

# Assessment of carbonation depth under natural and accelerated carbonation conditions

Shaik Hussain, Dipendu Bhunia and S.B. Singh

This paper deals with the effect of accelerated carbonation on mechanical properties and durability of unreinforced concrete. Concrete with water binder ratios of 0.35, 0.50 and 0.65 were cast and kept in accelerated carbonation chamber under controlled conditions for a period of 1 year. Specimens were removed at predefined time intervals and tested for compressive strength, flexural strength, modulus of elasticity, volume of permeable pores and depth of carbonation. The depth of carbonation obtained from the accelerated carbonation conditions are used to predict the carbonation depths under natural concentration of carbon dioxide using Fick's law and the values are compared to those obtained from a structure 60 years old.

## 1. INTRODUCTION

Concrete as one of the basic construction materials, is likely to withstand aggressive environments and maintain its durability without hindrance. But being a porous material, it is susceptible to ingress of various substances through its interconnected capillary pores. When carbon dioxide ( $\text{CO}_2$ ) from atmosphere comes in contact with the hydration products of cement, it changes the physical and chemical properties of the concrete. This process is termed as carbonation of concrete [1-3].

Carbonation is a physiochemical process, which involves the diffusion of carbon dioxide in the gaseous phase of the concrete pores and the dissolution of  $\text{CO}_2$  in the pore water as

carbonic acid ( $\text{H}_2\text{CO}_3$ ). It constitutes the formation of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions and the dissolution of hydration products of cement such as  $\text{Ca}(\text{OH})_2$  to release  $\text{Ca}^{2+}$  and hydroxyl ions and the formation of  $\text{CaCO}_3$  [4]. This reaction of  $\text{Ca}(\text{OH})_2$  is considered to be the most responsible reason for the reduction of the pH value of the pore solution of the concrete [5] which being around 12.6-13 is observed to fall to less than 9 [6]. This fall in the value of pH is held responsible for the initiation of depassivation phenomena of rebar embedded in the concrete, further exposing the rebar to potential corrosion threats. This is called carbonation-induced corrosion. Therefore it is extremely crucial to study the carbon dioxide ingress in concrete in accordance to the duration of exposure to predict the time taken by the products of carbonation to reach the rebar.

Though the process of carbonation of reinforced concrete, in terms of durability proves to be a malady, it is likely to improve the mechanical properties of unreinforced concrete. Because the carbonation product  $\text{CaCO}_3$  has higher molar volume than that of  $\text{Ca}(\text{OH})_2$  and C-S-H, a decrease in porosity is evident [4]. This decrease in porosity may improve the mechanical properties such as compressive strength, flexural strength, split tensile strength and modulus of elasticity of the carbonated concrete. It is to be noted here that, only surface porosity of concrete is decreased under carbonation [7-9]. The reason for which may be explained because the ingress of carbon dioxide is limited to a certain depth.

The factors that mainly influence the rate of carbonation are type and amount of pozzolanic material, the water binder ratio, the porosity of the material, the moisture in the vicinity and the duration of curing [10,11]. Amongst all the above-mentioned factors, the amount of moisture plays a principal role in governing the kinetics of carbonation. A low relative humidity dries up the concrete capillary pores and makes it difficult for the carbon dioxide to enter the pores irrespective of how porous the medium is. On the contrary high relative humidity condense the water in pores of concrete and delays carbon dioxide diffusion. Therefore for ideal conditions of carbonation, the relative humidity is to be maintained between 50-70% [12, 13].

The atmospheric concentration of carbon dioxide is 0.03-0.04% by volume. This considerably less concentration of carbon dioxide is the reason why the process of natural carbonation takes more than a decade to initiate [14]. To predict the long-term performance of concrete after natural carbonation, the process can be accelerated either by increasing the concentration of carbon dioxide in the vicinity or by increasing the atmospheric pressure [5]. Though few researchers still debate about how reliable the results of accelerated carbonation are in comparison to the natural process, Yongsheng et al., [14] proposed that the results of micro-structural analysis of natural and accelerated carbonation showed same phase compositions and similar XRD peak intensities.

This paper deals with the experimental investigation on the compressive strength, flexural strength, modulus of elasticity, volume of permeable voids and depth of carbonation of the unreinforced concrete exposed to accelerated carbonation for up to 1 year. To study the behavior of water binder ratios on the carbonation of concrete, water binder ratios of 0.35, 0.5 and 0.65 are adopted. Further, from the laws of diffusion,

**Table 1. Chemical composition of cement**

Chemical composition	OPC 43 grade (%)
SiO <sub>2</sub>	20.27
Al <sub>2</sub> O <sub>3</sub>	5.32
Fe <sub>2</sub> O <sub>3</sub>	3.56
CaO	60.41
MgO	2.46
SO <sub>3</sub>	3.17
Loss on ignition	3.55

**Table 2. Physical characteristics of cement**

Physical Characteristics	OPC 43 grade
Density (kg/m <sup>3</sup> )	3090.15
Specific gravity	3.15
Fineness (%)	8
Normal consistency	33

and the depth of carbonation obtained from the accelerated carbonation conditions, depth of carbonation under natural exposure conditions are predicted and compared with results obtained from the experimental investigation from a structure that is subjected to degrading natural environment for 60 years.

## 2. EXPERIMENTAL PROGRAM

### 2.1. Materials

Ordinary Portland cement (Grade 43) was used in the present experimental program, the chemical compositions of which are listed out in Table 1. The physical characteristics of the cement are given in Table 2. Crushed basalt with a specific gravity of 2.77 was used as a coarse aggregate and sand as fine aggregate has a specific gravity of 2.42. The size of coarse aggregates were in a range of 12.5 to 20 mm while fine aggregates were in a range of 0.075 to 4.75 mm. Water reducing admixture has been used to attain a slump of 100±20 mm to make the concrete workable. Its specific gravity was found to be 1.08. Concrete mix proportions for the various mixes used are presented in Table 3. The specimens were kept in carbonation chamber for 7, 28, 60, 120, 180, 240, 300 and 365 days after moist curing for 29 days. After the process of accelerated curing, the specimens were removed and

**Table 3. Design mix proportions of concrete**

Mix proportions for 28 day strength of 30-35 MPa in kg/m <sup>3</sup>				
Water binder ratio	Cement	Water	Fine Aggregate	Coarse Aggregate
0.35	450	157	557	1088
0.50	394	197	655	1125
0.65	304	197	734	1114

tested for their predestined experiments. These results are compared to concrete specimens associated with 7 and 28 days of water curing.

**2.2. Carbonation environment**

To compensate the process of natural carbonation, which normally takes few decades, the concrete specimens are subjected to high amounts of carbon dioxide in a controlled environment. The concentration of carbon dioxide was fixed to 5% and the relative humidity ranged from 50% to 70%. The temperature of the chamber in which the specimens were kept was maintained at 25°C to 35°C.

**2.3. Tests procedure**

To evaluate the carbonation effects on mechanical properties of concrete, several experiments such as compressive strength, flexural strength and modulus of elasticity were performed. Depth of carbonation and volume of permeable voids were also measured to study the durability aspects of carbonated concrete. To measure the compressive strength and volume of permeable voids, concrete cubes of (15×15×15) cm<sup>3</sup> were cast, flexural strength, depth of carbonation and modulus of elasticity were measured by casting prisms of (10×10×50) cm, (15×15×90) cm and cylinders of 30 cm height and 15 cm diameter respectively. They were then removed carefully from moulds and placed in water for an age of 28 days. Once the process of water curing was accomplished, the specimens were removed from water and dried in air for a day (temperature being 40°C) and kept in carbonation chamber after cleaning with a dry cloth. After the requisite duration of curing, the specimens were removed from the chamber and tested.

Tests for compressive and flexural strengths were carried out using the methods suggested in IS 516 [15]. The test for modulus of elasticity includes the testing of cylindrical specimen under axial compression and measuring the strain.

Depth of carbonation was measured by spraying phenolphthalein pH indicator. The indicator is a phenolphthalein 1% ethanol solution with 1g phenolphthalein and 90 ml ethanol diluted in water to 100 ml [16]. The carbonated zone, where Ca(OH)<sub>2</sub> is converted to CaCO<sub>3</sub>, remains colorless and the zone where the value of pH was above 9.5, turns purple in color. Volume of permeable voids was measured by the method suggested in ASTM C642 [17].

The concrete specimens once removed from carbonation chamber were kept in oven for 24 hours and weighed. This process was repeated until the difference between two successive readings was within 0.5% of the lesser weight. The specimens were then immersed in water for 48 hours and weighed after its surface was dried. The readings were

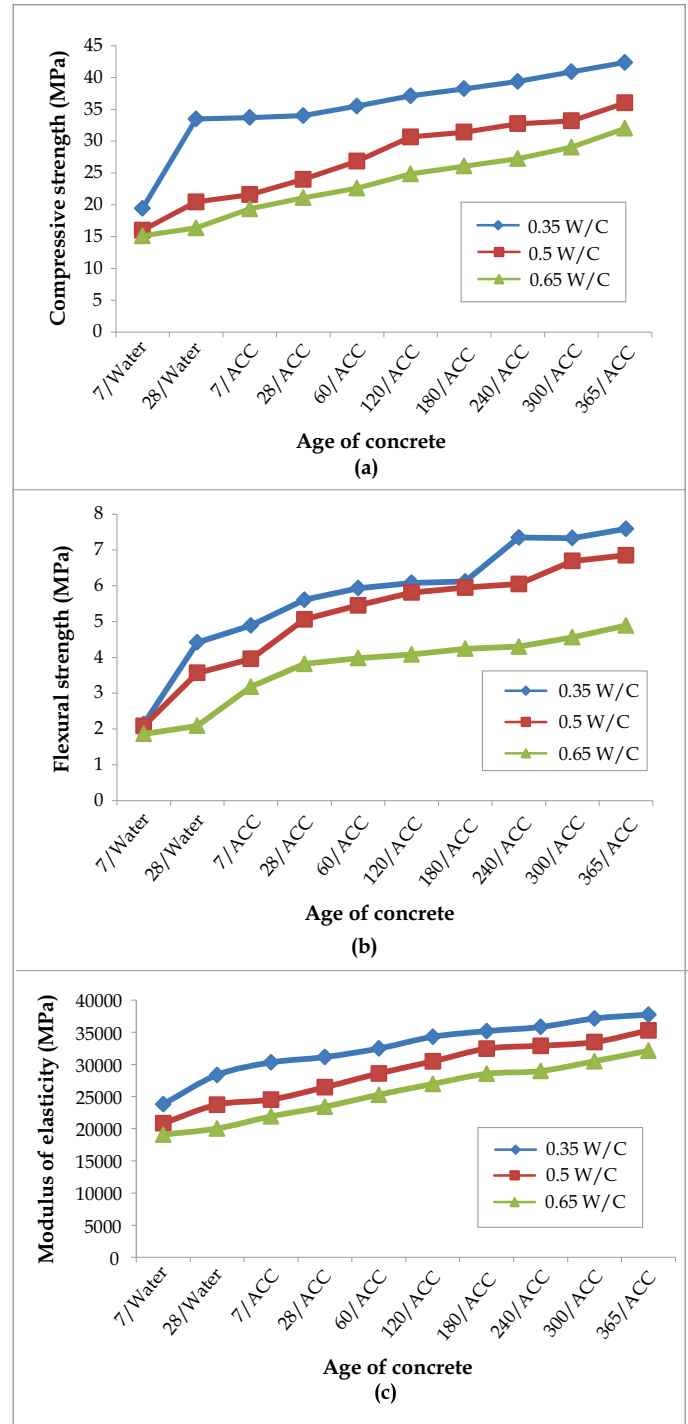


Figure 1. Mechanical properties vs Age of concrete

taken till the difference between the readings was less than 0.5%. After this the specimens were subjected to rigorous boiling for 5 hours and then weighed after 14 hours. Finally the specimens were suspended in water and their apparent weights were taken. The calculation of volume of permeable voids (%) was done by the formulae mentioned in ASTM C 642 [17].

To validate the results obtained from the predicted values of depth of carbonation under natural carbon dioxide exposure, depth of carbonation was found for a building that was subjected to environmental concentrations of CO<sub>2</sub> for 60 years, and rigorous change in climatic conditions with the temperature ranging from 48°C during month of June to 1°C during December.

### 3. EXPERIMENTAL RESULTS AND DISCUSSIONS

#### 3.1. Mechanical properties

##### 3.1.1 Influence of age of carbonation

The compressive strengths, flexural strengths and modulus of elasticity for different duration of carbonation of each mix proportion curing are shown in Figure 1 (a - c) respectively. From the figures it is perceived that the accelerated carbonation has some beneficial effects on concrete. These mechanical strengths increased with an increase in the duration of accelerated curing. The increase in compressive strength, flexural strength and modulus of elasticity for

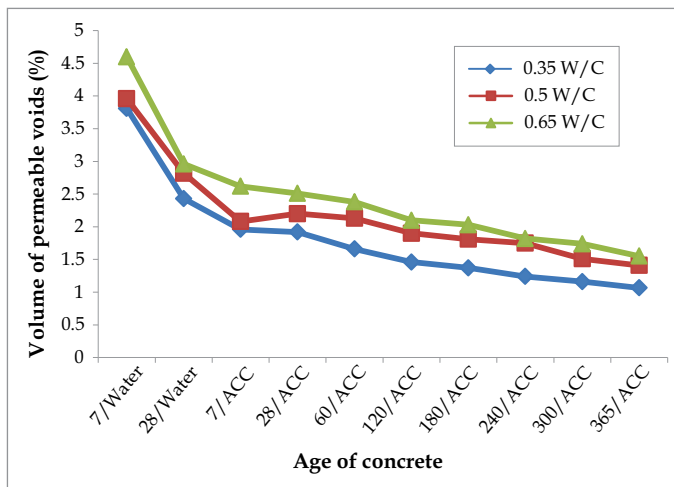


Figure 2. Volume of permeable voids vs Age of concrete

365 days of accelerated curing over an age of 28 days water curing is remarkable. This increase may be accounted for the greater volume of CaCO<sub>3</sub> over Ca(OH)<sub>2</sub>.

##### 3.1.2 Influence of water binder ratio

The results shown in Figure 1 demonstrate the compressive and flexural strengths and modulus of elasticity of the three types of concrete mix designs used in the present experimental study. The concrete mix proportion with highest water binder ratio has shown least mechanical strength compared to the other mixes. This decrease is particularly adamant in concrete mix proportion with the water binder ratio of 0.65.

#### 3.2. Durability

##### 3.2.1. Volume of permeable voids (%)

The test results for the volume of permeable voids are presented in Figure 2. As shown in the figure, the percentage of voids has decreased with the age of accelerated carbonation. The drop is highest for the concrete mix with the least value of water-binder ratio.

##### 3.2.2 Depth of carbonation

The depth of carbonation is the measure of the depth till which CaCO<sub>3</sub> has formed. From Figure 3, it is evident that the depth of carbonation has increased with age of accelerated carbonation. The depth of carbonation is observed to be highest in the concrete mix proportion with highest water

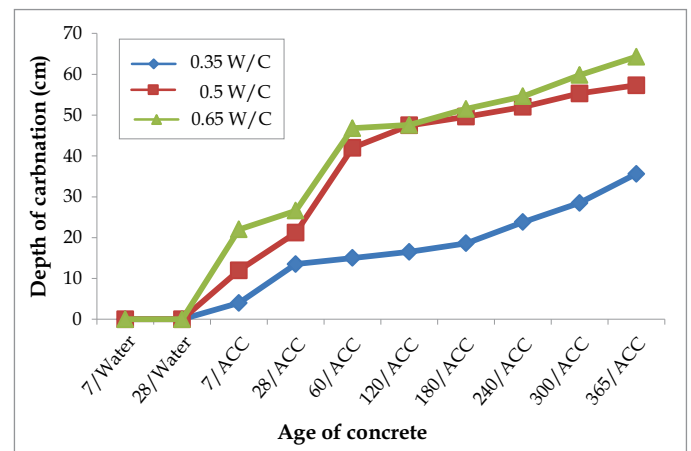


Figure 3. Depth of carbonation vs Age of concrete

binder ratio. It is because of the decrease in compressive strength and open pore structure that makes the concrete with highest water binder ratio have highest the depth of carbonation.

**4. PREDICTION OF CARBONATION DEPTH FOR ENVIRONMENTAL EXPOSURE**

To understand the kinetics of carbonation in real life, i.e., for an exposure of concrete to natural concentration of carbon dioxide (0.03- 0.04%), it would take more than a decade to completely comprehend the study, which is why increasing the carbon dioxide concentration, accelerating the process contemplates it.

Though results from accelerated carbonation tests have been used to predict the carbonation depths on long-term natural exposures [5], there still lies a conjecture on how to extrapolate the real performance from accelerated tests [18-20]. This is certainly a complex phenomenon because the natural exposure conditions differ greatly from the controlled accelerated conditions where the humidity and temperature are maintained constant. This predominantly changes the mass transfer properties [21].

It is a well-established directive that the carbonation depth progresses with duration of exposure. Nevertheless the rate of carbonation decreases with time and is usually considered proportional to square root of exposure time [5]. This assumption holds good even in the case of accelerated carbonation exposure.

This can be well explained by Fick’s second law of diffusion in which the diffusion causes the concentration to change with time. Assuming a uni-directional flow the partial differential equation can be written as,

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \dots(1)$$

where  $D$  is the diffusion coefficient ( $m^2/s$ ),  $\phi$  is the concentration ( $g/m^3$ ),  $t$  is time (s) and  $x$  is the position [carbonation depth in (m)].

Usually, the progression of carbonation depth is considered as the square root model of time. The equation was first proposed by Tuutti [22] and was written as,

$$x = k\sqrt{t} \dots(2)$$

where  $x$  is carbonation depth,  $t$  is duration of exposure and  $k$  represents coefficient of carbonation.

The coefficient of carbonation can be determined by another approach theoretically, which uses the first law of diffusion. Fick’s first law of diffusion relates the diffusive flux to the concentration under the assumption of steady state. It states that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient. In one (spatial) dimension, the law is given by the following equation.

$$J = -D \left( \frac{\partial \phi}{\partial x} \right) \dots(3)$$

where  $J$  is the diffusion flux ( $g/m^2.s$ ).

Upon further simplification of Eq. (3) and relating the expression  $k$  in terms of concentration, the rate of carbonation can be written as, [23,24]

$$k = \sqrt{\frac{2D\phi}{m}} \dots(4)$$

where  $k$  is rate of carbonation ( $m/s^{0.5}$ ) and  $m$  is amount of  $CO_2$  required to react with alkali phases ( $g/m^3$ ) contained in unit volume of sample. Assuming the values of  $D$  and  $m$  as sample properties constants for each concrete, a relationship of carbonation coefficients can be generated in terms of carbon dioxide concentrations. Thus the ratio of coefficient of carbonation for accelerated and natural conditions can be expressed as,

$$\frac{k_{acc}}{k_{nat}} = \frac{\sqrt{\phi_{acc}}}{\sqrt{\phi_{nat}}} \dots(5)$$

where  $\phi_{acc}$  and  $\phi_{nat}$  are carbon dioxide concentrations in natural and accelerated exposure conditions respectively.

A linear relationship between  $k_{acc}$  and  $k_{nat}$  has been assumed in the literature review [25,26]. The ratio of carbonation coefficients of both accelerated and natural conditions from Eq. 2 can be related to those of the theoretical values obtained from the Eq. 5. To rationalize the above assumption, survey of literature has been done to find any relation that considers the

theoretical and practical carbonation coefficients on a single platform. Khunthongkaew et al., [27] in his research exposed the concrete samples for a carbon dioxide concentration of 4% by volume, where the ratios of carbonation coefficients of accelerated and natural carbonation, under experimental evaluation and theoretical formulae differed by 4.29%. Ohga et al., [28] in a similar research when exposed the concrete to carbon dioxide concentration of 7%, kept indoor, the ratios differed by 3.81%. Chin[29] considered the carbon dioxide concentrations of 7% and 12%, and deduced the ratios of carbonation coefficients under both conditions. He found that the ratios have had a deviation of 1.62% and 5.02% respectively for the concentrations.

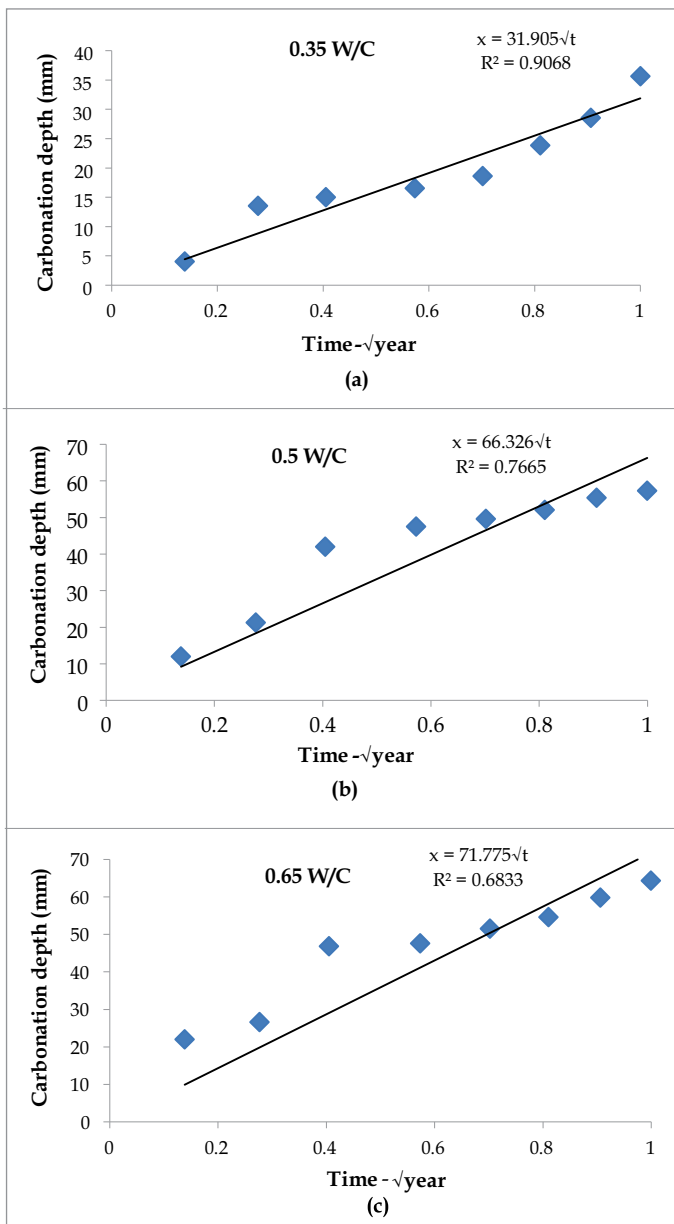


Figure 4. (a-c) Carbonation depth vs Time

Figure 4 (a-c) shows the depth of carbonation and coefficient of carbonation for water binder ratios adopted in the present paper. The predicted values for coefficient of carbonation under natural exposure conditions are determined by equating the ratios obtained from Eq. 2 and Eq. 5. The depth of carbonation in accordance to these carbonation coefficients is plotted in Figure 5, which shows the predicted depth of carbonation every 10 years for a period of 60 years.

It is evident from the Figure 5 that the depth of carbonation is least in the concrete with water binder ratio 0.35; where as a marginal difference in depth of carbonation of concretes with water binder ratios of 0.50 and 0.65 is observed. 60 years of concrete exposure to natural concentration of carbon dioxide (0.03%-0.04%) yielded a depth of carbonation of 46 mm for a water binder ratio of 0.65, which was attained in 60 days under accelerated carbonation conditions.

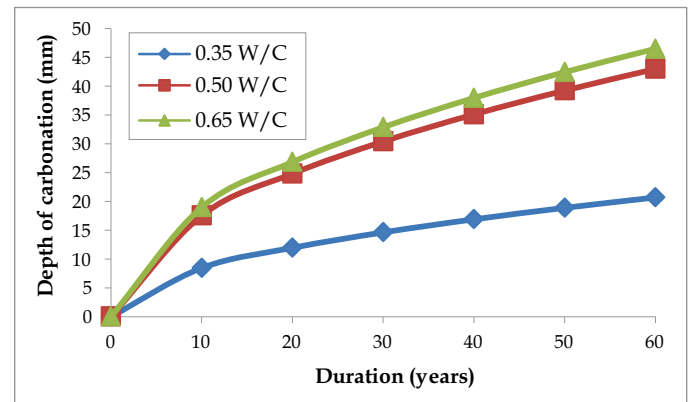


Figure 5. Predicted depth of carbonation depth under environmental exposure to CO<sub>2</sub>



**Table 4. Depth of carbonation of 60 years old structure**

Floor	Elements / Locations	Depth of Carbonation (mm)
Ground Floor	Columns	17
	Beams	22
	Ceiling Slabs	26
1 <sup>st</sup> Floor	Columns	23
	Beams	30
	Ceiling Slabs	26

The results of depth of carbonation found for a building with an age of 60 years is tabulated in Table 4. Drilling a cylindrical core of diameter 75 mm and spraying phenolphthalein indicator found the depth of carbonation.

As no information has been found on the field about the grade of concrete and water binder ratio involved during the construction of the structure, it is not possible to determine the water binder ratio that we could relate to the accelerated conditions. Given the Indian code of practice at that time, the water binder ratio is presumed to be between 0.45-0.50.

The depth of carbonation obtained from the predicted values by equating Eq. 2 and Eq. 5 for a water binder ratio of 0.50 as seen in Figure 5 for 60 years is 40mm. But the original maximum value for the depth of carbonation from Table 4 has been found to be 30 mm. The depths of carbonation predicted from the accelerated conditions adhere to the controlled conditions of temperature and humidity where as the structure when exposed for 60 years to the natural carbon dioxide and the weather, withstands varying temperature and humidity. This explains the difference in the values of depths of carbonation. The other reason for this difference might be because of the relatively lower  $R^2$  value for the equation of depth of carbonation in Figure 4(b).

## 5. CONCLUSIONS

Unreinforced concrete when exposed to higher carbon dioxide concentrations increases its surface porosity, which in turn enhances its mechanical properties. Concrete with three water binder ratios 0.35, 0.50 and 0.65 were used to test for their mechanical strength and durability. It is observed that the compressive strength, flexural strength and modulus of elasticity have increased with the duration of the accelerated carbonation exposure. The depth of carbonation too, as

expected has increased. It is highest for the concrete with a water binder ratio of 0.65. Volume of permeable voids has reduced with the duration of exposure, owing to the decrease in surface porosity. The depth of carbonation under natural concentration of carbon dioxide is predicted for an age of 60 years for the accelerated tests using laws of diffusion. The depth of carbonation for a structure 60 years old has been obtained and compared to the predicted values. It is observed that the values differ in its magnitude, which might be explained because of the controlled conditions of accelerated curing chamber, whereas the structure exposed to natural environment has no such restraints.

## Acknowledgements

Department of Science & Technology (SERB), New Delhi, supported the research presented in this paper. Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of the sponsors.

## References

- Castellot M, Andrade C, Turrillas X, Campo J, Cuello GJ. Accelerated carbonation of cement pastes in situ monitored by neutron diffraction. *CemConcRes* 2008;38:1365-1373.
- Rostami V, Shao Y, Boyd AJ, He Z. Microstructure of cement paste subject to early carbonation curing. *CemConcRes* 2012; 42: 186-193.
- Bertos MF, Simons SJR, Hills CD, Carey PJ. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO<sub>2</sub>. *J Hazard Mater* 2004;B112:193-205.
- Thierry M, Villian G, Dangla P, Platret G. Investigation of the carbonation front shape on cementitious materials: Effects of the chemical kinetics. *CemConcRes* 2007; 37:1047-1058.
- Simsomphon K, Franke L. Carbonation rates of concretes containing high volume of pozzolanic materials. *CemConcRes* 2007; 37: 1647-1653.
- Jack Chi M, Huang Ran, Yang CC, Effects of carbonation on mechanical properties and durability of concrete using accelerated testing method. *J Mar Sc Tech* 2002; 10: 14-20.
- Verbeck GJ, Carbonation of hydrated Portland cement. *ASTM Sp. Tech. Publ* 1958; 205: 17-36.
- Leber I, Blakely FA. Some effects of carbon dioxide on mortars and concrete. *J Amer ConrInst* 1956; 53: 295-308.
- Dias WPS. Reduction of concrete sorptivity with age through carbonation. *CemConcRes* 2000; 30: 1255-1261.
- Roper H, Baweja D. Carbonation-Chloride interactions and their influence on corrosion rates of steel in concrete. *Durability of Concrete, ACI* 1991; 126: 295-315.
- Veleva L, Castro P, Hernandez G, Schorr M. The corrosion performance of steel and reinforced concrete in a tropical humid climate. *A Review. Corros Rev* 1998; 16: 235-284.

12. Wierig H. Long time studies on the carbonation of concrete under normal outdoor exposure, RILEM Seminar 1984: 239-249.
13. Saeki T, Ogha H, Nagataki S. Mechanism of carbonation and prediction of carbonation process of concrete, Concrete Library of JSCE 1991; 414: 23-36.
14. Yongsheng JI, Yingshu Y, Jianli S, Yuqiang MA, Shaoping L. Comparison of concrete condition and high CO<sub>2</sub> concentration environments. J Wuhan Univ Tech mater 2010: 515-522.
15. IS 516: Methods of tests for Strength of Concrete, New Delhi, India 1959.
16. Fukushima T, Yoshizaki Y, Tomosawa F, Takahashi K. Relationship between neutralization depth and concentration distribution of CaCO<sub>3</sub>-Ca(OH)<sub>2</sub> in carbonated concrete. Adv Conc Tech, ACI 1998; 179: 347- 363.
17. ASTM C 642 - 06 Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, Philadelphia, USA 2006.
18. Sanjuán MA, Andrade C, Cheyrezy M. Concrete carbonation tests in natural and accelerated conditions. Adv Cem Res 2003;15:171-80.
19. Ishida T, Maekawa K, Solitan M. Theoretically identified strong coupling of carbonation rate and thermodynamic moisture states in micropores of concrete. J Adv Concr Technol 2004;2:213-22.
20. Muntean A, Meier SA, Peter MA, Böhm M, Kropp J. A note on limitations of the use of accelerated concrete-carbonation tests for service-life predictions. Germany: Universität Bremen; 2005.
21. Neves R, Branco F, Brito J. Field assessment of the relationship between natural and accelerated concrete carbonation resistance. Cem Conc Res 2013; 41: 9-15.
22. Tuutti K, Corrosion of steel in concrete. Cem Conc Res Inst, CBI Res Nr. Foo 4: 82.
23. Bakker RFM, Corrosion of steel in concrete. In: P. Schiessl, ed. Rep Tech Com 60-CSC RILEM 1998: 22-65.
24. Richardson MG, Carbonation of reinforced concrete: its causes and management. New York CITIS 1988.
25. Parrott LJ. A review of carbonation in reinforced concrete. UK: BRE; 1987.
26. Gehlen C. Probabilistische Lebensdauerbe rechnung von stahlbetonbauwerken Zuverlässigkeitsbetra chtungen zur wirks amenvermeidung von bewehrungskorrosion. Germany: German Committee for Structural Concrete (DafStb); 2000 [in German].
27. Khunthongkeaw J, Tangtermsirikul S, Leelawat T. A study on carbonation depth prediction for fly ash concrete, Const Build Mat 2006; 20: 744-753.
28. Ohga H, Nagataki S. Prediction and evaluation of the depth of carbonation of concrete by the accelerated tests, Concrete Library of JSCE 1989; 12: 93-106.
29. Chin MS, Carbonation of concrete M. Eng. Thesis, National University of Singapore, Singapore, 1991.



**Shaik Hussain** received his Bachelors and Masters Degree from Andhra University College of Engineering, Visakhapatnam; is a research scholar in Birla Institute of Technology and Science, Pilani campus. His areas of interest are carbonation of concrete and its effects on corrosion of reinforcement and Earthquake Engineering are his research interests.

**Dipendu Bhunia** holds Bachelors and Masters Degree from Bengal Engineering College, Howrah; PhD from IIT, Roorkee. He is an Assistant Professor in the Department of Civil Engineering, Birla Institute of Technology and Science, Pilani Campus. His research interests include performance based seismic design, concrete technology and energy efficient construction.



**S.B. Singh** is an ACI member. He is associate member of ACI Committee 440 and Professor of Civil Engineering Department in Birla Institute of Technology and Science, Pilani Campus. He is also a member of American Society of Civil Engineers and Indian Concrete Institute. He has been post-doctoral fellow at LTU in Michigan and has been awarded P.E. license from the state of Michigan, USA. He is also serving as editorial board member of various journals.