



# IJRASET

International Journal For Research in  
Applied Science and Engineering Technology



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# INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

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**Volume: 4**

**Issue: V**

**Month of publication: May 2016**

**DOI:**

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# Review on Carbonation Induced Corrosion in Concrete

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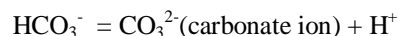
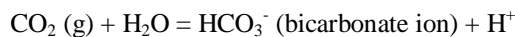
**Abstract--Carbonation is one of the major reasons for the decrease in pH of the concrete. This reduction in turn will lead to the deterioration of the passivating layer around the steel bar and opens a way for the corrosion to occur. Several factors that are controlling carbonation includes: Relative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

**Key words--Carbonation, Relative Humidity, Temperature, Carbon dioxide, Corrosion.**

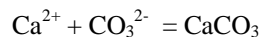
## I. INTRODUCTION

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. Carbonation is due to the fact that in the presence of carbonate ions, the calcium ions in the pore solution precipitate and form calcium carbonate. The atmosphere contains substantial amounts of carbon dioxide. Gaseous CO<sub>2</sub> cannot, however, react directly with the hydrates of the cement paste. Thus the CO<sub>2</sub> gas must first dissolve in water and form carbonate ions that in turn will react with the Ca ions of the pore water. The type of carbonate ions depends on the pH. When CO<sub>2</sub> comes into contact with water at neutrality it forms bicarbonate. Inside concrete, the pH is high and as a result the bicarbonate dissociates and forms carbonate ions. Thus in the carbonated layer bicarbonate forms but closer to the uncarbonated cement paste this carbonate ions form (due to higher pH) and precipitate calcium carbonate crystals (CC). Calcium carbonate exists in three crystallographic forms, aragonite, vaterite and calcite. Calcite and vaterite are commonly found in carbonated concrete. Presumably the metastable vaterite will transform into stable calcite over time.

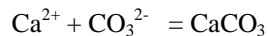
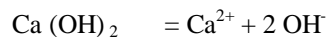
The carbonation process can be described by the following chemical equations;



The carbonate ion will react with Ca ions in the pore solution.



This will lead to lower concentration of Ca<sup>2+</sup> which in turn will lead to dissolution of primarily calcium hydroxide (CH). The solubility of CC is much lower than that of CH.



Thus Ca (OH)<sub>2</sub> (CH) will dissolve and CaCO<sub>3</sub> (CC) will precipitate and the process will continue until all of the CH is consumed. Apart from CH, the cement paste contains calcium silicate hydrate (C-S-H) and ettringite/monosulphate (AFt/AFm). These components are in equilibrium with and stabilized by high pH and Ca ions in the pore solution. Thus when the CH is consumed the pH and the Ca ion concentration drops and the C-S-H will dissolve congruently. Monosulphate (AFm) will decompose at a pH of around 11.6 and later the ettringite (Aft) will decompose at a pH of around 10.6.

At pH < 9.2 (when the phenolphthalein change colour) none of the original Ca containing phases remain. Most of the Ca from the C-S-H will be bound to calcium carbonate but some Ca will always remain in silica gel. The following equation tells us that, during the chemical reaction, the C-S-H releases CH which is carbonated and that this process gives a C-S-H with lower contents of CaO.

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$$C-S-H (1) = C-S-H (2) + CH \text{ where } Ca/Si (2) < Ca/Si (1)$$

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

## II. CO<sub>2</sub> CONCENTRATION, RELATIVE HUMIDITY AND TEMPERATURE

CO<sub>2</sub> 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. Optimal conditions for carbonation occur at a RH of 50% (range 40% to 90%). This is because when the RH is lesser than 40%, CO<sub>2</sub> cannot dissolve and when the RH is greater than 90%, diffusion of carbon dioxide will be inhibited by the water that has filled the pores and hence CO<sub>2</sub> cannot enter the concrete.

Hongzhi Cui et al., (2015), conducted the accelerated carbonation test at five different CO<sub>2</sub> concentration levels of 2%, 10%, 20%, 50% and 100% by volume, temperature of 20°C and RH of 70%. Salvoldi B G et al., (2015) stored the concrete specimens in an environmental room for 60 days at a relative humidity of  $45 \pm 2.5\%$  and  $20 \pm 2^\circ\text{C}$ . After 6 weeks they found a mass loss of less than 0.3%/week. Thereafter the specimens were placed in the carbonation chamber for 14 days where the relative humidity was kept constant at  $65 \pm 5\%$  and the temperature was kept constant at  $20 \pm 2^\circ\text{C}$ . They maintained a CO<sub>2</sub> concentration of  $2 \pm 0.1\%$ . Chandrasekariah T et al.,(2014), done the pond curing and after 28 days of curing, they exposed the specimens to CO<sub>2</sub> 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  $20 \pm 2^\circ\text{C}$ . They maintained the RH of about 66% by a saturated saline solution and the CO<sub>2</sub> concentration of 50% by volume. They kept a low CO<sub>2</sub> flow even after filling of the enclosure to replace any leaking CO<sub>2</sub> and the consumed by the sampler. Jian Geng & Jiaying Sun (2013) , cured the samples in water at  $20 \pm 2^\circ\text{C}$  for 26 days and thereafter they were dried for 48 h at  $60 \pm 2^\circ\text{C}$  to accelerate the carbonation. All surfaces of the dried samples were sealed by paraffin, except for two opposing side surface. Finally they conducted the accelerated carbonation test at  $20 \pm 5^\circ\text{C}$  and  $70\% \pm 5\%$  RH with  $20\% \pm 3\%$  carbon dioxide concentration in the testing chamber. Talukdar S 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 they conducted the experiment at four different laboratory scenarios with each scenario running for 8 weeks. The four scenarios adopted by them are as follows: 30°C, 65% RH & 6% CO<sub>2</sub>; 25°C to 45°C, 65% RH, 6% CO<sub>2</sub>; 30°C, 50% to 90% RH, 6% CO<sub>2</sub>; 30°C, 65% RH, 6 to 10% CO<sub>2</sub>. Khunthongkeaw J et al., (2006), maintained the temperature and RH of 40°C and 55% respectively. Also, they conducted the experiment at a CO<sub>2</sub> concentration of 4%. Cengiz Duran Atis (2002), de-molded the specimens after 24 h 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. Bakharev T (2000), maintained the alkali activated slag concrete and ordinary portland cement concrete at 10% to 20% CO<sub>2</sub> in air at 70% RH for a period of 4 months.

## III. VARIATION OF CARBONATION DEPTH

Hongzhi Cui et al., (2015), investigated the variation of carbonation depth using the cubic specimens. They found that the concrete carbonation depth increased with increased CO<sub>2</sub> concentration but the significance is reduced when the CO<sub>2</sub> 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 they 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. Salvoldi B G (2015), Showed that the plain cement concrete (CEM I) carbonated the least, closely followed by the SF mixes. The FA and 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. They also 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



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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, they 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% FA replacement concrete and NPC 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 NPC concrete for both curing conditions. Khunthongkeaw J 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. Bakharev T et al., (2001), concluded that the Alkali Activated Slag concrete of Grade 40 has lower resistance to carbonation than that of OPC concrete.

### IV. THEORETICAL STUDY ON CARBONATION

Steady state diffusion follows Fick's first law  $J = -dc/dx$ . 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  $\text{CO}_2$  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, we can apply Fick's second law:  $(\partial c / \partial t) = D (\partial^2 c / \partial x^2)$ , where  $\partial t$  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  $\text{CO}_2$  with the material is instantaneous (i.e. diffusion of  $\text{CO}_2$  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  $K_{ac} = (C_d.k_e)/(\sqrt{Y_s}\sqrt{t_{sl}})$ , Silva R V 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 ( $\text{mm year}^{-0.5}$ );  $k_e$  is the environmental parameter, being 9.9 for environmental class XC3 and 15.0 for environmental class XC4; and  $t$  is the exposure time to  $\text{CO}_2$  (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 RA 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. Salvoldi B G 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  $\text{mol/m}^3$ ,  $\beta$  is the relative humidity factor,  $t_e$  is the effective time of exposure,  $a$  is the amount of carbonatable material in  $\text{mol/m}^3$ . Finally, they 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  $X = k_c t^{1/2}$ . Talukdar S (2012) et al., created a numerical model involving simultaneous solution of the transient diffusion and reaction equations of  $\text{CO}_2$  and  $\text{Ca}(\text{OH})_2$ . The model successfully includes the effects of variations in various properties such as porosity, humidity, temperature, atmospheric  $\text{CO}_2$  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 ( $\text{m}^2/\text{s}$ ),  $Q$  = flow rate of gas B ( $\text{m}^3/\text{s}$ ),  $f_A$  = molar ratio of gas A in gas B,  $L$  = thickness of specimen (m), and  $A$  = cross sectional area ( $\text{m}^2$ ). They finally concluded 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, they used the fick's first law of diffusion to find the carbonation coefficient:  $J = -D (\delta c / \delta x)_t$ , where  $J$  is a carbon dioxide flux ( $\text{g/m}^2 \text{ s}$ ),  $D$  is a diffusion coefficient ( $\text{m}^2/\text{s}$ ),  $c$  is a  $\text{CO}_2$  concentration ( $\text{g/m}^3$ ) and  $x$  is a depth of

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penetration (m). They arrived at an equation  $dm = C_o Adx$ , where  $C_o$  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, they compared the final equation with the Fick's second law and arrived a final equation as follows to find the carbonation coefficient:  $k = \sqrt{(2Dc_1/c_o)}$ . Khunthongkeaw J 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:  $D_{n,t} = A \cdot D_a \sqrt{t}$ . 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. 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. CONCLUSION

General conclusions drawn from the above literature review is given below:

Optimum temperature for the carbonation to occur is at  $20 \pm 2^\circ C$

Optimum Relative Humidity for the carbonation to occur is at 40 to 90%.

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%).

Ternary systems (Portland cement, silica fume, fly ash) will show higher carbonations than that of uni - cement systems.

Carbonation depth increased with the increase in the w/c ratio.

The resistance to carbonation of Recycled Fine Aggregate Concrete (RFAC) can be improved by adding fly ash, because the Fly ash addition will help to enhance the microstructure of RFAC.

In the steady state, Fick's first law of diffusion to find the carbonation coefficient is  $J = D (\delta c / \delta x)_t$ . 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).

In the non steady state, where concentration changes in both space and time, we can apply Fick's second law to find the Diffusion Coefficient:  $(\partial c / \partial t) = D (\partial^2 c / \partial x^2)$ , where  $\partial t$  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.

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