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Validation Exercise at European Level on Natural Chloride Diffusion Test and Natural and Accelerated Carbonation Testing

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Abstract. *The work summarizes the results of the interlaboratory testing made in the committee CEN/TC51/WG12 on the standardized procedures for carbonation (EN 12390 – 10 and part 12) and chloride diffusion (EN 12390-12). The exercise was made by 13 different laboratories on 8 different concrete compositions with w/c ratios of 0.4, 0.5 and 0.6. The results indicated repeatability of 10-22% for natural carbonation (outdoors protected from rain and controlled chamber respectively), of around 5% for accelerated carbonation (at 4% of CO_2 concentration), and 23% in the Apparent diffusion coefficient for natural chloride diffusion and 13% for the chloride surface concentration.*

Keywords: *Carbonation, Chlorides, Testing Performance, Stantarization.*

1 Introduction

The need to improve the performance of concrete structures in aggressive environments and the need to increase the use of concretes made with non-traditional cements (low carbon among other) have promoted the change from prescriptive to performance based standards. The committee CEN/TC51/WG12 has developed several testing methods of assessment the performance of concrete with respect to the exposure classes of EN 206 related to reinforcement corrosion, more specifically methods that concern the carbonation resistance and chloride penetration.

The procedures are described in the standards:

1) Natural carbonation - EN 12390 – 10: "Testing hardened concrete – Part 10: Determination of the relative carbonation resistance of the concrete at atmospheric levels of carbon dioxide "that considers two methods at natural carbon dioxide concentrations: one in chamber controlling humidity (65±5%) and temperature (20±2ºC) and the other simply exposed outdoors sheltered from rain,

2) Natural chloride diffusion - EN/TS 12390-11: 2009: "Testing hardened concrete. Part 11: Determination of the chloride resistance of concrete. Unidirectional diffusion" method based on natural diffusion with three different modes of contact of the salt solution with one face of the specimen [Immersion (DCL1), Ponding (DCL2) and Inversion (DCL3)] and a concentration profile after 90 days of contact with the chloride solution is used to fit Fick's law in order to calculate the chloride surface concentration, C_s and the apparent Diffusion Coefficient, D_{ap}.

3) Accelerated carbonation - EN 12390-12: "Testing hardened concrete - Part 12: Determination of the carbonation resistance of concrete - Accelerated carbonation method" using a chamber at 4% of carbon dioxide concentration also with controlled humidity (65±5%) and temperature (20±2ºC).

In present work is summarized the interlaboratory validation program made to establish the

precision (repeatability and reproducibility) of these methods. It has to be emphasized the joint effort made, in particular by the Institute of Construction Sciences of CSIC-Spain where the specimens were prepared and shipped and of the participant laboratories, which were 13: 1) CRIC-Belgium, 2) Lafarge- France, 3) LRPC-France, 4) VDZ-Germany, 5) Politecnico de Milano -Italy, 6) SINTEF-Norway, 7) ISCMOIB/OMMB-Poland, 8) CBI- Sweden, 9) KEMA-The Netherlands, 10) TNO- The Netherlands, 11) SGS INTRON - The Netherlands, 12) Dundee University. UK and 13) IETcc-CSIC -Spain. And shown in Table 1

2 Experimental

The specimens were cubic of 15 cm of side (figure 1). The cement type and class were chosen to be: CEM II/A-LL 42.5 R and CEM II/B-V 32.5 R. For the preparation of the specimens the aggregate was “round shaped” siliceous, and the slump class was S3 (100 – 150 mm). Some tests were carried out in order to fit the dosage for the required slump class, using a superplasticizer.

Figure 1. Specimens in the molds in the left side and in the right when demolded placed inside the chamber for curing.

The required number of specimens (two specimens per each test method and concrete mix) were prepared in a horizontal mixer. Two batches were necessary due the large number of specimens.

The specimens consisted in 8 different concrete compositions (see Table 1) with w/c ratios of 0.4, 0.5 and 0.6 for structural class S4 for exposure classes:

- of carbonation XC2 (wet, rarely dry) and XC4 (cyclic wet and dry) and
- for chlorides: XS1/XS2/XS3 (sea water attack) and XD3 (deicing salts cyclic wet and dry).

Once prepared and cured 28 days in standardized conditions the specimens were sent to each laboratory. together with the forms to be filled with the results.

Table 1. Concrete compositions tested and some properties.

		CARBONATION				CHLORIDE			
		MIX 1	**MIX 2**	**MIX 3**	**MIX 4**	**MIX 5**	**MIX6**	**MIX7**	**MIX8**
Cement type		CEM II/A-LL 42.5R		CEM II/B-V 32.5R		CEM II/A-LL 42.5R		CEM II/B-V 32.5R	
Cement	**amount** (kg/m^3)	295	296	296	300	345	351	349	357
Water	(l/m^3)	144	173	144	175	137	173	138	176
w/c ratio		0,49	0,58	0,49	0,58	0,4	0,49	0,4	0,49
Gravel	(kg/m^3)	1 049	1 011	1 054	1 025	1 005	977	1 019	993
Sand	(kg/m^3)	857	827	861	838	816	793	827	806
Superplasticizer (% cement weight)		0,60	0,20	0,50	0,15	0,79	0,23	0,57	0,10
Density	(kg/dm^3)	2 260	2 265	2 294	2 285	2 273	2 313	2 330	2 330
Air content	(%)	5,75	4,9	5,15	3,75	5,7	3,8	4,4	2,3
Slump	(cm)	11	10	12	10	10	10	13,5	10

With respect to the chloride testing, three procedures were considered as the normal practice in different countries (figure 2):

- DCL 1- by **immersion** of the specimen in the solution previous protection of the perimetral face with and epoxy resin,
- DCL2- by placing a **"pond**" with the solution on the flat top face of the specimen and
- DCL3- similar to procedure 1) but **inverting** the specimen and making the contact with the solution only on the top flat face.

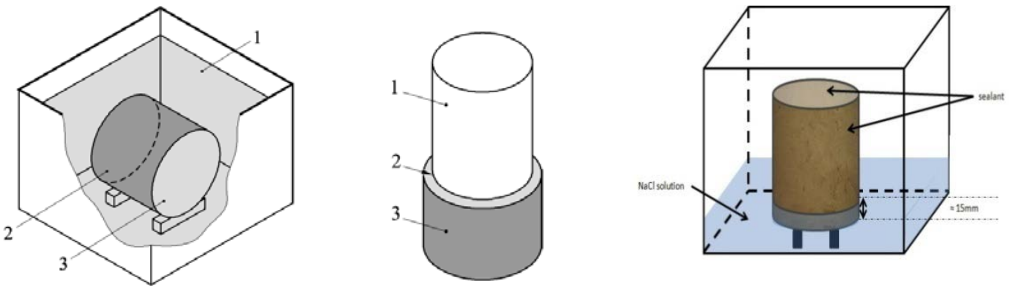

Figure 2. The three alternative modes of contact of the specimen with the salt solution in the chloride diffusion test.

In the chloride testing, it has to be emphasized is that the precision was also made on the fitting of Fick's law equation to the profiles in order to delimit the acceptable regression coefficient. The fitting procedure described in EN 12390-11:2015 indicates that the first

chloride value nearer of the concrete surface should be not considered in the fitting and the last values should be that in which the chloride concentration is C_i and C_i + 0,015 % (zero point). The objective of the analysis has been: 1) to establish the scatter of the regression coefficients R^2 obtained by each laboratory and from it the minimum value to be accepted in any fitting, and 2) the influence of the operator in the results from the profile fitting.

The carbonation test required two chambers, one at atmospheric carbon dioxide concentration and the other at 4% CO_2 concentration. The other exposure was atmospheric but protected from rain. In figure 3 is shown the average temperature and humidity of the towns of the laboratories.

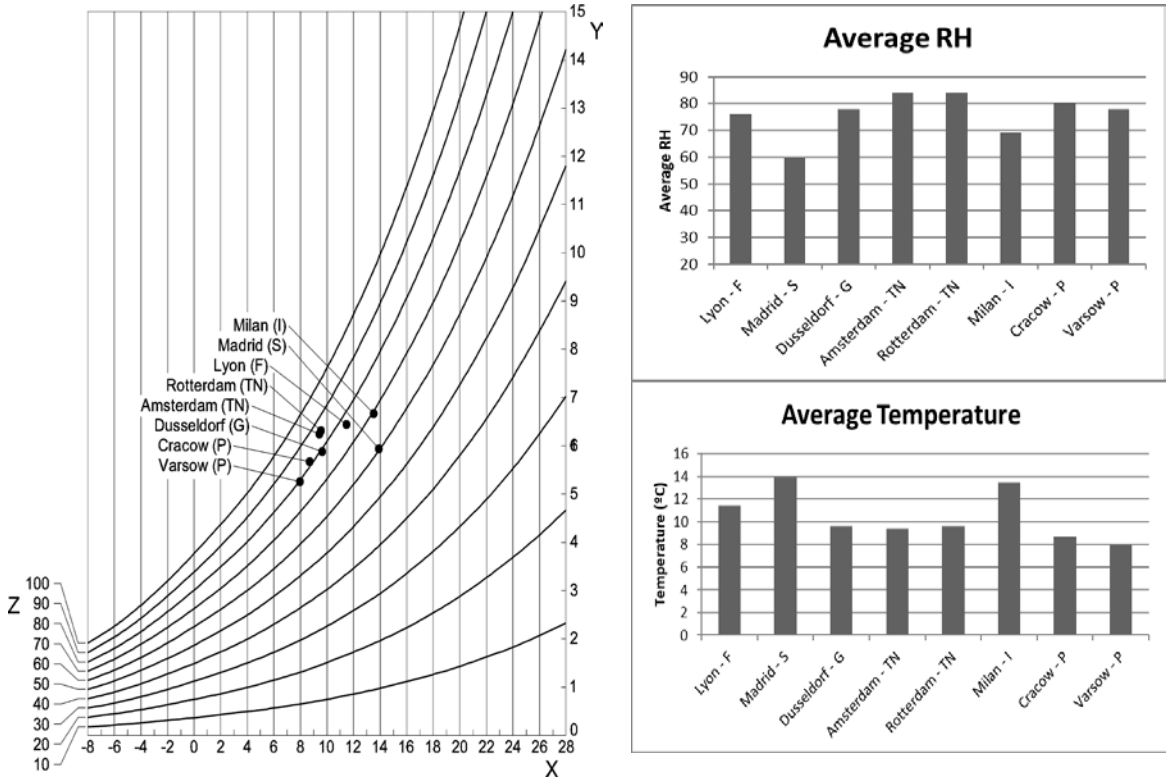

Figure 3. Sicrometric graphic of climatic parameters a as average temperature and relative humidity of the different towns where the specimens were exposed outdoor sheltered from rain

The statistical treatment has been made following ISO 5725-2: "Determination of the accuracy (trueness and precision) of measurement methods and results. Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method". According to this standard, the parameters to be calculated are the *mean value (m)*, the *repeatability standard deviation (sr)*, the *reproducibility standard deviation (sR)*, and the relationship between *m and (sr), (sR)* .In addition, the values of the *repeatability and reproducibility, r and R*, calculated for a 95% of probability have been also derived.

3 Results and Discussion

The compressive strength at 28 days of wet curing is given in Table 3.

Table 2. 28d compressive strength test results**.**

	Compressive strenght (MPa)							
	Mix 1	**Mix 2**	**Mix 3**	**Mix 4**	**Mix 5**	**Mix 6**	**Mix 7**	**Mix 8**
Average	**46.3**	**33.1**	**39.7**	**25.8**	**48.9**	**45.4**	**50.7**	**36.5**
Cv(%)	**1.4**	**2.9**	**5.0**	**10.6**	**9.5**	**8.6**	**5.0**	**4.0**

After the testing the results were submitted and treated for establishing the precision of each test type.

The results shown in Tables 4 and 5 indicated a repeatability for the samples tested of 10-22% for the carbonation rate *kc* in natural carbonation (outdoors protected from rain and controlled chamber respectively), of around 5% for the carbonation depth in the accelerated carbonation (at 4% of CO_2 concentration), and 23% in the Apparent diffusion coefficient for natural chloride diffusion and 13% for the chloride surface concentration.

Table 3. Precision data in carbonation rate (CEN/TS 12390-10) at about one year testing

Precision of carbonation rate expressed in terms of coefficient of variation	CV_r (%)	r (%)	CV_R (%)	R (%)
Outdoors protected from rain NCA1 *kc* ±	10	29	25	71
Controlled climatic chamber NCA2 *kc* ±	22	60	31	85
Accelerated carbonation (4% CO_2 conc.) depth ±	5	8.5	14	24

It has to be mentioned that the accelerated carbonation test was made using 4% carbon dioxide concentration while this amount was not finally approved and then, although presented in this work, this testing condition was changed for a 3% carbon dioxide. This is because several countries considered the 4% as risky high concentration because the possible damage of high proportions of CO_2 to the lower calcium ratio in the silicates when mineral additions are used (Galan et al. 2013).

Table 4. Precision data for EN 12390-11:2015

Precision of chloride diffusion expressed in terms of coefficient of variation	CV_r (%)	r (%)	CV_R (%)	R (%)
D_{nss} x 10^{-12} (m^2/s) ±	23	65	33	92
C_s (% concrete mass) ±	13	37	19	54

Regarding the fitting procedure its repeatability and reproducibility values are presented in Table 6. The averaged value resulted of 0.978 and then the minimum acceptable value of the regression coefficient was selected to be $R^2 = 0.95$.

These values are taken into consideration in the new method for classification of concretes

in Exposure Resistance Classes (ERC's) adopted recently in the new version still under balloting of Eurocode 2-structural concrete. The new classification in ERC's will be described in the new version of EN 206-100.

4 Conclusion

The main conclusions that can be drawn up are the following:

- The accelerated carbonation ranks the concrete mixes in a different manner than the natural exposure, and then it seems not appropriate to use CO_2 concentrations of 4%..
- In spite of the different climates of the participating laboratories both methods of natural carbonation give similar precision and are equally robust.
- The three test conditions of the chloride diffusion tests give similar diffusion coefficients, being a bit better the ponding test but they can be considered equally robust.
- Different operator or mathematical program does not introduce sources of error in the fitting procedure of the chloride profile. They present always a very high regression coefficient whose limit value can be considered $R^2 \geq 0.95$.

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