

Recycling Electric Arc Furnace Slag as Unconventional Component for Building Materials

Maria Chiara Bignozzi*, Franco Sandrolini*, Fernanda Andreola°, Luisa Barbieri° and Isabella Lancellotti°

**Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Via Terracini 28, 40136 Bologna, Italy. E-mail: <mchiara.bignozzi@mail.ing.unibo.it>, <franco.sandrolini@unibo.it >*

° Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, Via Vignolese, 905/a, 41100 Modena, Italy. E-mail: <andreola.fernanda@unimore.it, <luisa.barbieri@unimore.it>, <isabella.lancellotti@unimore.it >

ABSTRACT

In this work a complete characterization of electric arc furnace slag (EAF-S) coming from an Italian steel production plant has been carried out with the goal to study if this type of waste is suitable to be used as cement constituent or aggregate for cement based materials. Exploiting the different chemical composition and grain size distribution of two types of EAF-S produced in different steps of the same industrial plant, mortar samples were prepared containing EAF-S as sand (from 10 up to 100%) or 25 wt% ordinary Portland cement replacement, respectively. Chemical and physical results agree with the requirements prescribed for cement and aggregate by European standards. Moreover, the mechanical performances determined on mortar samples seem promising, although an active participation of EAF-S in the hardening process has not been detected.

INTRODUCTION

Steel production is a very demanding productive process in terms of energy costs, gas emissions and waste generation [EPA]. Blast furnaces have a severe impact on the environmental pollution, however granulated blast furnace slag is recycled as constituent of cement (blast furnace cement, CEM III according to EN 197-1). At present, the electric arc furnace (EAF) technology is also widely used, permitting steel manufacturing mainly from steel scraps, with limited amounts of iron scrap, pig iron, and direct reduced iron. From an environmental point of view, steel production by EAF can be considered as a less severe process than that carried out in blast furnace, however different types of slag are also produced. Electric arc furnace slag (EAF-S) is generated in the furnace and in the refining process (also known as secondary metallurgy process): the different origin produces two types of slag characterized by a different chemical composition. Taking into account that fifty millions tons per year of EAF-S are produced worldwide, with about twelve millions tons produced by

Europe [Kourounis et al. 2007], the importance to find a successful recycling route for this material appears clearly evident. Building materials field seems suitable to reach this goal: blended cements containing waste of different nature (fly ash, silica fume, blast furnace slag, etc.) and concrete produced with recycled aggregates coming from construction and building demolitions are important examples of how waste can be used as new raw material. However, waste can not simply be introduced in cement based materials mix-design: chemical, physical and mechanical tests of the recycled material have to be carried out to ensure a good compatibility with cement, water and natural aggregates thus avoiding deleterious reactions that could lead to disruptive effects in the final product.

Several researches have recently been developed on the possibility to recycle EAF-S in cement and/or concrete [Shi 2002; Kourounis et al. 2007; Muhmood et al. 2009; Rodriguez et al. 2009] and EAF-S chemical stability was investigated [Frías Rojas et al. 2004; Setién et al. 2009]. The presence in EAF-S of minerals, such as calcium oxide and periclase, sensitive to weathering requires particular attention in the slag selection, as the delayed formation of expansive products is usually very dangerous for cement based building materials.

The aim of this study is to find a fruitful application for two types of slag coming from the same productive plant located in Italy. The studied EAF-S comes from the furnace (henceforth named black slag, BS) and ladle (henceforth named ladle slag, LS), where the refining process occurs: BS and LS represent about 2/3 and 1/3 of the total slag produced, respectively. Both BS and LS are classified as not hazardous waste in according with the European Waste Catalogue (European waste code 10.02.02) [EWC], but so far are not involved in any recycling route. As the two types of investigated slag have different grain size distribution, they have been used trying to keep the number of further treatments as low as possible. Accordingly, ladle slag, being produced as very fine powder, was used as cement replacement (25 wt%), whereas BS, due to its larger size, was used as sand for mortar samples preparation.

A mineralogical, chemical and physical characterization of BS and LS has been carried out to establish if their role in working as aggregate or cement constituent may be suitable. Finally, mortar samples were prepared containing BS or LS as sand (from 10 up to 100%) or 25 wt% ordinary Portland cement replacement, respectively. The performances of the new materials based on the investigated EAF-S are reported, discussed and compared with those of reference samples.

EXPERIMENTAL INVESTIGATION

Materials

The two typologies of slag investigated in this work, BS and LS, were kindly supplied by Acciaieria di Rubiera SpA, Casalgrande, RE, Italy: a highly representative sample was directly collected in the steel productive plant. Both the slag types are usually wetted and piled in sheltered outdoor environment, before landfill dismissing that usually occurs every 2-3 months. BS sample is constituted by large pieces (1-5 cm), whereas LS is a fine powder. Then, BS was ground in a laboratory ball mill to obtain a sand-like grain size distribution with the aim to use

this slag as aggregate for mortar samples. For LS, the fraction > 0.106 mm was eliminated by sieving to obtain a cement-like grain size distribution. The size distribution curves for BS and LS, determined by sieving and a laser particle-size analyzer (Mastersizer 2000, Malvern Instruments) respectively, are reported in Figure 1 and Figure 2.

BS and LS chemical analysis was conducted by X-Ray fluorescence spectrometer (XRF, PW 1414, Philips) for the main elements. X-ray analysis was carried out by a powder diffractometer with Ni-filtered Cu $K\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation (PW 3710, Philips) in the $5-70^\circ 2\theta$ range. The crystalline phases were determined by comparison with tabulate data on the JCPDS files. Chloride and sulfate (SO_3) content as well as loss of ignition (LOI) were determined following the specific procedures for cement and aggregates chemical analysis reported in the European standards EN 196-2 and EN 1744-1 respectively.

Ordinary Portland cement (OPC) CEM I 52.5 R (EN 197-1, Italcementi, Calusco d'Adda (BG) Italy) was used for paste and mortar samples preparation: its grain size distribution is reported in Figure 2. Silica sand with normalized grain size distribution according to EN 196-1 (Figure 1) was used for mortar preparation.

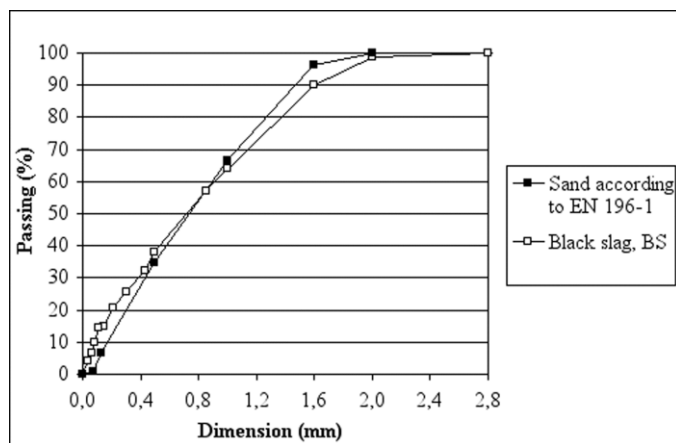


Fig. 1. Grain size distribution of BS and normalized sand

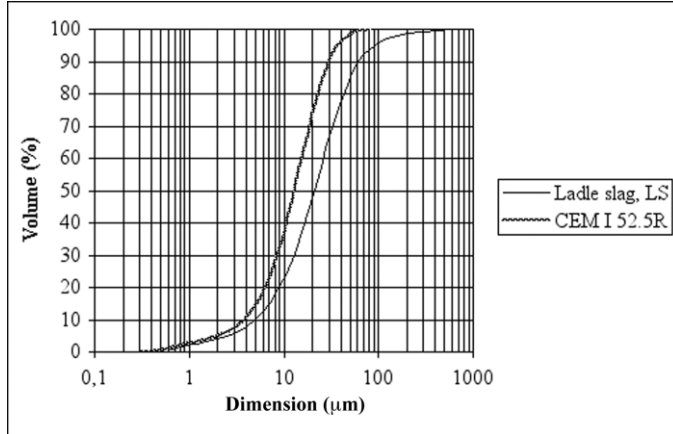


Fig. 2. Grain size distribution of LS and CEM I 52.5 R

Samples preparation

Different mortar samples were prepared using LS or BS as cement or sand replacement respectively. The LS based binder was prepared by dry mixing 25 wt% of LS and 75 wt% of CEM I 52.5 R: the amount of slag selected as cement replacement was set on the basis of compositional range of CEM II blended cement as reported in EN 197-1. Mixing was carried out for 30 min to ensure a repeatable mix. Reference binder was 100% OPC CEM I 52.5 R. Initial cement setting time and soundness were determined on pastes of normalized consistence by Vicat method and Le Chatelier apparatus respectively, according to EN 196-3. BS based mortar was prepared replacing different amount of sand (0, 10, 30, 50 and 100 %) with BS.

Mortar samples were prepared by Hobart mixer according to the normalized mix-design (binder, sand and water in a weight ratio of 1:3:0.5) reported in EN 196-1 for cement mechanical strength determination. Mortar samples mix design is reported in Table 1. Prismatic samples (40x40x160 mm) were prepared and marked with M, followed by BS or LS according to the slag used in the mix-design. MLS samples were cured for 2, 7, 28, 90 days and MBS for 7 and 28 days at 20°C and R.H. > 95%. When necessary, MBS samples are marked by a number indicative of the percentage of sand replaced by BS (e.g. MBS-50 means a mortar sample containing 50% of normalized sand replaced by BS). Mortar prepared with 100% CEM I 52.5 R as binder and 100% normalized sand was identified as MREF.

Table 1. Mix-design of the investigated mortar samples

	CEM (wt %)	LS (wt %)	Water (wt %)	Sand (wt%)	BS (wt %)
MREF	22.2	-	11.1	66.7	-
MLS	16.7	5.6	11.1	66.7	-
MBS-10	22.2	-	11.1	60.0	6.7
MBS-30	22.2	-	11.1	46.7	20.0
MBS-50	22.2	-	11.1	33.3	33.3
MBS-100	22.2	-	11.1	-	66.7

Samples Characterization

Flexural (S_f) and compressive strength (S_c) of mortar samples was determined by an Amsler-Wolpert machine (100 kN) at a constant displacement rate of 50 mm/min and reported as average of at least three measurements. Water absorption test at atmospheric pressure was carried out on hardened mortar prisms: firstly, samples were weighted after being immersed in water for 24 hours or up to reaching a constant mass (M_w), then they were weighted after being dried at 100 °C for 24 or up to reaching a constant mass (M_D). Water absorption was calculated by the following equation: $WA\% = 100 \cdot (M_w - M_D) / M_D$. Scanning electron microscopy (SEM) analysis was carried out by means of XL 40 Philips instrument on samples undisturbed fracture surface previously coated with Au/Pd by vaporization under vacuum.

RESULTS AND DISCUSSION

Oxide chemical analysis (Table 2) shows the compositional range determined by different sampling of the two investigated slag typologies; moreover the chemical composition of BS and LS used in the present work is also reported. EAF-S compositions strongly depends on its origin: BS is rich of Fe_2O_3 and mainly contains CaO, SiO_2 , Al_2O_3 , MnO as other constituents; LS has higher content of CaO, SiO_2 , Al_2O_3 and lower Fe_2O_3 than BS, according to the process occurring in the ladle. Both BS and LS differ from the chemical composition of ground granulated blast furnace slag ($CaO \approx 36-42$, $SiO_2 \approx 35-39$, $Al_2O_3 \approx 8-12$, $MgO \approx 4-12$ wt%) normally used for the production of blast furnace cement (CEM III) thanks to its hydraulic properties.

The mineralogical composition of BS and LS agrees with the chemical analysis above reported. In fact the main phase present in the both typologies is dicalcium silicate (C_2S). In particular, the XRD spectrum of BS shows sharp peaks characteristic of crystalline phases, and a broad band (2θ : 20-30°) indicating the existence of an amorphous phase. The crystalline phases identified were: silicates, such as Ca_2SiO_4 Larnite, syn (β - C_2S) (ICDD # 33-302), $Ca_2(Al,Fe)_2O_5$ Brownmillerite, syn (ICDD # 30-226) and $MnSiO(SiO_4)$ Manganese Silicon Oxide Silicate (ICDD # 188-1232), iron oxides, such as FeO wustite (ICDD # 6615) and Fe_3O_4 magnetite (ICDD # 19-629) and iron silicates as $(Mg,Fe)_2SiO_4$ Wadsleyite (ICDD # 37-415). By XRD, the presence of MgO as periclase in BS was not detected. The XRD spectrum of LS highlighted the presence of calcium-magnesium-aluminium silicates as Ca_2SiO_4 Olivine (γ - C_2S) (ICDD # 180-941), $Ca_2(Al(AlSi)O_7)$ Ghelenite (ICDD # 174-1607), $Ca_{12}Al_{14}O_{33}$ Mayenite, syn (ICDD #170-2144) and iron silicates as $(Mg,Fe)_2SiO_4$ Wadsleyite (ICDD # 37-415) and Iron Magnesium Calcium Silicate (ICDD #172-1915). Traces of CaS Oldhamite, coming from the desulfuration process, MgO as periclase and $Ca(OH)_2$ were determined. Both BS and LS XRD spectra are not reported for brevity's sake.

Mineralogical analysis of BS and LS agrees with the crystalline phases analysis reported in the literature for the same kind of slag after weathering [Frías Rojas et al. 2004; Setién et al. 2009]: for BS the amount of free CaO and MgO is very low (< 0.5%), then the delayed formation of expansive products is not expected. In LS the traces of periclase and portlandite, detected by XRD, suggest a higher content of the two oxides: for this reason a soundness test was carried out and the results are reported below.

As the aim of this work is to study if BS and LS can be suitable adopted as aggregate or cement constituent in mortar mix-design, chemical parameters such as chloride and sulfate content were determined following the procedures required for cement and aggregates by European/Italian standards (Table 3 and Table 4). Moreover, physical (initial setting time, soundness) and mechanical (compressive strength) properties were determined for the LS based binder and compared with those exhibited by OPC-CEM I 52.5 R (Table 5 and Table 6). Chemical parameters of BS and LS fulfill the limits set by the standards. Moreover, the LS based binder exhibits a physical behavior very similar to that of CEM I 52.5 R. Soundness test carried out with Le Chatelier apparatus in accelerated curing conditions is very important to establish if the amount of free CaO and MgO in the binder promotes the formation of expansive products. For the LS based binder here investigated such expansion is negligible and below the limit of EN 197-1.

Table 2. Chemical composition of BS and LS (oxide wt%)

	BS range (wt %)	BS investigated (wt %)	LS range (wt %)	LS investigated (wt %)
Fe ₂ O ₃	32 – 43	32.68	2 – 3	3.85
MnO	4 – 6	4.60	0.05 – 0.50	0.32
CaO	32 – 44	37.98	41 – 66	55.24
K ₂ O	0.03 – 0.05	0.23	0.04 – 0.2	0.22
Al ₂ O ₃	3 – 10	6.98	17 – 20	13.69
P ₂ O ₅	0.2 – 0.4	0.40	-	0.10
TiO ₂	0.3 – 0.7	0.32	0.04 – 0.2	0.20
MgO	2.0 – 4.5	3.65	2.2 – 7.7	3.22
SiO ₂	12-16	15.18	20 - 25	23.85
V ₂ O ₃	0.09 – 0.5	0.13	-	0.01

Table 3. Chemical properties of LS and CEM I 52.5 R (average of 2 measurements)

	LS	CEM I 52.5 R	Limits set by EN 197-1 for cement
Chloride (wt %) EN 196-2	0.01	0.04	≤ 0.1
Sulfate (SO ₃ wt %) EN 196-2	0.38	0.65	≤ 3.5
Loss of Ignition (wt %) EN 196-2	2.69	3.61	≤ 5.0

Table 4. Chemical properties of BS (average of 2 measurements)

	BS	Limits set by UNI 8520-2 for aggregates
Chloride (wt %) EN 1744-1	0.03	≤ 0.03
Sulfate (SO ₃ wt %) EN 1744-1	0.20	≤ 0.2 ≤ 0.8
Total Sulfur (wt %) EN 1744-1	0.20	≤ 1.0 ≤ 2.0

Table 5. Physical properties of CEM I 52.5 R and LS based binder (average of 2 measurements)

Binder	100% CEM I 52.5 R	75% CEM I 52.5 R + 25% LS	Limits set by EN 197-1		
			32.5 R	42.5 R	52.5 R
Initial Setting Time (min)	107	106	≥ 75	≥ 60	≥ 45
Soundness (mm)	0.2	0.4	≤ 10	≤ 10	≤ 10

As far as concern mechanical requirements, Europeans standard EN 197-1 sets for each kind of cement a division based on cement mechanical strength (32.5, 42.5 and 52.5 N/mm² determined at 28 days of curing). However, it has been recently considered necessary to separate common cement (OPC, lime OPC, etc.) from special cements, that are those binders having hardening process not mainly dependent on the hydration of calcium silicate. Accordingly, EN 197-4 has been issued in 2004: this standard defines and gives the specifications of three distinct low early strength blast furnace cements. For this reason the compressive strength of LS based binder samples has been compared with the reference mortar MREF and the limits proposed by both EN 197-1 and 197-4. The data, reported in Table 6, highlight that compressive strength of MLS is higher at all curing time than the limits required for a 42.5 R cement, regardless its nature (common or special cement). However, MLS exhibits lower mechanical performances than those prescribed for a 52.5 R cement: in fact at 2 days of curing S_c for MLS is greater than the limit set by EN 197-4, but lower than the limit set by EN 197-1, and at 28 days S_c does not reach the threshold value of 52.5 MPa.

Table 6. Compressive strength at 2, 7 and 28 days of curing and relevant limits by EN 197-1 and 197-4

Sample	MREF	MLS	Limits set by EN 197-1 and EN 197-4		
			32.5 R 32.5 L	42.5 R 42.5 L	52.5 R 52.5 L
Compressive Strength @2days (MPa)	40.4	27.0	≥ 10 n.s.	≥ 20 n.s.	≥ 30 ≥ 10
Compressive Strength @7days (MPa)	59.4	42.1	n.s. ≥ 12	n.s. ≥ 16	n.s. n.s.
Compressive Strength @28days (MPa)	63.2	50.4	≥ 32.5 ≥ 32.5	≥ 42.5 ≥ 42.5	≥ 52.5 ≥ 52.5

Figure 3 reports flexural and compressive strength as a function of curing time for MLS and reference samples MREF. The cement substitution by LS leads to lower mechanical properties than those of M-REF; moreover, MLS performances do not change extending the curing time up to 90 days, whereas MREF samples still develops mechanical strength. The behaviour detected for MLS samples suggests that LS is not chemically involved in the hardening process, however it collaborates in mortar strengthening thanks to a filler effect. Water absorption data (Table 7) confirm mechanical measurements: MLS shows WA% higher than MREF at all the investigated curing times, thus indicating a larger open porosity for LS based samples.

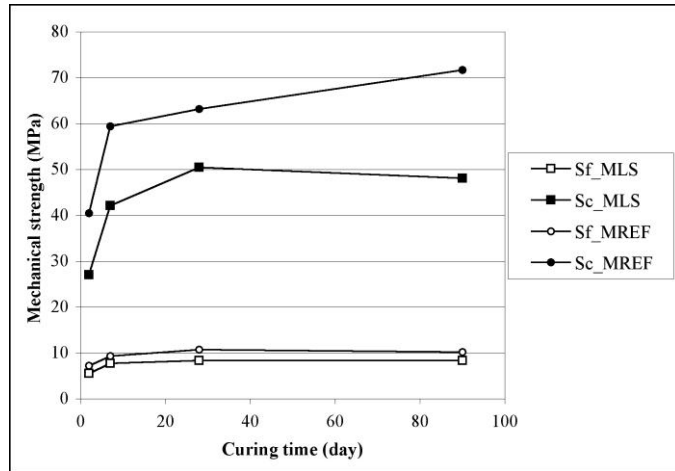


Fig. 3. Mechanical properties of mortars MLS and MREF (□, ○ flexural strength; ■, ● compressive strength)

The mechanical properties of MBS samples at 7 and 28 days of curing are reported in Figure 4 as function of BS content replacing the normalized sand. Both the compressive and flexural strength increase with BS and curing time, thus indicating that BS amount does not interfere with cement hydration reactions. However, analyzing water absorption measurements of MBS samples reported in Table 7, it is evident that the introduction of black slag leads to an increase

in the porosity sample. MBS mortar exhibit a WA% of about 8.4% and this value slightly increase with BS content. The porosity of MBS can be ascribed to the shape of black slag: accordingly workability reduction was registered at the fresh state with the increasing content of BS in mortar mix-design.

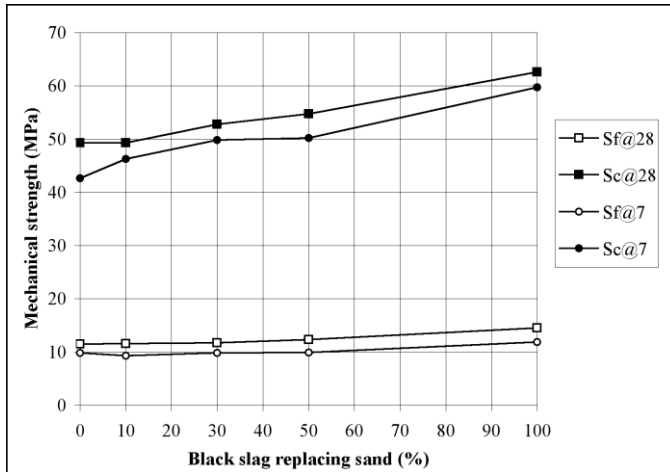


Fig. 4. Mechanical properties of mortar samples containing BS as sand replacement
Table 7. Water absorption (WA%) of MLS, MBS and MREF samples at different curing time

Sample	Curing time (day)	WA (%)	Sample	Curing time (day)	WA (%)
MLS@2	2	7.4	MBS-100	7	8.6
MLS@7	7	7.3	MBS -50	7	8.4
MLS@28	28	7.6	MBS -30	7	8.4
MLS@90	90	7.5	MBS -10	7	8.3
MREF@2	2	6.7	MBS -100	28	9.1
MREF@7	7	6.4	MBS -50	28	8.5
MREF@28	28	6.6	MBS -30	28	8.6
MREF@90	90	6.2	MBS -10	28	8.5

Figure 5 shows two SEM images of the slag based mortar samples: for MBS-100 cured at 28 days (Figure 5a), a black slag particle used as sand is clearly visible as well as the absence of a continuous phase between slag and cement paste. Such separation is consistent with previous data. For MLS cured at 90 days (Figure 5b), no separation occurs between silica sand and LS based paste, however a large number of pores of about 10 μm size are evident all over the matrix. More investigations are currently running to analyze the chemical composition of the LS-cement matrix with the aim to assess if LS works only as filler or, somehow, is chemical reactive.

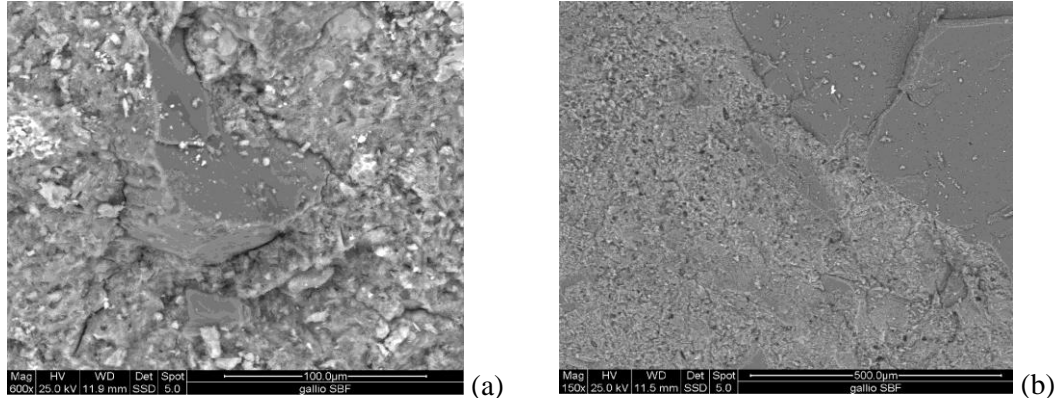


Fig. 5. SEM observations on slag based mortar samples: (a) MBS-100 cured at 28 days; (b) MSL cured at 90 days

CONCLUSIONS

The main conclusions from the experimental work carried out can be as follows:

- From a chemical and physical point of view, the investigated black and ladle slags are suitable to be used in cement conglomerates as sand and cement replacement, respectively. The exposition to outdoor environment during their storage in the industrial plant for a period of about 3 months is enough for both the slag types to avoid delayed formation of expansive products in their future applications.
- Mechanical performances of slag based mortar samples are promising, however both BS and LS increase the total open porosity of the specimen.
- LS does not seem chemically reactive: its contribute to mortar strengthening is limited to a filler effect. Indeed, more investigations are necessary to analyze the chemical composition of LS-cement hardened phase.
- From the current study, the possibility to realize unconventional building materials based on electric arc furnace slag coming from the same industrial plant appears feasible, but with some drawbacks that need to be controlled and, when possible, overcome.

ACKNOWLEDGEMENTS

Acciaieria di Rubiera S.p.A. (RE, Italy) is kindly acknowledged for the financial support to the research.

REFERENCES

- EN 196-1. "Methods of testing cement - Part 1: Determination of strength." *CEN European Committee For Standardization*, Brussels, Belgium, 35 pages.
- EN 196-2. "Methods of testing cement - Part 2: Chemical analysis of cement." *CEN European Committee For Standardization*, Brussels, Belgium, 52 pages.
- EN 196-3. "Methods of testing cement Part 3: Determination of setting times and soundness." *CEN European Committee For Standardization*, Brussels, Belgium, 18 pages.

- EN 197-1. "Composition, specifications and conformity criteria for common cements." *CEN European Committee For Standardization*, Brussels, Belgium, 52 pages.
- EN 197-4. "Composition, specifications and conformity criteria for low early strength blastfurnace cements." *CEN European Committee For Standardization*, Brussels, Belgium, 20 pages.
- EN 1744-1. "Tests for chemical properties of aggregates. Chemical analysis" *CEN European Committee For Standardization*, Brussels, Belgium, 46 pages.
- EPA. (2009). Inventory of U.S. greenhouse gas emissions and sinks: 1990 – 2007, EPA 430-R-09-004.
- EWC (European Waste Catalogue). < <http://www.environment-agency.gov.uk/>>.
- Frías Rojas, M., Sánchez de Rojas, M. I. (2004). "Chemical assessment of the electric arc furnace slag as construction material: Expansive compounds." *Cement and Concrete Research*, 34(10), 1881-1888.
- Kourounis, S., Tsivilis, S., Tsakiridis, P.E., Papadimitriou, G.D., and Tsibouki, Z. (2007). "Properties and hydration of blended cements with steelmaking slag." *Cement and Concrete Research*, 37(6), 815-822.
- Muhmood, L., Vitta, S., and Venkateswaran, D. (2009). "Cementitious and pozzolanic behavior of electric arc furnace steel slags." *Cement and Concrete Research*, 39(2), 102-109.
- Rodriguez, A., Manso, J.M., Aragón, A., and Gonzalez, J.J. (2009). "Strength and workability of masonry mortars manufactured with ladle furnace slag." *Resources, Conservation and Recycling*, 53(11), 645-651.
- Setién, J., Hernández, D., and González, J.J. (2009). "Characterization of ladle furnace basic slag for use as a construction material." *Construction and Building Materials*, 23(5), 1778-1794.
- Shi, C. (2002). "Characteristics and cementitious properties of ladle slag fines from steel production." *Cement and Concrete Research*, 32(3), 459-462.
- UNI 8520-2. "Aggregates for concrete. Additional provisions for the application of EN 12620. Part 2: Requirements." *UNI Ente Nazionale Italiano di Unificazione*, Milano, Italy, 14 pages.