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The pore solution phase of carbonated cement pastes

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Abstract

Samples of hydrated cement pastes were exposed to atmospheres with various carbon dioxide concentrations at relative humidities controlled by different saturated salt solutions. When carbonated throughout their thickness, as indicated by the phenolphthalein test, they were resaturated with water and subjected to pore solution expression and analysis. The effects of the various carbonating environments on the pore solution composition and on aspects of the pore structure and mineralogy of the carbonated products are reported. Implications regarding the likely effects of different accelerated carbonation regimes on the corrosion behaviour of steel in concrete are discussed. In particular, it is shown that the use of saturated sodium nitrite solution to control the relative humidity of atmospheres with high concentrations of carbon dioxide may cause an evolution of gaseous oxides of nitrogen, which can result in the contamination of the pore solution with nitrite and nitrate salts.

Keywords: Carbonation; Cement paste; Pore solution; Pore size distribution; Mineralogy

1. Introduction

When steel is embedded in dense concrete of good quality, it is surrounded by a hydrated cement matrix containing pore electrolyte with a typical pH value in the range 13–14 [1]. In this alkaline environment, the steel is normally protected from corrosion by a passive film of oxide that acts as a barrier to the anodic dissolution of the metal. Carbonation of concrete, however, reduces the initially high pH value of the pore solution phase to a level at which the passive film can break down, allowing the steel to corrode at a rate determined primarily by the electrolytic conductivity of the carbonated material [2,3].

Because natural atmospheric carbonation is a slow, diffusion-controlled process that can take many years to penetrate through a typical thickness of concrete cover applied to reinforcing steel [4], laboratory studies of carbonation-induced corrosion are often carried out with specimens subjected to some form of accelerated carbonation. This commonly involves exposing the concrete to an atmosphere with high carbon dioxide concentration and relative humidity in the range 50–80%, controlled by means of a saturated salt solution. There is very little available published evidence of the possible influence of such accelerated exposure regimes in modifying the corrosion-related properties of the carbonated materials concerned.

The research described in this paper was therefore undertaken to clarify whether the accelerated carbonation regimes, required to produce carbonated cement paste for laboratory investigations over reasonable time scales, may affect the corrosion-related properties of concrete. The work involved the chemical characterisation of the pore electrolytes within hydrated cement pastes that were exposed to atmospheres with three different concentrations of carbon dioxide at relative humidities, controlled by five different saturated salt solutions. The features of the pore structure and the mineralogy of the carbonated specimens were also determined.

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2. Experimental procedures

2.1. Preparation of hydrated cement paste specimens

The cement used was a standard Ordinary Portland Cement (OPC), sieved through a 150-μm mesh to remove coarse particles. Its chemical analysis and potential mineralogical composition were as shown in Tables 1 and 2, respectively. Deionised water was added to the cement to produce a paste of water to cement ratio 0.6, which was blended thoroughly by hand for about 5 min with a spatula. The mixture was then poured into cylindrical PVC containers (49 mm diameter by 75 mm in height), compacted lightly by vibration and rotated end over end at 8 rpm for at least 24 h to minimise segregation and bleeding. After 7 days, the specimens were demoulded before being cured in saturated air at 20 °C for 14 days and then at 38 °C for 84 days. The cylinders were finally cut, perpendicular to their axis, into 5-mm-thick discs by means of a mechanical hacksaw.

2.2. Carbonation of cement pastes

The 5-mm-thick discs were placed in an upright position on specially constructed racks maintained at room temperature (approximately 22 °C) within sealed tanks, as illustrated in Fig. 1. The air within the tanks was conditioned by placing one of five saturated salt solutions in their bases and stirring periodically. The saturated salt solutions were sodium chloride (NaCl), sodium nitrite ($NaNO_2$), ammonium nitrate (NH_4NO_3), magnesium nitrate ($Mg(NO_3)_2.6H_2O$) and sodium dichromate ($Na_2Cr_2O_7.2H_2O$). The expected variation with temperature of the equilibrium relative humidity of air over each saturated salt solution is shown in Table 3. Measured values of relative humidity, determined with a hand-held Vaisala HM 34 Humidity and Temperature Meter that was connected via sealable ports in the sides of the tanks, were generally found after about 24 h to be within 2% of the equilibrium levels expected at 22 °C. When these near-equilibrium relative humidities had been recorded, the carbon dioxide levels within the various tanks were then varied by pumping one or another of the following gas mixtures through them for 30 min each day: 100% CO_2, 5% CO_2 (with 21% oxygen and 74% nitrogen) and approximately 0.03% CO_2 (air).

Table 1
Chemical analysis of OPC

Material	wt.%
CaO	63.86
SiO_2	19.07
Al_2O_3	5.13
Fe_2O_3	2.83
SO_3	3.25
MgO	1.35
Na_2O	0.11
K_2O	0.74
Cl	0.015

Table 2
Potential phase compositions of OPC (wt.%)

C_3S	C_2S	C_3A	C_4AF
61.16	8.54	8.81	8.61

To monitor the depths of carbonation, freshly broken pieces of hydrated cement paste were sprayed with phenolphthalein indicator solution, which changes from colourless below a pH value of approximately 9.2 to red above this pH value [5]. Thus, the depth from the exposed face at which a colour change to red is just visible gives a simple indication of carbonation depth. All the specimens in a particular environment were deemed to be carbonated when sample discs remained colourless throughout their thicknesses after the phenolphthalein test.

2.3. Pore solution analysis

Once the discs appeared to be carbonated throughout, as determined by the method described above, they were converted to a saturated, surface-dry condition by the following method that was intended to minimise the possibility of significant leaching. The technique involved placing the weighed discs on platforms above deionised water in sealed tanks and adding deionised water to each disc by pipette at a rate of 0.1 ml/day. Any very minor quantities of excess water that were not absorbed within 24 h were carefully removed by lens tissue, and the discs were reweighed daily until practically constant weights were achieved. Once saturated, five discs from each particular carbonation atmosphere were stacked together to form a cylinder (approximately 25 mm in height) and subjected to pore solution expression at a pressure of up to 300 MPa applied by means of a device similar to those described elsewhere [6,7].

The pore solutions were analysed by pH measurement and titration (for hydroxyl, carbonate and bicarbonate ions) using a Pye Unicam pH electrode in conjunction with a Philips digital pH meter. A Dionex DX-500 ion chromatography system, operated as described elsewhere [8], was used to measure all other significant anions (chloride, nitrite,

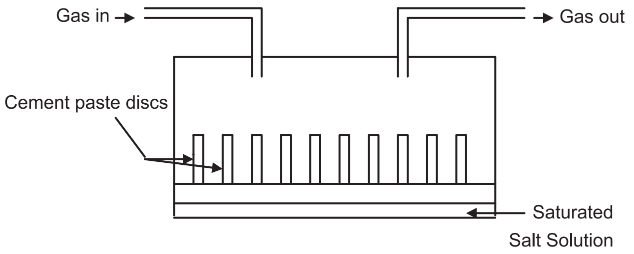

Fig. 1. Experimental setup used for the carbonation of cement paste discs.

Table 3
Relative humidity of air over saturated salt solutions (B.S. 3718: 1964)

Saturated salt solution	Temperature (°C)		
	20	25	30
	Relative humidity (%)		
Sodium chloride	76	75	75
Sodium nitrite	65	65	63
Ammonium nitrate	65	62	59
Magnesium nitrate	55	53	52
Sodium dichromate	55	54	52

nitrate and sulfate) and cations (sodium, potassium, calcium, magnesium and ammonium).

Analysis for bicarbonate and carbonate ions involved the titration of a 1.0 ml sample of pore solution with 1 mmol/l nitric acid whilst monitoring the pH. The titration of a carbonate solution with nitric acid is expected to result in two inflections, one around pH 9 and the other around pH 4. The first coincides with the point of conversion of carbonate to bicarbonate and the second with complete neutralisation [9]. No such clear inflections were, in fact, observed, and many of the solutions had an initial pH below 9. However, the quantity of 1 mmol/l nitric acid needed to convert the pore solution to pH 4 was recorded. From this and published pK_a data for the system $CO_3^{2-}/HCO_3^-/H_2CO_3$ [10], the maximum amounts of carbonate and bicarbonate present in the pore solution were estimated.

2.4. Analysis of porosity and related features

To determine the bulk density of the various carbonated specimens, discs were vacuum saturated for 24 h, and their weights immersed in water were recorded (W_1). They were then removed from water, dried with a lens tissue and their saturated, surface-dry weights (W_2) were recorded in air. The bulk densities were calculated according to Archimedes' principle (see Eq. (1)):

$$\text{Bulk density}\left(\text{g/cm}^3\right) = W_2/(W_2 - W_1) \tag{1}$$

Estimates of the 'coarse capillary porosity' were then made by exposing the saturated, surface-dry discs to an atmosphere of 90.7% relative humidity at a temperature of 22 °C until practically constant weights (W_3) were recorded. The relative humidity of 90.7% was achieved by placing the specimens over a saturated solution of hydrated barium chloride ($BaCl_2 \cdot 2H_2O$) within an airtight container. The coarse capillary porosity measured in this way represents the pores greater than approximately 30 nm in width [11] and is given by Eq. (2):

$$\text{Capillary porosity}(\%) = [(W_2 - W_3)/(W_2 - W_1)] \times 100 \tag{2}$$

To obtain simple estimates of total porosity, each specimen was finally dried at 105 °C for 24 h and its weight (W_4) was recorded. Total porosity data, which were estimated from Eq. (3), are of course very loosely defined here in view of the ill-characterised nature of the evaporable water:

$$\text{Total porosity (\%)} = [(W_2 - W_4)/(W_2 - W_1)] \times 100 \tag{3}$$

For comparison, 2.5 to 3 g samples obtained from of each of the carbonated specimens in a saturated, surface-dry condition were dried by evacuation after solvent replacement with propan-2-ol [12,13] and subjected to mercury intrusion porosimetry, using a Micromeritics Pore Sizer 9310. The intruded pore volumes (cm^3/g), measured at the maximum applied pressure of 30,000 psi (approximately 210 MPa), were recorded to provide an estimate of the total volume of pores of diameter larger than about 5 nm, assuming that the Washburn equation may be applied with typical values for the surface tension (0.485 N/m) and contact angle (117°) of mercury [14]. Again, it should be noted that the assumptions of mercury intrusion porosimetry are widely acknowledged to be subject to considerable uncertainties and that the technique is used here purely to provide comparable data for the various specimens.

To assess the main mineralogical changes induced by carbonation in the various environments, dried specimens were ground to fine powders and subjected to analysis by X-ray diffractometry (XRD) with Cu–Kα radiation.

3. Results and discussion

3.1. Pore solution composition

The ionic concentrations and pH values of the pore solution extracted from cement pastes subjected to different atmospheres are presented in Tables 4 and 5.

These data indicate that, for all the expressed pore solutions analysed, the sums of charge associated with the detected anions ($\sum^-$) and the detected cations ($\sum^+$) were balanced to within the expected accuracy of measurement. This strongly suggests that all the ions that were present at significant concentrations within the expressed pore solutions have been accounted for in the analysis.

The analysis of pore solution expressed from the noncarbonated cement paste of the same composition as those studied in this investigation had indicated that the liquid contained mainly potassium and sodium hydroxides and that the pH value was 13.49, corresponding to a hydroxyl ion concentration of 307 mmol/l [15]. As expected, the carbonated specimens all yielded pore solutions with hydroxyl ion concentrations of less than 1 mmol/l (pH <11), and the specimens exposed to carbonation in atmospheres with a high CO_2 concentration were more completely neutralised than those exposed to air. This shows that, although the phenolphthalein test can roughly indicate the depth of carbonation, it does not reflect the degree of carbonation [16].

Table 4
Concentration of anions (mmol/l) in the pore solution of hydrated cement paste after carbonation in various atmospheres

Saturated Salt solution	CO_2 concentration (%)	pH	OH^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	$\sum^-$
NaCl	100	7.4	3×10^{-4}	20.5	–	–	16.7	–	5.4	59.3
$NaNO_2$	100	7.2	2×10^{-4}	16.3	123.7	33.7	12.6	–	15.8	214.7
NH_4NO_3	100	9.6	4×10^{-2}	11.4	–	–	15.3	0.9	4.4	48.2
$Mg(NO_3)_2.6H_2O$	100	7.4	3×10^{-4}	23.4	–	–	18.0	–	5.8	65.2
$Na_2Cr_2O_7.2H_2O$	100	7.1	1×10^{-4}	23.4	–	–	20.3	–	6.9	70.9
NaCl	5	8.7	5×10^{-3}	13.1	–	–	19.7	–	2.8	55.3
$NaNO_2$	5	10.4	0.3	10.8	22.3	0.4	19.3	1.5	0.8	76.2
NH_4NO_3	5	9.9	0.1	12.0	–	–	24.1	0.5	1.3	62.6
$Mg(NO_3)_2.6H_2O$	5	10.9	0.8	7.5	–	–	2.0	9.8	3.1	35.0
$Na_2Cr_2O_7.2H_2O$	5	10.8	0.6	11.2	–	–	6.9	8.2	2.1	44.1
NaCl	0.03	10.7	0.5	4.1	–	–	1.2	7.6	3.0	25.2
$NaNO_2$	0.03	10.6	0.4	8.0	15.8	0.3	11.4	7.6	3.8	66.3
NH_4NO_3	0.03	10.6	0.4	7.5	–	–	10.9	6.5	3.3	46.0
$Mg(NO_3)_2.6H_2O$	0.03	10.9	0.8	8.4	–	–	1.9	8.0	2.0	31.0
$Na_2Cr_2O_7.2H_2O$	0.03	10.7	0.5	8.9	–	–	5.0	6.1	2.4	34.0

Only a small fraction of the total sodium and potassium ions present in the specimens were retained in solution after carbonation, and the concentrations of the soluble carbonate and bicarbonate ions were also low. This shows that carbonation results in the enhanced binding of alkali metal ions by the solid products of carbonation, the most likely effect being sorption by hydrous silica gel, formed as a result of the decalcification of C-S-H [16].

The overall concentrations of the electrolytes present in carbonated specimens produced in the various environments were generally far lower than that of the original non-carbonated material and were mainly confined within a fairly narrow range, approximately 55±15 mmol/l. For the specimens exposed over saturated sodium nitrite solutions, however, this was not always so and, in these cases, significant quantities of nitrite ions and lesser quantities of nitrate ions, derived from the saturated salt solution, had entered the carbonated specimens and were associated with the presence of additional calcium ions in the pore solution. This effect was very much more pronounced in the case of specimens carbonated at high CO_2 concentration than in those carbonated in air and can probably be attributed to a series of reactions of the following nature, or similar:

$$2NaNO_2 + CO_2 = Na_2CO_3 + NO\uparrow + NO_2\uparrow$$

$$Ca(OH)_2 + NO + NO_2 = Ca(NO_2)_2 + H_2O$$

$$2Ca(OH)_2 + 4NO_2 = Ca(NO_2)_2 + Ca(NO_3)_2 + 2H_2O$$

$$2Ca(OH)_2 + 4NO + 3O_2 = 2Ca(NO_3)_2 + 2H_2O$$

The practical implications of the above reactions, in terms of their possible effects on the corrosion behaviour of steel embedded in concrete subjected to accelerated carbonation in an atmosphere whose relative humidity is controlled by saturated sodium nitrite solution, may be significant in some cases. The nitrite ion is well known to function as an anodic inhibitor of corrosion of steel in concrete [17], and, in the case where specimens were carbonated in 100% CO_2 over saturated sodium nitrite solution, the eventual concentration of nitrite ions in the pore solution phase was in excess of 120 mmol/l. Air-

Table 5
Concentration of cations (mmol/l) in the pore solution of hydrated cement paste after carbonation in various atmospheres

Saturated salt solution	CO_2 concentration (%)	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	$\sum^+$
NaCl	100	–	3.8	9.9	0.9	20.8	57.1
$NaNO_2$	100	–	4.0	12.4	8.4	78.5	190.2
NH_4NO_3	100	–	1.7	5.5	–	20.3	47.8
$Mg(NO_3)_2.6H_2O$	100	–	5.2	11.4	1.0	22.1	62.8
$Na_2Cr_2O_7.2H_2O$	100	–	9.9	16.5	2.0	19.6	69.6
NaCl	5	–	3.9	8.9	–	22.3	57.4
$NaNO_2$	5	–	6.8	19.2	–	26.9	75.8
NH_4NO_3	5	–	6.5	16.0	–	22.9	68.3
$Mg(NO_3)_2.6H_2O$	5	–	0.3	0.6	–	19.1	39.1
$Na_2Cr_2O_7.2H_2O$	5	–	0.5	1.2	–	25.0	51.7
NaCl	0.03	–	3.0	14.5	–	12.3	42.1
$NaNO_2$	0.03	–	4.1	13.9	–	26.4	70.8
NH_4NO_3	0.03	–	3.5	13.2	–	18.2	53.1
$Mg(NO_3)_2.6H_2O$	0.03	–	3.1	26.4	–	7.1	43.7
$Na_2Cr_2O_7.2H_2O$	0.03	–	0.7	1.1	–	23.1	48.0

saturated aqueous solutions containing 100 mmol/l of nitrite have been found to passivate steel even in the presence of chloride at 10 mmol/l [15]. It would seem, therefore, that if specimens are being subjected to accelerated carbonation, with a view to studying the behaviour of steel in concrete that is intended to simulate the long-term composition of the naturally exposed material, the use of saturated sodium nitrite solution to control the relative humidity in an atmosphere of high CO_2 concentration should preferably be avoided.

A further interesting feature of the results shown in Table 4 is the observed variation in chloride ion concentration in the pore solution phase of the different types of carbonated specimen with the CO_2 concentration of the atmosphere concerned. It was found that a higher proportion of the chloride, present as an impurity in the cement, is released into the pore solution when carbonation is performed in 100% CO_2 rather than air. This is consistent with the findings of research conducted elsewhere [18], in which carbonation-induced decomposition of bound chloride from solid phases, such as calcium chloro-aluminate hydrates, has been demonstrated:

$$\begin{aligned}&3CaO.Al_2O_3.CaCl_2.10H_2O + 3CO_2\\&\quad + 3H_2O = 3CaCO_3 + 2Al(OH)_3 + CaCl_2 + 10H_2O\end{aligned}$$

The effect, coupled with the reduced hydroxyl ion concentration associated with the accelerated carbonation regime, implies that the pore solution phase is rendered more aggressive to embedded steel than naturally carbonated concrete exposed to the air would be.

3.2. Porosity and related features

The results of the water desorption experiments are presented in Table 6. These show that, as the carbon dioxide concentration increases, there was an apparent increase in bulk density and an associated decrease in the total porosity of the pastes, but a simultaneous increase in their coarse capillary porosity. The increase in bulk density and decrease in total porosity are also reflected in the mercury intrusion porosimetry data for total intruded pore volume, as shown in Fig. 2. These trends may be explicable in terms of an increasing degree of carbonation at the higher carbon dioxide concentrations, because previous research has shown that the carbonation of OPC pastes causes a marked densification of the material [19,20]. The contrary tendency of the coarse capillary porosity (pores wider than 30 nm) to increase with an increasing degree of carbonation is also in accord with previous findings [20]. This is important with respect to the corrosion-related properties of concrete, as these coarse pores provide the major interconnected pathways along which aggressive substances, such as chloride ions, can most readily penetrate the cement matrix from the environment. It is therefore apparent that cement pastes, carbonated in CO_2-enriched atmospheres, are more susceptible to chloride penetration than those carbonated in air.

Confirmation that the degree of carbonation was affected by the carbon dioxide concentration of the exposure environment is provided by the results obtained from X-ray diffraction studies, as shown in Table 7. These indicate that, at the highest carbon dioxide concentration, the transformation of portlandite to calcium carbonate in the form of calcite (with lesser quantities of vaterite and very little aragonite) was almost complete. This was so also for most of the specimens carbonated in 5% carbon dioxide. For the specimens carbonated in air, however, it was apparent that significant quantities of unreacted portlandite remained within the material, presumably enclosed by solid products of carbonation in view of the low pH of the pore solution, as indicated by the phenolphthalein test and by the analyses reported in Table 4. The mineralogy of the calcium carbonate present in the air-carbonated specimens was also different, with significant quantities of aragonite appearing in addition to the calcite and vaterite forms that predomi-

Table 6
Water desorption results for hydrated cement paste after carbonation in various atmospheres

Saturated salt solution	CO_2 concentration (%)	Bulk density (g/cm^3)	Capillary porosity (%)	Total porosity (%)
NaCl	100	1.992	22.15	38.21
$NaNO_2$	100	1.996	22.17	38.19
NH_4NO_3	100	1.993	22.87	38.67
$Mg(NO_3)_2.6H_2O$	100	1.992	23.07	39.17
$Na_2Cr_2O_7.2H_2O$	100	1.993	22.94	39.69
NaCl	5	1.984	15.58	39.62
$NaNO_2$	5	1.982	16.02	41.54
NH_4NO_3	5	1.990	16.75	41.21
$Mg(NO_3)_2.6H_2O$	5	1.982	15.81	41.19
$Na_2Cr_2O_7.2H_2O$	5	1.985	16.29	41.05
NaCl	0.03	1.960	4.44	43.35
$NaNO_2$	0.03	1.968	11.03	43.64
NH_4NO_3	0.03	1.960	16.15	45.31
$Mg(NO_3)_2.6H_2O$	0.03	1.960	3.54	44.16
$Na_2Cr_2O_7.2H_2O$	0.03	1.963	3.72	44.27

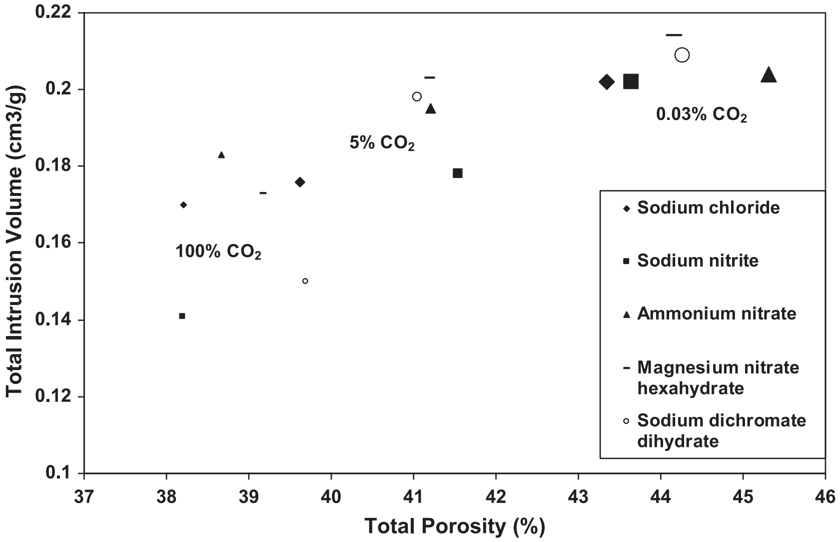

Fig. 2. Relationship between total intruded pore volume from MIP and total porosity from water desorption for cement pastes carbonated over various saturated salt solutions in atmospheres with 0.03% CO_2 (large symbols), 5% CO_2 (medium-sized symbols) and 100% CO_2 (small symbols).

nated in specimens carbonated at the higher carbon dioxide concentrations.

4. Conclusions

This research has elucidated changes induced by carbonation in the composition of hydrated cement pastes of water/cement ratio 0.6, which had been made with OPC of equivalent soda content 0.6% and which, prior to being carbonated, contained an alkaline pore electrolyte phase (pH value approximately 13.49) in which the major dissolved species were potassium, sodium and hydroxyl ions. The principal findings were as follows:

(i) The carbonation of the material in various atmospheres with relative humidity values in the range 50–80%, followed by resaturation with water, reduced the ionic strength of the pore electrolyte substantially and lowered its hydroxyl ion concentration to a near-neutral value (<1 mmol/l).

(ii) Although all specimens were assessed as carbonated throughout their thickness by the phenolphthalein test, the measured pH values of their expressed pore

Table 7
XRD results for hydrated cement paste after carbonation in various atmospheres

Saturated salt solution	CO_2 concentration (%)	Largest peak intensity			
		Calcite	Vaterite	Aragonite	Portlandite
NaCl	100	VS	M	W	W
$NaNO_2$	100	VS	M	ND	ND
NH_4NO_3	100	VS	M	ND	ND
$Mg(NO_3)_2.6H_2O$	100	VS	M	W	ND
$Na_2Cr_2O_7.2H_2O$	100	VS	M	ND	ND
NaCl	5	VS	M	ND	ND
$NaNO_2$	5	VS	W	ND	ND
NH_4NO_3	5	VS	W	ND	W
$Mg(NO_3)_2.6H_2O$	5	VS	M	W	M/S
$Na_2Cr_2O_7.2H_2O$	5	VS	M	W	M
NaCl	0.03	S	M	M	S
$NaNO_2$	0.03	VS	M	M	M
NH_4NO_3	0.03	VS	W	M	M
$Mg(NO_3)_2.6H_2O$	0.03	S/M	M	M	S
$Na_2Cr_2O_7.2H_2O$	0.03	S	M	M	M

Key

VS	S	M	W	ND
Very strong	Strong	Medium	Weak	Not detectable

solutions varied significantly with the carbon dioxide concentration of the carbonating atmosphere.

(iii) The mineralogy and pore structure of the solid phases present in the carbonated specimens also varied significantly with the carbon dioxide concentration of the carbonating atmosphere, as did the proportion of chloride ions released into the pore solution from impurities in the cement.

(iv) Except in cases where saturated sodium nitrite solution was employed, the composition of the pore solution phase of the carbonated specimens was not greatly affected by the nature of the saturated salt solutions used to control the relative humidity of the carbonating atmosphere; thus, none of the detected anions (chloride, sulfate and bicarbonate/carbonate) or cations (calcium, potassium and sodium) was present at a concentration of higher than 25 mmol/l.

(v) The use of saturated sodium nitrite solution led to the evolution of gaseous nitrogen oxides, which were apparently absorbed into the pore solution phase of the carbonated specimens as nitrite ions (with lesser amounts of nitrate ions) and balanced by additional dissolved calcium ions; for the specimens exposed to carbonation in 100% carbon dioxide, this resulted in a concentration of nitrite ions in the pore solution in excess of 100 mmol/l.

(vi) Because nitrite ions can act as anodic inhibitors of corrosion of steel, it is suggested that alternative methods to those involving the use of saturated sodium nitrite solution are preferable for controlling the relative humidity of carbon-dioxide-enriched atmospheres in studies of accelerated carbonation and its effects on corrosion of steel in concrete.

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