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THE EQUIVALENT PERFORMANCE CONCEPT APPLIED TO CARBONATION OF CONCRETE.

APPLICATION DU CONCEPT DE PERFORMANCE EQUIVALENTE AUX BETONS EXPOSES A LA CARBONATATION.

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ABSTRACT – Carbonation is a widely spread degradation of reinforced concrete and may be combined with other more severe exposures. In all cases, requirements for durability were based on prescriptions, such as minimum cement content and maximum water/cement ratio. However, according to the equivalent performance concept of the new standard NF EN 206-1, a new concrete mixture will be deemed to be satisfactory if its potential durability is at least as good as a reference concrete mixture. The experimental study shows the variability of performances of concrete mixtures which comply with the minimum requirements from standard. The work includes accelerated carbonation test and commonly used durability tests (porosity, permeability, chloride migration test, MIP), and results suggests that carbonation does not mainly depend on porosity.

RÉSUMÉ – La carbonatation est l'action environnementale la plus répandue et peut être combinée à des expositions plus sévères. Dans tous les cas, l'approche normative de la durabilité restait fondée sur une obligation de moyens. Cependant, la nouvelle norme NF EN 206-1 permet également par le concept de performance équivalente de qualifier un béton par comparaison à un béton de référence conforme à l'obligation de moyens. Cette étude expérimentale montre la variabilité des performances de bétons pourtant conformes aux valeurs limites seuils de la norme. Le programme comprend à la fois un essai de carbonatation accéléré et la détermination d'indicateurs de durabilité tels que la porosité, la perméabilité et un coefficient de diffusion des chlorures. Il montre la dépendance relativement faible de la vitesse de carbonatation aux caractéristiques du réseau poreux.

1. Introduction

As carbonation of concrete involves carbon dioxide (CO₂), most of structures and buildings are exposed to this type of degradation. Carbonation consists in chemical reaction between CO₂ from air and concrete portlandite Ca(OH)₂ and results in a drop of pH of surface concrete, which may lead to corrosion of reinforcement and spalling of concrete. So carbonation has to be taken into account in the design of most of concrete mixtures, to ensure appropriate durability of structures. Specifications for concrete durability have been based for a long time on prescriptive requirements. Threshold values of cement content,

water/binder ratio, compressive strength, and maximum mineral admixture contents are given in French standard. They are meant to warrantee a 50-year lifespan for concrete buildings and structures. However, such an approach does not draw benefits from advances in concrete research and may not be accurate enough. The new standard on specifications of concrete EN 206-1 has taken into account the need for performance-based specifications through the *equivalent performance concept*. Equivalent performance has to be shown by comparison with a reference concrete mixture, which complies with prescriptive requirements for a given exposure. The comparison may be made through durability tests that have to give appropriate evaluation of performance of concrete exposed to a given degradation, such as carbonation. According to this concept a methodology is being designed for every exposure (carbonation, chloride penetration, freeze/thaw cycles, chemical attacks). This experimental study deals with reference concrete mixtures. The purpose is to investigate the variability of performances of concrete mixtures which comply with prescriptive requirements, i.e. threshold values, in order to provide data to choose reference concrete. Moreover, as the experimental study includes an accelerated carbonation test, assessment of general durability indicators (Baroghel-Bouny et al., 2004) and mercury intrusion porosimetry tests, it is meant to give information on the effect of composition parameters such as aggregates, binder, water/cement ratio and curing on carbonation. It is also hoped that results from this study help to understand the relation between global properties and carbonation (Roy et al., 1998).

2. Experimental program

2.1 Materials, mixture proportions and curing

Eight concrete mixtures have been designed by choosing two values of each following composition parameters, namely: water/binder ratio, composition of binder, aggregates, as shown in Table I.

The two water/binder ratios, 0.63 and 0.58 were chosen from the maximum values for XC-XC2 and XC3-XC4 classes (defined in NF EN 206-1, Table NA.F.1). These classes respectively correspond to carbonation, from ordinary to high risk. Binder contents comply with the same requirements, they are the minimum values given in French standard. The same Portland cement CEM I 52,5 N was used in all concrete mixtures. Fly ash content of B1, B2, B5, and B6 concrete mixtures is the maximum mineral admixture content which comply with prescriptions from the standard. Two different aggregates mixtures were used to investigate the effect of aggregate type and aggregate mixture density, to have interfacial transition zone and porosity varied. Boulonnais sand and gravel are crushed dense limestone (WA24 = 0.7 %), they have been used in other laboratory studies and their main feature is a high proportion of fine elements. Graves de mer gravels and Pilier sand are sand-lime sea aggregates, they have a low fine elements proportion and a relatively high porosity (WA24 = 2 %). Very fine sand was used in B8 concrete to compare the effect of mineral admixture (fly ash) and aggregate mixture density.

Two batches of each concrete were made and cast in 7 x 7 x 28 cm molds (for accelerated carbonation test) and cylindrical \emptyset 11 x 22 cm molds. After 24 hours of sealed curing, the first set of specimens was cured under water for 28 days, and will be referred to as "24 h – Water". The second set of specimens was sealed cured until concrete reached 50

% of the minimum 28-day characteristic strength from standard, which is 20 MPa for XC1-XC2 classes, and 25 MPa for XC3-XC4 classes. Then they were cured in a room at a constant temperature of 20° C and a constant relative humidity of 50 % RH for 28 days. They will be referred to as "50 %".

Exposure classes	XC1, XC2					XC3, XC4				
(kg/m^3)	B1	B2	B3	B7	B8	B4	B5	B6		
G Boulonnais 12/20	541	561				541	561			
G Graves de mer 10/20			553	553	553			553		
G Boulonnais 4/12	416	432				416	432			
G Graves de mer 4/12			446	425	452			446		
S Boulonnais 0/4	992	915				980	900			
S Pilier 0/4			819	880	712			805		
Fine sand SIFRACO 0/1	-	-	-	-	-	-	-	144		
Cement (C) CEMI 52,5N	260	207	207	260	260	280	223	223		
Fly ash (FA) Cordemais	-	89	89	-	-	-	95	95		
(k = 0, 6)										
W _{eff}	163.	163.8	163.8	163.8	163.8	162.4	162.4	162.4		
	8									
WRA (Glénium 27)	3.82	3.65	0.97	0.50	0.60	3.67	2.98	1.69		
W _{eff} /Binder content	0.63	0.63	0.63	0.63	0.63	0.58	0.58	0.58		
Binder content (C+k.FA)	260	260	260	260	260	280	280	280		
FA/(FA+C)	0	0.30	0,30	0	0	0	0.30	0.30		
Fine elements (< 125 µm)	447	468	317	283	289	465	488	339		
Volume of paste V_p (L)	318.	328.3	271.4	256.3	258.4	322.3	339.7	283.5		

Table I. Mix proportions.

2.2 Durability tests

The 16 previously described materials underwent the same set of durability tests, after 28 days. Each test was done on three samples from the same batch, except the mercury intrusion porosimetry test, which was done on two samples after 90 days.

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Compression tests were carried out just after sealed curing and after 28 days. Gas permeability was measured to the AFPC-AFREM procedure, at a relative pressure of 1.00 bar, to assess apparent permeability, and between 2 bar and 4 bar, to assess intrinsic permeability by Klinkenberg approach.

Accelerated carbonation test was done according to the AFPC-AFREM procedure, in a carbonation chamber at 20°C and 65 % RH, with 50 % CO_2 by Laboratoire Matériaux et Durabilité des Constructions (LMDC) in Toulouse, France. Porosity was also measured according to the AFPC-AFREM procedure by LMDC. Chloride diffusivity was assessed from a steady state migration test called LMDC Test.

3. Results and discussion

3.1 Global properties

Compressive strength, porosity, gas permeability, chloride diffusivity may be considered as general durability indicators (Baroghel-Bouny et al., 2004). Comprehensive results are given in table II. Each result is a mean value, from three tests on different samples.

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	Strength (MPa)		Porosity		Porosity/ Volume of		Apparent gas		Intrinsic permeability	
	(IVII a)		(70)				permeability			
					paste (%)		(10^{-7} m^2)		(10^{-7} m^2)	
	24 h -	50 %	24 h -	50 %	24 h -	50 %	24 h -	50 %	24 h -	50 %
	W		W		W		W		W	
B1	47,8	36,2	12,7	14,4	40,0	45,2	1,8	11,8	2,6	9,8
B2	40,0	31,2	13,7	15,0	41,6	45,6	8,0	23,0	3,1	21,3
B3	35,4	25,3	14,1	17,3	52,1	63,7	5,2	33,4	4,4	20,2
B7	37,8	31,3	13,6	17,3	52,9	67,4	4,9	24,9	4,3	17,3
B8	37,7	29,4	13,2	15,4	51,1	59,7	4,2	30,7	3,9	18,7
B4	52,1	38,6	14,2	13,9	44,0	43,2	35,6	20,1	6,5	10,2
B5	52,7	38,8	14,2	15,7	41,8	46,3	1,0	26,3	3,1	8,1
B6	37,5	32,5	15,1	15,9	53,1	56,2	14,4	21,4	4,2	12,5

Table II. General durability indicators.

A 20-MPa characteristic strength was required for B1, B2, B3, B7, and B8 concrete mixtures (XC1-XC2 class), and a 25-MPa characteristic strength was required for B4, B5, and B6 concrete mixtures. 28-day compressive strengths were from 50 % (B6) to 139 % (B1) higher than required. As concrete mixtures comply with maximum Water/Binder ratios and minimum binder contents, this result may seem surprising. However, the highest compressive strengths were measured on concrete including crushed limestone aggregates (B1, B2, B4, and B5). The sand contains 7 % of fine elements (< 80 µm), which are not taken into account in binder content. So fine element contents (given in Table I) could explain this difference. The difference in compressive strength of concrete mixtures including crushed limestone or sea aggregates may also come from densities of aggregate mixtures and actual Water/Binder ratios. Effective water content (W_{eff}) differs from added water by water which is absorbed by aggregates. This is assessed by WA24 (water which is absorbed after 24 hours), given for each type of sand or gravel. Sea gravels were more porous and had a WA24 of 2 %, instead of 0.7 % for limestone gravel. But during batching and curing gravels may not absorb so much water, so the real water content of paste is higher for concrete made of sea gravels, and strength is lower.

Porosity results show the same trend and Porosity/Volume of paste ratios are consistent with strengths. Volume of paste has been defined as $W_{eff.}$ + Volume of fine elements (<125 µm), it is given in Table I. 125 µm is the maximum size of cement grains. If it is assumed that porosity of concrete is porosity of paste, Porosity/Volume of paste ratios give porosity of paste (Table II). It is closely linked to aggregate type, and the significant differences are consistent which what was assumed about real water content of paste to explain differences in strengths. Use of fine sand in B8 concrete mixture reduces concrete porosity and porosity

of paste, especially for dry curing ("50 %"). Fly ash would not have such a positive effect on density, and would only have a chemical part. But global properties have been assessed after 28 days, and positive effect of pozzolanic reaction might not have been observed yet.

The type of curing seems to have a significant effect, especially on gas permeability, as shown in Table II. This does not only come from curing conditions but also from configuration of samples for durability tests. Compressive strengths of studied concrete mixtures are significantly higher than required characteristic strengths. So strength at the end of sealed curing is less than 50 % of real 28-day compressive strength. It actually ranges from 22 % (B1 50 %) to 31 % (B6 50 %). So because of drying hydration rate of surface concrete of "50 %" samples is relatively low and explains the increase in transfer properties, such as gas permeability. Finally, for the "50 %" curing condition, the stronger concrete undergoes the worst curing conditions. This discrepancy between required and real compressive strength and its consequences on real curing is also to be kept in mind to analyze results from carbonation test. But configuration of samples and testing device may also be taken into account to explain effect of curing conditions on gas permeability. This is assessed on cylindrical Ø 11 x 5 cm specimens sawed from Ø 11 x 22 cm samples. As gas flux is transverse, it may flow through surface concrete layer, which is likely to be more permeable, for the "50 %" curing condition, because of early drying. In real atmospheric conditions, air or gas gets into concrete from the surface, so configuration and effect of curing conditions on durability may be different.

3.2 Accelerated carbonation test

The result of the accelerated carbonation test is carbonated depth. It is assessed by a colorimetric method on a cross section of prismatic 7 x 7x 28 cm samples, at 7, 14, 21, 28 and 56 days. 28-day carbonated depths are given in Figure 2.



Figure 1. Results of accelerated carbonation test and durability tests.

Standard deviations are given on first graph of Figure 1. In spite of dispersion of some results, significant differences may be observed. Most of carbonation depths ranged from 4 to 12 mm, whereas Water/Binder ratio and Binder content were kept constant. So the accelerated carbonation test is interesting in a performance based approach, as it is

sensitive. Moreover classifications of materials seem not to be affected by curing condition, which may be useful in a comparative approach.

Effects of composition parameters and curing conditions appear on the results of the accelerated test. "Dry" cured ("50 %") concrete generally had higher carbonation depth than concrete cured under water, except B6 50 % concrete. It should be noted that this result may not be relevant, as it is not consistent with other properties of the same material (see Table II) or results for B3 concrete (Figure 1), which had the same binder and aggregates.

Water/Binder ratio had not systematically the expected effect on carbonation, as B1, B7, and B8 concrete mixtures (W/B = 0.63) showed lower carbonated depth than B4, B5, and B6 concrete mixtures (W/B = 0.58). But the difference between the two W/B ratios is relatively low, and the difference between the water contents – respectively 163.8 and 162.4 L/m^3 – is even more reduced (0.9 %), as binder content also varied. So the accelerated test might not have been sensitive enough to show the difference, which also occurred for other properties, such as porosity and gas permeability. The effect of fly ash is clearer and has already been reported (Papadakis, 1999). From concrete mixtures which had the same aggregates and W/B ratio, it may be deduced a negative effect of fly ash. That may be explained by a lower portlandite content of the hydration products. Moreover, pozzolanic reaction reduces portlandite content. The effect of aggregates could have been more complicated. Moreover the test may not be sensitive enough to draw conclusions, and "50 %" curing may lead to better curing for sea aggregates concrete mixtures than limestone aggregates concrete mixtures, as shown in 3.1. As far as water cured concrete are concerned, from B1/B7, B2/B3, and B5/B6 concrete mixtures, it may be deduced that the crushed limestone aggregate lead to better resistance against carbonation. This may come from the quality of the interfacial transition zone between paste and aggregates or from density of the mix, as the sea aggregates mix lacks fine elements. In B8 concrete mixture, fine sand was added, and the concrete seemed to have a better behavior than B7.

In Figure 1 the second graph results from durability tests are plotted against carbonation depth. The highest sensitivity was shown with gas permeability, but no good correlation between global properties and carbonation may be deduced from these results. For instance the same porosity can be associated with very different carbonation rates. This has already been shown in literature (De Schutter and Audenaert, 2004)

3.3 Mercury intrusion porosimetry

As global properties may be difficult to analyze, mercury intrusion porosimetry (MIP) tests have been carried out. Pore size distribution curves and quantitative results, such as porosities, median and average pore diameters, may be useful to analyze properties of concrete.

MIP tests were carried out on B4 concrete samples, after 28 days and 90 days, to investigate the effect of curing condition, as shown in Figure 2. The porous mode which appears clearly at 28 days for "50 %" curing tended to decrease, but it could still be observed after 90 days, and it had an influence on median pore diameter.

Median pore diameter may be used as a quantitative result to be linked to global properties. In Figure 3, compressive strength is plotted against macroporosity, which is defined as porosity for pore diameters > 50 nm. Compressive strength decreases with an increase in porosity, which is to be linked to W/B ratio of paste.



Figure 2. Pore size distribution of B4 concrete mixture.

In Figure 4, intrinsic permeability is plotted against median pore diameter. Equations can be found in literature to link porosity and permeability, through MIP and other data. From the results of the study, median pore diameter seems to be a relevant parameter as far as gas permeability is concerned.



Figure 3. Compressive strength.

Figure 4. Intrinsic permeability.

4. Conclusions

This research includes accelerated carbonation test and a comprehensive study of porosity of 16 concrete mixtures. It can be used as a work on standards to translate prescriptions into data on potential durability and as an investigation on durability of concrete exposed to carbonation.

In the standard context, the objective was to investigate performances of reference concrete mixtures for XC exposure classes. Experimental data from accelerated test and other durability tests have shown significant variability of properties and resistance to carbonation. Carbonation depths after 28 days of accelerated test range continuously from 4 to 12 mm, whereas the studied concrete mixture had the same binder content and water/binder ratio, in the standard meaning. These results will be to taken into account for the choice of reference concrete mixtures, in order to avoid mixtures leading to the worst performances. Durability tests must be sensitive enough, and must show appropriate repeatability and reproducibility, to be use in the comparative approach of the equivalent performance concept. The accelerated carbonation test, according to AFPC-AFREM procedure, is sensitive enough to draw conclusions in spite of the dispersion of the results, and its reproducibility has been investigated (AFPC-AFREM, 1997).

This experimental work gives data on the effect of composition parameters and curing conditions. The effect of binder type was found to be more significant than the effect of aggregates type or water/binder ratio. So, for these types of concrete mixtures, carbonation would mainly depend on chemical behavior, rather than density of concrete, and a study on portlandite content of paste and concrete would bring useful data. Saturation degree of concrete has not been assessed but it could explain some trends, as CO_2 diffusivity is much higher in dry concrete than in saturated porosity. Curing condition is a major parameter, but it has to be defined precisely, and one has to pay attention to the configuration of samples and testing device.

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