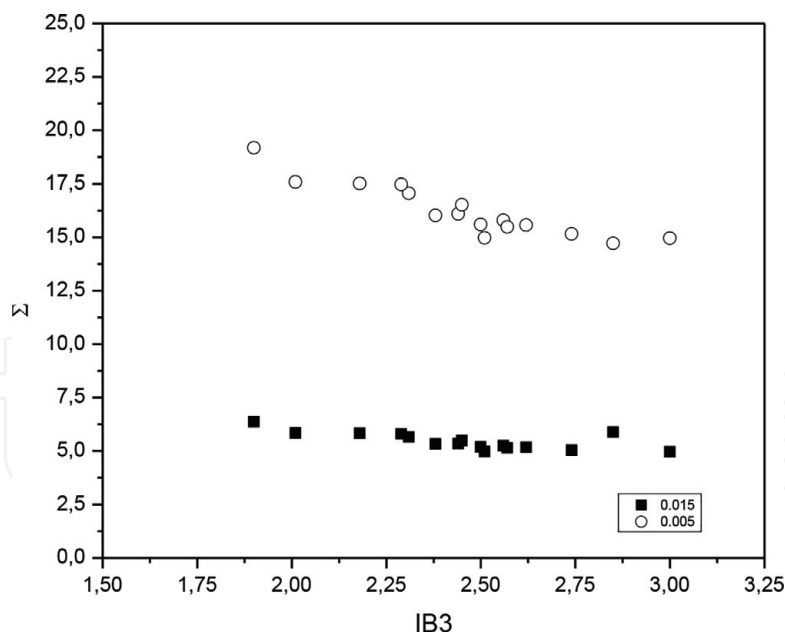
Figure 5.
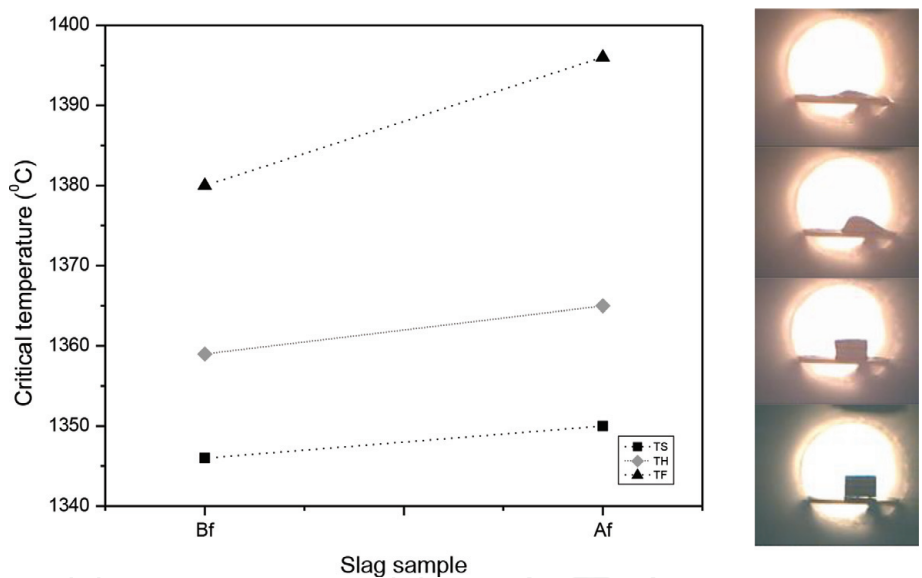*Incidence of IB3 on foaming index Σ.*

Figure 6.
Average critical temperature values (melting behavior) of the slags before and after foaming practice.

foaming) slags are between 1345 and 1380°C. However, for A_f slags (after foaming), an increase $\approx$ 3% of critical temperatures was determined.

During slag foaming, when carbon is injected into the slags, gas bubbles are formed around the carbonaceous particles. It is necessary to take into consideration that different carbonaceous materials could produce different impact on slag foaming. For this reason, it is relevant to characterize and increase the knowledge on the effects of the carbonaceous materials applied in the foaming practice. Chemical and structural characteristics of three carbonaceous materials were studied. In **Table 4**, results of the chemical characteristics of carbonaceous materials are informed. Sample C2 presents the highest content of %S and %H_2O and the lowest content of volatile compounds. Ash content is around 11% in materials C1 and C2 (typically in metallurgical cokes). Nevertheless, material C3 contains very low percentage of ash because it is a petroleum coke. Moreover, it presents the highest carbon content. Sulfur content is similar in all samples.

Carbonaceous material	% H_2O (at 105°C)	%Ash	%Volatile	%C	%S
C1	0.76	11.81	1.84	86.35	0.62
C2	1.02	10.95	1.38	87.67	0.70
C3	0.61	0.20	2.24	97.56	0.63

Table 4.
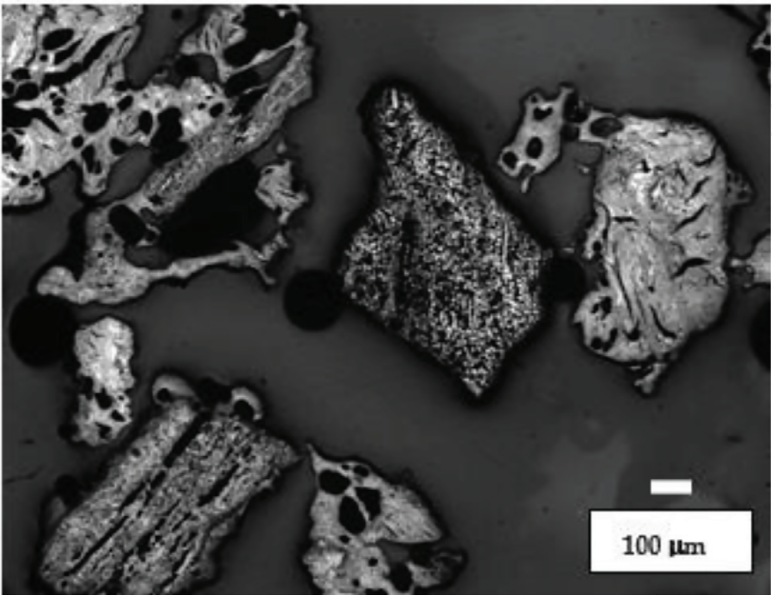*Chemical characteristics of carbonaceous materials.*

Figure 7.
Different types of porous carbonaceous particles identified.

Size distribution of carbonaceous particles was determined by ASTM sieves. It was observed that sample C1 has particles of small sizes, sample C2 also contains particles of up to ≈ 0.75 mm, and sample C3 presents particles between 0.80 and 2.5 mm. The morphology, the phases present, and the porosity of the carbonaceous particles were studied by light and scanning electron microscopy including EDS analysis. Different types of carbonaceous particles were identified in all the samples (**Figure 7**). Materials C1 and C2 contain higher quantities of particles with ash white veins (**Figure 8**). This result is consistent with the %Ash experimentally determined.

The morphology, size, and distribution of pores in each type of carbonaceous particles are variable. There are irregular, spherical, and elongated pores of different sizes and proportion in the particles observed. It was possible to establish that sample C3 has the largest proportion of pores with different sizes (800–50 μm), and samples C2 and C1 present porous with sizes between 350 and 50 μm. Rahman et al. [19] informed that metallurgical cokes (such as materials C1 and C2) promote gas emissions one order higher (in magnitude) than the synthetic coke. This is explained by the higher chemical interaction in contact with the slag, due to the reduction of the oxides present in the ash and FeO content. To control foam height, carbonaceous particles can be added to slag with adequate size and low volatile content. This is another alternative to avoid the risk of slopping. It is important to highlight that the foaming index decreases as the size of carbonaceous particle increases. Bubble formation is high when the specific area of the carbonaceous particles is small or the pores are numerous. On this base, material C3 is the most favorable for the slag foaming practice due to the size and distribution of the pores.
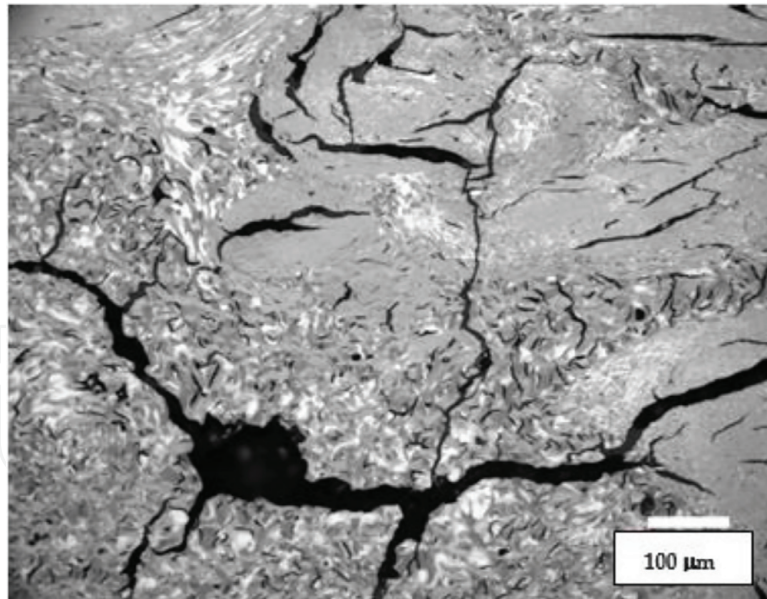
Figure 8.
Detail of one particle with considerable white ash veins.

Furthermore, the ash content of materials C1 and C2 allows predicting rapid gas generation, which is not favorable for foam stability.

Based on these results, it is possible to confirm that the evolution of properties (viscosity and surface tension) of BOF slags during the operation represents the key to obtain the best aptitude for foaming practice, avoiding the risk of slopping. High viscosity is perhaps the most obvious factor in the stabilization of BOF-converter foams, and it retards the rate of drainage in the films of the bubbles. Nevertheless, surface tension is also a relevant physical property that should be taken into account to predict foam behavior. Both properties, high viscosity and surface tension, are determined by the chemical composition and the evolution of the slag at process conditions. Carbonaceous materials also exert an effect in the foaming practice; it is possible to recommend the addition of petroleum coke (material C3) in the foaming practice, because of its ash low content, high proportion of large pores, and higher carbon content.

3. EAF slags reused in the foaming practice

Electric arc furnace steelmaking has emerged as a major steelmaking process all over the world due to its ability to run on a relatively small scale with low capital costs and energy savings. Steel scrap is the preferred metallic charge material, and sponge iron is also used regularly in most plants in order to dilute tramp elements introduced through the scrap [1, 17]. The growth of the arc furnace-based steel industry has been encouraged by modern arc furnaces of large capacity and ultra-high power, electrical efficiency improvement, and metallurgical efficiency through oxygen lancing or the co-jet technology. In conventional EAF steelmaking, natural gas is generally used as a supplementary energy source. Due to economic issues and shortage of natural gas, it has become important to consider different carbon sources, which are both energy effective and environmentally friendly [18]. In addition, the decrease of refractory consumption is a crucial topic of consideration for all steel plants.

Not only does the slag foaming practice protect the equipment covering the arcs and the refractory lining (the furnace roof and sidewalls from excessive heating and radiation), but it also reduces the arc noise, decreases electrode and electricity

consumption, and has present a significant impact on improving thermal efficiency. The foamy slag provides an insulating layer to the melt, thereby reducing energy loss. Slag foaming involves the expansion of molten slag by CO gas bubbles evolving from chemical reactions at the slag-metal interface. Slag viscosity and surface tension control the movement of bubbles in the liquid. Foaming was generally found to improve as surface tension decreases, increasing slag viscosity and suspension of second-phase particles. The reaction between FeO present in the slag and carbon is strongly endothermic. It is important to note that sulfur additions suppressed slag foaming and tended to increase the size of CO gas bubbles. An increase in silica concentration promotes lower surface tension of slag and leads to smaller CO gas bubbles and their easier escape from the slag. The injection of oxygen and carbonaceous materials in industrial EAF furnaces creates highly dynamic and nonsteady state conditions. Oxidation and reduction reactions continuously change slag composition, and chemical reactions produce CO gas that also changes significantly with time [19].

In agreement with BOF foaming practice, the rate of gas generation was found to be an important parameter in carbon-slag interactions and needs to be optimized to maintain optimum levels/duration of gas entrapment by the slag and foaming behavior. The type of carbonaceous material added affects the foaming practice. Metallurgical cokes affect foaming because of the ash content. Natural graphite, on the other hand, produces excellent slag volumes but slow reduction of iron oxide. Slower rates of gas generation and higher surface tension values cause slag to trap gases and sustain foaming. Slag foaming height is well connected to carbon injection rate and slag chemical properties. Bubble sizes in EAF slags are $\approx$ 1–2 mm. In general, bubble number in the slag foam is greater than the number of coal particles. One particle of coal can form more than one bubble. In EAF steelmaking, the foam becomes less stable toward the end of the process.

4. Reused of ladle slags

The amount of ladle slag generated in the steelmaking is important. The former method of recycling ladle slag is pouring the molten slag from a ladle to another or making ladle slag ingot [3]. The ingot production is complex. However, nowadays three main types of ladle slag recycle products are used depending on the particle size and chemical composition: (a) desulfurizing agent in hot metal pretreatment, (b) as a product to substitute converter flux, and (c) as a product to substitute ladle flux. It is possible to reduce steelmaking cost and get ecofriendly benefits, recycling ladle slag.

Ladle slags present similar melting behavior respect synthetic flux ($T_s \cong 1334°C$, $T_f \cong 1346°C$) and also have a good inclusion absorptivity. For this reason, they constitute an alternative for ladle flux substitution. Slag low-melting point possibilitates the application in ladles during secondary refining process reducing the fluorspar or lime additions. Finally, lumps of slags could be added in BOF to improve dephosphorization.

5. Slags reused as concrete raw material

Slag is a partially vitreous byproduct of the process of smelting ore, which separates the desired metal fraction from the unwanted fraction. Blast furnace slag is furthermore classified into granulated blast furnace slag and air-cooled blast furnace slag. Granulated blast furnace slag is produced by quenching molten

furnace slag with high-pressurized water [20]. Blast furnace slags cooled in air constitute a crystallized material used as raw material instead of sand in the production of concrete. In the case of water applied during granulated slag production, it is possible to recover heat from the slag quenching water, thereby reducing energy consumption. Blast furnace slag is obtained at 1300–1400°C; viscosity is around 0.4–1.0 poise; the chemical composition mainly includes FeO, CaO, MgO, SiO_2, Al_2O_3, TiO_2, S, and C; the alkalinity (CaO/SiO_2) is 1.2; and the alkalinity [($CaO + MgO$)/SiO_2] is around 1.5. A lot of research has focused on the reuse of blast furnace slag to make building materials. Crystallized slag sand is added to Portland cement in particles of ≈ 3.15 mm. The chemical and mineralogical composition of Portland cement is detailed in **Table 5**. Senani et al. [21] informed that concrete with crystallized slag sand addition presents good physical and mechanical properties. This study confirms that the additions of blast furnace slags (0–4 mm of size) in concrete (up to 20–25%) result in good compressive strength (≈30 MPa after 28 days) for the grades of concretes tested.

The use of blast furnace slag as artificial rocks is also possible because they are similar to semi-hard stones. As a recyclable material, they support resource conservation by substituting nonrenewable natural stone. Land and marine applications include seaport and airport civil engineering projects, coastal protection structures, seaweed bed rehabilitation, and land surface coverage [22]. This type of slag may represent a good alternative to reduce the cost of cement production, contribute to environment protection, and provide enormous social and economic benefits.

Brand and Roesler studied different basic steel slags: energy optimizing furnace (EOF), electric arc furnace (EAF), and arc oxygen decarbonization (AOD), as aggregates in concretes [23]. However, for civil applications, exhaustive controls are carried out in order to determine contents of Ba, Cd, Cr, Mo, Ni, Pb, V, and Zn, in order to avoid soil contamination. The content of sulfates or sulfides is also controlled to avoid SO_2 emissions causing air pollution. It was found that steel slag is volumetrically unstable as compared to blast furnace slag due to the content of expansive oxides such as MgO and CaO. In the case of basic slags, the authors propose to modify the surface of the aggregates by blending them with a slurry mixture of fine quarry dust and cement in order to avoid the expansion and to reduce the porosity. Another possibility is the use of steel slag as a binder or filler replacement in composite materials in civil engineering production. These binder or

Chemical composition of Portland cement	Range (%)	Mineralogical composition	Range (%)
CaO	56–63	C_3S	50–65
Al_2O_3	4–6	C_2S	10–25
SiO_2	19–27	C_3A	9–12
Fe_2O_3	2.5–3.5	C_4AF	7–11
MgO	1–2		
Na_2O	0.1–0.6		
K_2O	0.3–0.6		
Cl^-	0–0.2		
SO_3	2–3		
CaO	0.5–2.5		

Table 5.
Chemical and mineralogical composition of Portland cement.

filler substitutes were mixed into composites, and their compressive strength was tested with good results.

6. Conclusion

The disposal and exploitation of residues from steelmaking plants are still an open problem because of the huge amount and the remarkable variety of waste materials. Slag recycling in the steel job constitutes a relevant way of reusing with important economic impact on refractory costs. The coating and foaming practices are very useful in BOF converters and EAF. The ladle slag recycling also represents an important alternative to reduce steelmaking cost, decreasing the consumption of fluorspar and lime (among others metallurgical applications), and get ecofriendly benefits.

The growing trend in the construction industry is to develop sustainable buildings. The principles underneath this movement bring new requirements with an emphasis on the rational use of material and energy resources by controlled minimization of total emissions produced. One of the possible ways of achieving sustainable development in the construction industry is to use easily renewable raw material resources and waste materials instead of limited and finite resources. In this sense, the interest shown by the professional community in aggregates based on secondary raw materials is increasing, and slags constitute a good alternative.

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