Influence of curing duration on accelerated carbonation of concrete and the uncertainties in its measurement

Shaik Hussain, Dipendu Bhunia and S B Singh

Department of Civil Engineering, BITS, Pilani, Rajasthan 333031, India

Abstract. Carbonation of concrete is a natural phenomenon of the ingress of carbon dioxide into pore structure of concrete leading to the lowering of pH value of pore solution of concrete. This causes the corrosion of steel in reinforced concrete. An acid-base indicator, phenolphthalein is usually used to identify the occurrence of carbonation in concrete. This paper deals with the influence of curing duration prior to accelerated carbonation of concrete. Various concrete samples with five design mixes with water binder ratio of 0.4, 0.45, 0.5, 0.55 and 0.6 have been pond cured for 7, 14 and 28 days and kept in accelerated carbonation chamber for 6 months. These specimens were tested for compressive strength, split tensile strength and depth of carbonation at an interval of 1 month. A generalized expression to predict the depth of carbonation in accordance with water binder ratio and curing duration has been developed. Also, scanning electron microscopic tests were conducted to study the microstructure of carbonated products. Results indicate that the concrete specimens subjected to pond curing of 28 days prior to accelerated carbonation had greater resistance to carbonation compared to the samples cured for 7 and 14 days. Also, the percentage of increase in compressive strength with respect to carbonation duration is highest for the mix with water binder ratio of 0.6

1. Introduction

Concrete is a composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregate [1]. The binding material being cement, hardened concrete too is impervious to water provided the concrete has less porosity. But upon prolonged exposure of concrete to aggressive environments, concrete loses its ability to remain impervious. Under such circumstances, concrete loses its durability.

Carbonation of concrete is usually referred to the effect of carbon dioxide (CO₂) on concrete. Once the concrete loses its impermeability, it allows the CO₂ in atmosphere to seep into concrete through its pores. When carbon dioxide (CO₂) from atmosphere comes in contact with the hydration products of cement, it changes the physical and chemical properties of the concrete [2-4]. Carbon dioxide in the air reacts with pore solution of concrete to from either carbonate ions or bicarbonate ions, depending on the pH of pore solution.

The carbonate ions react with the calcium phases of cement to precipitate calcium carbonate (CaCO₃) which has low solubility compared to calcium hydroxide (Ca(OH)₂) [5]. The dissolution of the calcium hydroxide will proceed until all the calcium phases are consumed to form calcium carbonate. The pore solution of concrete has a pH of 12–13 [6]. After complete carbonation, the pH value of concrete reaches 8.3 [7]. Minimum pH of 11.5 is required to keep the passive layer on reinforcement
stable [8]. But, when the concrete is completely carbonated and the pH falls to 8.3, the passive layer around the reinforcement obliterates leaving the steel reinforcement in reinforced concrete to potential corrosion threats. This is called carbonation-induced corrosion usually measured by the depth of carbonation.

The depth of carbonation of concrete depends on several factors like porosity of freshly hardened concrete, exposure conditions and duration of concrete curing prior to the carbonation.

The objectives of the present study are to study the effect of pre-carbonation water curing duration and water binder ratio on the kinetics of accelerated carbonation and its influence on mechanical properties of concrete; also, to identify the carbonation products of C-S-H in concrete.

Since it would more or less take a decade of prolonged exposure to natural concentration (0.03–0.04%) of carbon dioxide for the process of carbonation to initiate, the concrete samples in the present study were exposed to accelerated carbon dioxide concentration of 5%.

2. Materials and Methodology

2.1. Cement
Ordinary Portland cement (Grade 43) was used in the present research. The chemical and physical characteristics of the cement are mentioned in Table 1 and Table 2, respectively. The physical tests of cement have been determined in accordance to the standard procedure specified in IS 4031 [9].

2.2. Aggregates
The Crushed basalt was used as coarse aggregate and sand was used as fine aggregate. The specific gravity and size range of the aggregates is mentioned in Table 3.

2.3. Concrete mix proportions
The design mix proportions have been prepared in accordance with the guidelines given in IS 10262 [10]. The mix proportions prepared for the present experimental study had ordinary Portland cement made with five water binder ratios (0.4, 0.45, 0.5, 0.55 and 0.6) that yielded a mean strength of 20 to 40 MPa. The mixes are designed for constant water content. The ratio of 20 mm to 10 mm coarse aggregate by weight in the design mixes is fixed to 60:40 by trial and error. Table 4 gives the details of design mix proportions and the notations assigned to them in the present study. The mix proportions MW1, MW2, MW3, MW4 and MW5 denote the ordinary Portland cement concrete mixes with water binder ratio 0.40, 0.45, 0.50, 0.55 and 0.6, respectively.

2.4. Exposure conditions and tests conducted
To overcome the difficulties of natural carbonation that would consume few years of exposure, the concrete specimens are cured in an accelerated carbonation with controlled humidity and temperature. The concentration of CO₂ in the chamber was maintained at 5%, the temperature was maintained at 30–35 °C and humidity was kept at 60–70%. To investigate the effect of per-carbonation water curing duration on carbonation resistance of concrete samples, they were removed from the water after a curing duration of 7, 14 and 28 days, cleaned with a dry cloth and kept in an oven at a temperature of 60 °C for a day and then kept in carbonation chamber for six months. The samples were then removed from carbonation chamber once every month to study the mechanical strength such as compressive strength, tensile strength and durability property, and depth of carbonation. Figure 1 shows the carbonation chamber used in the present study.

Concrete cubes of 15×15×15 cm are used to measure compressive strength. The cubes are placed in such a manner that the load is applied to opposite sides of the cubes as cast. The load is axially applied without any shock and increased continuously at a rate of approximately 140 kg/sqcm/min as specified in IS 516–1959 [11]. The maximum load sustained by the specimen is recorded and divided by cross-sectional area to obtain the compressive strength of the specimen.

Concrete cylinders of 15 cm diameter and 30 cm height are cast and tested to measure the split tensile strength of carbonated concrete. The specimens were placed in the centering jig with packing strip
and/or loading pieces carefully positioning along the top and bottom of the plane of loading of the specimen. The load is to be applied without shock and increased continuously at a nominal rate within the range 1.2 N/ (mm2/min) to 2.4 N/ (mm2/min). The maximum load taken by the specimen before failure is noted and the split tensile strength of the concrete cylinder is found.

The depth of carbonation is measured through concrete cylinders of diameter 15 cm and height 30 cm. After carbonation, the cylinders are split and phenolphthalein indicator is sprayed onto the split faces of the cylinders from the plain face. The indicator is a phenolphthalein 1% ethanol solution with 1 g phenolphthalein and 90 ml ethanol diluted with water to 100 ml [12]. The carbonated zone, where Ca(OH)₂ is converted to CaCO₃, remains colorless and the zone where the value of pH is above 9.5, turns pinkish purple in color.

| Table 1. Chemical composition of cement |
|----------------------------------------|
| Chemical composition | OPC 43 grade (%) |
| SiO₂ | 20.27 |
| Al₂O₃ | 5.32 |
| Fe₂O₃ | 3.56 |
| Al₂O₃ + Fe₂O₃ | 8.88 |
| CaO | 60.41 |
| MgO | 2.46 |
| SO₃ | 3.17 |
| Loss on ignition | 3.55 |

| Table 2. Physical characteristics of cement |
|---------------------------------------------|
| Physical Characteristics | OPC 43 grade |
| Density (kg/m³) | 3090 |
| Specific gravity | 3.15 |
| Finess (%) | 8 |
| Normal consistency (%) | 33 |

| Table 3. Aggregates size and specific gravity |
|-----------------------------------------------|
| Physical Characteristics | Fine aggregate | Coarse Aggregate |
| Size range (mm) | 0.075 - 4.75 | 12.5 - 20 |
| Specific gravity | 2.42 | 2.77 |

| Table 4. Concrete design mix proportions (kg/m³) |
|------------------------------------------------|
| Mix Name | Water binder ratio | Cement | Water | Fine Aggregate | Coarse Aggregate |
| MW1 | 0.40 | 450 | 180 | 590 | 1201 |
| MW2 | 0.45 | 400 | 180 | 621 | 1211 |
| MW3 | 0.50 | 360 | 180 | 649 | 1212 |
| MW4 | 0.55 | 327 | 180 | 676 | 1211 |
| MW5 | 0.60 | 300 | 180 | 701 | 1204 |
3. Results and Discussions

3.1. Compressive strength

The trend of compressive strength changes with respect to carbonation curing duration for 7 day, 14 day and 28 day pre-carbonation water curing are presented in Figures 2 (a-c). The compressive strength has increased with the duration of carbonation irrespective of water binder ratio. The gain in strength is highest for the concrete samples that are water cured at 28 days with higher water-binder ratios as shown in Figure 3 which shows the compressive strength of samples with water binder ratio 0.5 for all pre-carbonation curing durations. The percentage gain in strength increased with the water-binder ratios. The percentage of increase in compressive strength with respect to carbonation duration is highest for the mix with water binder ratio of 0.6. The concrete mix with water binder ratio 0.6 had an increase in strength of 53%, 95% and 69% for the pond curing duration of 7 days, 14 days and 28 days pre-carbonation respectively. This is because the low porosity of the concrete mixes with lesser water-binder ratios hinder the diffusion of carbon dioxide into concrete resulting in the lesser-carbonated products. Thus, because the formation of calcite in mixes with lower water-binder ratios is relatively less, the gain in strength is minimum.
3.2. Split tensile strength

It can be seen from Figures 4 (a-c) that though the split tensile strength has increased with the duration of carbonation irrespective of water binder ratio, the increment in strength is marginal and very arbitrary. For the concrete samples cured in water for 7 days prior to carbonation, the concrete mix with water binder ratio of 0.40 had very little increase in the split tensile strength for carbonation duration of 6 months. This increase in strength is the least for mixes with water-binder ratios of 0.55 and 0.60 for concrete cured for 14 days and 28 days, respectively. Figure 5 shows the variation in split tensile strength for water bonder ratio 0.5 for all pre-carbonation water curing durations.
3.3. Depth of carbonation

From Figures 6 (a-c), it is observed that the depth of carbonation increases with the duration of carbon dioxide exposure. The concrete mixes with 7 days and 14 days pond curing have shown higher depths of carbonation than those cured for 28 days as shown in Figure 7. This is because of the poor porosity of the mixes, not completely cured or undergone complete hydration. The ingress of carbon dioxide into such mixes was easy. Once the concrete is cured for 28 days, the depth of carbonation of the mixes upon accelerated carbonation has reduced compared to 7 and 14 days pond cured samples. The percentage increase in the depth of carbonation from a water binder ratio 0.4 to 0.6 is highest at carbonation duration of 2 months. This trend is observed in all the three pre-carbonation pond-curing durations (7, 14 and 28 days). It can be inferred that the carbonation activity is at its extreme at 2 months of carbonation duration. After this duration the activity has gradually dwindled. This is due to the formation of calcium carbonate on the top surface of the concrete specimen, which blocks the further diffusion of carbon dioxide into concrete confirming that the steady state diffusion of carbon dioxide into concrete does not apply in the process of carbonation.
4. Expression to predict the carbonation depth

A relation between depth of carbonation and the compressive strength of concrete measured after being exposed to high amounts of carbon dioxide is generated. The values of carbonation depth and compressive strength obtained from the present study and those available in literature have been taken and represented graphically (Figure 8). Roy et al. [13] have studied the durability of concrete by accelerated carbonation for a period of 1, 4, 8 and 16 weeks with a carbon dioxide concentration of 6%. In a research done by Khunthongkeaw et al. [14], the depth of carbonation under natural and accelerated conditions of carbon dioxide concentrations has been compared and a relation has been formulated based on the carbon dioxide concentration, relative humidity and time of exposure. Cengiz[15] in his research emphasized on the influence of fly ash on accelerated carbonation of concrete and deduced that 50% replacement of fly ash has shown lesser carbonation compared to 70% replacement and normal Portland Cement Concrete. The values of carbonation depths and compressive strength obtained from the above mentioned works have been taken and represented in a graph along with the work done in the present research.

From Figure 8, the Equation (1) for the depth of carbonation is
where, ‘d’ is depth of carbonation in mm, ‘t’ is number of days of carbonation exposure in Days, ‘w’ is the water binder ratio of the mix and ‘S’ is compressive strength of the specimen.

5. Scanning Electron Microscopy (SEM)

Samples have been studied under SEM to find the microstructure of ordinary Portland cement mortar mix after hydration before being exposed to accelerated carbonation. The presence of calcium hydroxide (CH) can be observed through the hexagonal prism morphology as shown in Figure 9 (a). In some cement mixes with small amount of calcium hydroxide where the carbonation progresses due to rapid decalcification of C-S-H, the carbonation products get intermixed into calcium silicate hydrates and become difficult to identify the morphology [16]. Hence Energy dispersive X-ray spectroscopy (EDS) of carbonation of C-S-H from Figure 9 (b) at a region marked ‘X’ is performed and shown in Figure 9 (c). The EDS has shown that the products are calcium, oxygen and carbon, owing to the presence of calcite.

![Figure 9. (a) SEM image of CH prior to carbonation; (b) C-S-H decalcification; (c) EDS pictography](image)

6. Conclusions

- The carbonation resistance of concrete is greatly influenced by the curing duration of concrete sample.
- The concrete samples that have had complete hydration show better resistance towards carbonation compared to the ones that were cured for 7 and 14 days.
- The initial pre-carbonation porosity plays a predominant role in resisting the progression of carbon dioxide into concrete.
- The increase in split tensile strength after carbonation is not as significant as compressive strength.
- An expression to predict the depth of carbonation from compressive strength and water binder ratio has been generated.

References

[1] ASTM C125-15b 2015 Standard Terminology Relating to Concrete and Concrete Aggregates, ASTM International, West Conshohocken, PA.
[2] Castellote M, Andrade C, Turrillas X, Campo J, and Cuello G. J 2008 Accelerated carbonation of cement pastes in situ monitored by neutron diffraction. *Cement and concrete research*, 38(12), 1365-1373.

[3] Rostami V, Shao Y, Boyd A J, and He Z 2012 Microstructure of cement paste subject to early carbonation curing. *Cement and Concrete Research*, 42(1), 186-193.

[4] Bertos M F, Simons S J R, Hills C D, and Carey P J 2004 A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂. *Journal of hazardous materials*, 112(3), 193-205.

[5] Bary B, Sellier A, 2004 Coupled moisture—carbon dioxide–calcium transfer model for carbonation of concrete *Cement and Concrete Research* 34, 1859-1872.

[6] Neville A M 1995 *Properties of Concrete*, Fourth Edition, Longman Group Limited, England.

[7] Papadakis V G, Fardis M N and Vayenas C G 1992 Effect of Composition, Environmental Factors and Cement-lime Mortar Coating on Concrete Carbonation *Materials and Structures* 25, 293-304.

[8] Schiessl P 1988 *Corrosion of Steel in Concrete*, Report of the Technical Committee 60-CSC, RILEM, Chapman and Hall, London.

[9] IS 4031 1999 Methods of physical tests for hydraulic cement, New Delhi, India.

[10] IS 10262 2009 Guidelines for concrete mix design proportioning, New Delhi, India.

[11] IS 516 1959 Methods of tests for strength of concrete, New Delhi, India.

[12] Fukushima T, Yoshizaki Y, Tomosawa F, and Takahashi K 1998 Relationship between neutralization depth and concentration distribution of CaCO₃-Ca(OH)₂ in carbonated concrete. *ACI Special Publication*, 179.

[13] Roy S K, Poh K B and Northwood D O 1999 Durability of concrete-accelerated carbonation and weathering studies *Building and Environment* 34, 597-606.

[14] Khunthongkeaw J, Tangtermsirikul S, and Leelawat T 2006 A study on carbonation depth prediction for flyash concrete *Construction and Building Materials* 20, 744-753.

[15] Cengiz D A 2003 Accelerated carbonation and testing of concrete made with flyash *Construction and Building Materials* 17, 147-152

[16] Berger R L, Young J F, and Leung K 1972 Acceleration of hydration of calcium silicates by carbon dioxide treatment *Nature* 240(97): 16-18.