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6 7	A STUDY ON THE DURABILITY OF STRUCTURAL CONCRETE INCORPORATING ELECTRIC STEELMAKING SLAGS
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15	ABSTRACT
<ol> <li>16</li> <li>17</li> <li>18</li> <li>19</li> <li>20</li> <li>21</li> <li>22</li> <li>23</li> </ol>	The durability of structural concrete mixes prepared with electric steelmaking aggregates is tested for use in normal and aggressive environments. Samples of "pumpable" and "self-compacting" concrete mixes are shown to have good physical characteristics, mechanical properties and dimensional stability. The mixes were subjected to severe freezing-thawing and drying-wetting tests up until deterioration, to assess their resistance to inland environments. Real immersion in the tidal zone of a harbor and laboratory tests on reinforcement bar corrosion were also performed to evaluate the quality and utility of this sort of concrete in marine environments. The behavior of the mixes in these exposure tests was satisfactory, confirming their suitability for use in structural applications exposed to different environments.
24	KEYWORDS: electric arc furnace slag, self-compacting concrete, durability, aggressive environments
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26	HIGHLIGHTS
27 28 29 30 31	<ul> <li>Self-compacting concretes containing EAF slag are shown to be of good quality.</li> <li>The accelerated ageing test results are positive in all concrete samples.</li> <li>The limestone fines content of the concrete greatly influences its durability.</li> <li>The EAF slag concretes exposed to marine environments show satisfactory behavior.</li> </ul>

## 32 1. Introduction

Some decades ago, the pioneering proposals to use electric steelmaking slags as aggregates in concrete were welcomed as a potential means of reusing steelmaking slag waste. In these initial studies, [1-15] several areas were proposed for the application of these products; among which their reuse in construction and civil engineering sectors that are consumer of vast amounts of natural resources [16-28]. The target is to substitute that consumption for reasonable amounts of by-products that would otherwise be transported to dumping sites. Electric arc furnaces are used for most steel manufacturing in southern Europe where the by-products from industrial steelmaking processes are now a topical research area, aiming to produce viable

40 products for use in construction and engineering projects [29-45].

41 Over the last decade, several international research groups outside the EU have also been engaged in 42 research into hydraulic and bituminous concrete including electric arc furnace slag (EAFS, oxidizing slag, 43 from the acid refining of liquid steel) and ladle furnace slag (LFS, reducing, from the basic refining of steel) 44 for use in construction [46-57]. The authors of this paper form part of an EU research group that is also 45 engaged in this task. After investigating efficient manufacturing methods of non-reinforced (massive) 46 concrete containing EAF and LF slags as aggregates over the past decade, this research group in Spain is 47 now investigating efficient manufacturing methods for structural concrete containing these slag aggregates. 48 Recent publications of these authors have shown advances in this field, in which there is still a significant 49 way to go [58-63].

- 50 The three main obstacles to this objective are as follows: the reduced workability of concrete in the fresh 51 state, the increased density of the hardened concrete, and the risk of losing its good properties after a long 52 service life, taking into account the singular characteristics of these aggregates and their potential 53 expansiveness [64-68]. Each of the above-mentioned drawbacks, and others that further studies might 54 unearth, will have to be successfully negotiated, to produce a manufacturing method for the construction 55 sector in relation to the use of EAF slag and LF slag in structural concrete.
- In this paper, the results of incorporating EAFS and LFS in structural concretes are reported. Two different types of concrete were manufactured, to assess their fresh state workability: "pumpable" concrete of high workability, class S3 and S4, and self-compacting concrete with good flowability showing a spread of over 500 mm from the Abrams cone [69-76]. Considering the inherent and well known loss of workability 60 [31,41,59,77] associated with the use of these aggregates, a careful dosing and the use of appropriate admixtures is indispensable.
- 62 The aim of this article is to analyze the results of several durability tests and long-term behavior tests on 63 various structural concretes (pumpable and self-compacting mixes) made using slag aggregates. The main 64 result reaffirms the suitability of slag aggregate concrete under severe environmental conditions. The 65 preparation of these concrete mixes and their characteristics have recently been published in a paper by the 66 authors [78]; therefore, previously published details on the main features of these manufactured concretes 67 will only be very briefly described in this paper.

# 68 2. Scope of the research

The specificity of concrete made with electric steelmaking slags that performs as a self-compacting mixture is a singular challenge. At present, little research in the scientific literature [79,80] has been reported on this question, and there is a gap in the literature relating to the durability studies of these concretes. These EAFS concretes will, undoubtedly, still require considerable analysis before their global behavior is comparable to conventional concrete mixes.

An initial assessment might suggest that concrete manufactured with electric steelmaking slags can be of lower durability than conventional concrete when exposed to aggressive environments, due to the porosity of these aggregates and other uncertain long-term characteristics of them. Some researchers with significant experience in this field also consider that these concretes are of poorer durability than conventional concrete

- 78 [31,81], although the chlorine intake is fairly similar in both types [82]. In this paper, these durability issues
- results reveal that, where possible, the aforementioned disadvantages may to some
- 80 extent be mitigated.
- 81 There are mainly two types of EAF slag aggregates that may be identified in the scientific literature: one

82 with greater cohesiveness, almost without porosity, higher stiffness, strength, and specific weight [82-84];

83 another, also with greater porosity and characterized by a lower stiffness and specific weight, even though

it has good mechanical strength [81]. In this work this second type of slag is used; thus the conclusions are

- 85 only valid for one kind of EAF slag and they have no universal validity.
- 86 Molds of cubic and prismatic specimens were prepared, using the same mixes proposed by the authors in a 87 recent article on this subject [78]. The main properties of the hardened concrete are discussed, i.e. 88 mechanical strength, porosity, capillary absorption and water penetration under pressure, as well as the 89 results of measuring long-term concrete shrinkage in the atmosphere.
- 90 To analyze the durability autoclave tests were performed on the mixes, anticipating an eventual expansion
- 91 of the aggregates. A series of classical freezing-thawing and wetting-drying cycles were also developed as 92 part of the inland durability tests: throughout which damage to the material was controlled by means of

92 part of the inland durability tests; throughout which damage to the material was controlled by means of 93 measuring the propagation speed of ultrasonic waves through its mass and a final evaluation of compressive

- measuring the propagation speed of ultrasonic waves through its mass and a final evaluation of compressive
   strength.
- 95 Subsequently, the long-term durable structural behavior of this material is analyzed as "reinforced concrete" 96 for use in saline-marine environments. For that purpose, several non-reinforced concrete samples were 97 exposed to coastal seawater in intertidal zones over varied periods of time. Chloride and sulfate ion

98 penetration within the specimens was monitored in those samples. Likewise, laboratory tests to evaluate

99 corrosion in reinforcement steel bars of these concretes were also performed. In this way, samples of slag

- 100 concrete reinforced with embedded ribbed steel bars were exposed in the laboratory to simulated seawater, 101 to estimate the electrochemical corrosion resistance of this steel-concrete ensemble widely used in marine
- 101 to estimate the electrochemical corrosion resistance of this steel-concrete 102 structures.
- Finally, some conclusions are advanced to facilitate the practical use of this sort (pumpable, selfcompacting) of reinforced concrete mixtures using electric arc furnace slag as aggregate (coarse and fine) and ladle furnace slag in construction, and the reliability of structural engineering elements in marine environments.
- 107

# 108 **3.** Materials and mixes

# 109 3.1. <u>Cement, water and natural aggregates</u>

A Portland cement type I 52.5 R was used in this research, except in one sample prepared with a Portland
cement type IV/B-V 32.5-N that included pozzolanic (fly ash) material in the mix; both in accordance with
UNE-EN 197-1 standard. Water with no compounds that might adversely affect the hydraulic cement mixes
was taken from the urban mains supply of the city of Bilbao (Spain).

A commercial crushed natural limestone with a fineness modulus of 2.9 units, a maximum size of 5 mm, and a bulk density of 2.6 Mg/m<sup>3</sup> was used as a fine aggregate in certain mixes. The same material was also used to increase the workability of other mixes (see Table 1) after screening through 0-0.6 mm and 0-1.18

mm sieve sizes, with fineness moduli of 0.7 and 1.5 units, respectively. Coarse crushed limestone aggregate

- 118 (5-12 mm) of the same density was also used in one case, see Table 1. The main mineral component of all
- these aggregates was calcite (95%). The gradation of all of the above-mentioned fractions is shown in
- 120 Figure 1. A suitable plasticizer and viscosity conditioner admixture was used to reduce the mixing water
- 121 and to obtain a good rheological behavior of mixes.

122 3.2. <u>Slags</u>

Electric Arc-Furnace slag (EAFS) crushed and sieved into two size fractions (fine <5 mm, coarse 5-12.5 mm), with a specific gravity of 3.42 Mg/m<sup>3</sup> and fineness modulus 3.9 and 6.1 respectively [78], supplied by the company Hormor-Zestoa, was used in this research. The chemical composition, some physical properties and mineralogical main components are detailed in Table 2. The grading of both fractions is shown in Figure 1.

128

#### Figure 1. Grading of aggregate fractions.

 $129 \qquad \text{An additional high-silica low-alumina ladle furnace slag (LFS) with a density of 3.03 \ \text{Mg/m}^3 \text{ and a fineness}}$ 

modulus of 0.75 units was also used; the amount of material passing the 40 micron sieve is 19%. Its chemical composition and other physical properties are detailed in Table 2 and its grading in Figure 1. A minor fraction of the total amount of LFS added to the hydraulic mixes could show binder properties in the same way as a supplementary cementitious material (SCM), as suggested in [85]; the rest of the LFS can be considered as an additional fine aggregate fraction. Some earlier works by the authors [86,87] contain more detailed descriptions of this type of LFS slag, also specifying properties complementary to the analyses presented in this study.

137

Mix Design (kg/m <sup>3</sup> )		P1	P2	P4	P5	SC1	SC2	SC3
CEN	4 I 52.5 R	300	300	350	350	350	350	210(*)
H	Fly ash							140
	Sieved fraction <0.6 mm		760					
Limastana	Sieved fraction <1.2 mm			450	680	680	900	900
Linestone	Fine aggregate <5 mm	1050				550		
	Medium aggregate 5-12 mm					720		
		80						
EVES	<5 mm		550	800	700		550	550
LAFS	5-12.5 mm	1050	750	1050	900		670	670
,	Water	160	200	180	180	180	195	195
Plasticizer (%	weight of cement)	2	2	2.5	2	2.5	2	2
Fresh density (Mg/m <sup>3</sup> )		2.6	2.65	2.84	2.75	2.46	2.62	2.65
Occluded air (% vol)		1.9	2.5	2.1	2.4	1.6	2.2	6.3
Slump/Spread i	160/	180/	180/	220/450	/580	/680	/560	

#### Table 1: Mix composition

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(\*) Equivalence of used cement type IV (EN 197-1).

Table 2: Chemical composition and physical characteristics of the slags

Compounds (in weight)	EAFS (all sizes)	LFS
Fe <sub>2</sub> O <sub>3</sub> (%)	22.3	1.0
CaO (%)	32.9	59.2
SiO <sub>2</sub> (%)	20.3	21.3
$Al_2O_3$ (%)	12.2	8.3
MgO (%)	3.0	7.9
MnO (%)	5.1	0.26
SO <sub>3</sub> (%)	0.42	1.39
$Cr_2O_3$ (%)	2.0	
$P_2O_5$ (%)	0.5	
TiO <sub>2</sub> (%)	0.8	0.17
Loss on ignition (%)	gain	0.5
MIP porosity average (%)	8.9	
Specific gravity (Mg/m <sup>3</sup> )	3.42	3.03
X-ray diffraction main	Wüstite-Ghelenite	Periclase-Olivine
compounds	Kirsteinite	Mayenite

# 140 3.3. <u>Mixes: Proportioning and fresh properties</u>

Seven different concrete mixes were prepared to study relevant aspects of their durability. Table 1 lists the details of their dosing. Mixes labeled Px can be considered as "pumpable mixes", while those labeled SCx can be considered as "self-compacting mixes", due to the evident differences in their workability, as reported in previous works by the authors [78]. The selection of mixes in the present article coincides with those used in the recent paper cited above, with the exception of mix P3.

The grading curves of all the mixes are shown in Figure 2, in which the passing percentage of ordinates is shown by volume, to avoid imprecisions due to the different densities of both aggregate types. Mix P1 could be considered as a sort of "reference specimen", as it contains electric arc furnace slag as a coarse aggregate, and crushed limestone as fine aggregate; however, as can be seen in Figure 2, the content of the fines fraction (passing through ASTM N° 200 sieve, 75 micron) is low compared with all the other mixes. This fines fraction (referring to total aggregates by volume, figure 2) amounts to 8% in P1 versus 9% in P4,

152 12% in P5 and 15-16% in the rest; moreover the aggregates together amount to about 75% by volume of 153 concrete in P1 and 70% in the rest of mixes. Thus, its value as a reference specimen is relative.

From among the self-compacting mixes, mix SC1 can also be considered as a "reference specimen", due to the exclusive use of limestone aggregates in its composition. Mix P2 has a composition that is close to a

the exclusive use of limestone aggregates in its composition. Mix P2 has a composition that is close to a self-compacting mix with respect to its percentage of fines, but includes a small proportion of ladle furnace slag, implying a slight loss of workability that was corrected by adding water in the fresh state.

The components of these different mixes were prepared in conventional mixers and cast in place in the fresh state mainly in cubic molds of 100x100x100 mm and prismatic molds of 70x70x280 mm. Additional samples of some mixes were cast for other tests, i.e. cylindrical 150x300 mm and cubic 150 mm specimens. Several tests were performed on the fresh mixes to verify their physical properties and their workability; some of these results appear in the lower rows of Table 1. Details on these in-fresh tests have been extensively described in [78], as previously mentioned.

164

Figure 2. Aggregate gradation of mixtures.

# 165 4. Hardened properties

# 166 4.1. <u>Density and mechanical strength</u>

167The dry densities of the hardened concretes are shown in Table 3, which correlate well with the fresh168densities shown in Table 1. The average density of the slag concretes increased from 10 to 15% with respect169to those of concrete made using coarse and fine limestone aggregates, i.e. values in the interval of 2.5 to1702.6 in almost all mixes versus 2.35 Mg/m³ shown by the SC1 mix.

The compressive strength results after 7, 28, 90, and 180 days of curing appear in Table 3, as an average of three consistent numerical values. The mixes prepared with I 52.5R cement showed a strength of over 45 MPa at 28 days. Mix SC3 prepared with the type IV cement only reached a similar strength after 180 days; the use of this sort of cement is not so advantageous in terms of structural efficiency (strength/density ratio), and it has the highest index of occluded air from among all the mixes, due to the singular interaction

between the plasticizer admixture and the pozzolanic addition (fly ash) [87].

177 The results of the compressive strength of the "pumpable" mixes were similar and fairly good in mixes P1 178 and P4; hence they are better-balanced mixes with regard to mechanical strength. Mix P2 contains a 179 significant proportion of ladle furnace slag that is not always favorable [88]. Mix P5 showed a lower 180 strength associated with higher (and even an excessive) fines fraction content (in relation to mechanical 181 strength); however, this additional fines fraction favored workability, essential in this case to obtain slumps 182 as high as 220 mm in the Abrams cone test. Mix P5 was the last step in "pumpable mixes" to obtain self-183 compacting mixes in the experimentation of this work. Finally, the results after the Brazilian test in terms 184 of tensile strength after 360 days, close to the level of 5 MPa, confirmed the good quality of the material 185 for structural applications.

Table 3. Hardened properties of mixtures

Property	P-1	P-2	P-4	P-5	SC-1	SC-2	SC-3	
Compressive strength at 7 days (MPa)	61	46	61	30	44	47	19	
Compressive strength at 28 days (MPa)	67	54	69	46	51	53	31	
Compressive strength at 90 days (MPa)	68	56	71	54	56	55	36	
Compressive strength at 180 days (MPa)	73	60	74	62	64	61	41(*)	
Brazilian test at 360 days (MPa)	5.0	5.2	5.9	5.5	4.4	4.6	5.4	
Dry density (Mg/m <sup>3</sup> )	2.51	2.5	2.63	2.59	2.35	2.53	2.5	
MIP porosity (% vol)	12.3	15.5	15.2	13.5	9.9	16.6	17.5	

<sup>187</sup> 

(\*) mix SC-3 showed 50 MPa after one year

188 Self-compacting mixes SC1 and SC2 showed lower compressive strength levels than the higher quality 189 pumpable concretes, P1 and P4, but similar to P2 and P5; the results of SC1 and SC2 at 28 days were in the 190 interval 50-55 MPa versus 65-70 MPa in a good pumpable concrete. The high fines fraction of the materials 191 and the higher water-cement ratio (indispensable to obtain the appropriate workability) weakened the short-192 term strength of the self-compacting mixes; in the long term, mixes SC1 and SC2 reached reasonable values 193 of 60-65 MPa. The global results (in both the fresh and the hardened state) obtained in the SC2 mix can be 194 qualified as excellent and represent the best performing self-compacting concrete to emerge from the former 195 work [78]. Mix SC3, made with cement type IV, reached 50 MPa after one year.

#### 196 4.2. MIP analysis

197 Mercury Intrusion Porosimetry (MIP) was employed, using an Autopore IV 9500 apparatus (Micromeritics) 198 at a pressure of 33,000 psi, to study the pore structure of samples held for 180 days in a moist chamber. 199 The specific results of the pore structure of a concrete that the MIP analysis provides are indispensable to 200 evaluate the resistance of concrete mixes to some types of deterioration. Recalling the general rule, the 201 porosity of these cementitious matrixes is in proportion with the water used in the mix, minus the water 202 fraction absorbed by the EAFS.

203 The values obtained in terms of global porosity were, in general, within the range of 12-16%, with the 204 exception of mix SC1 containing conventional limestone aggregates. It should be noted that the 205 measurement of total porosity represents the addition of capillary matrix porosity from mixing water and 206 EAF slag porosity. The EAF slag represents between 40% and 60% of total concrete volume. The MIP 207 porosity of the EAFS was within an interval of 6-14% (in our case close to 9% as included in Table 2), and 208 the most frequent pore sizes were between 0.03 and 80 microns, as in Figure 3, but the structure of this 209 porosity differs from that of the cementitious matrix: it arises from the cooling of the slag and the associated 210 phenomenon (slag foaming, gas vacuoles, phase transformations, and thermal contractions...). In fact, the 211 water absorption of this kind of EAF slag (of higher porosity) is, in general, higher (in the order of 4-8% 212 [59,78,85]) than that shown by natural aggregates (lower than 4%). The excellent compressive result of the 213 P4 mix was accompanied by a higher MIP porosity value, an illogical situation at first sight, although 214 explainable, because it had the highest EAFS content of all the mixes.

215 The pore size frequency distribution of the mixes is shown in Figures 4a, 4b, and 4c. In Figure 4a the 216 differential intrusion curve of mixes P1 and SC1 are shown; in Figure 4b mixes P4 and P5 show the capillary 217 porosity of the cementitious matrix added to that coming from the particles of EAF slag inside the sample 218 (peaks between 200 and 50,000 nm) and, finally, the pore distributions of mixes P2, SC2 and SC3 are 219 shown in Figure 4c. In all cases, a significant peak (maximum frequency) is evident in the vicinity of 100 220 nm (between the pore sizes of 40-150 nm), mainly due to matrix capillary porosity.

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- 222 223

Figure 3. MIP results on two EAF samples used in this work. Figure 4a, 4b and 4c. MIP differential intrusion in mixes.

224 4.3. Dimensional stability - Shrinkage. Prismatic specimens of 70x70x280mm in size were used to evaluate dimensional changes, due to the longterm dry shrinkage of the concrete mixes. These sample dimensions are acceptable for testing the mixes with a maximum aggregate size of 12 mm. Two samples of each mix were kept in a "conditioned chamber" at 50% RH and 20°C of temperature over several months after their removal from the molds. Their elongation was controlled in a "classic" rigid frame of 300 mm, equipped with a suitable micrometer for length measurement. Measurements were recorded every hour, day, or week, depending on the rate of length variation.

232 Figure 5 represents the evolution of the shrinkage length for all mixes, where each point is the average of 233 the measurements on two samples; the measured values were almost-constant from an age of 90 days. As 234 Figure 5 shows, shrinkage values are globally smaller in the self-compacting mixes than in the pumpable 235 mixes. As stated in recent works [87,89], the mixes with EAF slag as aggregate generally showed a slightly 236 higher dry shrinkage than the mixes containing natural aggregates, due to the lower elastic modulus of this 237 EAF slag type in comparison with the higher stiffness of the natural aggregates; in this case, the higher the 238 proportion of EAF slag, the greater the contraction of the mix. If we take into account the higher volumes 239 of EAF slag in several pumpable mixes (except P-1), the long-term results are coherent with these 240 statements. Mix SC-1 contained no EAF slag and had the smallest shrinkage value; on the contrary, mix P-241 4 that contained EAF slag had the highest shrinkage values and showed the highest contraction from among 242 the pumpable mixes.

As stated in a previous work [87], the influence of a pozzolanic addition such as fly ash can slightly increase the shrinkage values, and the presence of ladle furnace slag can, due to its expansion, slightly mitigate those values. However, these effects are not visible in the concrete mixes tested in this study, due to the decisive influence of coarser aggregate stiffness; hence the final shrinkage rate of mix SC-3 is close to that of mix SC-2.

248

Figure 5. Shrinkage contraction of mixes

# 249 4.4. <u>Water penetration under pressure</u>

250 Conventional tests on the penetration depth of water under pressure were performed on the concrete mixes 251 in accordance with the EN 12390-8 standard [90]. The results provide an idea of concrete permeability and, 252 therefore, an idea of the durability of these mixes in tests where permanent interaction with water plays a 253 decisive role. The samples (cylindrical, 150x300 mm) had undergone one year of curing in a moist room 254 (20°C, 98%RH) and were previously immersed in liquid water until saturation (until constant weight). Table 255 4 shows the results in terms of the evaluation of the water penetration area (maximum and average depth 256 of penetration), measured on the region of the sample in which the liquid water is visible after breakage in 257 a Brazilian test. The indirect tensile strength of the samples was also evaluated in this final rupture test [91].

In general, the mixes containing EAFS showed better resistance to water penetration (impermeability) than concrete mix (SC-1) made with natural aggregates. As shown in Table 4, the maximum of all the EAFS mixes was below 20 mm in the water penetration test, which is a very good result in terms of mix quality. Good durability results would be expected in tests exposing the slag concrete to water; unfortunately, this result only represents one among various factors that influence the global durable behavior of the concrete.

263

 Table 4. Test results of water penetration under pressure.

Mix	P-1	P-2	P-4	P-5	SC-1	SC-2	SC-3
Maximum (mm)	16	18	14	10	25	19	15
Average (mm)	10	8	9	7	16	8	7

264

265 4.5. <u>Capillary absorption of water</u>

Capillarity tests were performed on samples following the UNE 83982 standard [90], "Determination of
the capillary suction in hardened concrete. Fagerlund method". These calculations are based on Darcy's
laws of water permeation in porous media. The tests were performed on dry specimens of mixes.

In this test, 100 mm edge cubic samples of each mix were halved (50 mm high each piece) and placed on a tray which has a 5 mm height water layer in the bottom. Water penetrates through the lower cut face of the sample (both aggregate and matrix are visible on that face, with no skin effect) and ascends by capillary action to the upper face. The mass gain of the sample was periodically evaluated. Curves representing this mass gain against the square root of time are drawn, as shown in Figure 6. The test ends when the absorption of water terminates and the mass of the saturated sample stabilizes and remains constant over time.

- 275
- 276

Figure 6. Capillary absorption of mixtures.

Figure 7. Mix SC3 showing high spherical porosity.

277 The Fagerlund method requires the calculation of three parameters; first, the resistance to water penetration 278 m; second, the effective porosity  $\varepsilon_e$ ; and third, the capillary absorption coefficient K. The first is a 279 representative value of resistance (inverse of speed) to the permeation process in square root units of time 280 divided by penetration height; the second represents the porosity of the available concrete that can be filled 281 by water, and the third is a global characteristic of the capillary process, in terms of its unitary mass of 282 absorbed water divided by the exposed surface and the square root of the time unit. This magnitude is really 283 a combination of the two former variables. The classical units for Darcy's law are used in calculations, 284 grams, minutes and centimeters.

285 The influence of these features on the durability of concrete in situations with the presence of water (rain, 286 sea, river) is decisive, as freezing-thawing or wetting-drying cycles and exposure to marine environments. 287 Concrete permeability and its resistance to the liquids penetration is also assessed in this test.

The results obtained for all of the mixes are compiled in Table 5; the differences between them are small except for mix SC3, made with cement type-IV, which included a high content of fly ash. This mix showed a lower slope than the other mixes under consideration (higher value of "m") in the rising zone of the curves. In Figure 7, the large amount of spherical pores can be appreciated, due to the occluded air of this mix (Table 1, value 6.3%). It is well-known that the abundance of these spherical pores leads to concrete mixes of low-permeability. Additionally, its higher effective porosity " $\varepsilon_e$ " is shown in this test, in coherence with the results of its MIP porosity.

295

Table 5. Capillary absorption results

	AWaiaht	$a_{aut} t_{aut} (min 0.5)$	m (min/am2)	- ( 3/ 3)	$V(\alpha/(m^2*1)min))$
	Aweight	sqrt $t_n$ (mm <sup>33</sup> )	m (mm/cm²)	$\varepsilon_{e} (cm^{3}/cm^{3})$	$\mathbf{K}$ (g/(m <sup>2</sup> , vmm))
	(g)				
P1	67.7	35	49	0.1354	1.93
P2	77.7	34	46	0.1554	2.29
P4	64.3	33	43	0.1286	1.96
P5	69.8	34	46	0.1396	2.06
SC1	71.2	35	49	0.1424	2.03
SC2	81.4	42	70.5	0.1628	1.94
SC3	90.6	66	172.8	0 1812	1 38

<sup>296</sup> 

Among the other mixes, the differences are of minor magnitude; the presence of ladle furnace slag in mix P2 led to a slightly higher capillary coefficient. The difference between mixes SC1 and SC2 deserves some comments; in the first state of the Fagerlund curve (before the sharp point in the abscissa " $t_n$ ") the curves coincide almost perfectly; in the second part of the curve, there is a gentle-slope in the last zone of SC2 in which other kinds of porosities (other than capillary porosity) are prevalent, the almost null porosity of the limestone aggregate and the high porosity of the EAF slag that constitute total effective porosity can be easily appreciated.

# **304 5. Durability tests**

# 305 5.1. <u>Autoclave test</u>

306 An autoclave test is a type of accelerated aging test to accelerate the potential expansion of some concrete 307 components over time (long term) and the eventual damage caused by this effect on the global concrete, 308 including the risk of breakage in the samples.

309 The test follows the instructions of Spanish standard NLT-361[92], entitled "Determination of the degree 310 of aging in steelmaking slag", in which one kilogram of irregular pieces of gravel-sized converter slag (LD 311 slag, BOF slag) are introduced with a liter of water into an autoclave at 2 bar and held at a constant heat of 312 130°C over four hours; the degree of disintegration of the original gravel pieces is evaluated by sieving and 313 constitutes the result of the test. Therefore, the logical situation would be to submit the original EAF slag 314 gravel to the NLT-361 test, as a prior condition before use of the slag in a serious and responsible way in 315 structural applications. However, in our case, it was considered preferable to perform this test on real 316 concrete using sufficiently and suitably hardened samples (after six months in a moist room); all detrimental 317 effects related to expansive phenomenon were tested together including eventual interactions between 318 cementitious matrix and slag aggregates.

Two concrete cubic samples of 100 mm were placed for a fairly lengthy period in the autoclave, to ensure the widest possible spectrum of detrimental effects, considered as thermally activated, in the same way as they would after centuries in structural concrete. The sequence of the operations was as follows:

- Initial warming-up, for 1 hour reaching 0.2 MPa (2 bar) and 130°C
- Maintaining heat for 160 hours (about one week)
- Cooling at room temperature during 10 hours
- Measurement of sample weight variation in the test
- Exposure to the environment over 200 hours
- Verification of external detriment and compressive test

The results of this test on the variation of specific mass, the appearance of superficial perturbations, and on compressive strength after a prudent period of post-test repose (one week) are summarized in Table 6; numerical values are the average of two specimen results. Figure 8 shows the appearance of a sample of mixture P-1 after the test, in which flaking and peeling along the in-front edge and at the corners may be appreciated in the foreground; the expansion of the largest slag pieces close to the specimen edge is responsible for the damage as they are visible in the image.

From the results of the autoclave test, two processes may be observed. Firstly, the pieces of slag swell and produce tensile stresses and subsequent micro-cracking in the neighboring matrix, an effect that is more detrimental near the edges of the pieces. Moreover, high stiffness in the cementitious matrix (lower ductility) is probably a harmful circumstance in view of the micro-cracking.

338 Regarding the results in Table 6, variations in density are not very significant and in general lead to 339 decreased density associated with loss of strength. Mixture SC-1 is probably the reference in this set of 340 mixtures, due to its lack of slag; its loss of strength can be attributed to the deterioration of the cementitious 341 matrix in this kind of test. Mixture SC-2 shows a loss of strength close to that of SC-1; it can be deduced 342 that the presence of slag in those proportions (lower than 40% in volume) will cause no visible detriment 343 associated with its eventual swelling. These digressions may be extended to mixture SC-3, in which the 344 effect of slag must be similar to that of SC-2 and the cementitious matrix obtained with cement type IV 345 showed no loss of strength; the detrimental factors affecting cementitious matrixes made with cement type 346 I were compensated in this SC-3 mixture by an "accelerated curing" of its matrix by developing the 347 pozzolanic reaction of fly ash.

- Among the "pumpable" mixes, the presence of LFS might be decisive in the deterioration of mixture P-2.
- 349 Other mixtures P-1, P-4 and P-5 presented a strength loss of around 30%. This value is partially due to the
- damage in the matrix, as has been shown in the SC1-2 mixes, enhanced by the swelling effect of the EAF
- 351 slag that is notoriously higher in these P-mixes due to their greater volumetric proportion of EAF slag.

Considering the particular severity of this test, the results should not discourage the use of these types of concretes in structural applications in buildings. There is no fear of spontaneous concrete weakening when used in real situations, in which a "normal" combination of temperature and humidity are present. The weakened strength of between 20% and 30% observed in this test should only be relevant in specially heated zones (hot zones in factories, heating building installations...).

Mixture	Variation of density	Compro Strength	essive (MPa)	Loss of	Appearance after 90 days of
	(%)	Before	After	Strength (%)	weathering
P-1	0.0	73	48.7	33	Edge flaked (see photo)
P-2	-0.4	60	36.2	40	Slight loss of mass
P-4	-0.1	74	50.3	32	Slight loss of mass
P-5	-0.5	62	43.6	30	Slight mass loss and crack
SC-1	-0.2	64	49.8	22	Normal
SC-2	-0.7	61	48.0	21	Normal
SC-3	-0.2	41.5	41.1	1	Normal

Table 6. Properties of slag concretes after autoclave test.

## 358

Figure 8. P1 sample after autoclave test

# 359 5.2. <u>Freezing-thawing tests</u>

360 Two 100x100x100 mm cubic samples from each of the mixes were tested in freezing-thawing tests after a 361 curing time of 90 days immersed in water. The whole freezing-thawing test comprised 122 cycles, each 362 lasting for two days, at which point the test was ended due to large-scale cracking apparition on the sample 363 surface (the cracking became apparent from cycle 105). A full 48-hour cycle involved 24 hours of storage 364 in a freezer at -15 °C followed by 24 hours of immersion in water at room temperature. The structural state 365 of the samples was periodically controlled by verifying their external appearance and by measuring the 366 ultrasonic pulse velocity, as an estimation of concrete integrity. Finally, a compressive test of the samples 367 was performed, and their final mass was measured; the results are compiled in Table 7.

Figure 9a shows the evolution of the Ultrasonic Pulse Velocity (UPV) test results over time; mixes P1, P2 and P4 showed a sharp fall; a low-content in limestone fines is the common characteristic. The presence of LFS in mix P2 is neither a favorable factor. As shown in Figure 9a and in Table 7, only a few mixes passed this perhaps overly severe test with a tolerable loss of strength and UPV; a loss of more than 25% of the initial value can be considered as a worrying damage. However, the set of compressive strength values of our mixes after the test, contained in the interval 37 to 48 MPa, resulted in no dramatic detriment in relation to their structural use. The loss of mass was also of the same magnitude in all mixes.

Considering both strength and UPV together, better behavior was shown by mixes P5, SC1, SC2 and SC3, which all shared the common characteristic of their higher proportion of limestone fines; this proportion has been demonstrated as more suitable than that of P1 and P4 mixes face to this durability test. Mix SC3 showed low capillary absorption-permeability, and the occurrence of fly-ash delayed pozzolanic reactions were reconstructive; in absolute terms, the compressive strength of the SC3 mix after the test is a good value.

Moreover, the type of porosity in SC1 explains its slightly lower UPV test results that differ from the UPV loss of the mixes containing EAFS that have two pore-types: pores in the matrix and pores in the slag. The additional porosity provided by EAFS to global concrete is not a positive factor. It may be recalled that the presence of EAFS in the concrete will not favor this kind of durability, as previously observed in [88]. Finally, the presence of LFS appears to have no favorable influence on the results.

- **Figure 9a.** UPV variations during freezing-thawing test
- 387 Figure 9b. UPV variations during wetting-drying test

# 388 5.3. <u>Wetting-drying tests</u>

389 The wetting-drying test was performed by following the guidelines of the ASTM D 559 standard [93], 390 although the standardized procedure was not rigorously followed, but adapted to these mixes and samples. 391 Once again, two cubic samples sized 100 mm for each mix were tested after a curing time of 90 days 392 immersed in water. The study comprised 148 cycles each lasting one day, with the end of the test defined 393 by the point at which the material loss (apparent from cycle 118) at the edges of the samples was considered 394 excessive. A full 24-hour cycle consisted of the immersion of the samples in water at room temperature for 395 16 hours, followed by forced oven-drying at 60 °C for 6 hours, and then by air cooling for 2 hours to avoid 396 thermal shock. As in the former case, the structural state of the samples was periodically controlled, by 397 verifying their external appearance and measuring their ultrasonic pulse velocity, as an estimation of the 398 integrity of the concrete. Finally, a compressive test on the samples was performed when evident 399 deterioration was detected and the final mass had been measured. Table 7 shows the average results of the 400 compressive tests, UPV and mass variation on samples subjected to the wetting-drying cycles and their 401 percentile variations; Figure 9b shows the evolution of the UPV results in this test.

402 As shown in Table 7, almost all the mixes (except P1 mix) passed this test with a tolerable loss of strength 403 and UPV, having the same order of magnitude for loss of mass in all mixes; the external aspects of several 404 samples after the test may be seen in Figure 10. It may therefore be stated that the behavior of the mixes 405 with EAF slag aggregate in the wetting-drying was acceptable. The better behavior, mainly in terms of 406 UPV, is once again evident in those mixtures with higher fines contents. As in the former case, the LFS 407 presence had no significant influence on the results. Also, the long-term structural reconstruction of the 408 pozzolanic reaction was effective in mix SC3.

409 Mix P1, which has normal porosity, normal capillary absorption and good strength, showed the worst 410 behavior. The co-existence of two types of aggregates (natural and slag aggregate), which have quite 411 different physical properties, in sizes larger than 1-2 mm (this aggregate size value could be the diffuse 412 border between whether it forms part of the concrete cementitious matrix), could be identified as a cause 413 of deterioration in a test characterized by severe thermal shocks. Additionally, in the range of 0-0.1 mm,

the amount of limestone fines is perhaps too low in mixture P1; a suitable fines content (amounting to 15-

415 16% by aggregate volume in the better performing mixes) is therefore a key variable in the durability tests.

416

 Table 7. Durability results in freezing-thawing and wetting drying tests

Mixture	Strength 90 days (MPa)	UPV (km/s)	Strength after F-T (MPa)	UPV after F-T (km/s)	Mass loss F-T (g)/2500	Strength after W-D (MPa)	UPV after W-D (km/s)	Mass loss W-D (g)/2500
P1	68	4.78	45.7 (-33%)	3.79(-21%)	39.5	40.2 (-41%)	3.51 (-27%)	127
P2	56	4.27	37.8 (-32%)	3.45 (-35%)	23.8	53.5 (-4.5%)	3.94 (-15%)	140.5
P4	71	4.75	41.6 (-41%)	3.46 (-27%)	60	68.9 (-3%)	4.39 (-8%)	162.6
P5	54	4.42	48.3 (-11%)	4.06 (-8%)	54.4	52.9 (-2%)	4.26 (-3.6%)	116
SC1	56	4.38	44.5 (-21%)	4.34 (-1%)	37.5	54.8 (-2.1%)	4.35 (-0.7%)	131
SC2	55	4.33	41.1 (-25%)	4.22 (-2.5%)	55.9	55 (0%)	4.32 (-0.2%)	158.5
SC3	41.5(*)	4.13	44.2 (+6.5%)	4.21 (+9.4%)	24	44.6 (+7.5%)	3.85 (-6.7%)	201.9
417	417 (*) SC3 result for strength after 180 days of curing in Table 3; pozzolanic hydration has place during the durability tests.							

418

419

Figure 10. External aspect of several samples after the wetting-drying test.

420

# 421 5.4. <u>Marine environment tests. Penetration of chlorine and sulfate ions.</u>

422 Over the past few years, one application of concrete made with EAFS as aggregate is the construction of 423 coastal defenses (dykes) against storms, in the breakwater structures of a marine environment. There is no 424 reason why the same kind of concrete may not be used in other on-shore structures such as docks, wharfs, 425 and quays. In view of these applications, further durability behavior studies of these reinforced concretes426 against saline water are very relevant.

427 The first part of this study is centered on ionic penetration into the concrete mass, while the second part 428 concerns reinforcement corrosion. Chlorine and sulfate ions (the most abundant and most pernicious to 429 concrete in sea water) permeate materials exposed to marine environments and sea immersed structures; 430 these ions potentially endanger steel reinforcement bars (rebars) and cementitious matrix, respectively, and 431 have to be monitored. Additionally, the chlorine presence in the concrete mass increases the leaching of the

432 Portlandite and can form additional harmful compounds.

433 When water disappears (mainly by spontaneous evaporation) from the concrete, the aforementioned ions 434 remain in the cementitious mass, probably combined in the existent compounds and dissolved in the present 435 moisture. Although this area is as yet unstudied, these ions could be able to diffuse in solid state or are 436 transported in liquid water; these last circumstances must be best verified. Following these assertions, it is 437 easy to understand that the direct use of Fick's diffusion laws for this question is not the best approach for 438 the authors, in whose opinion the Darcy laws are the most appropriate for use in the future. It must also 439 remembered that if the pH of the concrete mass is basic, the corrosion of steel rebars in marine environment 440 is moderate despite the presence of chlorine ions.

The practical exposure of the samples to marine environments was done by suspending them in cages, at level zero of the Pasaia Donibane port. Hence, the samples suspended at "elevation zero" or at the "central level" of the intertidal zone, were exposed to tidal movements twice a day. They were soaked, as a result, for 12 hours every day and were exposed to the atmosphere over the remaining time, undergoing two wetting-drying cycles every day. The duration of the tests was classified into two groups, short-term tests

446 during one year and long-term tests, over five years.

447 The concrete mixes used in these tests were chosen as follows. In the short-term test, all the concrete mixes 448 described in section 3 of this article were tested. In the long-term test, mix P4 was used as an EAFS concrete; 449 additionally, another mix identical to P4 in volume and gradation of materials, but containing limestone 450 aggregates, named P4CA, was used as a conventional aggregate concrete. These two mixes were also used 451 in the next section, to analyze the corrosion problems of the concrete reinforcement bars.

452 In general, two 100x100x100 mm cubic samples of each mix were used in the short-term test. Following 453 exposure to the marine environment, suitable smaller pieces were cut from the initial samples, to observe 454 their internal zone, from external face to the center, along a 50 mm fracture surface broken few minutes 455 before the observation. The broken smaller pieces were placed in a nitrogen scanned chamber of a low-456 vacuum pressure scanning electron microscope, to evaluate the presence and concentration of the 457 aforementioned ions from the external periphery to the center of samples. In this way, backscattered 458 electron images were obtained and the energy-dispersive X-ray micro-analysis spectrography technique 459 was used to define the chemical composition.

460 Figure 11 shows the evolution of the chlorine and sulfur concentrations in the short-term test, from the 461 periphery to the center of the samples, in the samples exposed to the marine environment obtained by the 462 mentioned micro-analysis technique. The evaluation of these elements was performed on chosen sites in a 463 recent fracture surface of the sample, increasing the distance from the periphery towards the center of the 464 cubes, performing the micro-analysis on a small area of the cementitious matrix; the visible aggregates 465 (slag or limestone) were avoided. Exponential equations were successfully used to adjust the numerical 466 results, instead of the more complicated error functions usual in diffusion phenomena in accordance with 467 Fick's laws. In several cases the whole set of numerical results (chlorine concentrations in mixes P1 and 468 P2, sulfur in P1) is represented by little triangles or squares, in other cases only the adjusted curve are 469 drawn, so that the number of points on the graph are not excessive.

470

Figure 11. Penetration of chlorine and sulfur in mixtures.

The proportion of chlorine in the cementitious matrix of the periphery of the pieces was especially high in

- 472 mix P1, with values close to 2%; they were also higher in mix P2 (about 0.8%) than in the rest of mixes,
  473 which showed periphery concentrations in the order of 0.3-0.5%. The concentration decreases as expected
- 475 which showed periphery concentrations in the order of 0.5-0.5%. The concentrations are order of 0.2%.

475 Considering an amount of 0.1% as a "classical threshold value" in the chlorine content of a concrete matrix, 476 it can be stated that some "pumpable" mixes showed a deeper penetration of chlorine (P1 and P2 in the 477 order of 50 mm); penetration rates of almost 35 mm were observed in mixes P4 and SC1 and 25 mm in 478 mixes P5 and SC2. Mix SC3 is the most resistant against this penetration (estimated at about 15 mm), in 479 coherence with its air-void structure and its low rate of capillary water uptake. Considering that the "cover 480 thickness" of 40 to 60 mm prescribed for concrete marine structures from the rebar to the external concrete 481 surface, was reached by the chlorine in all mixtures after one year of exposure, the results are not reassuring. 482 The presence of EAFS could be said to have little effect on the penetration rate of chlorine ions in the 483 concrete mass by permeation-diffusion, in comparison with the SC1 mix made without EAFS. It appears 484 compulsory to evaluate the durability of the EAFS structural concrete (containing steel reinforcement) 485 under marine conditions in other ways, as it is performed in the tests described below and in section 5.5.

- 486 Concerning the penetration of sulfur, mix P1 was the only mix that showed values higher than "normal" 487 concrete values (a normal value of sulfur content in concrete could be calculated in the following way: 18% 488 sulfur in gypsum x 4% of gypsum in cement x 30% of cement in matrix = 0.2%); the rest of the mixes 489 showed values of sulfur content in the vicinity of 0.2% throughout the whole sample section. The sulfur 490 content at the center of the P1 sample was close to 0.5%; at the periphery the value was around 1%. The 491 dangerous risk of the appearance of secondary ettringite or thaumasite in the peripheral zone of the concrete 492 pieces is, in general, low except for the P1 mix; however, no evidence of either Candlot salt or Fridel's salt 493 formation was found in P1.
- 494 It has to be remembered that the poor behavior of mix P1 (with the lower content in limestone fines) in a 495 marine environment withstanding the penetration of pernicious ions is coherent with the poor results of the 496 wetting-drying test using urban supply water. It should be remembered that marine exposure in the intertidal 497 zone means that a wetting-drying cycle is repeated twice a day. The results of mix P2, containing a small 498 proportion of ladle furnace slag, were also poor but less detrimental than P1. In general, self-compacting 499 mixes perform better in these short-term tests in the marine environment; it can be concluded that the 500 presence of ladle furnace slag is not positive, and the presence of suitable amounts of limestone fines (up 501 than 12%) is clearly positive.
- 502 In the long-term test, 150x300 mm cylindrical samples were exposed to a marine environment for over five 503 years. The analyses were performed on concrete mixes P4 (with EAFS) and P4CA (with limestone 504 aggregate), using 200 mm portions in length of the aforementioned  $\Phi$ 150x300 mm cylindrical samples, 505 obtained after an initial transversal cut that shortened the overall length (300 mm) by 100 mm. The cut 506 bases are visible in Figure 12 as two semi-circular forms in the foreground of the photo, following breakage 507 of the 200-mm length piece in a Brazilian test. Figure 12 shows the test result of a pernicious ion search of 508 mix P4 (EAF slag aggregate), where the macroscopic change of color shows evidence of the presence of 509 ions.
- 510

# Figure 12 a Sample P4 after chloride. b after carbonation penetration analysis.

511 A recently broken surface, Figure 12a, was sprayed with a silver nitrate solution, in order to detect ionic 512 chloride penetration. If chlorine ions are present in a proportion higher than a certain threshold, the natural 513 surface color will remain unchanged (periphery of sample); on the contrary, if the proportion of chlorine is 514 lower than the threshold, the surface will become slightly darker (center of sample). Obviously, this test 515 yields broad results (all standardized tests of this sort show low accuracy), but it is nevertheless useful to 516 ascertain a general state of the samples; the most significant variable is the value of the threshold, which 517 must be near the maximum content of chlorine allowed by usual standards. In Spain, this value is fixed at 518 0.4% of cement content, a value equivalent to about 0.1% in the cementitious matrix of our mixes. The

519 active chemical reagent used in our test was prepared to change the light shading at the aforementioned 520 threshold.

The results of chloride penetration revealed total penetration after five years in the natural (limestone) aggregate mix, P4CA, i.e. 75 mm of the radius. The permeation-diffusion of chlorine in this concrete mix is revealed as active after five years. However, in the case of mix P4, see figure 12a, the average penetration was near the middle of the radius, and was fixed at 30 mm; obviously, on the cut base (front of the image) the dark zone is emergent. The presence of the slag in this P4 concrete mix is seen as positive in terms of less active chlorine penetration after five years (long-term).

- 527 The evaluation of carbonation (or excessive Portlandite lixiviation due to the chlorine presence) performed 528 on the aforementioned mixes, P4 and P4CA, was done with a similar test, by spraying a phenolphthalein 529 solution on the recently broken surface of the samples. As is well known in chemical analysis, a pH>9.5 530 corresponds to an intense pinkish color in the solution that extends across the visible surface. Unlike the 531 global spraying method on the broken surface after the Brazilian test for the detection of chlorides, in this 532 case only one significant region of the broken surface was sprayed, shown in Figure 12b, so that the ordinary 533 tone of the concrete remained as a reference in the unsprayed region. The dark pink color appeared very 534 quickly, indicating a high value of pH.
- The results of this latest test showed that carbonation or lack of Portlandite was non-existence in both concrete mixes after five years of exposure to tidal zones. The pH was higher than 9.5 units in the breaking surface of mixes P4 and P4CA, revealing the abundant presence of Portlandite in the concrete mass as a factor that determines a high pH, collaborating in the protection of the reinforcement steel bars. This is undoubtedly an encouraging result for the use of our concrete mixes in marine environments.

# 540 5.5. <u>Corrosion of reinforcement bars.</u>

541 Structural concrete is a composite material consisting of concrete and steel reinforcement bars (rebars); the 542 tensility of the steel withstands the tensile forces and the compressive forces are supported by the concrete 543 mass. Several aspects of this composite (steel-concrete) coupling are decisive in achieving this effect; 544 among which, the role of the concrete mass in the protection of the reinforcement steel bars against 545 electrochemical corrosion in aqueous environments containing chlorine ions may be mentioned.

546 The concrete protects the steel from environmental corrosion at two levels; firstly, as a physical barrier of 547 low permeability (covering concrete layer), and secondly as an electro-chemical protector, assuring a basic 548 pH in the vicinity of the steel bars. If the pH of the concrete mass is sufficiently basic, despite the presence 549 of chlorine ions, their corrosive attack on the rebars will be less aggressive.

- A study of the durable properties of EAF slag concretes reinforced by steel bars is reported in this section, in an attempt to analyze the protection that this kind of concrete has against marine corrosion, in comparison with the protection given by ordinary aggregate concrete or "conventional concrete" (in this case, concrete
- 553 made with crushed limestone aggregate).

558

559

- EAFS concrete and conventional concrete, both including reinforcement bars, were tested in the followingway:
- Durability tests (wetting-drying with seawater, saline fog chamber submission) were performed on samples of reinforced concrete.
  - 2. Electrochemical corrosion variables (current density and electrochemical potential) were periodically controlled on the steel reinforcement.

560 The samples consisted of 150 mm x 150 mm cubes, into which a small steel structure formed of 10 mm 561 diameter bars was embedded. Figure 13 shows the internal layout and the external appearance of these 562 specimens. The emergent central steel bar was used as an electric contact to perform the measurements,

563 which reflect the electrochemical evolution of the internal steel structure.

564 The concrete mixes used in these tests were chosen as in the former section. Mix P4 was used as an EAFS 565 concrete; and mix P4CA, identical in volumetric proportions to P4 employing limestone aggregates in 566 substitution of EAFS, was used as a conventional aggregate concrete.

567 Fi

Figure 13. External appearance of samples and internal rebar layout

The corrosion risk of rebars embedded in a cementitious material depends on their electrical potential. In general, its evaluation follows the specifications of the ASTM C-876 standard [93], which indicate that an electrical potential lower than -400 mV corresponds to a very high risk. In our testing, the values were always in this risk zone except in the first moments of the durability tests.

572 The measure of electrical current density (or electrical intensity divided by area of exposed surface) is a 573 measure of the corrosion rate of the steel rebars. Hence, the main results of these tests center on the 574 measurement of the current density over time in the corresponding wetting-drying and saline fog chamber 575 tests. The limit between active and passive corrosion is placed at 0.1-0.2  $\mu$ A/cm<sup>2</sup>, which in terms of 576 generalized corrosion implies around 1-2  $\mu$ m/year. Table 8 indicates these effects.

577

 Table 8. Steel reinforcement corrosion current density from ASTM C-876.

$I_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	Corrosion
< 0.1	Low
0.1-0.5	Moderate
0.5-1	High
>1	Severe

578

579 The wetting-drying test was performed using artificial marine water containing 19 grams of chlorine ions 580 per kilogram of water from the dissolution of pure sodium chloride (30 gr per liter). The samples were 581 soaked and dried in the same way as previously described in the corresponding wetting-drying section. In 582 this case, the thermal shock was voluntarily mitigated, avoiding disintegration of the concrete mass. The 583 samples were electrochemically controlled performing ten measurements on the sample submerged in water 584 every 10 cycles, and the results are represented in the graphs in Figure 14a and b, alongside an image of 585 the EAFS samples at the end of the test (Figure 14c). It is relevant to point out that the numerical results 586 are highly scattered in this kind of tests and that very many measurements must be taken before the average 587 results of the data cloud reveal a particular tendency.

588 The average results shows a "step" visible in the graph, probably associated with the moment at which the 589 chloride ions penetrated the concrete up to the steel bars in an "effective" way; the initial transient state 590 corresponds to a "first less-detrimental phase" before the "more worrying" arrival of chlorine ions. 591 Throughout this first phase of the test (around the initial 150 to 200 cycles), the corrosion rate can be 592 considered almost constant and with a low average in both types of concrete. In the case of the EAFS 593 concrete, the value was 0.11 µA/cm<sup>2</sup>, while the value in conventional aggregate (CA) concrete was about 594  $0.17 \,\mu\text{A/cm}^2$ , with a moderate risk of corrosion according to the data in Table 8 and in accordance with the 595 corrosion potential measurement.

596 In the subsequent (last) phase of the test, from cycles 200 to 330, the corrosion rates were higher; the 597 behavior of the concrete containing natural aggregates was worse than the behavior of the EAFS concrete, 598 0.77 versus 0.40  $\mu$ A/cm<sup>2</sup>, with notable corrosion risks in both cases, confirmed by a corrosion potential 599 lower than -0.4 volts. The difference between the behavior of the two types of concrete, in terms of standard 600 electrochemical evaluations of corrosion is, in fact, notorious but not "enormous" in this test. The protection 601 of the steel rebars in a marine environment is more effective in the concrete containing electric arc furnace 602 slag as aggregate than in the concrete containing conventional aggregate, and the "structural life" of EAFS 603 concrete elements will be almost twice that of the CA concrete.

604Figure 14a. Corrosion rate in the conventional aggregate (CA) concrete after wetting-drying test.605Figure 14b. Corrosion rate in the EAFS concrete after wetting-drying test.

#### Figure 14c. Image of EAFS samples after the test

The saline fog chamber test was performed following the specifications in standard EN ISO 9227. An aqueous solution of NaCl (30 grams per liter, as in the previous tests) is sprayed into the atmosphere in a sealed chamber, in which the samples are immersed. This test is extended over 3000 hours, with electrochemical measurements every 200 hours performed in the same way than in the former case. After the test, the surface appearance of the samples was normal, see Figure 15c; and the corrosion rates of the two mixes throughout the test are shown in the graphs 15a and 15b.

613 After around 1500 hours of exposure, in a similar way to the explanation of the results of the earlier chlorine 614 ion penetration tests, both mixes increased their corrosion rates from low to much higher values. The values 615 in the first phase were  $0.1\mu A/cm^2$  in the EAFS concrete and  $0.3 \mu A/cm^2$  in the conventional aggregate 616 concrete. In the second phase (from 1500 to 3000 hours), the values rose to  $0.28 \,\mu\text{A/cm}^2$  and  $1.5 \,\mu\text{A/cm}^2$ , 617 respectively, remaining almost constant until the end of the test. In this test, the long-term values reached 618 by the slag concrete were moderate according Table 8, while those of the conventional concrete were really 619 severe; this situation denotes a worrying corrosion rate in the conventional concrete, in contrast with 620 tolerable corrosion damage in the slag concrete. The corrosion potential measurements indicated a high risk 621 in both cases.

# 622<br/>623Figure 15a. Corrosion rate in the conventional aggregate (CA) concrete after saline fog test.623<br/>624Figure 15b. Corrosion rate in the EAFS concrete after saline fog test.624Figure 15c. Image of CA samples after the saline fog test

625 In summary, the electrochemical corrosion rates of the steel rebars embedded in the conventional concrete 626 (P4CA) clearly showed a gradual evolution that was more detrimental than the corrosion rates of the P-4 627 mix made with steelmaking aggregates. In the opinion of the authors, the EAFS concrete is over time 628 capable of maintaining higher pH values in the concrete mass than the conventional concrete, as a 629 consequence of which these mixes show slower steel corrosion rates in comparison with conventional 630 concrete. This result can probably be associated with the slow lixiviation of (free) lime by the slag aggregate 631 to cementitious matrix that maintains a more basic pH for a long time. The basic pH of the slag concrete 632 mass mitigates the electrochemical attack of chloride ions and produces a notorious overall delay in the 633 detrimental corrosion of the rebars.

Additionally, the hypothesis that the scarce presence of small metallic particles of iron (sized 0.5 to 2 mm)
and the abundant presence of iron oxides in the slag can favorably (albeit slightly) influence the global
behavior of the mixes against rebar corrosion should not be discounted [58]. It is in fact a hypothesis that
should be confirmed in the future through long-term marine tests.

## 638 6. Conclusions

639 The conclusions of this study are summarized as follows:

640 The reuse of electric arc-furnace slag in concrete manufacturing has, when properly performed, produced 641 good quality mixes in terms of workability and mechanical strength. Pumpable and self-compacting 642 concrete mixes have been successfully obtained and the pore structure and several physical properties as 643 strength, capillarity, porosity and shrinkage of these EAFS concretes are similar to those of reliable 644 concretes incorporating conventional aggregates.

645 The durability of concrete mixes that incorporate electric arc furnace slag as aggregate is, in general, fairly 646 good. On the contrary, the presence of ladle furnace slag is not positive. The eventual expansive processes 647 associated with slag appeared in autoclave accelerated aging test; the most favorable behavior of slag 648 concretes is showed by the self-compacting mixes SC2 and SC3.

In aqueous environments, after freezing-thawing and wetting-drying tests the comparisons between these
 EAFS mixes and other more conventional mixes have neither shown clear benefits nor excessively

- 651 detrimental effects. Furthermore, the self-compacting mixes usually performed better than the more 652 conventional "pumpable" mixes of concrete.
- 653 The well-balanced content of limestone fines in mixes seems to be an outstanding variable in relation to its 654 durability. This statement is supported by the results of mentioned physical tests affecting concrete 655 integrity, and by chemical verification of the presence of chlorine and sulfur in the concrete mass.
- 656 The advantageous resistance to steel rebar corrosion of the concretes incorporating electric arc furnace 657 aggregates in marine environments was apparent in the electrochemical corrosion tests. The lixiviation of 658 Ca-ions to the cementitious matrix due to the presence of free-CaO in the slag, can be considered very 659
- positively in relation to the long-term preservation of steel reinforcements.

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