EVALUATION OF THE DEGRADATION OF LF SLAG AND ITS IMPACT ON THE DECARBURIZATION OF THE LADLE REFRACTORY LINING

Marcos N. Moliné[a], Analía G. Tomba[a], Pablo G. Galliano[b]

[a]INTEMA (CONICET), Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina

[b]Tenaris REDE AR (CINI), Dr. Simini 250, 2804 Campana, Argentina

ABSTRACT

MgO-C and Al2O3-MgO-C bricks are widely used as working lining in the steelmaking ladles. Due to their carbon content they are particularly susceptible to high temperature oxidation. These bricks are exposed to such conditions after casting and during the ladle preheating.

At the end of each heat, LF slag remains partly adhered to the walls, generating a coating that can act as a barrier, protecting the refractory to decarburization. The slag also suffers transformations during cooling such as hydration and pulverization, which can affect its protective capacity.

For this reason, physico-chemical characterization of a steelmaking ladle slag and the evaluation of its integrity under different conditions are carried out in this work. The degradation of the slag by weathering is evaluated through its granulometric evolution at different times for several months. In each case, samples were also characterized by different techniques: X-ray fluorescence, X-ray diffraction and thermogravimetric analyses.

At short time, degradative processes concerning CaO are observed. At longer time, degradation of MgO and changes in calcium aluminates are also detected. These transformations involve volumetric expansions and then, the slag disintegration. These changes will affect the protective capacity of the slag on preventing decarburization of working lining refractories in empty ladle conditions.

Keywords: steelmaking slag, degradation, carbon-containing refractories, lining

INTRODUCTION

MgO-C and Al_2O_3-MgO-C bricks are widely used in working linings of steelmaking ladles. Due to their carbon content, these materials are susceptible to be oxidized by air or combustion atmospheres during its campaign. This risk is present after the ladle leaves the continuous casting machine and before it receives the liquid steel in the following heat. After ladle casting step is finished, a film of steelmaking ladle furnace (LF) slag covers the refractory lining and remains partly adhered to it. This slag coating, which is mainly composed of CaO, SiO_2, MgO and Al_2O_3, can have a beneficial effect on the lining providing a barrier against refractory decarburization. As far as the ladle is cooled down the remaining slag is solidified. In this stage, several phases crystallize from the liquid state. Further cooling down to room temperature can lead to additional phase transformations and reactions involving those crystallized phases. Some of these reactions can be strongly deleterious for the materials integrity, leading to a rapid degradation and pulverization

of the solid slag. Ambient degradation of steelmaking ladle slags has been mainly attributed to the presence of phases that show an expansive behavior due to hydration (mainly by reaction with ambient moisture) and carbonation (by combination with CO_2 gas from air) reactions with high volume variations. Tab. 1 resumes main phases and reactions involved, together with their volumetric and mass variation.

Slag weathering is conditioned by chemical, mineralogical and microstructural properties of the material, as well as by the thermal and atmospheric conditions during this process. [1,2]. Characterization studies of steelmaking slags and evaluation of their degradation pattern have been reported and have a great value when looking for better alternatives for re-using or recycling these materials in different industrial processes. However, no studies have been done on the evaluation of the degradation of these slags when they are coating ladle bricks under operation. And little is known about how do degradation affects slag protective role against in service refractory lining decarburization.

Tab. 1: Reactions involved in slag degradation. [3]

Reaction		Variation	
		vol%	wt%
$CaO + H_2O$	$\rightarrow Ca(OH)_2$	100	32
$Ca(OH)_2 + CO_2$	$\rightarrow CaCO_3 + H_2O$	10	35
$MgO + H_2O$	$\rightarrow Mg(OH)_2$	120	45
$Mg(OH)_2 + CO_2$	$\rightarrow MgCO_3 + H_2O$	15	45
$C_3A + 10H$	$\rightarrow CAH_{10} + 2C$	65	65
$C_{12}A_7 + 8H$	$\rightarrow 6C_2AH_8 + A$	80	15
$CAH_{10} + CA + H$	$\rightarrow C_2AH_8 + AH_3$	-40	-25
$C_2AH_8 + CA + H$	$\rightarrow C_3AH_6 + AH_3$	-20	0

C=CaO; A=Al_2O_3; H=H_2O

In this work, the degradation of an industrial steelmaking slag was studied by evaluating the evolution of its physical and chemical properties with increasing weathering time. The aim of this work is to get knowledge about the degradation mechanism of a steelmaking ladle slag under different conditions. This work is part of a research focused on the impact of the slag on the behavior of steelmaking carbon-containing refractory bricks.

MATERIALS AND METHODS

A representative batch of ~20 Kg of LF steelmaking slag was used for this study. The used batch was divided in four granulometric fractions by using ASTM sieves: a) < 1.4 mm (14 mesh); b) 1.4 to 4.0 mm (5-14 mesh); c) 4.0 to 7.2 mm (5-3 mesh); and d) > 7.2 mm (3 mesh). From now on

these fractions will respectively name as GFff, GFf, GFc and GFcc.

Each of these four fractions was characterized at the starting point of the weathering test ("test starting point'). Evaluation of each of these fractions was done after 1, 3, 7, 21, 35, 49, 70 and 126 days from the test start with the aim to follow up slag degradation at room temperature under ambient conditions during the weathering period. For that purpose, the following characterization techniques were selected: a) particle-size distribution (granulometry) by sieving; b) chemical composition by X-ray fluorescence (XRF); c) mineralogical composition by X-ray diffraction (XRD); d) thermogravimetric analysis (TGA).

Granulometric evolution of every fraction was done by using the same ASTM sieves employed for the initial separation (3, 5 and 14 meshes). Chemical composition of main oxides was determined by XRF using a Thermo Electron ARL model 9900. Mineralogical composition was analyzed by X-ray diffractometry (XRD). For that aim, a Philips Analytical PW 1830/40 diffractometer was used, with 40 KV, 30 mA and Cu radiation (Kα=1.5418 Å). X-ray patterns were acquired from 10° to 75° 2θ with a step of 2°/min. Thermogravimetric analyses (TGA) of the powdered slag samples were performed at 10 °C/min up to 1000 °C in airflow with a Shimadzu TGA-50 equipment.

RESULTS AND DISCUSSION

a) Granulometric analysis

Granulometric evolution (Fig. 1) is displayed as the weight % of each fraction with respect to that weight of the entire slag batch (19.50 Kg). At the starting point of the weathering test, proportion of each fraction was: 57.6 wt.% of GFff (<1.4 mm); 12.1 wt.% of GFf (1-4 mm); 6.9 wt.% of GFc (4-7.2 mm); and 23.3 wt.% of GFcc (>7.2 mm).
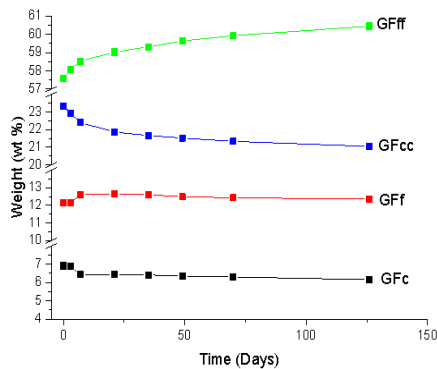

Fig. 1 – Granulometric fractions evolution vs. time of weathering.

GFcc and GFff exhibit a quite symmetric mass evolution in Fig 1. In general terms, we can consider that GFcc is losing weight due to fine particles generation resulting from weathering reactions. As a result, GFff is being enriched by the fine particles generated from the other fractions during the test. Although weight modifications along the test can be also affected by degradation reactions such as hydration and carbonation (see Table 1), results are

mainly showing surface pulverization of GFcc particles along the test that produces very fine particle fragments smaller than 1.4 mm which fall directly to GFff. In a sense, both types of curves can be used as indicators of the degradation evolution by slag pulverization. Intermediate conditions would be expected for GFc and GFf fractions; according to observed results, a slight tendency to lose mass prevailed in both granulometric fractions after the first samplings.

Fig. 1 also shows a particular slope change at the beginning of all curves. This was attributed to the fact that surface hydration of reactive phases is expected to be already present before the starting point of the weathering test. Friction during sieving could help the detachment of the previously hydrated and weak degraded layer of the particles. This can explain the initial higher rate of weight mass changes that were observed in all samples, but mainly in GFcc and GFff. After that, when sampling frequency decreases and the sieving operation interfered in a lesser extent in the barrier detachment, the evolution of the granulometric distribution is considered to be more representative of the degradation rate of each fraction.

b) Chemical and mineralogical analysis

Chemical composition of the granulometric fractions obtained by XRF is reported in Tab. 2, including only the main components. No significant changes were observed in the chemical composition of each fraction along the degradation test.

Tab. 2 – XFR chemical composition (wt.%)

ID	CaO	Al$_2$O$_3$	SiO$_2$	MgO	FeO
GFff	53.8	21.8	8.8	6.5	1.2
GFf	52.6	21.7	9.5	7.4	2.5
GFc	51.1	20.1	10.5	7.1	4.3
GFcc	46.6	14.3	13.0	6.4	9.6

Enrichment in Ca- and Al-containing compounds in the finest granulometric fraction takes place, whereas it has lower quantities of Fe- and Si-containing phases.

XRF data help the analysis of the mineralogical phases present and their evolution during the degradation by XRD. Fig. 2 shows the results of XRD patterns of the four granulometric fractions that were obtained 21 days after test start. Due to the large amount of obtained data, results from other weathering condition are not shown. In the case of Fig. 3, a comparative evolution of the XRD patterns of the two extreme granulometric fractions (GFff and GFcc) from 3 to 18 weeks of weathering is present.

In all the cases, the XRD analyses were focused on those phases that are mainly involved in slag degradation and showed variations along the test. Identified phases were classified in four groups according to their main components: Ca, Mg, Calcium Aluminates and Fe groups. Main results regarding the distribution and evolution of phases obtained from XRD analysis are resumed below.

Ca group

- CaO (C): it was found in every granulometric fraction, being in higher content in coarser fractions. A reduction of

its amount was observed in every fraction when increasing weathering time.

- Ca(OH)$_2$ (CH): it was detected mainly in finer fractions. An increase of its main peaks intensities predominates over longer times, mainly in GFff.

- CaCO$_3$ (C$\underline{C}$): identified in finer granulometric fractions at the beginning, increasing its amount at longer times by carbonation of Ca(OH)$_2$ during the test.

Mg group

- MgO (M): it is present in similar amounts in every granulometric fraction at the beginning of the test. A reduction in its amount was observed with the testing time, mainly in the coarser fraction.

- Mg(OH)$_2$ (MH): it was identified in every granulometric fraction at the beginning of the test. No significant variation in its relative content was observed for longer times. This can be a consequence of a balance between MgO hydration and Mg(OH)$_2$ carbonation.

- MgCO$_3$ (M$\underline{C}$) similar amounts were identified in every fraction when the weathering test was started. An increase of the main peaks intensity of this phase was appreciated for longer times, especially in the finer fractions.
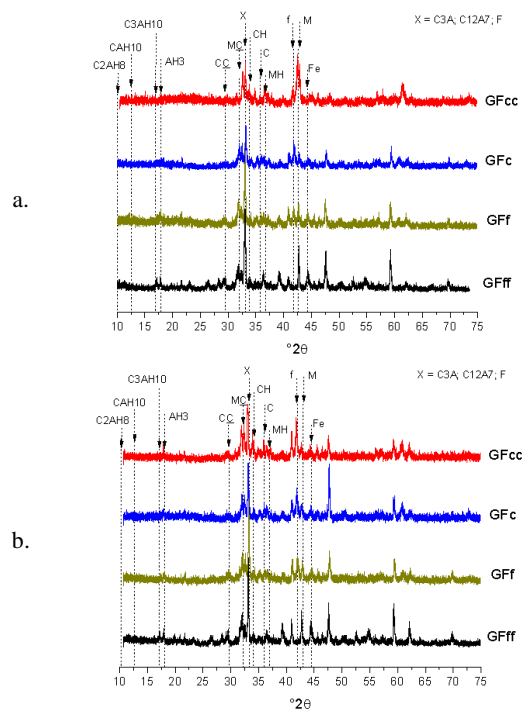

Fig. 2 – XRD patterns of granulometric fractrions: a. 21 days (3 weeks) and b. 126 days (18 weeks).

Calcium aluminates group

- C$_3$A/C$_{12}$A$_7$: main peaks of these phases were overlapped, being the most intense in all of XRD patterns (32.3° 2θ). These aluminates were found in every granulometric fractions at all weathering times. A decrease in the content for longer times was observed, mainly in finer fractions.

- CAH$_{10}$: low intensity of hydrated phase peaks made the analysis difficult. An increase of the amount of this solid was detected in GFff over longer times.

- C$_2$AH$_8$: main peaks detected in GFff fraction for long weathering times.

- C$_3$AH$_6$ + AH$_3$: they were observed only in the two finer granulometric fractions at the beginning of the test. For longer times, an increase of peak intensities in every granulometric fraction was observed. Finally, AH$_3$ amounts were similar between every fraction. Instead, C$_3$AH$_6$ peaks were more intense in GFff.

Fe phases:

No significant changes in the intensity of the main peaks were observed in the phases of this group as function of sampling time.

- Fe: similar amounts were detected in every fraction.

- FeO (f): it was identified only in the three coarser granulometric fractions in similar quantities.

- Fe$_2$O$_3$ (F): this phase is difficult to be identified since its main peak overlaps with those of C$_3$A/C$_{12}$A$_7$.
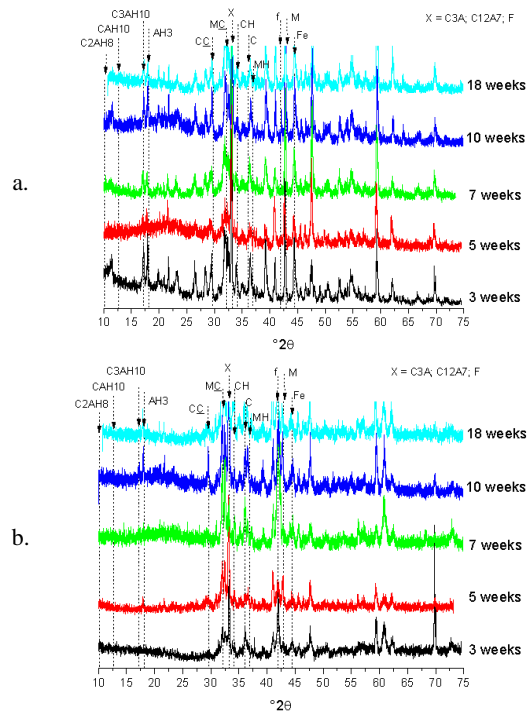

Fig. 3 – XRD patterns at different times: a. GFff, b. GFcc.

c) **Thermal analysis**

Previous results showed evidences of hydrated and carbonated phases in different slag fractions that were analyzed after different weathering times. These phases are expected to show weight losses when subjected to thermal treatments. For that reason, a set of thermogravimetric analysis (TGA) of all the studied slag samples were done. As an example, TGA curves of all samples after 21 of weathering test are shown in Fig. 4. Remarkable weight losses at temperatures lower than 600°C are observed, mainly in the case of the finer and most degraded fraction, GFff. These weight losses were mainly assigned to dehydration of previously identified phases such as Ca(OH)$_2$, Mg(OH)$_2$ and hydrated calcium aluminates.
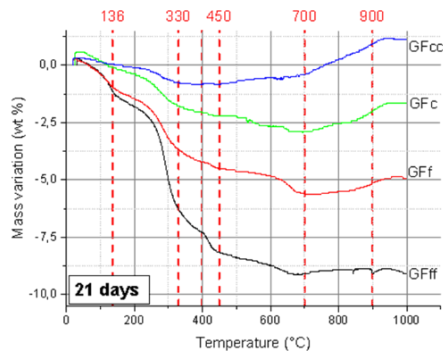
Fig. 4 – TGA curve after 21 days.

For the analysis of the weight evolution at higher temperatures, the following phases and possible reactions must be taken into account. Among them are: $MgCO_3$ decarbonation and iron oxidation, which are expected to occur between 450 and 600 °C, and reactions of $CaCO_3$ and FeO, which take place in the same range of temperature, between 700 and 800 °C. Nevertheless, carbonated phase produces weight loss due to CO_2 eliminations, whereas iron oxidation led to weight increase. TGA mass variations results suggest that the finest fractions have higher concentration of carbonates; instead, the coarser fractions have more iron containing phases in agreement with XRF data [2,4,6].

TGA of each granulometric fraction showed some distinct behavior along the degradation testing time. GFff has several phases coming from degradation process. Mass variations in the thermal range associated to hydrated calcium aluminates such as CAH_{10}, C_2AH_8 and C_3AH_6 (130 - 330 °C) were observed. The higher mass losses in TGA curves were displayed in the thermal range associated to dehydration of C_3AH_6 (250 - 300 ºC); moreover, this loss increased for longer times. This fact suggests the subsequent hydration reactions of calcium aluminates and intermediate hydrates to C_3AH_6. In the case of GFcc, this fraction was slightly degraded when the test started. Regarding GFc and GFf, they showed a trend to reduce the mass losses at longer times, becoming similar to GFcc, as occurred with the granulometric evolution.

d) Slag degradation mechanism

Main reactions with volumetric changes that are involved in the degradation of steelmaking LF slag are: CaO hydration and carbonation, MgO hydration and carbonation and calcium aluminates hydration.

In the case of the steelmaking LF slag that was studied in this work, results showed that CaO hydration and carbonation were the most relevant reactions at the beginning of the degradation process. High initial proportions of $Ca(OH)_2$ and $CaCO_3$ in finer granulometric fraction confirm this fact.

Considering the volumetric expansions in Tab.1, MgO and calcium aluminate hydrations should be more deleterious for the integrity of the slag particles. However, according to experimental data, these reactions are slower than CaO

hydration, which produces a slightly smaller volume change. Thus, MgO and calcium aluminate reactions with humidity produce the slag pulverization at longer times. In agreement with this, hydrated phases were detected in finer granulometric fractions after several weeks, and their amounts continued growing for longer times.

The effects of other weathering and thermal conditions on slag degradation have also been evaluated, with the aim to simulate possible in service conditions during ladle cycle, and will be reported elsewhere. Positive related results were also obtained during in-plant trials [7]. Further work in this direction is on going.

CONCLUSION

Moisture is the primary cause of slag degradation at room temperature. Hydration reactions of present phases such as CaO, MgO and calcium aluminates several phases produce volumetric expansion that finally promotes slag pulverization. CaO hydration is considered the first responsible of the initial degradation, while MgO and calcium aluminates hydration are responsible of slag pulverization at longer times. Further processes also take place such as $Ca(OH)_2$ and $Mg(OH)_2$ carbonation from ambient CO_2. Although these reactions also involve volumetric expansion, they mainly occur in the hydrated finer fraction of the slag. For that reason, they are not playing a major role in the slag pulverization process.

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