

UNCERTAINTIES IN PREDICTION AND EVALUATION OF CARBONATION PROPAGATION: RECENT DEVELOPMENTS

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ABSTRACT. The carbonation of concrete is a phenomenon influenced by various interdependent parameters. The major of these parameters may be grouped into external parameters such as CO₂ diffusion coefficient, exposure temperature, relative humidity, concentration of CO₂, curing period and stress level of the concrete and internal parameters such as microstructure for with and without supplementary cementing materials (SCM), water/ binder ratio, amount and type of superplasticizers, presence of Griffith's flaws in concrete, age of concrete etc. Several publications exist in literature on the study of carbonation of concrete carried out from different angle of considerations. Huge data base have been developed, however, generalization of these data poses an almost impossible task to the concrete experts as there is innumerable variability in experimental conditions and ingredients of the concretes tested and the specimens taken for conduction of tests. Several studies have employed numerical and statistical modeling techniques to predict the depth of carbonation as a function of age of concrete, compressive strength of concrete and other parameters affecting carbonation of concrete. This paper looks into these issues of uncertainty in prediction and evaluation of carbonation propagation.

Keywords: Carbonation depth & coefficient, numerical prediction, experimental investigation

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INTRODUCTION

During carbonation CO_2 is fixed by the hydrated cement paste and thereby the mass of the concrete increases. Especially $\text{Ca}(\text{OH})_2$ reacts readily with CO_2 and CaCO_3 is formed. Other hydrates also decomposed like hydrated silica, alumina, and ferric oxide being produced [43]. When, however, $\text{Ca}(\text{OH})_2$ is depleted, for instance by secondary reaction with pozzolanic silica, the carbonation of calcium silicate hydrate C-S-H, is also possible. When this occurs, not only is more CaCO_3 formed, but also silica gel which is concurrently formed has large pores, larger than 100 nm, which facilitates further carbonation [26]. The concrete's residual unhydrated cement compounds such as C_3S & C_2S react with CO_2 in the presence of H_2O further carbonating the concrete [29]. When concrete dries and carbonates simultaneously, the increase in mass on carbonation may not occur at some stage [16, 55]. Carbonation shrinkage is probably caused by dissolving of crystals of $\text{Ca}(\text{OH})_2$, while under a compressive stress (imposed by drying shrinkage) and depositing CaCO_3 in spaces free from stress. If carbonation proceeds to the stage of dehydration of C-S-H, this also produces carbonation shrinkage [39].

In this paper several issues like beneficial and detrimental effects of carbonation, carbonation of concrete containing blended cements, effect of loading/ stress level, relative humidity, high temperature, period of curing, water binder ratio, compressive strength of concrete on carbonation have been discussed in detail. Effect of carbonation on corrosion and service life of bridge and other structures also have been presented. Several studies dealing with statistical/ numerical modeling of carbonation have been also discussed.

EFFECTS OF CARBONATION

Beneficial effects of carbonation

IS 13311 (Part 2) 1992 details the effect of carbonation of concrete surface on rebound number. Carbonated concrete gives an overestimate of strength which in extreme cases can be upto 50 %. It is possible to establish correction factors by removing carbonated layer and testing the concrete with the rebound hammer on the uncarbonated concrete. A study has been conducted where carbonation is intentionally applied to freshly cast concrete pipes, wherein CO_2 reacts with anhydrous phases to form strength contributing hydrates and carbonates [18].

Because CaCO_3 occupies greater volume than $\text{Ca}(\text{OH})_2$ which it replaces, the porosity of carbonated concrete is reduced. Also, water released by $\text{Ca}(\text{OH})_2$ on carbonation may aid the hydration of hitherto unhydrated cement. These changes result in increased surface hardness, increased strength at the surface [44], reduced surface permeability [64], and reduced moisture movement [59] and increased resistance to those forms of attack which are controlled by permeability [16]. It is well known that carbonation increases the density, strength, modulus of elasticity, and shrinkage of the concrete [40].

Kim et al. (2009) studied the effect of carbonation on rebound number and compressive strength of concrete, which has been mentioned by IS 13311 (pt 2) : 1992. A strength reduction

coefficient is generally applied to the evaluated strength to compensate the effect of surface carbonation. A new equation for this strength reduction coefficient that can consider the influence of strength level was developed based on field test data extracted from technical reports of the Korea Research Institute of Standards and Science and four universities. Over a wide range of strength levels, the equation shows good agreement with strength reduction coefficients established experimentally.

Detrimental effects of carbonation

Carbonation affects durability of concrete, as pH of the concrete pore solution is reduced from 12 to less than 9 causing the formation of CaCO_3 [34, 52]. This affects passivation state of embedded steel. When the low pH front reaches the vicinity of the surface of the reinforcing steel, the protective oxide film is removed and corrosion takes place, provided oxygen and moisture necessary for the reactions of corrosion are present [16]. Because of the presence of coarse aggregate, the 'front' does not advance perfectly as a straight line. In many cases, corrosion can take place even when the full carbonation front is still a few millimeters away from the surface of the steel if partial carbonation has taken place.

RATE OF CARBONATION

The diffusion of CO_2 is a slow process if the pores of the hydrated cement paste are filled with water because the diffusion of CO_2 in water is 4 orders of magnitude slower than in air [16]. On the other hand, if water is insufficient in the pores, CO_2 remains in gaseous form and does not react with the hydrated cement.

The highest rate of carbonation occurs at a relative humidity of between 50 and 70 %. Under steady hygrometric conditions, the depth of carbonation increases in proportion to the square root of time, which is a characteristic of sorption rather than diffusion, but carbonation involves an interaction between CO_2 and the pore system. The carbonation resistance of the concrete can be expressed using Fick's first law of diffusion [63]. To express the depth of carbonation, D in mm, as $D = K t^{0.5}$, where, K = carbonation coefficient in $\text{mm/year}^{0.5}$, and t = time of exposure in years. The value of K is often more than 3 or 4 $\text{mm/year}^{0.5}$ for low strength concrete [16]. Broadly, in a concrete with w/c of 0.60, a depth of carbonation of 15 mm would be reached after 15 years, but at a w/c of 0.45 only after 100 years [66].

The expression involving the square root of time is not applicable when the exposure conditions are not steady [16]. In particular, if the surface of the concrete is exposed to a variable humidity, with periodic wetting, the rate of carbonation is reduced because of slowing down of diffusion of CO_2 through saturated pores in the hydrated cement paste. Conversely, sheltered parts of a structure undergo carbonation at a faster rate than those exposed to rain, which significantly slows down the progress of carbonation.

In a single building made all of the same concrete, there may be considerable variation of carbonation depth. Overall, the greatest depth of carbonation can be 50 % more than the smallest

depth [60]. Small variations of temperature have little effect on carbonation but a high temperature increases rate of carbonation unless drying overshadows the temperature effect [16].

MEASUREMENT OF CARBONATION

To measure the extent of carbonation the techniques, viz., chemical analysis, X-ray diffraction, infra-red and Raman spectroscopy and thermo-gravimetric analysis. The thermo-gravimetric analysis (TGA) method tests the concentration distribution of $\text{Ca}(\text{OH})_2$ and CaCO_3 while the X-ray diffraction analysis (XRDA) tests the intensity distribution of $\text{Ca}(\text{OH})_2$ and CaCO_3 . The fourier transform infrared spectroscopy (FTIR) test method detects the presence of C-O in concrete samples on the basis for determining the presence of CaCO_3 . With a solution of phenolphthalein in diluted alcohol, free $\text{Ca}(\text{OH})_2$ becomes colored pink, while the carbonated portion remains uncolored [23, 31, 32].

Chang and Chen (2006) conducted the experimental investigation of concrete carbonation depth. Concrete specimens were prepared and subjected to accelerated carbonation under conditions of 23°C temperature, 70% RH and 20% concentration of CO_2 for 8 and 16 weeks. The three methods to determination of carbonation depth, e.g., TGA, XRDA and FTIR along with phenolphthalein test were used. The TGA, XRDA and FTIR results showed that the depth of carbonation front is twice of that determined from phenolphthalein indicator.

CARBONATION OF CONCRETE CONTAINING BLENDED CEMENTS

In spite of numerous publications on carbonation propagation in blended cement concrete, useful generalization is not an easy task [16]. Towards this, it is important to understand the microstructure of hardened cement paste made up of pozzolana cement, ground granulated blast furnace slag cement etc.

The effect of supplementary cementing materials (SCM) on concrete resistance against carbonation and chloride ingress has been studied [17]. The silica fume and low and high calcium fly ash have been used as SCM. Experimental investigations simulating main deterioration mechanisms in reinforced concrete have been carried out. It was seen that the carbonation depth decreases as aggregate replacement by SCM increases, and increases as cement replacement by SCM increases. New parameter values were estimated and existing mathematical models were modified to describe the carbonation propagation. The mathematical model yields a complex non-linear system of differential equations which are solved numerically for the unknown concentration of materials involved. The theoretically and experimentally carbonation depths matched well.

Portland pozzolana cement

The observations stated herein relate to Class F fly ash. Bier (1987) has shown that the depth of carbonation is greater when the amount of $\text{Ca}(\text{OH})_2$ present is lower. It follows that the presence

of fly ash results in rapid carbonation [16]. It is also observed that the more is the amount of pozzolanic material, deeper the carbonation depth develops [53]. However, reaction products between pozzolanic silica and $\text{Ca}(\text{OH})_2$ result in denser structure of the HCP so that its diffusivity is reduced and carbonation is likely to be slowed down. For this to happen, good curing is essential [37, 54, 61].

There are contradictory conclusions, in published literature reported in this paragraph, on a similar type of fly ashes [26, 65]. Many studies have reported that higher carbonation has been found in concrete containing fly ash when compared to normal Portland cement (NPC) concrete [3, 27, 36, 62]. Ogha and Nagataki (1989) reported increase in carbonation coefficient with the increase in replacement ratio of fly ash and air content [49]. Contrary to these studies, in a case , where a 25 year old fly ash foundation concrete was examined and it has been reported that there has been no carbonation in the fly ash concrete specimens [28].

Blast furnace slag cement

Poorly cured concrete containing blast furnace slag cement exhibits higher carbonation [38]. It has been observed that the increase in rate of carbonation is greater when fly ash is used with Portland blast furnace slag cement. When the GGBFS plus fly ash content is more than 60%, the increase in carbonation is greater, the greater is the fly content. Depths of 10 to 20 mm after one year's exposure have been reported [50]. Using a concentration of CO_2 of 2 %, it was found that the depth of carbonation of well cured concrete containing fly ash or blast furnace slag is greater by a factor of a least 2 than when Portland cement is only present [26]. Extensive carbonation of C-S-H in concrete in service has been reported [42].

Sulfate resisting cement

Sulphate resisting cement leads to a 50 % greater depth of carbonation than Portland cement [46]. Carbonation of concrete containing regulated set cement is also increased [58].

High alumina cement

Reaction of calcium aluminate hydrates CAH_{10} and C_3AH_6 with CO_2 gives rise to carbonation forming CaCO_3 and alumina gel, which have lower strength than the hydrates. At the same strength as NPC concrete, high alumina cement concrete exhibits twice as high carbonation [66].

FACTORS INFLUENCING CARBONATION

The physico-chemical phenomena influencing the rate of carbonation are discussed [52]. The diffusivity, a function of pore system of the hardened cement paste significantly influences carbonation. The type of cement, water cement ratio, curing history, and degree of hydration also

influences carbonation depth. The effect of curing has been studied in detail [25, 45]. The latter has reported that increasing the period of wet curing from 1 day to 3 days reduces the depth carbonation by about 40 %.

Effect of loading on carbonation

The effect of loading on carbonation penetration in reinforced concrete elements has also been studied [68]. Concrete tensile micro-cracking due to mechanical loading enhances the diffusion of CO₂ and other aggressive agents from concrete cover to the reinforcement. Concrete carbonation was studied on two 13-year-old reinforced concrete beams always stored in a loaded state subjected to atmospheric carbonation. Tensile microcracking in reinforced elements are characterized by the tensile stress in steel rebar as microcracking network is almost impossible to characterize. It was concluded that the carbonation depth increases with increasing tensile stress in the elements.

Carbonation and corrosion

Carbonation of HCP in which bound chlorides are present has a similar effect of freeing the bound chlorides and thus increasing the risk of corrosion. An increased concentration of chloride ions in pore water to occur 15 mm in advance of the carbonation front has been found [35, 36]. This harmful effect is in addition to the lowering of the pH value of the pore water, so that severe corrosion may well follow [16]. The presence of even a small amount of chloride in carbonated concrete enhances the rate of corrosion induced by the low alkalinity of the carbonated concrete [33].

The carbonation-induced reinforcement corrosion in silica fume concrete has been investigated by [11]. The paper concludes that when used in concentrations greater than 10% , silica fume increases the potential for carbonation-induced reinforcement corrosion.

Effect of carbonation on Service life of structure [2]

Service life of a concrete bridge structure subjected to carbonation has also been predicted [2]. Carbonation-induced corrosion in concrete occurs in high CO₂ environment. The risk of carbonation of a concrete bridge in an urban area was evaluated by measuring the carbonation rate and concrete cover depth at three different parts: the sound, cracked and construction joint parts of cover concrete. The safety factor method and the Monte Carlo simulation are representative techniques of modeling the risk of carbonation. Carbonation rate was evaluated to be 4.0 mm/year^{0.5}. A decrease in the rate of carbonation by about 20% resulted in a 50 % increase in the corrosion free life, while a decrease of 60% carbonation rate significantly increased the service life by about 500%. The carbonation-free service life calculated by the safety factor method was almost identical to by the Monte Carlo simulation.

Compressive strength vs carbonation depth

As far as strength is concerned, in a situation conducive to continuing carbonation, concrete with a strength lower than 30 MPa is highly likely to have undergone carbonation to a depth of at least 15 mm in a period of several years [48]. Following two Tables from [54] show some typical relationship between strength and carbonation depth.

Table 1 Depth of carbonation as a function of strength [54]

EXPOSURE	DEPTH OF CARBONATION AFTER 50 YEARS, mm	
	25 MPa CONCRETE	50 MPa CONCRETE
Sheltered outdoors	60 to 70	20 to 30
Exposed to rain	10 to 20	1 to 2

Table 2 Maximum depth of carbonation in sheltered concrete Outdoors in UK [54]

28 DAY STRENGTH (MPa)	DEPTH OF CARBONATION AFTER 30 YEARS, MM
20	45
40	17
60	5
80	2

From Parrott's data, it could be concluded that for sheltered concrete outdoors in the UK or a similar climate, in 90 % of the cases, the depth of carbonation will not exceed the values shown in above Table 1 and 2 [16]. A study has been conducted to assess the correlation between the extent of carbonation and compressive strength of concrete [3]. Based on the statistical analyses of his study and others [49, 57], a relation was proposed as,

$$\text{Depth of carbonation (mm)} = - 0.18 * \text{Compressive strength (MPa)} + 16.18$$

Thus, it is observed that higher the strength, lower will be the carbonation depth.

Effect of Curing period on carbonation

The variation of carbonation depth for the three grades of concrete have been studied. The cubes were cured for 28, 56, 90, 120 days and subsequently subjected to an accelerated carbonation process at a carbonation chamber with CO₂ concentration of 10% for an exposure duration of 150 days at 27⁰C and 65 % relative humidity. The depth of carbonation was determined by spraying 1 % phenolphthalein in 70% ethyl alcohol that changes from colourless to purple when pH > 9 (CPC-18, 1988). EN 13295: 2004 (CEN 2004) specifies an accelerated laboratory method for measuring the resistance against CO₂ penetration through repair products and systems.

Table 3 Mix proportions for different grades of concrete [5]

MIX DESIGNATION	CEMENT CONTENT (kg/m ³)	w/c	MIX PROPORTION (OPC:W:FA:CA)	COMPACTING FACTOR
C1	300	0.55	1:0.55:2.06:4.37	0.90
C2	320	0.45	1:0.45:1.98:4.60	0.84
C3	360	0.40	1:0.40:1.88:4.59	0.82

Table 4 Carbonation depth for different grades of concrete specimens [5]

CURING PERIOD T (days)	T = 150 DAYS					
	CARBONATION DEPTH (mm)			% REDUCTION		
	C1	C2	C3	C1	C2	C3
28	28.2	24.2	19	NA	NA	NA
56	25	22.1	16.5	11.35	8.68	13.16
90	22.2	19	13	21.28	21.49	31.58
120	18.6	15.2	10	34.04	37.19	47.37

NA = not applicable

Both the carbonation coefficient and depth decreased with the increasing curing period. From the plot of variation of carbonation coefficient vs curing period by [5, 6], one can infer that the carbonation coefficient decreases parabolically (rather close to exponentially) with longer curing period. With the w/c decreasing from 0.55 to 0.40, carbonation coefficient, k, reduced by a factor 3. The data suggests that curing period plays an important role in developing the carbonation resistance of concrete.

A comparison of carbonation depth has been carried out in OPC (mix designated as C1, C2 and C3) vs PPC (F1, F2 and F3) keeping mix ratio and other ingredients same as shown in above Table [5, 6]. The following two tables show the results of compressive strength and carbonation depth.

Table 5 Compressive strength of different grades of concrete [6]

TIME (days)	COMPRESSIVE STRENGTH (MPA)					
	C1	F1	C2	F2	C3	F3
28	31.76	40.94	42.81	54.88	51.20	58.02
56	38.06	47.24	46.14	58.43	53.82	64.37
90	39.44	48.76	46.25	61.35	54.13	68.40
120	40.12	50.08	47.82	63.25	56.48	69.78

Table 6 Measured carbonation depths for different grades of concrete [6]

TIME (days)	CARBONATION DEPTH (mm)					
	C1	F1	C2	F2	C3	F3
28	28	26	24	20	19	15
56	25	24	22	18	17	14
90	22	18	21	14	12	11
120	19	15	18	13	10	9

From the above results, it can be seen that F series specimens containing fly ash shows higher resistance to carbonation.

Effect of carbonation on leaching of trace elements

The effect of carbonation on the leaching behaviour of major and trace elements from concrete made with OPC and fly ash using a tank leach test has also been studied [15]. The cumulative release of Cr in the test increased proportionally to carbonation depth. More V was released from carbonated concrete [15].

Effect of recycled concrete aggregate on carbonation

A study has been reported in [20] on compressive strength and resistance to chloride ion penetration and carbonation of recycled aggregate concrete with varying amount of fly ash and fine recycled aggregate. Compressive strength of mortar and concrete which used recycled concrete aggregate (RCA) gradually decreased as the amount of the recycled materials increased. The measured carbonation depth did not indicate a clear relationship to the fine RCA replacement ratio, but the recycled aggregate concrete could also attain adequate carbonation resistance.

Effect of water /binder ratio on carbonation

A study has been conducted accelerated carbonation of concrete made with fly ash for water – cementitious material ratios ranged from 0.28 to 0.55 [3]. Five types of concrete mixtures were prepared as M0 with normal Portland cement with no fly ash, M1 and M2 made of 70 % fly ash replacement with and without superplasticizer, whereas, M3 and M4 were made with 50% fly ash replacement. Accelerated carbonation in controlled chamber at nearly 5% concentration of CO₂ is performed at temperature of 20⁰C for two values of relative humidities as 65% and 100% [3].

In a discussion on the paper [3], it has been pointed out that the actual water to binder ratio for M3 and M4 concretes are 0.33 and 0.30 respectively [21]. This w/b ratio is drastically lower than that of NPC concrete (0.55). Thus, there is a serious inconsistency and hence, the above conclusion merits further scrutiny.

The results obtained in [3] are presented in Tables below:

Table 7 Accelerated carbonation depth (mm) of concrete cured at 65% RH at 20⁰C [3]

MIX NAME/ INITIAL CURING TIME	W/(FA+C)	3 DAYS	7 DAYS	28 DAYS	3 MONTHS
M0	0.55	9.60	8.50	6.50	5.00
M1	0.28	14.10	12.80	10.40	8.40
M2	0.29	14.90	13.40	11.30	8.90
M3	0.33	10.30	9.80	6.30	4.50
M4	0.3	9.80	9.30	5.70	3.80

Table 8 Accelerated carbonation depth (mm) of concrete cured at 100% RH at 20⁰C [3]

MIX NAME/ INITIAL CURING TIME	3 DAYS	7 DAYS	28 DAYS	3 MONTHS
M0	9.10	7.40	4.50	3.30
M1	13.30	10.90	6.50	4.60
M2	13.80	11.70	7.30	5.00
M3	8.70	8.40	3.20	1.80
M4	9.60	7.50	2.10	1.60

From the above results it can be inferred that the carbonation depths are not significantly influenced by the use of superplasticizers as M1 and M2 or M3 and M4 have almost similar values. Although, it has been reported that a dosage of above 0.5% by weight of cement in concretes resulted in slightly higher carbonation depths. Furthermore, the effect of type of superplasticizers is also an important factor [3, 70].

Similar to the studies [5, 6], it is observed that moist curing conditions significantly reduce the extent of carbonation. For both moist and dry curing conditions, the concrete M1 and M2 made with 70 % fly ash replacement with cement carbonated more than that of NPC (M0) concrete and 50 % fly ash replacement concretes (M3 and M4). This finding that addition of fly ash in concrete increased the carbonation depth in comparison with NPC concrete is clearly in agreement with the other published results [27, 35, 41, 49, 51]. Byfors (1985), Ogha and Nagataki (1989), Paillere et al. (1986), Kasai et al. (1983)] . However, the mixtures M3 and M4 showed similar or comparable carbonation depth to NPC concrete at 3 and 7 days of initial curing period. Furthermore, the mixtures M3 and M4 showed lower carbonation depth than that of NPC concrete at 28 days and 3 months of initial curing period. These findings are in disagreement with the conclusions of several studies [27, 35, 41, 49, 51].

Effect of Relative humidity on carbonation

The accelerated carbonation of a blast-furnace cement concrete varying the relative humidity for 0.03% and 10% CO₂ exposure have been studied [7]. The maximum carbonation was observed to occur at RH level of 50%. The following Table presents the results obtained. The mix proportion used are 1200 kg gravel, 650 kg coarse sand, 310 kg cement (HK40 – a Belgian granulated slag cement) & 185 l of water. The water cement ratio of 0.6 was chosen rather high to facilitate faster carbonation.

Table 9 Effect of relative humidity on carbonation [7]

RELATIVE HUMIDITY (%)	CABONATION DEPTH (mm) AT CO ₂ CONCENTRATION OF 50 %	CABONATION DEPTH (mm) AT CO ₂ CONCENTRATION OF 0.03 %
90	4.9	0.5
80	5.6	0.5
70	7.5	0.8
60	8.0	0.6
50	8.5	1.4
40	6.8	0.9

Extent of carbonation in SCC and NVC

Natural carbonation of self-compacting concrete has been also investigated in [63]. Eight different concretes were used, four self-compacting concrete (SCC) and four normally-vibrated concrete (NVC). The carbonation rate was found to be lower in SCC than NVC due to the fact that limestone fines produce less porosity and finer micro-structure. An expression is proposed to estimate carbonation rate in concrete from the volume of pores over 0.065 μm and threshold diameter.

Table 8 Carbonation depth & coefficient for SCC & Normal concrete [63]

MIX	AGE 9 MONTHS	AGE 42.5 MONTHS	CARBONATION COEFFICIENT (mm/month ^{0.5})
S-65-32	6.4	12.1	1.99
S-55-32	4.5	9.3	1.47
S-55-42	2.8	6.7	0.99
S-45-42	1.2	4.0	0.51
N-65-32	7.1	16.5	2.45
N-55-32	5.0	11.2	1.69
N-55-42	3.5	8.4	1.23
N-45-42	1.8	4.9	0.66

The depth profiling of carbonates formed during a natural carbonation of mortars with one face exposed directly to rain and the opposite face sheltered has been measured and compared in [9]. As expected and explained in [16], due to pore blocking by periodic rain water, the amount of carbonates formed on mortars sheltered from rain is generally higher. The CO₂ diffusion coefficients calculated on the basis of the distribution of carbonates are of the same magnitude as those measured by a direct method. A threshold value of diffusivity appears when the sand concentration is progressively increased. Six different mortars with w/c ranging from 0.4 to 0.9 were exposed and analyzed. The carbonation kinetics has been defined in greater detail as

$$x = \sqrt{\frac{2Dc}{a}} \sqrt{t}$$

where,

x = carbonation depth at time t,
D = the effective diffusivity of CO₂,
c = concentration of CO₂ in the atmosphere, and
a = the concentration of the reactive components.

Here D is not a constant but function of degree of hydration, on location (curing effect, wall effect), moisture content, the temperature. The CO₂ diffusion is enhanced by an increase in temperature, whereas, the moisture content is reduced, providing more space for gas diffusion which further increases gas diffusivity.

Effect of high temperature curing on carbonation [13]

The effect of high temperature curing on the strength and carbonation of pozzolanic structural light weight concretes has been studied in [13]. Mixes having relatively high replacement level of PFA at 25, 40 and 55% and silica fume at 5, 10, and 15% by weight were considered. The results indicated that accelerated curing at 60°C for 3 days improved 28 day compressive strength of the PFA and SF incorporated mixes but resulted in higher carbonation of the mixes compared with that under normal temperature curing. The increase in carbonation of a concrete mix with 25% PFA replacement level was marginal. At higher replacement levels of PFA and SF, further lower strength and higher carbonation was observed. However, if PFA and SF is added as an aggregate replacement, the carbonatable constituents of cement are not reduced, which slows down carbonation.

Da Silva et al. (2009) studied the sources in variations when comparing concrete carbonation results [4]. In spite of various reported studies, there is a need for information that could allow an adequate interpretation of the results of the standardization process. Several experimental results were analyzed together by the authors. Thereby, the authors have discussed the possible sources of variations when interpreting and comparing carbonation results in accelerated tests. A methodology in terms of standardization of specimen size and procedural steps to minimize their influence have been proposed. Round robin tests, among different laboratories, are suggested to verify the results of this methodology. Several main indicators used in carbonation depth have been provided by the authors as

Table 9 pH indicator and color range [4]

pH INDICATOR	COLOR RANGE
Phenolphthalein	Colorless violet pH 8.0 - 9.8
Thymolphthalein	Colorless blue pH 9.3 – 10.5
Alizarin yellow GG	Colorless yellow pH 10.0 - 12.0
Alizarin yellow R	Yellow-red pH 10.1 – 12.0

The use of correction factor for carbonation depth as function of normalized penetration depth p (= penetration depth in cylinder/external diameter) in cylinders (Moreno, 1999) has been provided and discussed.

Effect of plastering on carbonation [69]

A study on effect of plastering on the carbonation of a 35-year-old reinforced concrete building located in a subtropical environment has been reported [69]. A significant reduction in carbonation was discovered for the columns and beams of building that was plastered and/or put tile/coating. There was no carbonation of concrete when the plaster thickness surpassed 50 mm. The measured carbonation depth and coefficient of carbonation rate of the building are 8.34 mm and $1.38 \text{ mm/year}^{0.5}$, respectively.

NUMERICAL MODELING OF CARBONATION

Analysis of carbonation behaviour in concrete using neural network algorithm and carbonation modeling was carried out [12]. Mix design components such as cement content, water to cement ratio, and volume of aggregate including exposure conditions to relative humidity are selected as neurons. Training of neural network has been carried out using back propagation algorithm. The diffusion coefficient of CO_2 from neural network are in good agreement with experimental data considering various conditions of w/c ratios (0.42, 0.50, & 0.58) and relative humidities (10%, 45%, 75% and 90%).

Numerically modeling has been carried out [19] on the interdependent multi-parameter real mechanism of carbonation considering interaction between the diffusion of CO_2 , the moisture and heat transfer, the mechanism of CaCO_3 formation and the availability of Ca(OH)_2 in the pore solution due to its transport by water movement. The authors developed a set of governing partial differential equations and solved numerically to calculate the depth of carbonation as a function of time considering all the chemical and physical aspects of carbonation process. The amount of CaCO_3 that forms in a unit time depends on the degree of carbonation (i.e., the availability of Ca(OH)_2), the temperature T , the CO_2 concentration, and the relative humidity h into the pore structure of concrete. Assuming the reaction between Ca(OH)_2 & CO_2 is of first order with respect to their concentration, its rate can be expressed as

$$v = \frac{\partial}{\partial t} (CaCO_3) = f(h, T) * [Ca(OH)_2][CO_2]$$

The results of simulation have been compared with experimental results of [35, 36]. It can be observed that a good agreement between the two has been obtained [19].

The prediction for concrete carbonation depth based on RBF neural network has also been carried out [8]. According to the main factors affecting concrete carbonation, prediction model for concrete carbonation depth is established based on the advantages of RBF neural network. Combining with the MATLAB mathematical software, it is used to test mathematical model by the experimental data. The prediction results show that the forecast results conform to the test results very well. A new form of carbonation depth formula used in China Academy of building research as

$D = \eta_1 \eta_2 \eta_3 \eta_4 \eta_5 \eta_6 \sqrt{t}$ where, η_1 = coefficient of cement consumption, η_2 = coefficient of water-cement ratio, η_3 = coefficient of fly ash, η_4 = coefficient of cement type, η_5 = coefficient of aggregate type, η_6 = coefficient of curing method, t = concrete carbonation time.

A statistical analysis has been performed on the carbonation coefficient in open air concrete structures [14]. The study is based on the results of over 100 measurements taken on existing structures upto 99 years old. The results were statistically analyzed to obtain correlations between K and factors such as structure age, the effect of painting, concrete compressive strength and exposure conditions.

A model for predicting carbonation depth of concrete containing low-calcium fly ash has been developed [22]. This numerical model has two parts : hydration and carbonation models. By applying the hydration model, the amount of hydration product that is susceptible to carbonate as well as porosity was obtained as function of curing age. Furthermore, the diffusivity of CO_2 in concrete and the carbonation depth of concrete were also determined.

A mathematical model for hysteresis phenomenon in moisture transport of concrete carbonation process has been proposed in [1]. The authors focus only on moisture transport in the process and propose an initial boundary value problem for a system of partial differential equations as a mathematical model.

Prevention of carbonation

Sakuta et al. (1987) have proposed the use of additives that absorb CO_2 which has entered the concrete, thereby, preventing carbonation. Also proper moist curing for longer period will save the concrete from carbonation [56].

CONCLUDING REMARKS

From the results based on several studies presented above, it is realized that there are several uncertainties on values of parameters to be adopted in experimental as well as numerical investigation of concrete carbonation. However, in this context, following issues needs mention and proper examination:

1. Similar data banks need to be generated in India on carbonation of concrete with and without superplasticizers, supplementary cementing materials in Indian climate. Since Indian climate ranges between two extremities, the experimental studies to be undertaken become multiplied.
2. Minimum cover to reinforcements in carbonation prone concrete to be adopted by codes could only be finalized based on the huge data base that will be generated and analyzed in detail.
3. The necessary depth of cover and the actual quality of concrete are interdependent, in so far as protection of reinforcement is concerned [16]. So at site proper quality monitoring and assessment must be ensured.
4. Poorly cured concrete containing blast furnace slag and other pozzolans exhibits higher carbonation. This may be verified in greater experimental details.
5. Statistical and numerical modeling of carbonation and thereby its prediction may be useful to assess the complex interdependence of numerous parameters affecting carbonation of concrete.

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