

The use of steelmaking slags and fly ash in structural mortars

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Abstract

The main objective of this work is to produce structural slag mortars of good mechanical strength and workability, while reducing the consumption of Portland clinker, the production of which is a growing source of environmental concern. In this context, the study looks at the preparation of these mortars with steelmaking slags (electric arc furnace slag, ladle furnace slag) in partial substitution of conventional aggregates, and as supplementary cementing materials, and the use of Portland cement that includes a notable proportion of fly-ash. A detailed examination of the characteristics of eight mortar mixes is described. Structural and mechanical analyses are performed on the mixes, to study the role of water-reducer and air-entrainment admixtures; also, shrinkage contraction and other volumetric variations of the mixtures are measured and evaluated. The long-term behavior of these slag mixes appeared acceptable, thereby opening a promising line of work that will eventually establish suitable conditions for their use. The strength-to-weight ratio of these mortars is encouraging although uncertainty persists over the use of air-entrainment admixtures and ladle furnace slag.

Introduction

The production of steelmaking slags around the world is increasing over time, despite the onset of the economic crisis. It is, therefore, essential to conduct research into applications for this by-product, to reduce its dumping in landfill sites and the production of excessive volumes of waste. By doing so, there would be less extraction of the natural resources that are necessary in those applications, which may otherwise be substituted by slags [1-3].

Several slag types may be listed in this context: blast furnace slag (BFS), basic oxygen-furnace slag (BOS), electric arc-furnace oxidizing slag (EAFS), ladle-furnace basic slag (LFS), argon-oxygen-decarburization slag (AODS), cupola-furnace slag (CFS), open-hearth furnace slag (OHS) and primary desulfurization slag (DS); and even milling scales (MS) [4, 5]. There are at present many research groups studying suitable and reliable applications for each slag type. The construction and building sector will undoubtedly employ most of these by-products [6-17].

Among the aforementioned slag types, BFS and CFS have the highest quality, which after rapid cooling and grinding show good hydraulic properties and excellent durability; the problems arising from their use are almost non-existent [18-21]. Although the performance of EAFS and LFS is less satisfactory [22-40], the objective of this present study is to demonstrate their successful application in several fields [41-60]. The most problematic slag type was obtained from the LD furnace (BOFS), the volumetric expansion of which was far from satisfactory [61-63].

Studies into the application of EAFS and LFS in hydraulic mixes, mortar and concrete, have been conducted by research teams throughout the world. Several groups may be found in the EU [46, 64-82], in Asia and in both South [83, 84] and North America [85, 86]; nevertheless, Asia is the continent with the largest number of such research teams, in both the Middle East [87-91] and the Far East [92-99].

In general, the use of these slags (EAFS and LFS) when applied as aggregates in hydraulic mixes has been relatively successful; the observation of hydraulicity is scarce and requires high particle fineness [100-103]. It is logical, at first, to give little or no consideration to the hydraulic factor in EAFS, the natural presentation of which is in the form of gravel. In contrast, a slight hydraulicity may be analyzed in the LFS, which is presented in the form of dust. The long-term behavior of the mixes obtained with these slags appears acceptable [67, 69, 70, 77, 79], which has opened a promising line

of research that will establish suitable conditions for its use. Several research groups in the EU (from Greece, Italy, Belgium, Germany and Spain) are in contact with the intention of establishing pre-normative rules for the use of these two slag types (EAFS and LFS) in mortar, concrete and bituminous mixes, including particular mixes as self-compacting concrete (EAFS), sprayed concrete (shotcrete) and self-leveling mortar (LFS).

The present work analyses the characteristics of several structural mortars in which these slags are used as aggregates (EAFS and LFS) and SCM (LFS) and it assesses the slight potential hydraulicity of the LFS. The main objective is to obtain good mechanical strength and suitable workability, so as to minimize the use of Portland clinker. Mortar density, due to the high specific weight of EAFS, and its durability are the most important factors to be taken into account; the role of the admixtures (fluidifying, water reducer and air-entrainment) is also thought to be essential. Shrinkage or volumetric contraction is an also relevant characteristic of these mortars, the study of which is necessary to obtain high-quality structural mixtures that contain steelmaking slags.

Materials

Water, cement and natural aggregates

Mains water, containing negligible levels of compounds that can negatively affect the preparation of mortar mixes, was taken from the urban supply of the city of Bilbao.

A Portland cement type IV/B-V 32,5-N, as per UNE-EN 197-1 standard [104] was used in the mixes, the chemical composition of which is shown in Table 1. Its low hydration heat and particle fineness is common in ordinary cements. Only a half of the binder is Portland clinker as its composition by weight of cement comprises 5% of calcium carbonate fines, 40% of fly ash type I, and 50% of Portland clinker, milled with 4% of gypsum.

	Cement IV/B-V	EAFS	LFS
Fe ₂ O ₃ (%)	3.9	22.3	1.0
CaO (%)	45.5	32.9	59.2
SiO ₂ (%)	28.9	20.3	21.3
Al ₂ O ₃ (%)	12.6	12.2	8.3
MgO (%)	1.8	3.0	7.9
MnO (%)	0.1	5.1	0.26
SO ₃ (%)	3	0.42	1.39
Cr ₂ O ₃ (%)	-	2.0	--
P ₂ O ₅ (%)	0.45	0.5	--
TiO ₂ (%)	0.65	0.8	0.17
Loss on ignition (%)	5.8 (C+CO ₂ +H ₂ O)	gain	0.5
Porosity (%)		2.6	--
Water absorption (%)		As-sand 3.51 / Fines 1.12	--
Blaine fineness (m ² /g)	0.385		0.138
Hydration heat (cal/g)	52 (at 7 days)		
Specific gravity (Mg/m ³)	3.07	As-sand 3.24 / Fines 3.54	3.03
X-Ray diffraction main compounds		Wüstite-Ghelenite- Kirsteinite, Ca-Mn- Oxide	Periclase-Olivine- celite

Table 1: Chemical composition (XRF) and other physical properties (EN-12620) of cement and aggregates

A natural siliceous fine aggregate of washed sand (SS) from Arija – Burgos, sized between 0.1 and 0.3 mm and with a fineness modulus of 0.47, was used. The quartz particles were rounded, with a specific gravity of 2.63 Mg/m³.

A commercial crushed natural-limestone aggregate (LS), of a size within the range of 0 and 5 mm was used in the mixes. The presence of calcite (95%) was detected as the main mineral. The specific gravity of the LS was 2.67 Mg/m³. Its size grading is represented in Figure 1, the fineness modulus of which was 2.9.

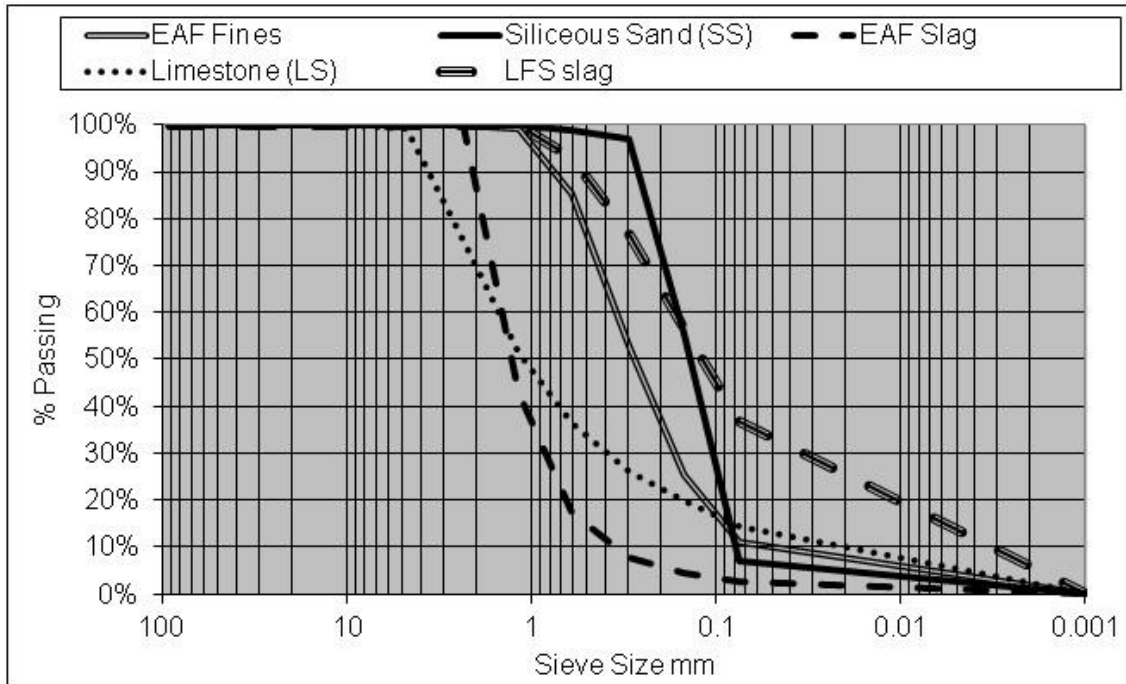


Figure 1: Grading curves of limestone sand (LS), EAF slag (two sizes), siliceous sand (SS) and LF slag.

Electric arc furnace slag

Crushed electric arc furnace slag was supplied by Hormor-Zestoa for use in this research work. Its global chemical composition and physical properties are detailed in Table 1 and its size grading is represented in Figure 1. The fineness modulus of the fine fraction (EAF Fines, EAF Fines) was 1.4, of a size smaller than 1 mm; the fineness modulus of the as-sand fraction (EAF Slag, EAF Slag) was 3.3, with sizes of between 0.2 and 2.3 mm.

The factors that influence EAF slag density are its internal porosity (occluded gas), the proportion of iron and manganese oxides (with a density higher than 5 Mg/m^3) and the metallic iron content (lower than one per ten thousand parts); its density was 3.24 Mg/m^3 in the as-sand fraction, and 3.54 Mg/m^3 in the fine fraction. X-ray diffraction analyzed the main crystalline components of the slag, also shown in Table 1. There was no noticeable presence of free lime or free magnesia; scarce amounts of uncombined free silica, with gehlenite, kirschsteinite and wüstite as the main compounds of the EAF Slag.

Ladle furnace slag.

Of the two main types of ladle furnace slag produced in the steelmaking industry (silica-saturated and alumina-saturated), a high-silica low-alumina LFS was used, the chemical composition and X-ray diffraction analysis of which is shown in Table 1. Its main compound is gamma-dicalcium silicate. Following spontaneous disintegration during cooling, it was kept dry and protected from external weathering in individual plastic bags. Its grading with a fineness modulus of 0.75 is shown in Figure 1. The Blaine specific surface was measured at $0.138 \text{ m}^2/\text{g}$.

This LFS contained free magnesia (periclase) and dicalcium silicate, as shown by XRD. It also contained an amount of around 15-20% of calcium aluminates (celite, mayenite), both potentially reactive in the presence of water, which produced hydrated-calcium-aluminates that slightly improved the mechanical strength of the mixes. The authors of this article have previously reported in [75] that roughly 30% of the mass of this slag type may be treated as supplementary cementitious material (SCM).

A previous work by the authors on the same LFS [105] established that the contents in potentially expansive compounds were 7% by weight of free-MgO and 6% by weight of free-CaO. The presence of typical sulfide compounds in the basic slag, such as olhamite-jasmondite, susceptible to oxidization, were also observed as well as their conversion to calcium sulfate at high temperature (see Figure 2, peak at 920°C , oxygen mass gain of 1.5%). This conversion can also happen more slowly at room temperature; subsequently, calcium sulfate is susceptible to produce secondary ettringite in the hardened state, with catastrophic results. Undoubtedly, the use of this kind of slag in hydraulic mixes is a notable risk and should be done in a controlled manner; the high amount of LFS used in some mixes of this work must be qualified as imprudent, as the global content of expansive compounds reached 4.4% (e.g. in M5).

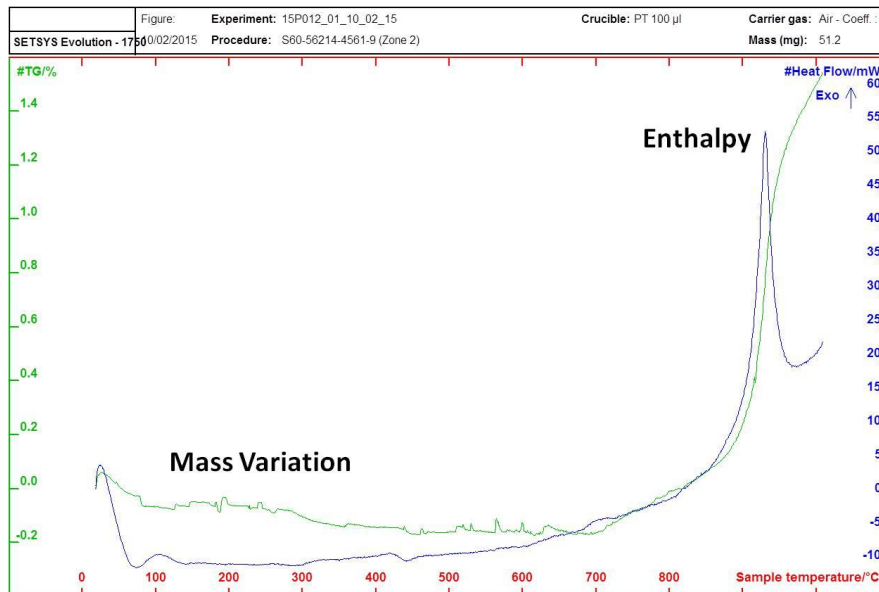


Figure2: Thermo-gravimetric curves of LFS slag.

Fresh Mixes

A water-cement-aggregate ratio of 1:2:6 ($w/c=0.5$), the classical in-weight proportions for structural mortars, was fixed for the reference mix (M1). The proportions of Portland clinker plus fly ash were 1:1.1+0.8:6.1. The reference aggregate was quarry-crushed limestone rock sized 0-5 mm (LS); hence, the proportions 1:1.9:6.1 were changed by volume to a ratio of 1:0.6:2.4 or roughly 25:15:60%.

Subsequent volumetric substitutions of the reference aggregate LS by other materials was done in an attempt to conserve (with limited success due to variations in porosity) the volumetric ratio matrix-aggregates in all the mortars; in doing so, seven additional mixes were prepared. The materials for the substitution were: siliceous sand (SS), electric arc furnace slag (EAFS), fine electric arc furnace slag (EAFF) and ladle furnace slag (LFS) in various combinations. It have to be taken into account the hydraulicity of the LFS; it is partially considered as an aggregate (70%), the rest of its amount (30%) have to be considered as SCM and replaced the Portland cement.

Two admixtures, a fluidifying-water-reducer and an air-entrainment agent, were used, the first of which to enhance the workability of all the mixes to obtain fluid mortars, and the second to introduce a controlled amount of air bubbles in the mass, thereby decreasing the density slightly. The workability objective was a runoff-slump on the flow table of over 170 mm; mixes M3, M4, M5 failed to reach this value, showing a typical loss of workability when the two kinds of slag (EAFS and LFS) were used. The shape and the superficial texture of EAFS fine particles (sharp, rough) are not

conducive to good workability, and the substitution of this slag in place of the natural aggregate leads to losses in the spreading of mixes, mainly in mix M3. On other hand, the effect of the air-entrainment admixture on entrained air was low in mixes containing LFS[98], as may be observed from the lower than expected values of M4 and M5; the other mixes behaved as expected.

Table 2 and Figures 3a and 3b show the composition and grading of the eight mixes. M1, M2 and M5 (Figure 3a) were mixes without EAFS, the proportioning of which were intended to fit the Fuller’s curve; the rest of the mortars contained EAFS and their grading curves were in general well-adjusted to the recommended ASTM C33 [106] interval, as shown in Figure 3b.

The mixtures were cast and kept in prismatic moulds for one day; they were then demolded and submerged in water until their corresponding tests. Two different kinds of prismatic moulds were employed: the standard 40x40x160 mm size for the measurement of both strength and physical properties (18 sample moulds from each mix), and special 25x25x250 mm size specimens (4 from each mix) to monitor dimensional variations (shrinkage-expansion).

Mortar	Components								
	Water	Cement IV/B-V	LS	SS	Aggregates			Admixtures	
					EAFS	EAFF	LFS	WR	AE
M1	257	513	1540	-	-	-	-	4	-
M2	257	513	1078	462	-	-	-	4	5
M5	257	289	1078	-	-	-	749	6	5
M3	257	513			747	1121		4	-
M3air	257	513	-	-	747	1121	-	5	5
M4	257	326	-	-	747	747	500	8	5
M6	257	513	308	-	747	747	-	4	5
M7	257	513	308	308	561	561	-	5	5
M8	257	513	-	616	1121	-	-	5	2.5

Table 2: Mix proportioning in kg per cubic meter of reference mortar.

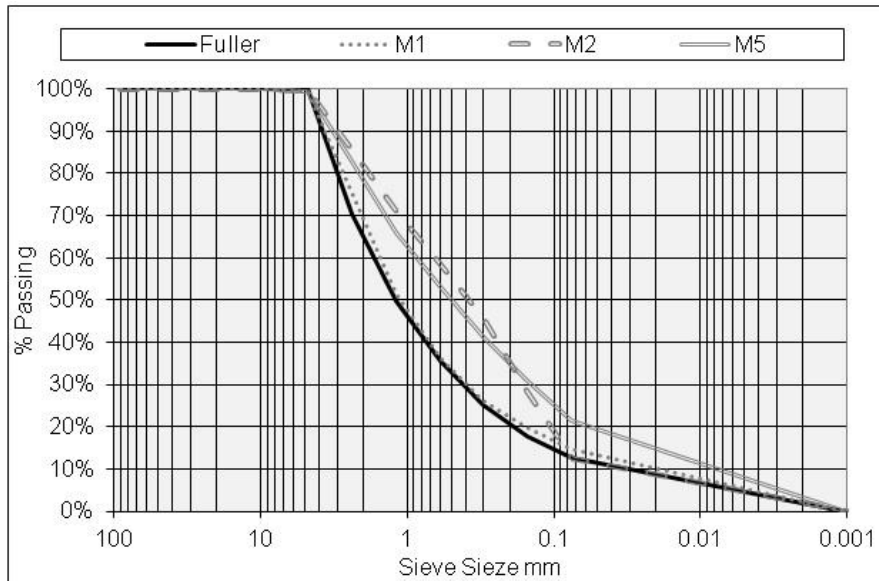


Figure 3a: Fuller curve & grading of mixes 1, 2, and 5.

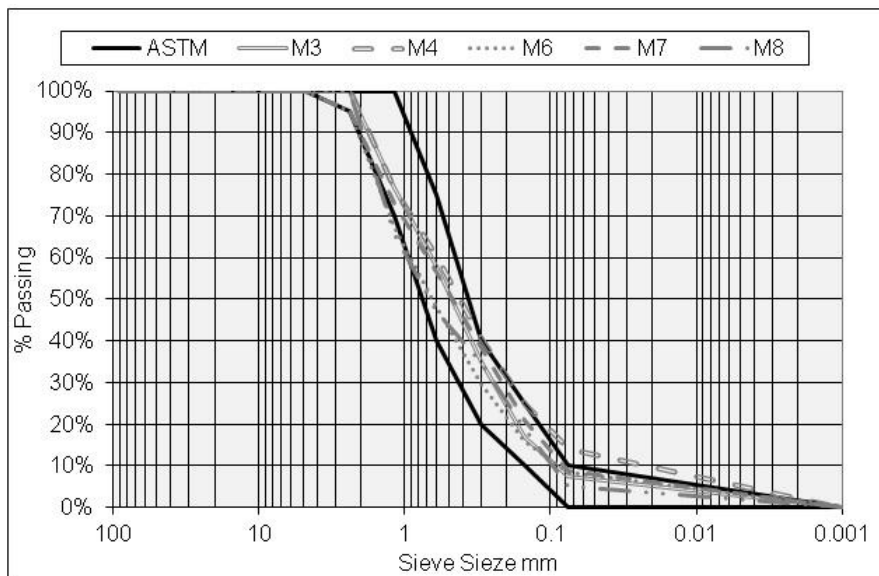


Figure 3b: ASTM C33 range and mixes 3,4,6,7,8

Physical characterization: density and porosity

The bulk density of the mixes was evaluated by the conventional measurement of in-air and submerged weight; additionally, the porosities and densities were evaluated by Mercury Intrusion Porosimetry (MIP). The results of these measurements and of the entrained air are shown in Table 3.

It should be noted that the MIP porosity in mixtures containing LFS and EAF slag (3-4-5-6-7-8), in which the accessible-to-mercury porosity of both slags is added to the capillary porosity of the cementitious matrix, should be higher than the others (1-2)

ceteris paribus (all other variables being similar). Figures 4a and 4b show the MIP-graphs for mixes M2 (usual capillary pore-size distribution in mixes 1-2-3-6-7-8) and M5 (exceptional capillary nano-pore size distribution due to inclusion of LFS, shown by M4 and M5, see also the size range in the third column of Table 3).

MIP porosity increased to values of over 20% in the EAFS mixes with 5% of an air-entrainment admixture (M3air, M6 and M7), except in mixtures M4 and M5. In these last two, it was observed that the presence of LFS “mitigated” the effect of this air-entrainment admixture, and changed the pore-size distribution due to the size of its own porosity, as shown in Figure 4b. The global MIP porosity amount for mixes M4 and M5 was a result of those two circumstances.

The apparent density measured by MIP revealed the presence and amount of heavy EAF slag; in fact, the resultant value of 3.11 Mg/m³ is fairly accurate in mixture M3 with 70% by occupied volume of EAF slag (average density value 3.4 Mg/m³) and 30% by occupied volume of hardened cementitious matrix (average density value 2.4 Mg/m³). Similar calculations can be applied to mixes M4-M6 (about 60% in volume of EAF, density value 2.98) and in the set M7-M8 (45% by volume of EAF, values 2.83-2.86). Moreover, the values of bulk density measured by MIP and by the conventional on-air/submerged method to assess the sample specific weight are quite coherent.

Mix	Porosity MIP % vol	Nano-Pores MIP size range	Bulk/Apparent density by MIP Mg/m ³	Bulk Density classical Mg/m ³	Fresh Density Mg/m ³	Air entrained % volume	Workability Spreading in mm
M1	13.1	5-80nm	2.22/2.56	2.22	2.30	2.1	175
M2	17.7	10-70 nm	2.04/2.49	2.03	2.14	8.2	180
M5	19.3	5-500nm	2.05/2.54	2.03	2.17	4.6	140
M3	16.7	5-60nm	2.59/3.11	2.60	2.72	3	115
M3air	27.6	10-60nm	2.25/3.11	2.21	2.36	7.3	130
M4	19.2	10-500 nm	2.41/2.98	2.39	2.52	4.1	160
M6	24.1	6-90nm	2.26/2.98	2.24	2.38	6.8	170
M7	25.7	5-60nm	2.10/2.83	2.06	2.21	7.1	170
M8	16.9	5-90nm	2.38/2.86	2.37	2.47	3.5	175

Table 3: Density and porosity of mixtures by MIP, and fresh properties.

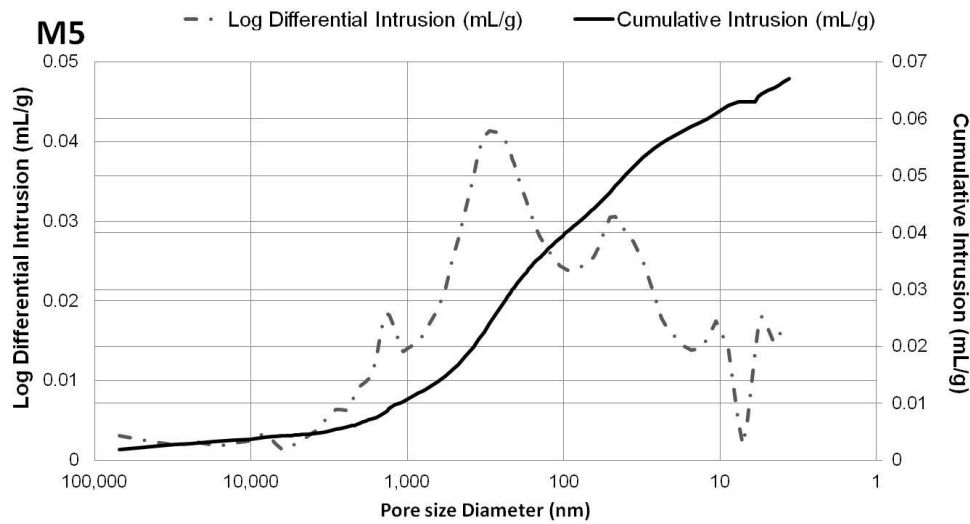
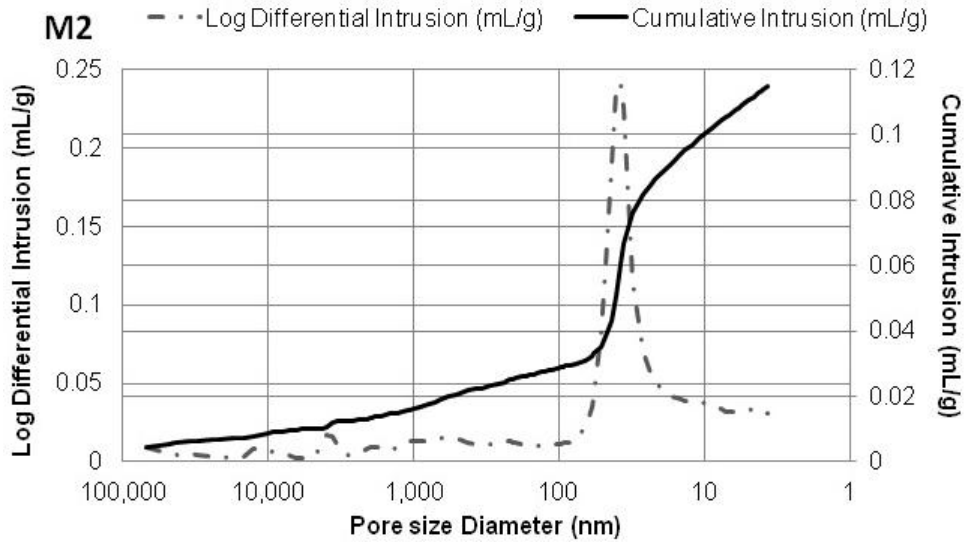


Figure 4: MIP pore size distribution in mixes M2 (4a) and M5 (4b).

Mechanical properties: compressive and flexural strength, stiffness

The time period of strength measurement for mixes based on type IV/B-V 32.5N cement with a high content (40%) of fly ash, a material of slow pozzolanic reactivity, extends to one year. For most engineering applications, long-term strength is not very relevant, although it is worth noting that when FA was used, long-term strength measurements were more suitable, due to the different evolution of strength over time. Additionally, it should be considered that most of the mixes contained only 280 kg of clinker and gypsum per cubic meter of fresh mass.

Two groups of mixes were prepared in this study: EAF slag and non-EAF slag mortars. The general trend stated in the scientific literature is once again very clear in this

research: mixtures containing EAF slag showed higher mechanical properties than comparable mixes containing natural aggregates. In fact, reference mixture M1 yielded good results in short and long-term tests, but mixture M3 was the strongest. Likewise, we may compare M4 versus M5, and M8 versus M2.

The poorer results of EAFS mixes M3air, M6 and M7 were evident; the porosity values (MIP and entrained air, Table 3) were too high and their mechanical properties decreased. The efficacy of the air-entraining admixture in the presence of EAFS was good in relation to density (15% lower in M3air than in M3) but detrimental in relation to strength (loss of 43%). Hence, its use must be reconsidered or seriously limited in structural mixes.

The good results for the long-term strength of mixes M4 and M5 that contained LFS confirms the role of LFS in enhancing the mechanical properties. We should remember that mix M4 contained EAF slag and 175 kg (53% of 326 kg) of clinker plus gypsum and that mix M5 contained 150 kg of clinker per cubic meter. Their poor short-term results may be noted, see strength at 3 days; the effect of both SCM (fly ash and LFS) was more evident after 28 and 90 days.

Mix M8 yielded good strength; its density (including an outstanding proportion of EAFS, 45% in volume) was only 6% higher than the reference mortar M1, with a 5% lower long-term strength. Finally, the results obtained for the M2 mix were as expected, on account of its characteristics.

The flexural strength of the mixes was varied and, in general, close to the compressive strength, but the value for mixtures M3 M4 and M8, containing EAFS, was remarkable. These better values shown in Table 4 show that EAF aggregate also had a favorable effect on this relevant property of structural concrete. Previous research [79] arrived at the same result, justifying it in terms of slag morphology, rough texture, and the different matrix-aggregate interfaces, which may create stronger links between binder and aggregate.

Ultrasonic pulse velocity, V , was used to estimate the stiffness in accordance with the formula [107]:

$$E = V^2 \frac{(1 + \nu)(1 - 2\nu)}{1 - \nu} \quad \text{usually } \nu = 0.2 \text{ in concrete}$$

The estimated stiffness values (not valid as Young's modulus) after 360 days are shown in Table 4; as usual for concrete, they correlate with the other mechanical properties. It is worth remarking that the stiffness values in mortars containing EAFS and LFS were lower than those of the reference mixes when the compressive strength was similar or comparable. This result was observed by authors in a previous work [46] and is probably explained by the fact that EAFS gravel stiffness is lower than that of natural aggregate stiffness, due to its internal porosity and the presence of iron oxides which have low rigidity.

	FLEXURAL STRENGTH (MPa)						COMPRESSION (MPa)						Stiffness E (GPa)
	3 Day	7 Day	28 Day	90 Day	180 Day	360 Day	3 Day	7 Day	28 Day	90 Day	180 Day	360 Day	
M1	4.52	7.78	8.17	9.01	9.49	9.84	18.93	28.01	39.71	57.59	63.70	68.2	41.1
M2	4.60	6.59	9.13	9.29	9.28	10.5	18.86	26.05	40.79	45.69	49.1	49.3	31.3
M5	1.64	3.37	6	6.53	8.09	9.59	6.13	18.23	35.39	42.2	48	49.2	28.6
M3	5.50	7.07	9.56	11.3	11.7	12.2	25.51	33.56	49.10	64.70	74.41	78.3	41.8
M3air	3.95	5.34	5.46	8.42	9.04	9.28	13.58	18.66	26.83	36.68	42.65	46.9	25.6
M4	1.34	3.62	5.16	9.34	10.2	11.3	3.66	13.33	29.98	52.26	58.1	61.7	32
M6	4.0	5.04	6.48	7.87	9.05	9.68	13.39	17.93	28.82	37.22	45.02	50.7	28.4
M7	4.98	5.12	6.43	7.35	7.97	8.16	17.25	19.97	27.00	32.74	37.8	41.7	25.2
M8	4.52	5.73	7.65	10.4	10.8	11.2	17.15	24.32	36.29	53.59	62.58	64.9	37.4

Table 4: Mechanical tests results

Analysis of physical and mechanical results

Reference mixture M1 is an excellent model for a comparison of aggregate packaging, because its grading adjusts quite well to Fuller's curve (see Figure 3a) for a maximum aggregate size of 4.75 mm; hence, the MIP capillary porosity was low (13.1%). Air represents only 2.1% in volume due to the high fluidity of the mixture as seen in Tables 3 and 4.

In Figure 3a, mixture M2, in partial substitution of the limestone in M1 by siliceous sand showed a worse fit with Fuller's curve. The use of an air-entraining admixture increased the air content and the MIP porosity and slightly decreased the density and, more remarkably, the mechanical strength; the benefit of the air-entrainment admixture is uncertain. Mixture M5 included LFS and limestone sand (LS), so as to observe the influence of the ladle furnace slag, considered a partial binder (SCM). Its aggregate grading adjusted poorly to the Fuller curve in the fines zone (sieve #200) and both its air content and its MIP porosity were low. As a result, its mechanical strength was similar to M2, despite the lower clinker content, so the long-term hydraulicity of

the LFS and its interaction with the fly ash in the cement should be considered positive. The role of LFS fines in relation to workability was considered negative.

Mixture M3 included EAFS in two sizes, as-sand (EAFS) 0.2-3 mm, and fines (EAFF) <1mm; this mixture of aggregate sizes meets the ASTM C33, as shown in Figure 3b. Despite the use of admixtures it showed poorer workability (the lowest slump) than the reference mix M1 and excellent mechanical properties. The entrained air in M3 was expected, due to low fluidity during its mixing. The fresh density of the M3 mortar decreased from 2.72 to 2.36 (13%) and its workability was improved by air-entraining admixture in the M3air mixture; the efficiency of the air-entraining admixture was good in the presence of the EAF slags, although the mechanical performance of M3air was poor compared to other results of this work. Comparing the main mixes of this batch, the fresh density of M3 was 18% higher and its strength was 15% higher than the reference mortar (M1).

Mixture M4 included EAFS and EAFF and the ladle furnace slag (LFS) used as the finer fraction had an excess of fines, as shown in Figure 3b; these amounts of aggregates had a negative effect on workability, because of the lack of fluidity produced by both slags. The results in terms of density were high despite the air-entraining admixture and the mechanical behavior of the mix with a low content of cement was good, as in M5.

Mixtures M6, M7 and M8 used heavy EAFS combined with natural aggregates; the adjustment to the ASTM C33 was good, and the densities were close to the reference M1 with the use of air-entrainment; however, the capillary porosity and entrained air increased due to the use of that admixture, decreasing their mechanical properties. Mixture M8 had the best performance from among these three mixes, low air-entrainment, good workability and mechanical strength, with a higher density than the reference mix.

Dimensional stability - Shrinkage

Two specimens (25x25x250 mm) of each eight mixtures (except M3, including M3air) were kept submerged in water following demolding, and a further two were kept in air, all of them in the same chamber at room temperature, 20°C±2. Their length was measured in a rigid frame equipped with a 0.01 mm precision apparatus. Figure 5 shows the evolution of the shrinkage length for all mixes, each point is the average of the measurements on two samples; the upper set of values corresponds to submerged

specimens and the lower set of values to in-air specimens. The measured values were almost-constant from an age of 250 days, as seen in Figure 5, although the in-air specimens were controlled throughout the year.

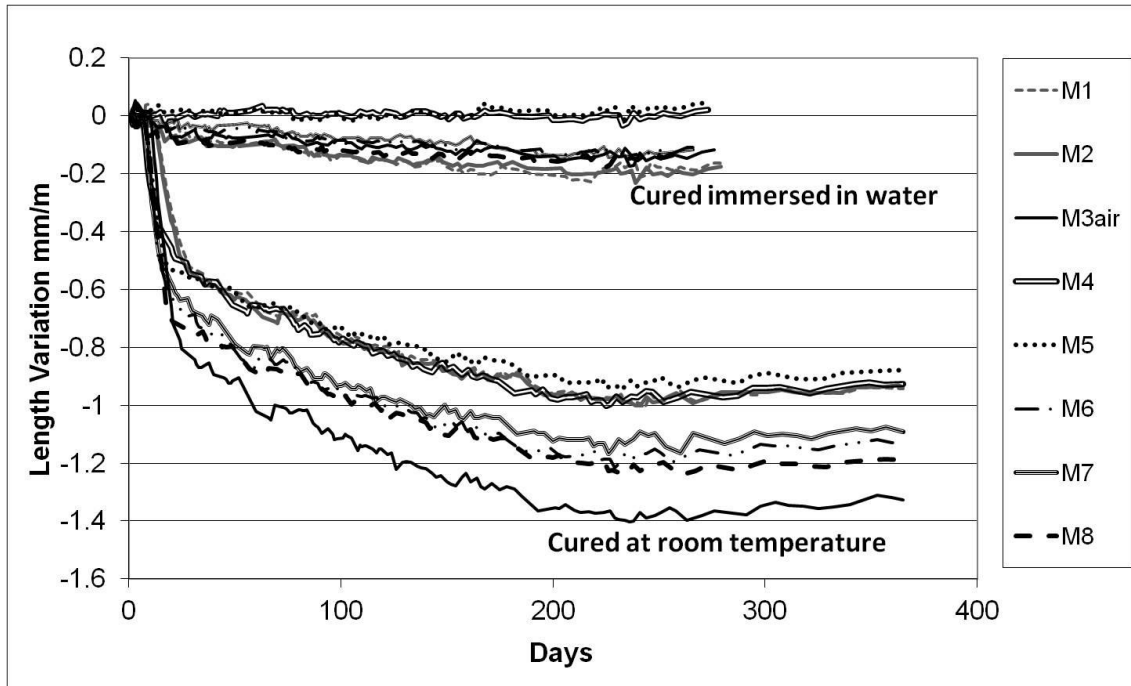


Figure 5: Evolution of specimen length over time: the upper curves refer to the submerged specimens and the lower curves to the in-air specimens.

In the submerged specimens, a contraction of about 0.2 mm/meter was noticeable in six mixtures, except those (M4-M5) containing LFS. The reaction of expansive components free-CaO and free-MgO in these specimens compensated the general trend towards slight contraction and their average value was almost zero. Contraction values of 0.2 mm/m were reported in the mixtures containing EAF slag and also in the reference mixtures M1-M2. This behavior is associated with the presence of large amounts of fly ash as pozzolanic material, the slow hydration of which produces this effect; the same effect occurs in the on-air specimens, giving rise to high global-shrinkage values.

The asymptotic values of the in-air specimens after 250 days differed widely, as may be seen in Figure 5. The asymptotic value of the shrinkage in the reference mix M1, and in the other almost-reference mix M2, was close to 1 mm/m, a value in this kind of mortars that usually represents an “acceptable maximum” in the world of structural mortars for construction.

Mixture M5, containing LFS but no EAFS, showed a value of 0.9 mm/m, a logical value owing to the superposition of the slight internal expansivity of some LFS compounds and the shrinkage shown by the reference mixes. In the same way, mixture M4 containing EAFS and LFS showed a value about 1 mm/m. It should be remarked that this expansion could be deleterious even though it may compensate shrinkage contraction. Mixture M3 (maximum content in EAFS) had 1.4 mm/m, and M6, M7 and M8 (lower content in EAFS) had values of between 1.2 and 1.1 mm/m. For instance, it appears evident that the growing presence of EAFS as aggregate in the mixtures increased their shrinkage contraction, associated with a lower elastic modulus [107] and it is even possible that a high amount of entrained air in mixtures containing EAF slag also favors this contraction.

Durability tests

The submerged specimens of mixtures (25x25x250 mm), cited in the former section, were held at room temperature water over 270 days and were then submerged in a 70°C temperature bath in a similar way to that proposed in the ASTM D-4792 standard; they were held for an additional 60-day period under these test conditions.

M3 and the other mixes without LF slag (M1-2-6-7-8) had no problems and there was a moderate expansion of their length over time in 70°C water, with values of between 0.1 and 0.2 mm/meter. The aforementioned expansion has to be deducted from the contraction value of 0.2 mm/m obtained in the shrinkage test of the former section. The final result in the global length variations of the relevant mixes was virtually zero.

However, the mixtures containing LFS, M4 and M5, showed an evident and detrimental expansion, as may be seen in Figure 6b, in which these specimens are curved and, especially in the case of M5, are even broken as well. The M3 specimens remained straight, as expected. The amount of LFS in these mixes was excessive with regard to durability and the effect of the expansive compounds was evident.

An additional durability test in which the specimens were submerged for 180 days in water and oven dried was performed in an autoclave test on cubic pieces of a size of roughly 25 mm obtained from other specimens. This test followed the norms detailed in Spanish NLT-361 standard "Determination of aging degree in steelmaking slag"; slightly different from the conventional autoclave test for Portland cement in that they were performed at a pressure 0.2 MPa over 48 hours. The result was mainly observed on the lateral plate faces of the pieces and in the presence of small particles that

disintegrated from the sample in each container; the results were graded as “integrity maintained”, “superficial scaling”, “general cracking” and “total destruction”.

The results for the behavior of the mixes was generally good (integrity maintained in almost all mixes M1-2-3-6-7-8) except in mixtures M4 and M5; once again, the mixes containing ladle-furnace slag, in which the expansive compounds played a fundamental role. The photo in Figure 6a shows the final state of mixture M4 specimen, resulting in “general cracking”; the result of mixture M5 was “total destruction”, in which the mass of the M5 specimen were reduced to as-sand particles.



Figure 6a and 6b: Samples after durability tests

Relevant SEM observations

A SEM analysis was performed on the fracture surface of the samples that were broken in the above-mentioned autoclave test. The technique is based on low-vacuum observation of backscattered electron (BSE) images, in which the samples were not electrically charged (neither sputtered with gold nor carbon). It was complemented by energy-dispersive X-ray analysis (EDX),

As is well-known, the internal expansion of some compounds included in the LFS produces long-term detrimental effects in the hardened mixes. Figures 7a and b show two expansive particles of different chemical composition found in the specimen of the M5 mix. As stated in the previous section on ladle furnace slag, the kind of LFS used in these experiments contained free-MgO, 7% by weight, and free-CaO in 6% by weight. It is expected that the expansive hydration or hydro-carbonation of these species [107] and their remarkable amounts will produce expansion and subsequent deleterious effects in the hardened mixes.

The particles of expanded compounds embedded in a stony hardened mass can be identified because of the notable cracking produced in their vicinity. Mapping of magnesium, calcium, silicon, oxygen and carbon in a large region of the fracture surface also identified these kinds of particles.

Indeed, Figure 7a shows a particle based on magnesium and oxygen and the presence of carbon, the elemental composition of which was obtained after micro-analysis EDX, shown in the lower-right-hand-side of the image. This particle was initially free-MgO, and the proportions obtained between Mg and O indicated that its current composition must be magnesium hydroxide (brucite), which is probably partially carbonated.

In a similar way, Figure 7b shows a particle of calcium carbonate, from an initial particle of free-CaO, firstly hydrated and subsequently carbonated throughout the accelerated aging durability test. Both particles were 20-30 microns large after their volumetric expansion and were partially or totally cracked by the mechanical stresses generated during the rupture of the specimen. They are surrounded by a cracked region of the cementitious matrix, in which the “granular” C-S-H detached particles may also be seen.

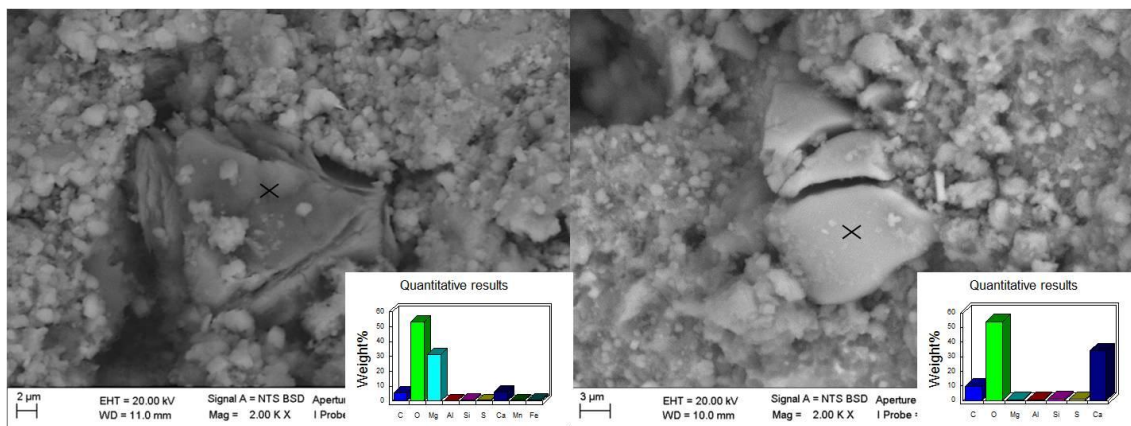


Figure 7: Brucite-magnesium carbonate (left) and Calcium carbonate (right)

Conclusions

The use of a Portland cement containing a notable amount of fly ash has proved positive in these structural mortar mixes: their workability was acceptable and the mechanical properties showed an excellent mechanical strength to clinker content ratio.

The compressive strength of 78 MPa was reached after one year with a mix employing EAF slag as aggregate; this compressive strength is promising in relation to the following step of performing similar concrete mixes. The stiffnesses of the mixes containing slag were, in general, lower than the stiffnesses of the natural aggregate mixes of similar strength.

The density of M3 was 18% higher and its strength was 15% higher than the reference mortar M1. The efficiency of the use of EAF slag in terms of structural use was (neither favorable nor unfavorable) intermediate. From this point of view, the feasibility of the use of these kinds of mortars in structural applications was positive.

From an engineering standpoint, the use of air-entraining admixtures in the EAF slag mortars is of no relevance, because the loss of strength (78.3 to 46.9 in M3) was not compensated by the gain in density (2.36 versus 2.72 in M3), and the eventual increase of workability due to its presence can be obtained using other admixtures that are not detrimental for the strength.

The long-term shrinkage of the mixes containing EAF slag as aggregate was significantly higher than the shrinkage of the reference mixes. The presence of ladle furnace slag hardly mitigated this outcome in an effective way despite its well-known expansivity.

Only mixtures M4 and M5, with a high content of LFS, were problematic in relation to durability. The others had few or no durability problems at all. However, any final decision on the maximum content of LFS in hydraulic engineering mixes will depend on the results of future in-depth studies performed on several kinds of LFS of variable composition and with varying contents of expansive compounds.

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