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Reduction of concrete sorptivity with age through carbonation

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Abstract

Ordinary Portland cement (OPC) concrete specimens that had been air-dried for 3.5 years were found to have an increase in weight and reduction in sorptivity, with weight and sorptivity changes being greater for specimens with higher original sorptivity. Since this was attributed to carbonation of the surface zone, the porosity differences between end slices and the specimen interior in cylindrical specimens from another test series (of 4 years of age) were measured, together with the depths of carbonation. It was found from sensitivity analyses performed on a neural network model that the porosity difference can be attributed, in increasing order of importance, to (i) depth of carbonation, (ii) original sorptivity (which reflects both the quality of the mix and the efficiency of curing), and (iii) whether the end slice was a top or bottom one (reflecting the direction of casting and compaction). Tests on existing structures also showed that sorptivity decreased with age and also that (carbonated) surface sorptivities were lower than interior sorptivities, further confirming that the reduction of sorptivity with age is due to surface carbonation and that this carbonation occurs in and benefits surfaces with poorer initial quality more. This implies that carbonation could have mutually compensatory effects on some aspects of concrete durability. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Aging; Carbonation; Curing; Porosity; Sorptivity

1. Introduction

Sorptivity, which is an index of moisture transport into unsaturated specimens, has been recognised as an important index of concrete durability, because (i) the test method used for its determination reflects the way that most concretes will be penetrated by water and other injurious agents and (ii) it is an especially good measure of the quality of the near surface concrete, which governs durability related to reinforcement corrosion [1]. For example, the extent of curing is considered to be a major influence on the quality of cover zone concrete, and sorptivity is very sensitive to the type and duration of curing [2].

This paper reports some results on the influence of age on sorptivity of ordinary Portland cement (OPC) concretes. It goes on to identify carbonation as the cause for the reduction in sorptivity that was observed with increase in age, and to substantiate this through the measurement of porosity and carbonation depths, and also through some tests on existing structures.

2. Materials and methods

The test programmes described were designed for other primary objectives, which are described below. Nevertheless, the specimens that were prepared for them were also used to study the influence of age on sorptivity, and to ascribe reasons for it. The cement used in all cases was OPC.

2.1. Test programme 1

A full factorial experimental programme was carried out to study the relative effects of (i) mix, (ii) slump, (iii) compaction, and (iv) curing on sorptivity. Two commonly used volume batched mixes were used for this programme, namely 1:2:4 and 1:1.5:3. The variation in slump corresponded to 0–10 mm for low slump and 100 mm for high slump.

The specimens were cast in cylindrical moulds of 100 mm diameter × 100 mm height. Half the specimens were

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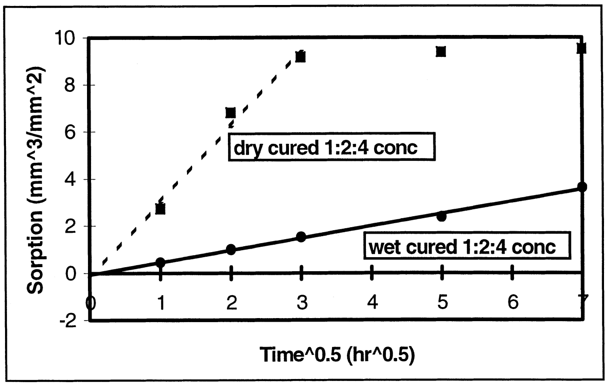

Fig. 1. Sorptivity plots for wet- and dry-cured 1:2:4 concrete.

vibrated for only quarter of the duration of the other half, which were subjected to full compaction on a vibrating table. After demoulding at 24 h, half the specimens were cured in water until an age of 28 days, while the other half were air-dried in the laboratory, where the temperature was around 27°C and the relative humidity around 85%. After this, all specimens were air-dried for around 6 months, until they reached moisture equilibrium with their surroundings, i.e., until specimen weights remained virtually unchanged. They were then coated on their cylindrical surfaces with an epoxy and made to absorb water from a shallow tray via sponges into their cast surfaces. The weights of specimens were measured after 1, 4, 9, 25, and 49 h of absorption, the initial weight also having been recorded. Weighing was done by removing specimens from their sponges, shaking off excess surface moisture, and placing them with their dry surfaces on an electronic pan balance, so that the absorbing surface would not be touched, and then returning them to their sponges within 15 s.

Sorptivity is defined as the slope of plots such as those in Fig. 1 between the volume of water absorbed per unit wetted surface area and the square root of time. In most cases the plots are linear up to 49 h of absorption, but in cases where sorption is very quick (e.g., for air-cured specimens), the linearity is confined to a shorter duration, reflecting the much higher sorptivity.

The study on the relative effects of mix, slump, compaction, and curing on sorptivity is described elsewhere [3]. However, in order to study the effect of age on sorptivity, these same specimens were subjected to sorptivity testing around 3.5 years after the original sorptivity testing had been performed. During the intervening period they were stored in the laboratory.

2.2. Test programme 2

This programme was devised to study more closely the effect of curing on sorptivity by varying both the duration and method of curing. In addition, actual external exposure conditions were simulated, and the testing extended to cover mortars as well as concretes, to study the effectiveness of plasters for increasing durability.

The sizes and method of casting for these specimens were as in Programme 1. Series A and B were 1:2:4 (w/c=0.60) and 1:1.5:3 (w/c=0.47) concretes, respectively. Series P and Q were 1:3 (w/c=0.56) and 1:5 (w/c=0.82) cement:sand mortars, while Series L was a 1:1:5 (w/c=1.00) cement:lime:sand mortar.

For each series, some of the specimens were water-cured in the laboratory for 0, 1, 3, 7, and 27 days after demoulding. Other specimens were kept outside the laboratory, exposed to direct sunlight. Some of these were wrapped in moist Hessian for 7 days, while others were placed in a box with a non-vapour-tight Perspex covering for 27 days. This covering ensured that the specimens would be exposed to the sun but shielded from rain; it also allowed evaporation of moisture from the specimens to take place.

After the above curing regimes, the specimens were air-dried in the laboratory and sorptivity testing carried out on them after coating, as in Programme 1. Subsequent to the sorptivity testing, the specimens were split in half along their axes, to obtain the depth of water penetration. After this, they were stored in the laboratory.

The results relating to the primary objective of this programme have been reported elsewhere [2]. However, around 4 years after their casting dates, some of these specimens (which had now been split into two) were sliced into five layers, perpendicular to their axes. Each layer of the specimen therefore had two pieces of 20 mm depth, which had their vertical edges trimmed so that triangular pieces were obtained. These pieces were used to measure the variation of properties with the depth of the original cylindrical specimens.

The depth of carbonation was measured by spraying a solution of 1% phenolphthalein in 70% ethanol; parts of the specimens that remained colourless (as opposed to turning

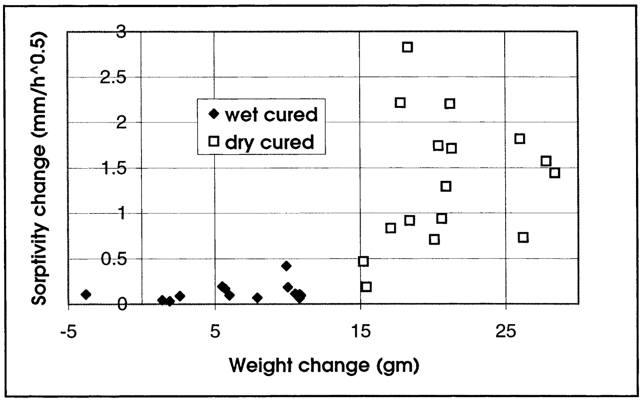

Fig. 2. Sorptivity change vs. weight change after 4 years of aging.

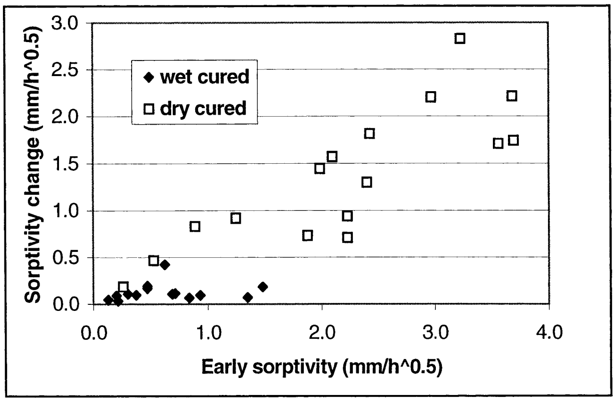

Fig. 3. Sorptivity change after 4 years of aging vs. early sorptivity.

pink/magenta) were considered as having been carbonated. In most cases, only the pieces from the top and bottom ends of the original cylinders showed carbonation.

The triangular pieces were also used to measure water permeable porosity. This was done by measuring the saturated surface dry weight (m_{sat}) and submerged weight (m_{sub}) after submerging the specimens in 0.5 m of water for 7 days. They were then oven-dried at 105°C for 3 days (during which it was established that no further weight losses were taking place), in order to obtain the oven dry weight (m_{dry}). The water permeable porosity is obtained as

$$[(m_{\mathrm{sat}} - m_{\mathrm{dry}})/(m_{\mathrm{sat}} - m_{\mathrm{sub}})] \times 100\%.$$

3. Experimental results

3.1. Influence of age on sorptivity

There was a consistent increase in weight and decrease in sorptivity for the specimens in the later test compared with the earlier one. The relationship between change in weight and change in sorptivity for all specimens is shown graphically in Fig. 2. It was also noted that the differences in weight and sorptivity are greatest for the air-cured specimens that had high initial sorptivities in the early test. Fig. 3 shows a clear positive correlation between early sorptivity and sorptivity change for the air-cured specimens; this correlation is not so clear for the water-cured ones.

Given that these OPC concrete specimens were around 6 months old even for the early test, it is unlikely that increased hydration accounts for the weight increases and sorptivity decreases 3.5 years later. It is likely that carbonation is the cause of this phenomenon, as discussed later in this paper. It

Table 1
Porosity, carbonation, and sorptivity measurements

Specimen	Slice (T/B)	Middle porosity (%)	End slice porosity (%)	Porosity differences (%)	Carbonation (mm)	Sorptivity (mm/h$^{1/2}$)
1:2:4 concrete, 0-day cure	B	10.15	9.07	1.08	5.0	0.834
	T	10.15	11.66	−1.52		
1:2:4 concrete, 27-day cure	B	10.75	10.18	0.58	4.0	0.469
	T	10.75	9.59	1.16	5.0	
1:1.5:3 concrete, 0-day cure	B	11.24	9.37	1.87	4.0	0.982
	T	11.24	18.92	−7.68	5.5	
1:1.5:3 concrete, 1-day cure	B	11.02	8.78	2.23	5.0	0.463
	T	11.02	11.04	−0.03	6.0	
1:1.5:3 concrete, 7-day cure	B	11.99	10.17	1.83	2.0	0.368
	T	11.99	14.00	−2.01	4.0	
1:1.5:3 concrete, 27-day cure	B	12.39	10.24	2.15	0.9	0.204
	T	12.39	16.01	−3.62	3.5	
1:1.5:3 concrete, Perspex cure	B	11.72	9.90	1.83	5.8	1.032
	T	11.72	12.10	−0.38	7.0	
1:1.5:3 concrete, Hessian cure	B	12.34	9.10	3.23	0.8	0.185
	T	12.34	17.05	−4.72	2.5	
1:3 mortar, 0-day cure	B	17.55	16.07	1.48	10.0	1.007
	T	17.55	16.05	1.50	14.5	
1:3 mortar, 27-day cure	B	17.19	14.73	2.46	6.0	0.413
	T	17.19	18.47	−1.28	5.5	
1:5 mortar, 0-day cure	B	19.73	15.83	3.90		2.605
	T	19.73	18.51	1.22		
1:5 mortar, 27-day cure	B	19.28	15.44	3.84		2.110
	T	19.28	20.16	−0.88		
1:1:5 mortar, 0-day cure	B	22.05	18.09	3.95	17.0	3.878
	T	22.05	22.71	−0.67	32.5	
1:1:5 mortar, 27-day cure	B	21.45	17.95	3.49	11.3	1.173
	T	21.45	22.33	−0.88	16.0	

is particularly to explore this hypothesis that the porosity and carbonation depth measurements were made on the specimens from Test Programme 2, 4 years after they were cast.

3.2. Porosity and carbonation depth measurements

Table 1 gives the porosity and carbonation depth measurements (at both top and bottom) for some of the specimens from Test Programme 2. It also gives the original sorptivity values obtained under Test Programme 2.

Table 1 gives the average porosity for the middle three slices and also the porosities of the top and bottom slices. The middle porosities do not appear to change with specimen curing regime, and are essentially constant for a given mix. However, the porosities of the top and bottom slices (where these terms are defined with respect to the direction of casting) differ considerably from the middle slice porosities.

This could be due to three reasons.

(i) The direction of casting would cause the bottom and top slices to have lower and higher porosities, respectively, as a consequence of the casting and compaction processes.

(ii) The curing regime would primarily affect surface layers, and hence cause differences between the end and middle slices, especially in poor curing regimes. This difference between end and middle slice porosities due to curing regime would also be greater in leaner mixes with higher porosities. It should be noted that the full factorial experiment in Test Programme 1 discovered that the mix-curing two factor interaction was as significant as the main factors of mix, slump and curing in their influence on sorptivity [3]. In the modelling of porosity changes described later, it was decided to represent this combined contribution from the mix and the curing regime by the original bottom surface sorptivity from Test Programme 2.

(iii) The carbonation of the end slices over 4 years would have reduced the porosity. The previously described decrease of sorptivity with age (albeit in another set of specimens — i.e., those for Test Programme 1) was attributed to such carbonation.

4. Modelling of porosity changes

An attempt was made to model the differences in top and bottom slice porosities (from the average middle porosity) as a function of (i) whether the slice was at the bottom or top, (ii) the mix type and curing regime, which was aliased by the original (Programme 2) bottom surface sorptivity, and (iii) the depth of carbonation.

A backpropagation neural network was employed for the above modelling [4], with the complete sets of data in Table 1 used for training (as the number of examples was small). A neural network is a model that tries to match inputs and outputs, whose dependencies are uncertain and/or non-linear. A binary representation was used for the end slice variable, which had two states (i.e., top/bottom), while a logarithmic transformation was applied to the carbonation and sorptivity values, in order to improve training [5]. The success of the training gives an indication of the existence of a dependency. Two hidden layers were used in the network, because the end slice input was not a continuous variable [6].

Although the trained network could not be tested because of the lack of data, it was used to study the sensitivity of the output. This was done by comparing the change in output (i.e., difference in end slice porosity from the average middle porosity, called "porosity difference") for changes in each input from its maximum to minimum value, while the other inputs were held at constant values [7].

Table 2
Sensitivity of porosity difference to surface type, sorptivity, and carbonation depth

Surface	Sorptivity	Carbonation	Porosity (%) difference	Porosity difference (%) change
Bottom	average	bottom deepest	1.77	
Bottom	average	bottom shallowest	3.67	
Top	average	top deepest	−1.36	
Top	average	top shallowest	−7.28	
Bottom	highest	bottom average	3.89	
Bottom	lowest	bottom average	1.24	
Top	highest	top average	−7.56	
Top	lowest	top average	1.04	
Bottom			2.64	6.43 (surface)
Top			−3.79	
	highest		−1.84	2.98 (sorptivity)
	lowest		1.14	
		deepest	0.20	2.01 (carbonation)
		shallowest	−1.81	

Table 2 shows the results of sensitivity analyses carried out on the above model, indicating the porosity differences predicted by the model for various combinations of surface, carbonation, and sorptivity values. The surface variable can have only two states, namely bottom and top and is represented by binary inputs. The sorptivity variable takes three values in Table 2, namely the highest, average, and lowest values of sorptivity in Table 1. The carbonation variable takes six values, corresponding to the deepest, average, and shallowest depths of carbonation from Table 1 in the bottom and top surfaces, respectively.

The lower part of the table indicates the "average" effects of changes in each of the three input variables from one end of their range to the other. It also indicates the porosity difference range that is associated with such changes. This shows that (i) a change in end slice (from bottom to top) resulted in a porosity difference change of 6.43%, (ii) the maximum change in sorptivity resulted in a porosity difference change of 2.98%, and (iii) the maximum change in carbonation depth resulted in a porosity difference change of 2.01%. This indicates that carbonation plays a reasonably significant part in reducing porosity.

5. Tests on existing structures

Tests on cores cut from concrete structures in Sri Lanka yielded average sorptivity values of 0.911 mm/h$^{1/2}$ (vertical surfaces of columns and beams of 30-year-old concrete), 0.892 mm/h$^{1/2}$ (bottom surfaces of slabs on 70-year-old concrete), and 0.674 mm/h$^{1/2}$ (top surfaces of slabs on 150-year-old concrete), further confirming that sorptivity decreases with age. This is despite the fact that average equivalent in-situ wet cube strengths also decreased with age, being 17.0, 12.6, and 7.6 MPa for the 30-, 70-, and 150-year-old concretes, respectively. The corresponding average depths of carbonation were 8, 41, and 67 mm, respectively, again pointing to carbonation as the cause for sorptivity reduction. Although it is likely that volume-batched 1:2:4 concrete was used for all three structures above, differences in the composition of the OPC may also have contributed to the differences in sorptivity, especially if the older cements had higher C_2S contents, which would have resulted in longer durations of hydration. The fairly low average depth of carbonation for the 30-year-old structure may be because the cores were taken from vertical surfaces exposed to rain, where carbonation would be less than in drier internal environments.

In the 30-year-old concrete structure referred to above, "twin cores" (cut from the same extracted core sample) were taken for testing from seven "bad" locations and five "good" locations ("good" cores being defined as those with zero depths of carbonation, and "bad" cores as those with non-zero depths). Obtaining zero carbonation depths from the phenolphthalein test in mature concrete is not uncommon [8]. However, it has been shown that the actual

Table 3
Test results from twin cores extracted from existing 30-year-old structure

Core ID	Sorptivity (mm/h$^{1/2}$)	Sorptivity ratio	Density (g/cm^3)	Strength (MPa)	Strength ratio	Carbonation (mm)
CMI-1G(O)	1.19	1.09	2.42	20.2	0.95	0
CMI-1G(I)	1.10		2.43	21.3		
PHI-G2(O)	0.64	0.44	2.38	17.2	1.13	0
PHI-G2(I)	1.46		2.44	15.3		
PHI-G5(O)	1.06	0.77	2.43	19.0	1.06	0
PHI-G5(I)	1.38		2.40	17.9		
CCI-B1(O)	1.27	1.02	2.45	13.3	1.09	0
CCI-B1(I)	1.24		2.45	12.2		
PHI-B8(O)	1.23	0.61	2.42	24.5	1.47	0
PHI-B8(I)	2.01		2.39	16.7		
PHI-B7(O)	1.43	0.89	2.47	12.7	0.71	30
PHI-B7(I)	1.61		2.44	17.8		
PHIIB11(O)	0.48	0.20	2.38	19.8	1.20	30
PHIIB11(I)	2.36		2.35	16.5		
RII-B5(O)	1.10	1.41	2.43	18.7	0.94	25
RII-B5(I)	0.78		2.45	19.9		
CCII-B2(O)			2.44	11.4	0.83	25
CCII-B2(I)	1.74		2.41	13.9		
KPI-B1(O)	0.57	0.12	2.44	15.5	1.86	5
KPI-B1(I)	4.65		2.44	8.4		
PHII-G9(O)	0.41	0.21	2.42	17.0	1.28	10
PHII-G9(I)	1.94		2.40	13.3		
RII-G3(O)	0.64	0.25	2.42	14.6	1.28	7.5
RII-G3(I)	2.57	2.40	11.4			
Average "good"	1.26	0.79	2.42	17.8	1.14	0.00
Average "bad"	1.56	0.51	2.42	15.1	1.16	18.93

carbonation front is deeper than indicated by this test [9], and all concrete surfaces would have experienced a measure of carbonation after 30 years.

The outer cores, designated with a suffix (O) were cut so that they incorporated the outside concrete surface (after the plaster was removed), while the inner cores, designated with a suffix (I) were taken from the interior of the extracted core. The results are given in Table 3 for sorptivity, density, and in-situ equivalent wet-cube strength. The ratios in Table 3 are those corresponding to the outer core values divided by inner core values.

Table 3 indicates that the mean strength of the good cores is a little higher and the mean sorptivity a little lower than that of the bad cores, as expected. The interesting feature in Table 3 is however that the sorptivity ratios are less than unity and the strength ratios greater than unity for both good and bad cores, indicating that the quality of the surface concrete is better than that of the interior concrete. This is particularly pronounced for the sorptivity ratio of bad cores (with non-zero depths of carbonation), and is further confirmation that carbonation reduces sorptivity, if not porosity. This also confirms the evidence in Fig. 3 that surfaces with poorer initial quality benefit more from carbonation, no doubt because they experience greater depths of carbonation.

6. Discussion

Blight [10] has reported that age (i.e., a 4-year exposure) reduced water absorption and attributed this to carbonation. Lampacher and Blight [11] tested properties of concrete sections at various depths in a 25-year-old concrete and reported that water sorptivity was lower in the cover zone, which was carbonated; this is akin to the results from the “twin cores” described before. They did find however that oxygen permeability was higher in the cover zone. A carbonation front has also been found to reduce chloride ion diffusion into concrete [12] and also to slow down sulphate attack [13]; some researchers have found however that carbonation reduces chloride binding [14].

It is also well established that carbonation reduces the capillary porosity. De Ceukelaire and Van Nieuwenburg [15] indicate that there is a solid volume increase of around 11% in the conversion of $Ca(OH)_2$ to $CaCO_3$; this involves an expansion of solid volume in the paste and hence a reduction of porosity. In addition, based on the molecular weights, there would be a 35% increase of weight as well. This would explain the decreases of porosity and sorptivity and increase of weight described in this paper.

An unequivocal validation of carbonation as the cause for sorptivity and porosity reduction can be made, if it can be shown that concrete in a carbon dioxide-free environment does not show such reductions. This however is outside the scope of this paper.

It should also be stated that the amount of $Ca(OH)_2$ available for conversion to $CaCO_3$ in blast-furnace slag and flyash cements is small. Furthermore, carbonation of the calcium silicate hydrate results in a reaction product with enhanced microporosity [15]. Hence, reduction in porosity with carbonation will not be generally exhibited by such concretes.

From a practical point of view, although carbonation leads to a reduced pH value in concrete and destroys the chemical protection given to the steel by concrete, given that it seems to actually reduce porosity and hence sorptivity in OPC concretes, it can be said to have some mutually compensatory effects on some aspects of concrete durability. In fact, this paper has shown that concrete surfaces with poorer initial quality benefit more from carbonation. This is probably why even some poorly cured concretes do not perform so badly in real structures — because the initially weak surface layer gets carbonated quickly and experiences a reduction in sorptivity. The aim in practice however should continue to be to produce a good quality surface zone in the concrete by good curing and to minimise carbonation.

7. Conclusions

1. Air-dried OPC concrete specimens experience an increase in weight and reduction in sorptivity with age; this can be attributed to carbonation of the surface zone.
2. Concrete surfaces with poorer initial quality, for example as a result of bad curing, show greater reductions in sorptivity as a result of subsequent carbonation.
3. The porosity difference between end slices and the specimen interior in cylindrical specimens with coated curved surfaces can be attributed, in increasing order of importance, to (i) carbonation in the end slices, (ii) richness of mix and efficiency of curing, and (iii) direction of casting and compaction.
4. The fact that (i) cores cut from existing structures (30 to 150 years old) showed increasing depths of carbonation and decreasing sorptivity with age, despite decreasing in strength, and that (ii) the sorptivities of carbonated outer cores was less than those of inner cores for “twin cores” (cut from the same extracted core) from the 30-year-old building, further confirmed conclusion (1) above. The fact that the ratio between the sorptivity of outer to inner cores was particularly low for highly carbonated locations also confirmed conclusion (2) above.

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