A Review on Carbonation Study in Concrete

Suba U
PG Student
Department of Structural Engineering
Anna University Regional Campus - Tirunelveli.

Dr. Srinivasan P
Senior Principal Scientist
CSIR - Structural Engineering Research Centre,
Chennai

Dr. Sakthieswaran N
Assistant Professor
Department of Structural Engineering
Anna University Regional Campus - Tirunelveli.

Abstract

Carbonation is one of the major reasons for the decrease in pH of cover concrete. This reduction in turn will lead to the deterioration of the passivizing layer around the steel bar and opens a way for the corrosion to occur. Several factors that are controlling carbonation includes: Relative humidity, Temperature and Carbon dioxide percentage. Various researches have been carried out on carbonation study. This paper reviews the experimental and theoretical studies on carbonation in concrete.
Keywords: Carbonation, Relative Humidity, Temperature, Carbon dioxide, Corrosion

_____

I. INTRODUCTION

Corrosion of reinforced concrete structures is the major problem, which leads to the deterioration of the entire structure. Two major causes which leads to the deterioration are carbonation induced corrosion and chloride induced corrosion. Through random distribution of pore spaces in concrete, the aggressive substances, such as chloride, carbon dioxide, oxygen, and moisture, may penetrate into the structure. This in turn will break down the passive layer around the bar and triggers the corrosion of reinforcing steel bars in concrete. It will also induce the cracking of concrete and finally deteriorate the load-bearing capacity of RC structure.

In general corrosion of reinforcement may occur due to (i) presence of CO_2, and (ii) presence of chloride ions. Carbon dioxide is an important trace in earth's atmosphere currently constituting about 0.04% (400 parts per million) of the atmosphere. The global annual mean concentration of CO_2 in the atmosphere has increased markedly since the industrial revolution from 280 ppm to 400 ppm as of 2015.The present concentration is the highest in the past 800,000 years and likely the highest in the past 20 million years.

Carbon dioxide concentration is increasing due to fossil energy consumption. The damage of RC structures due to carbonation was reported to increase due to increasing CO_2 concentration. Concrete carbonation should be carefully considered in the durability design of RC structures especially those in metropolitan cities where the rise in CO_2 concentration is accelerating. The straight cause of carbonation is the presence of CO_2 in the surrounding environment of the concrete.

Carbonation is process, in which carbon dioxide from air penetrates into the concrete structures and then reacts with the calcium hydroxide which leads to the formation of calcium carbonate. In another aspect CO_2 is not reactive by itself. But, in the presence of moisture, it changes into dilute carbonic acid and attacks the concrete and reduces the alkalinity of concrete.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The pH of the pore water in the hardened cement paste is generally between 12.5 to 13.5. The formation of carbonate will reduce the pH of the pore water in the cement paste to 9, which in turn will destroy the passivizing layer around the steel bar and initiate the corrosion.

The present paper focused on review on factors influencing accelerated carbonation testing, carbonation behaviour of various types of concrete, the variation of the carbonation depth and the theoretical study on carbonation.

Carbonation depth is the average distance, measured in mm, from the surface of the concrete or mortar where CO_2 has reduced the alkalinity of the hydrated cement to an extent such that an indicator solution based on phenolphthalein remains colourless.

II. CO₂ CONCENTRATION, RELATIVE HUMIDITY AND TEMPERATURE

Accelerated carbonation is a method in which carbonated samples can be obtained in a short time and can be served as the basis for predicting the carbonation behaviour of concrete under real atmospheric environments. CO_2 concentration, relative humidity and temperature are the main factors that are to be maintained in the accelerated carbonation chamber. A very dry concrete does not carbonate due to the lack of water needed for ions to form and subsequently react and form calcite. On the other hand, carbonation is also slow in wet conditions. The maximum carbonation will occur at a specific RH, a specific open porosity and specific type of binder. Moreover, it also depends on the geometry of the capillary system, which in practice means that it depends on the water/binder ratio, degree of hydration and type of binder as mentioned above. Optimal conditions for carbonation occur at

a RH of 50% (range 40% to 70%). This is because, when the RH is lesser than 40%, CO_2 cannot dissolve and when the RH is greater than 70%, diffusion of carbon dioxide will be inhibited by the water that has filled the pores and hence CO_2 cannot enter the concrete.

Hongzhi Cui et al., (2015), conducted the accelerated carbonation test at five different CO_2 concentration levels of 2%, 10%, 20%, 50% and 100% by volume, temperature of 20˚C and Relative Humidity (RH) of 70%. B. G Salvoldi et al., (2015) stored the concrete specimens in an environmental room for 60 days at a relative humidity of 45 ± 2.5% and temperature of 20 ± 2˚C. After 6 weeks, a mass loss of less than 0.3%/week was found. Thereafter, the specimens were placed in the carbonation chamber for 14 days where the relative humidity was kept constant at 65 ± 5% and the temperature was kept constant at 20±2˚C. A CO_2 concentration of 2 ± 0.1% was maintained in the chamber. T. Chandrasekaraiah et al.,(2014), done the pond curing and after 28 days of curing, the specimens were exposed to CO_2 concentrations of three intensities (30%,60% and 90%) in the carbonation chamber for different periods of 24, 48 and 72 hours. Mohamed Rabehi et al., (2013), carried out the accelerated carbonation test at the temperature of 20±2˚C. The RH of about 66% was maintained by a saturated saline solution and the CO_2 concentration of 50% by volume. A low CO_2 flow was maintained even after filling of the enclosure to replace any leaking CO_2 and the consumed by the sampler. Jian Geng & Jiaying Sun (2013), cured the samples in water at 20 ± 2˚C for 26 days and thereafter the specimens were dried for 48 h at 60 ± 2˚C to accelerate the carbonation. All surfaces of the dried samples were sealed by paraffin, except for two opposing side surface. Finally, the accelerated carbonation test was carried out at 20 ± 5˚C and 70% ± 5% RH with 20% ± 3% carbon dioxide concentration in the testing chamber. S. Talukdar et al., (2012), removed the sample from the water bath after 28 days of water curing and then allowed the samples to attain the equilibrium condition of 20˚C and 60% RH over a further 28 days before being placed in the carbonation chamber. Then, the experiment was carried out at four different laboratory scenarios with each scenario running for 8 weeks. The four scenarios adopted by S. Talukdar are as follows: 30˚C, 65% RH & 6% CO_2; 25˚C to 45˚C, 65% RH, 6% CO_2; 30˚C, 50% to 90% RH, 6 % CO_2; 30˚C, 65 % RH, 6 to 10% CO_2. J. Khunthongkeaw et al., (2006), maintained the temperature and RH of 40˚C and 55% respectively. The experiment was conducted at a CO_2 concentration of 4%. Cengiz Duran Atis (2002), de-moulded the specimens after 24 hours and kept some of the specimens at 20˚C with 65% RH, some of the specimens were cured at 20˚C with 100% RH until the time required for testing. T. Bakharev (2000), maintained the alkali activated slag concrete and ordinary portland cement concrete at 10% to 20% CO_2 in air at 70% RH for a period of 4 months.

III. VARIATIONS OF CARBONATION DEPTH

Hongzhi Cui et al., (2015), investigated the variation of carbonation depth using the cubic specimens. It was found that the concrete carbonation depth increased with increased CO_2 concentration but the significance is reduced when the CO_2 concentration is higher than 20%. Eehab Ahmed Badreldin Khalil & Mohamed Anwar (2015), came to know that for the mixes with 0% Fly ash (FA) and 0% Silica fume (SF), the carbonation rate was found to be 60% and 390% for the W-C of 0.5 and 0.6 respectively with respect to the W-C 0.4. For the set with 25% FA and 5% SF, the carbonation rate was found to be 108% and 285% for W-C 0.5 and 0.6 respectively with respect to the W-C 0.4. For the set with 25% FA and 10% SF, it was found to be 129% and 251% for W-C 0.5 and 0.6 with respect to the W-C 0.4, respectively. Finally, it was concluded that the variation in the SF does not affect the increase in the carbonation rate much, while the percentage of FA increased the carbonation rate considerably. B. G Salvoldi (2015), Showed that the plain cement concrete (CEM I) carbonated the least, closely followed by the Silica Fume (SF) mixes. The Fly Ash (FA) and Ground Granulated Blast Furnace Slag (GGBS) mixes performed similarly, both carbonated more than the CEM I and SF mixes. Mohammed Rabehi et al., (2013), showed that the carbonation depth increased with the increase in the w/c ratio. Also, it was concluded that the carbonation is a decreasing function of the compressive strength. Jian Geng & Jiaying Sun (2013), analyzed the effect of the cement replacement ratio by fly ash on the carbonation depth and it was revealed that the carbonation depth initially decreased and then increased with increased replacement ratio from 10% to 30%, and then reached the minimum at 20%.Also, it was found that the workability of recycled fine aggregate concrete was improved well at low w/b ratio, because the use of fly ash helped Recycled Fine Aggregate concrete (RFCA) to obtain a more compact structure. The resistance to carbonation of RFAC was improved by adding fly ash because the fly ash addition enhanced the microstructure of RFAC. According to Cengiz Duran Atis (2003), fly ash concrete made with 70% replacement ratio showed higher carbonation than that of 50% fly ash replacement concrete and Normal Portland Cement concrete for both moist and dry curing conditions. Fly ash concrete made with 50% replacement ratio showed lower or comparable carbonation than that of control Normal Portland Cement concrete for both curing conditions. J. Khunthongkeaw et al., (2006)., arrived at a result, that the carbonation depth of concrete and mortar specimens measured until 24 months were equivalent to the cement-only samples. The increment was drastic, when the fly ash content was higher than 30%. At the fly ash content of 50%, the carbonation coefficient was approximately two to three times as large as that of the cement-only mixture. T. Bakharev et al., (2001), concluded that the alkali activated slag concrete of Grade 40 has lower resistance to carbonation than that of ordinary portland cement concrete.

IV. THEORETICAL STUDY ON CARBONATION

Steady state diffusion follows Fick's first law J =D (dc/dx) .Where *J* is a quantity of a component passing through unit area per unit time, i.e. it is in this case the net transport rate of CO_2 and carbonate ions through a unit area and dc/dx is the concentration gradient/slope of molar concentration. D is a diffusion coefficient, a material property that depends on permeability, which in the

case of concrete is the connective porosity. The carbonation process is, however, more complicated as it is a combination of gas and liquid transport, but it can still be simplified with Fick's laws.

Fick's second law gives depth of alteration/carbonation and not the amount of material that is being altered. In the non -steady state, where concentration changes in both space and time, Fick's second law can be applied: $(\partial c / \partial t) = D (\partial^2 c / \partial x^2)$, where ∂t is a time factor, c is concentration and *x* is surface area. Several attempts have been made to establish a linear relationship between the coefficients of accelerated carbonation and those of natural carbonation of concrete. Thomas P. Hills et al., (2015), approximately found the carbonation depth using the following assumptions: (i) All gases within and without the cementitious material are ideal gases; (ii) The reaction of CO_2 with the material is instantaneous (i.e. diffusion of CO_2 is the rate-determining step); (iii) Diffusion is one-dimensional and conforms to Fick's first law of diffusion; (iv) The initial concentration of species which can carbonate in the concrete does not vary in space.

Based on the two methodologies, $x = (k_{ac}/k_e) (\sqrt{t})$ and $K_{ac} = (C_d.k_e)/ (Y_s\sqrt{t_{sl}})$, R.V Silva et al., (2015), estimated the required accelerated carbonation resistance of a reinforced Recycle Aggregate Concrete (RAC) exposed to natural carbonation conditions. Here, x is the carbonation depth (mm); k_{ac} is the coefficient of accelerated carbonation (mm year $^{-0.5}$); k_e is the environmental parameter and t is the exposure time to CO_2 (year); c_d is the reinforcement cover design value (mm); Y_s is the safety factor, being 1.0 for environmental class XC3 and 1.25 for environmental class XC4; and t_{sl} is the specified service life (year). From the distribution of accelerated carbonation coefficients of mixes containing recycled aggregate and the threshold values, it was concluded that the Recycled Aggregate Concrete (RAC) is a suitable material for reinforced concrete structures subjected to carbonation induced corrosion.

B. G Salvoldi et al., (2015), proposed a carbonation model in which oxygen permeability of concrete was used as an input parameter. $x = (2D_{dry}c\beta t_e)/a$, where x is the predicted carbonation depth, D_{dry} is the effective dry diffusion coefficient calculated with the oxygen permeability as input, c is the ambient carbon dioxide concentration in mol/m^3, ß is the relative humidity factor, t_e is the effective time of exposure, a is the amount of carbonatable material in mol/m^3.Finally, it was concluded that the equation enables prediction of time dependent carbonation depths of concretes based on the environmental exposure, mix design and oxygen permeability of the concrete.

Jian Geng & Jiaying Sun (2013), established a relationship between the carbonation depth and exposure time of recycled fine aggregate concrete using the fick's law $X = k_c t^{1/2}$. where X is the carbonation depth (mm), K_c is the carbonated coefficient, and t is exposure time (days).Talukdar S (2012) et al., created a numerical model involving simultaneous solution of the transient diffusion and reaction equations of CO_2 and Ca $(OH)_2$. The model successfully includes the effects of variations in various properties such as porosity, humidity, temperature, atmospheric CO_2 concentrations and chemical reaction rates. Those models were successfully used to predict the accelerated carbonation test results.

Sang Hwa Jung et al., (2010), used the following formula to find the diffusion coefficient of gas: $D_A = (Q.f_A.L) / (1-f_A).A$. Where D_A = diffusion coefficient of gas A (m^2/s), Q = flow rate of gas B (m^3/s), f_A = molar ratio of gas A in gas B, L = thickness of specimen (m), and A = cross sectional area (m^3). Finally, it was found that the diffusion coefficient of carbon dioxide increases with an increase of water to cement ratio.

Kritsada Sisomphon & Lutz Franke (2007), used the fick's second law to find the carbonation depth. Also, fick's first law of diffusion was used to find the carbonation coefficient: $J = D (\delta c / \delta x)_t$. where J is a carbon dioxide flux (g/m^2 s), D is a diffusion coefficient (m^2/s), c is a CO_2 concentration (g/m^3) and x is a depth of penetration (m). A equation $dm = C_oAdx$ was arrived by Kritsada Sisomphon & Lutz Franke, where A is the surface area and C_o represents an amount of CO_2 (g/m^3) required to react with alkali phases contained in a unit volume of a sample. After integrating this equation, the final equation was compared with the fick's second law and a final equation was arrived as follows to find the carbonation coefficient: $k = \sqrt{(2Dc_1/c_o)}$. c_1 is a CO_2 concentration in the environment.

J. Khunthongkeaw et al., (2006), used the following linear equation to relate the carbonation depth tested in natural environments at any ages with the accelerated carbonation depth defined in their study: $D_{n,t} = A . D_a \sqrt{t}$. Where $D_{n,t}$ is the carbonation depth of concrete normal exposed in natural environment for 't' months, D_a is the carbonation depth of the same concrete tested in the accelerated carbonation chamber for one month (mm), t is the exposure time in a real environment (months), A is the slope of the relationship, which is dependent on the environmental conditions.

Anna V. Saetta et al., (1993), described the governing equations of moisture, heat and carbon dioxide flows through concrete within the framework of a distributed parameter model. A numerical procedure based on the finite element method was developed to solve the set of equations. Since the diffusion of carbon dioxide into concrete depends on the moisture content in the pores and on the temperature, as well as on carbon dioxide atmospheric concentration, the equation of CO_2 diffusion is coupled with the differential equations governing the heat and mass flow in the drying process of the material. Comparisons with experimental tests were also carried out. Finally, it was came to that, it holds a good agreement that the short term tests of reference follow the classical square root relationship between depth of carbonation and time.

V. CONCLUSIONS

General conclusions drawn from the above literature review is given below:
1) Optimum temperature for the carbonation to occur was at 20 ± 2°C
2) Optimum relative humidity for the carbonation to occur was at 40 to 60%.

3) The increase of carbonation depth was found to be high when concrete samples were exposed to low concentrations of CO_2 (i.e. 2-20%); but low when the concentrations of CO_2 were high (i.e. 50-100%).

4) Ternary systems (Portland cement, silica fume, fly ash) show higher carbonation depths than that of uni - cement systems.

5) Carbonation depth increases with the increase in the w/c ratio.

6) The resistance to carbonation of Recycled Fine Aggregate Concrete (RFAC) was improved by adding fly ash, because the fly ash addition helped to enhance the microstructure of recycled fine aggregate concrete.

7) In the steady state, Fick's first law of diffusion can be used to find the carbonation coefficient: $J = D (\delta c / \delta x)_t$. Where J is a carbon dioxide flux (g/m^2 s), D is a diffusion coefficient (m^2/s), c is a CO_2 concentration (g/m^3), and x is a depth of penetration (m).

8) In the non-steady state, where concentration changes in both space and time, Fick's second law can be applied to find the Diffusion Coefficient: $(\partial c / \partial t) = D (\partial^2 c / \partial x^2)$, where ∂t is a time factor, c is concentration and x is surface area. It can also be expressed using the square root theory as $X = k_c \sqrt{t}$.

This paper focused on the optimum temperature, relative humidity and the CO_2 percentage to be used in accelerated carbonation test. Also, this paper reviewed on the theoretical study on carbonation.

REFERENCES

[1] BS EN 13295:2004, "Products and Systems for the protection and Repair of concrete structures - Test Methods - Determination of Resistance to Carbonation.

[2] Anna V. Saetta, Bernhard A. Schrefler & Renato V. Vitaliani (1993), "The Carbonation of Concrete and the Mechanism of Moisture, Heat and Carbon Dioxide Flow through Porous Materials", Cement and Concrete Research, Vol. 23, pp. 761-772.

[3] T. Bakharev, J. G Sanjayan & Y. B Cheng (2001), "Resistance of alkali-activated slag concrete to carbonation", Cement and Concrete Research,Vol.31,pp. 1277-1283.

[4] Björn Lagerblad (2005), "Carbon dioxide uptake during concrete life cycle - State of the art", Swedish Cement and Concrete Research Institute, ISBN 91-976070-0-2, ISSN 0346-8240.

[5] Cengiz Duran atis (2003), "Accelerated carbonation and testing of concrete made with fly ash", Construction and Building Materials, Vol.17, pp.147-152.

[6] T. Chandrasekaraiah, H. Anantharam, M. Krishnamurthy, K.V Manjunath, M.N Hegde (2014), "Accelerated testing of deteriorated concrete Structures due to carbonation", International Journal of Research in Engineering and Technology, Vol.03 , eISSN: 2319 -1163 , pISSN: 2321-7308.

[7] Eehab Ahmed Badreldin Khalil (2015), "Mohamed Anwar Carbonation of ternary cementitious concrete systems containing fly ash and silica fume", Water Science, Vol.29, pp.36 - 44.

[8] Hongzhi Cui , Waiching Tang , Wei Liu , Zhijun Dong & Feng Xing (2015), "Experimental study on effects of CO_2 concentrations on concrete carbonation and diffusion mechanisms", Construction and Building Materials, Vol. 93, pp.522- 527.

[9] Jian Geng & Jiaying Sun (2013), "Characteristics of the carbonation resistance of recycled fine aggregate concrete", Construction and Building Materials, Vol. 49, pp. 814-820.

[10] J. Khunthongkeaw, S. Tangtermsirikul & T. Leelawat (2006), "A study on carbonation depth prediction for fly ash concrete", Construction and Building Materials, Vol.20, pp. 744-753.

[11] Kritsada Sisomphon & Lutz Franke (2007), "Carbonation rates of concretes containing high volume of pozzolanic materials", Cement and Concrete Research, Vol.37, pp. 1647-1653.

[12] Mohamed Rabehi, Bouzidi Mezghiche & Salim Guettala (2013), "Correlation between initial absorption of the cover concrete, the compressive strength and carbonation depth", Construction and Building Materials, Vol.45, pp.123-129.

[13] B.G Salvoldi, H. Beushausen & M.G Alexander (2015), "Oxygen permeability of concrete and its relation to carbonation", Construction and Building Materials, Vol.85, pp. 30-37.

[14] Sang Hwa Jung, Myung Kue Lee, Seong Lo Lee & Byung Hwan Oh (2010), "Experimental Investigation on Diffusion Coefficient of Carbon Dioxide for Sustainable Construction Materials", Coventry University and the University of Wisconsin Milwaukee Centre for By-products Utilization Second International Conference on Sustainable Construction Materials and Technologies ISBN 978-1-4507-1487-7.

[15] R.V Silva, R. Neves, J.de Brito & R.K Dhir (2015), "Carbonation behaviour of recycled aggregate concrete", Cement & Concrete Composites, Vol.62, pp. 22-32.

[16] R.K Talukdar, N. Banthia & J.R Grace (2012), "Carbonation in concrete infrastructure in the context of global climate change - Part 1 Experimental results and model development", Cement & Concrete Composites, Vol.34 pp.924-930.

[17] Thomas P. Hills, Fabiana Gordon, Nicholas. H Florin & Paul S. Fennell (2015), "Statistical analysis of the carbonation rate of concrete", Cement and Concrete Research, Vol.72, pp 98 - 107.

[18] M.S Shetty (2012), "Concrete technology Theory and Practice", S. Chand & Company Ltd.