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Review Paper

Reviewing the Carbonation Resistance of Concrete

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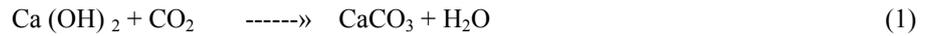
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ABSTRACT

The paper reviews the studies on one of the important durability properties of concrete i.e. Carbonation. One of the main causes of deterioration of concrete is carbonation, which occurs when carbon dioxide (CO_2) penetrates the concrete's porous system to create an environment with lower pH around the reinforcement in which corrosion can proceed. Carbonation is a major cause of degradation of concrete structures leading to expensive maintenance and conservation operations. Herein, the importance, process and effect of various parameters such as water/cement ratio, water/binder ratio, curing conditions, concrete cover, super plasticizers, type of aggregates, grade of concrete, porosity, contaminants, compaction, gas permeability, supplementary cementitious materials (SCMs)/ admixtures on the carbonation of concrete has been reviewed. Various methods for estimating the carbonation depth are also reported briefly

1   Introduction

Concrete is such a porous material that various substances can penetrate through interconnected capillary pores. The porosity of the concrete allows movement and retention of water and carbon dioxide (CO2). The CO2 gas is present in the atmosphere at approximately 0.03% by volume of air [1] and the cement industry contributes about 7% of the total worldwide CO2 emissions. The production of one ton of Portland cement (PC) generates approximately 0.55 tons of chemical CO2 and requires an additional 0.39 tons of CO2 in fuel emissions for baking and grinding, accounting for a total of 0.94 tons of CO2. Durability of concrete is a relative property since it simultaneously depends on the chemical and physical characteristic of concrete and environmental conditions. Carbon dioxide in the atmosphere diffuse through the empty pores of concrete and reacts with the hydration products leading to initiation of carbonation process. Carbonation of concrete is commonly defined as the chemical reaction between CO2 present in the atmosphere and the cement hydration products such as calcium hydroxide Ca(OH)2, calcium silicate hydrate (CSH), calcium aluminate hydrate (CAH) resulting in formation of calcium carbonate (CaCO3).

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$$Ca\,(OH)_2 + CO_2 \quad ------\!» \quad CaCO_3 + H_2O \tag{1}$$

$$Ca^{2+} + CO_3^{2-} \quad -----------\!» \; CaCO_3 \tag{2}$$

These reactions lead to a decrease in the pH of the liquid of the pores and in moist conditions with low pH values, embedded reinforcement in concrete starts corroding. A layer of passive oxide forms around the reinforcement steel which protects it against corrosion. Generally, two limit states can be identified with regard to service life. The first limit state ends when the steel is de-passivated. The second limit state is based on cracking of the concrete cover due to which oxides generated during corrosion [2]. The steel reinforcing bars are protected from corrosion by a thin oxide layer which forms on their surface due to the high alkalinity (pH > 12.5) of their environment, i.e. the surrounding concrete, if the pH-value of this environment drops below 9, or if chloride ions penetrate up to the surface of the reinforcement, the protective oxide layer is destroyed, and the corrosion of the steel rebar is initiated. When $Ca\,(OH)_2$ and hydrated CSH are transformed into $CaCO_3$, the hydroxide concentration in the water of the pores is reduced which results in promoting corrosion of the steel reinforcement in the presence of water and oxygen. Reinforcement corrosion is considered as one of the critical stages for determining service life of a concrete structure.

2 Importance of Carbonation

Durability is defined as the capability of concrete to maintain the long-term structural performances. The atmosphere, water and the soil are the environments to which concrete is exposed. In these environments, concrete subject chemical and physical attacks. These attacks are sulfate attack, acid attack, carbonation, alkali-aggregate reaction, freezing–thawing, abrasion, etc. [3]. Performance of concrete against all of these attacks is named as durability. Water ingress is one of the most important reasons that increase the deterioration of concrete. Carbonation is a major risk for reinforced concrete because it lowers alkalinity of the concrete to such an extent that iron may rust and spall the cover. The service life includes a certain propagation period of corrosion during which the cross-sectional area of steel is progressively decreased, the bond between steel and concrete is reduced and the effective cross-sectional area of concrete is diminished due to spalling of the cover [2]. In the design of concrete structures, carbonation is one of the many important factors that determine their service life. Frequent maintenance and conservation operations or even entire replacement are required for less durable concrete structures, which is associated with the consumption of more raw materials and energy. This phenomenon may affect the serviceability of the structure (e.g. fall of concrete debris), its stability (due to detachment of concrete cover and reduction of thickness of steel reinforcement) and also the aesthetic appearance (cracks in concrete, rust spots, exposed bars, general decay). Increase in the durability of the concrete from 50 to 500 years would mean a reduction of environmental impact by a factor of 10. Due to corrosion of steel and spalling of concrete, structural and aesthetic aspects are thereby compromised which leads to high repair and rehabilitation costs for the damaged structures.

3 Carbonation of Normally Vibrated Concrete made with Natural Aggregates

Carbonation is a major cause for deterioration of concrete structures and mainly depends on various parameters like water cement ratio, water binder ratio, curing regimes, addition of admixtures, curing compounds, porosity, type of concrete and aggregates, cover, super plasticizer, relative humidity, temperature and concentration of carbon dioxide. The influence of these parameters on the carbonation of normally vibrated concrete (NVC) made with natural aggregates (NA) is discussed below:

3.1 Effect of water/cement (w/c) ratio

Carbonation was found to depend mainly on the w/c ratio whatever be the mix constituents. Studies revealed that the w/c ratio was found to be the most reliable parameter in predicting the resistance of NVC to carbonation. Results were obtained from one week accelerated carbonation which was compared with one year accelerated carbonation. With curing period of seven days, it was predicted that carbonation depth was found to be directly dependent/ proportional to w/c (Fig.-1) [4]. Carbonation depth increases with increase in w/c ratio and with the age of NVC [5]. The depth of carbonation was reduced considerably by reducing the w/c ratio. It was found that for NVC mixes with lower w/c ratio (0.4), a linear relationship with low values of carbonation depths were observed but as w/c ratio (0.6-0.7) increases a continuous increase in carbonation depths were also observed [6]. The rate of water flow is increased with increase in w/c ratio due to change in

pore structure under both carbonated and non-carbonated conditions. Decrease in w/c ratio resulted in decrease in concrete carbonation. Study of NVC in hot arid regions confirmed that with decrease in w/c ratio, carbonation also decreases [7].
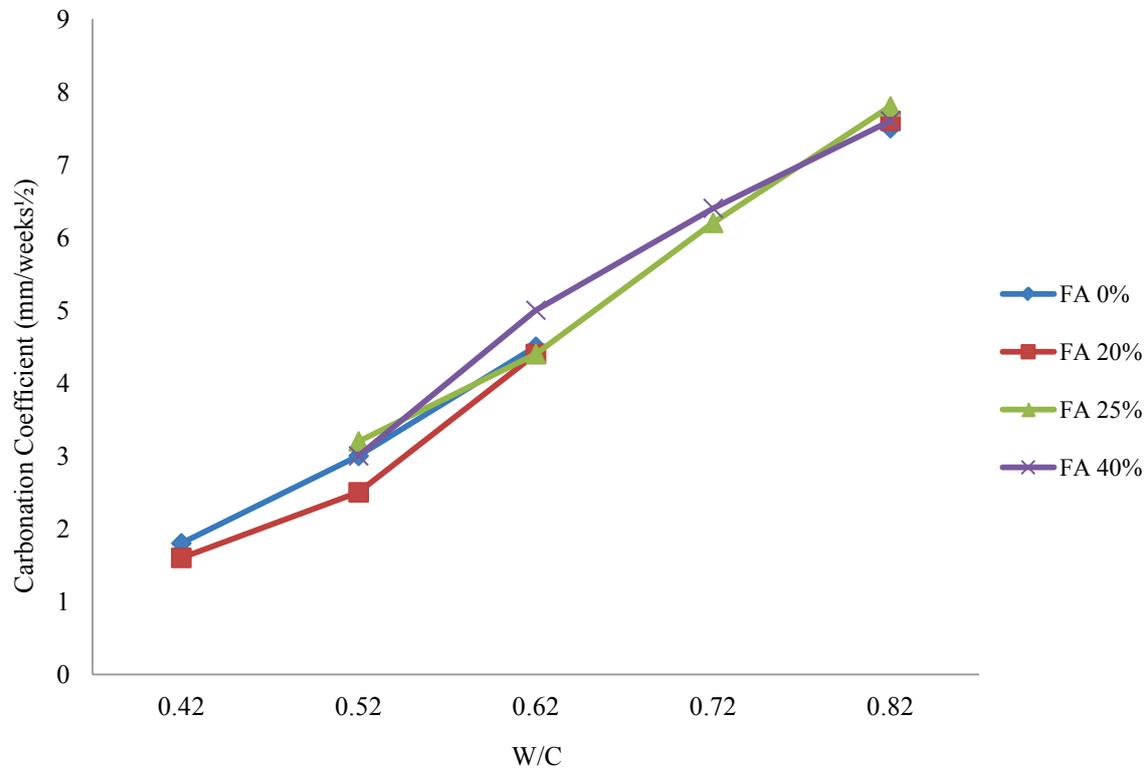

Fig. 1 Carbonation coefficient vs w/c ratio and fly ash content [4].

3.2 Effect of water curing and amount of cement

It was found that carbonation depth is inversely proportional to the curing time and vice versa. Results obtained from 1 day, 7 days, 21 days and 28 days clearly justified the above statement. From Fig.-2 & Fig.-3 it was found that when the curing periods were increased from 1-28 days, the depth of carbonation was reduced to extent of 61, 43, 25 and 17% [6]. Concrete carbonation rates decreased with an increase in water curing period. Delay in water curing period resulted in higher rates of concrete carbonation. Based on this study a relation was suggested between carbonation depth and exposure time ($d_k = Kt^{0.5}$) where d_k is the average depth of carbonated surface layer (mm), K is a factor whose magnitude depends on concrete properties and curing conditions, and t is the time of exposure to CO_2 in days. It was found that carbonation depth reduces up to 53% and K values for the mixes reduces to 39-30% if curing time increases from 3 days to 28 days [8]. Curing time has a large effect on the durability of commonly used NVC and one day curing is not sufficient whatever be the cement content (range between 300 and 420 kg/m^3). Previous studies have found that whatever be the curing time, carbonated depth decreases with increasing cement content. With increase in the cement content and curing period from 1 to 28 days durability increase from 10%-30%. It was also found that increasing the curing period up to 3 days is sufficient for NVC with the cement content up to 380 kg/cum; but for other type of concretes with higher cement contents, curing period must be longer. The experimental study confirmed the results which contains mainly four mixes, naming from B1-B4 in which cement content (from 300 Kg/m^3 to 420 Kg/m^3) and gravel on sand ratio (G/S: 1.0 - 1.15) increases and water to cement (w/c: 0.65-0.48) decreases respectively. Since with increase in cement content, compressive strength increases (expressed in terms R_{28}) and this directly affects the carbonation depths. The effect is clearly shown in Table 1. the curing effect also depends on cement type at some extent such that prolonged curing period improves durability of concretes made with cements which contain slag [9]. Longer initial curing period helps in reducing the carbonation depth. It was also found that initial curing for prolonged period proved to be most beneficial in reducing carbonation depth [10]. Also mixes under normal water curing observed lower carbonation than mixes under hot water curing. Comparison of study in terms of

carbonation was done and the effect of carbonation under hot water curing for both normal weight concrete (NWC) and light weight concrete (LWC) was studied and it was found that LWC mixes have lower carbonation depths than NWC mixes. For PC based mixes, longer moist exposure in normal curing produced better hydration than hot curing, causing denser pore structure in PC concrete under normal curing than under hot curing which helps in lowering the carbonation depth.
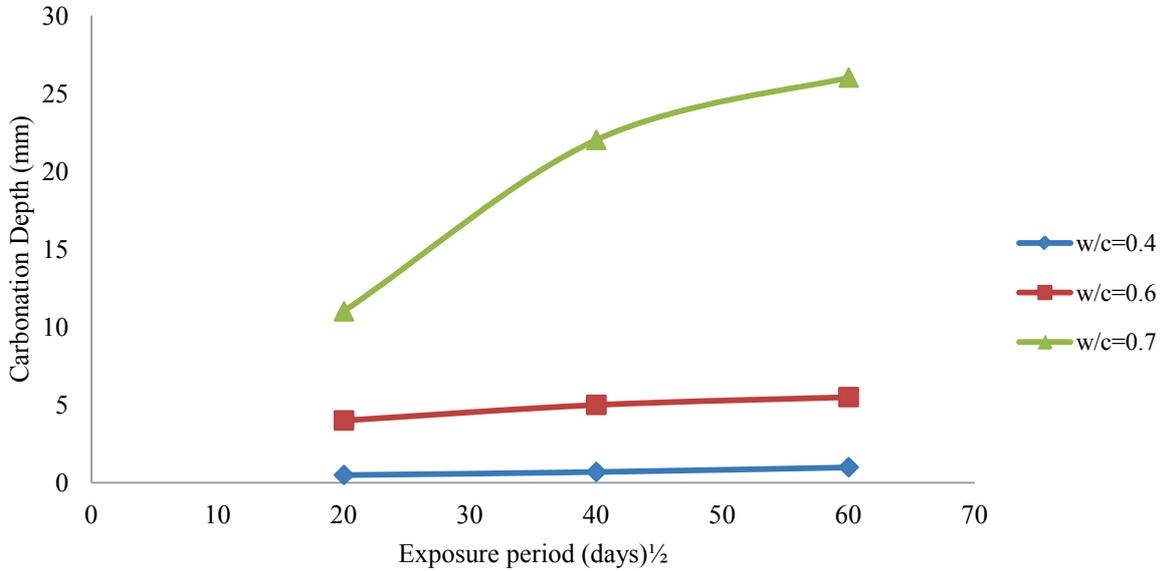

Fig. 2 Carbonation depth vs exposure period for 7-days water cured concrete with varying w/c ratios [6]
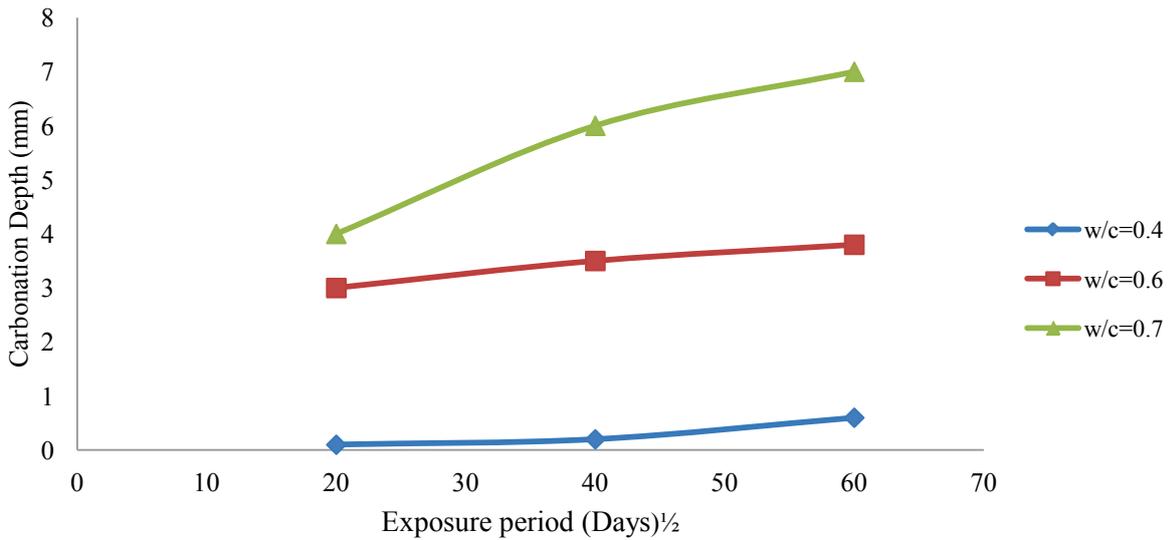

Fig. 3 Carbonation depth vs exposure period for 28-days of water curing with varying w/c ratios [6].

Table 1- Carbonation depths (mm) of four different mixes (B1-B4) with altered curing and exposure periods [9]

Concrete	Properties	Curing Days	Exposure 90 days	Exposure 180 Days	Exposure 360 Days	Exposure 540 Days
B1	C =300 Kg/m^3	1	6.5	11	13	15
	W/C =0.65	3	4	6	9.5	13
	R$_{28}$ =25.1 MPa	28	3	5	6	9
B2	C =340 Kg/m^3	1	5.5	10	12	13
	W/C =0.61	3	3.5	5	6	8
	R$_{28}$ =32.6 MPa	28	2.5	4	4.5	6
B3	C =380 Kg/m^3	1	4.5	9	10	11.5
	W/C =0.53	3	3	5	5.5	7
	R$_{28}$ =37.8 MPa	28	2	3.5	4	5
B4	C =420 Kg/m^3	1	4	7.5	8.5	9.5
	W/C =0.48	3	2.5	4	3.5	4
	R$_{28}$ =43.5 MPa	28	1.5	3	3	3.5

Study revealed that insufficient initial hot water curing results in greater carbonation of LWC and carbonation depth for all NVC mixes under accelerated curing was higher than that of NVC mixes under normal curing because during hot water curing amount of calcium hydrates (CH) is decreased and more CSH is produced hence hot water cured concretes lacked the moist curing of 3 days as compared with normal water curing due to pozzolanic reaction. Hot water curing with certain quantity of admixtures like fly ash (FA) and silica fumes (SF) helps in increasing compressive strength up to some extent as compared to normal water curing. Accelerated curing with admixtures helps in providing more strength as compared to normal curing; simultaneously carbonation depth for all concrete mixes increases than that of concrete under normal curing. Normally vibrated concrete made with light weight aggregates (LWA) experiences more carbonation depths in hot water accelerated curing [1]. To improve carbonation resistance, sufficient water curing of at least seven days is necessary for PC based concrete, whereas, an extended curing age of water is required for ground granulated blast furnace slag (GGBFS), FA and SF concretes [11].

Curing compounds based on sodium silicate exhibited higher carbonation than samples brushed with curing compounds based on resin and wax emulsion. Specimens cast and exposed during the winter exhibited lower carbonation than those cast and exposed during summer. Specimens brushed with curing compound based on resin performed best in hot and arid climates and curing compounds based on resin and emulsion were as effective as six days of water-curing which helps in reducing carbonation and coatings based on ethylene copolymer dispersion or acrylic resin were found effective in preventing carbonation up to 600 days [7]. The use of epoxy resin showed better protection than the use of acrylic and siloxane resins, also composition of the concrete is an important factor affecting the diffusion of carbonation. The desired life of a structure can be enhanced by providing proper protection treatments [2].

3.3 Effect of air curing

A study was done on both newly made specimens in laboratory and on existing building by providing air and water cured exposure. Carbonation depth measurements were made on the specimens from 2 and 4 years after they were cast and the weights of specimens were measured after 1, 4, 9, 25, and 49 hours of absorption of water. The initial and final weights

after air dried curing were recorded. It was concluded that air dried concrete specimens experience an increase in weight and reduction in sorptivity with age [12]. Air cured NVC shows a loss in strength relative to equivalent NVC made with NA which is water cured and the strength differences increases with curing period. It was also found that chances of increase in carbonation depths in air dried curing are much higher than the specimens which cured in water as higher loss of strength is observed in air dried curing concrete [13]. The water curing has a beneficial effect on all the tested mixtures. The carbonation depths were about 20–50% lower in the case of water curing than in the case of air curing. The above statement was justified from the values obtained from different mixes (A1, A2, A3, A4) in which A1 (CEM I 52.5N type) and A4 (CEM II/B-V 32.5 R type) were taken as base mixes and A2 and A3 were mixes having 30% and 50% replacement of cement with FA. The super plasticiser content and water to powder ratios varies in all mixes starting from 0% in A1, 0.3% in A4, 0.7% in A2, 3% in A3 and 0.6 in A1, 0.54 in A4, 0.53 in A2 and 0.41 in A3 respectively. The results shown in Fig.-4 and Fig.-5 were compared and it was clearly observed that carbonation depth values were higher in case of air curing than water curing [14].
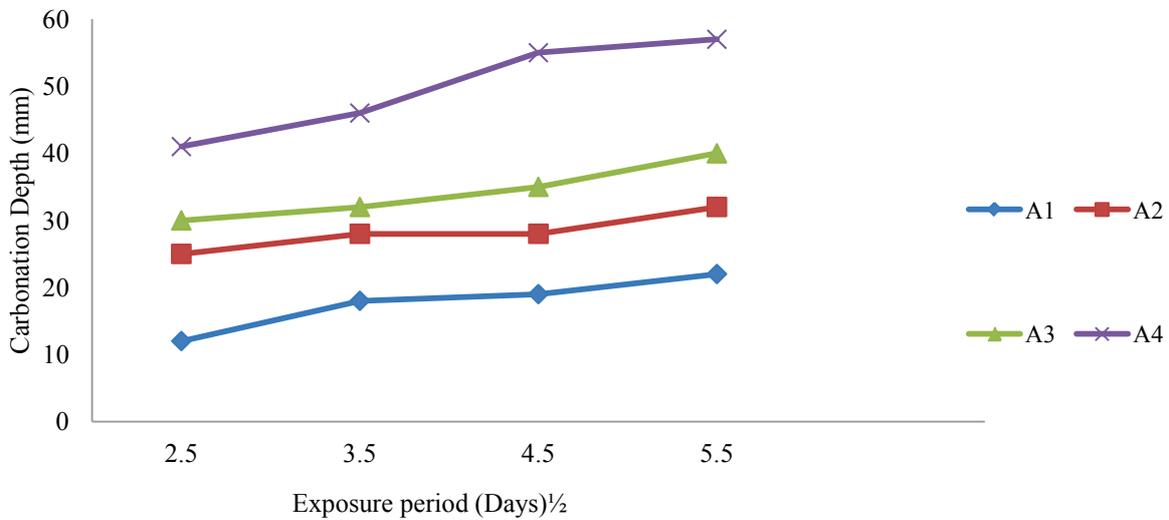

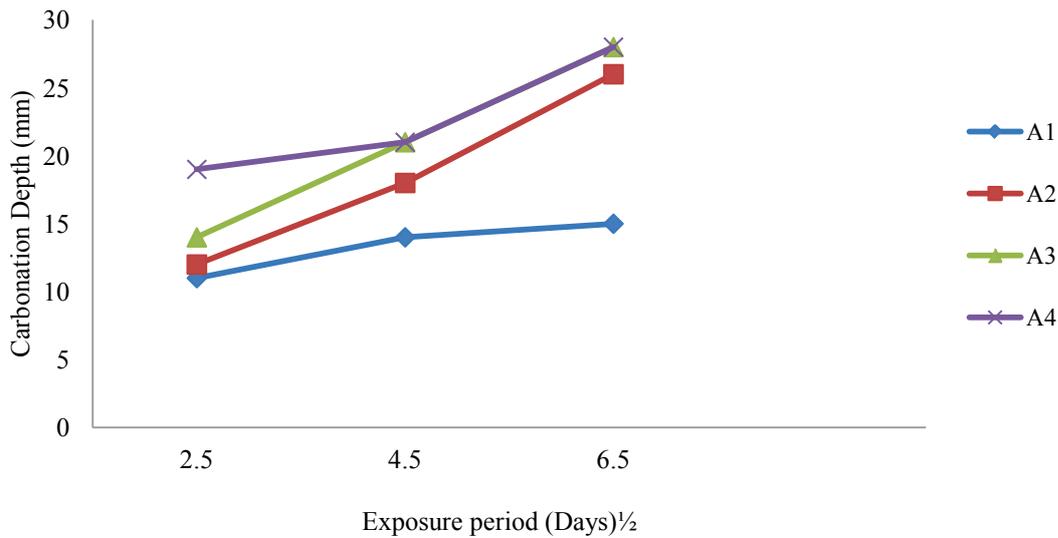**Fig. 4 Carbonation depth vs exposure period after air-curing [14].**

Fig. 5 Carbonation depths vs exposure periods after water-curing [14].

3.4 Effect of water/binder (w/b) ratio

Carbonation is greatly affected by w/b ratio. Lower w/b ratios do not affect much on carbonation depth values but higher ratios completely deteriorate other properties. Also the relation between compressive strength and gas permeability depends upon w/b ratios [15]. Carbonation depth for NWC and LWC mixes increased with the increase in w/b ratio. The decrease in w/b ratio in NVC mixes replaced with FA is due to the refinement of pores which results in reducing the carbonation coefficient (CC). Carbonation increases with the increase of w/b ratio and the decrease of binder content (Fig.-6). Also it was found that with increase in w/b ratio, value of slump of NVC increases with considerable increase in carbonation depths in both NWC and LWC mixes [1]. At lower w/b ratio, with 30% replacement of FA improves the compressive strength, and results in a marginal increase in carbonation depth but on the other hand at higher w/b ratio with FA replacements, significantly effects on all other properties [16].
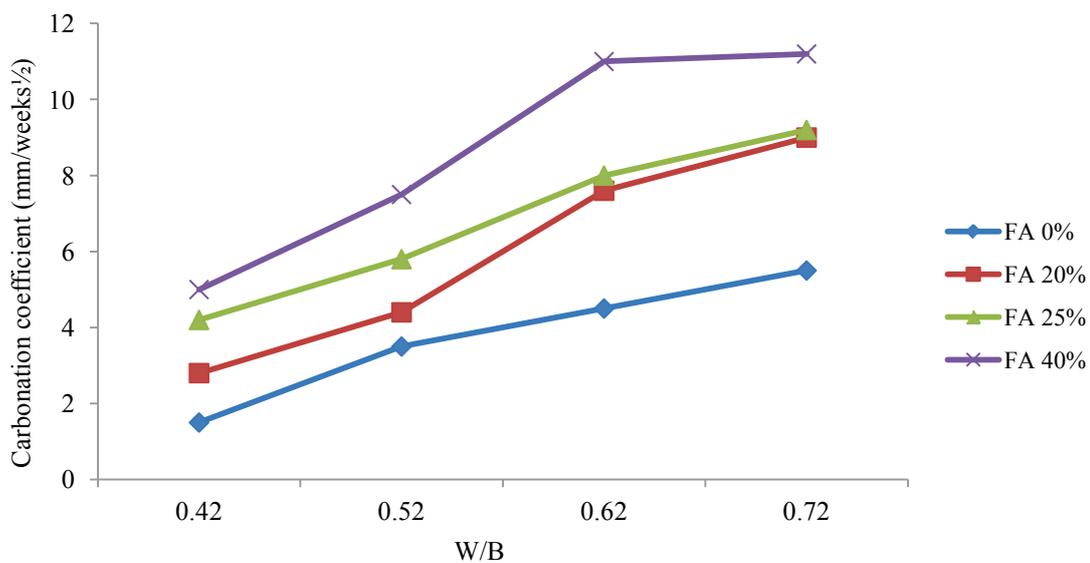

Fig. 6 Influence of water/binder ratio on the carbonation depth of concrete with different levels of fly ash [4].

3.5 Effect of admixtures

Different industrial wastes such as FA, GGBFS, SF, Metakaolin (MK) etc. are now used in the construction industry as these admixtures help in improving the various properties of concrete. The parameter of high strength is the most important which helps in reducing the carbonation phenomena as it is observed from previous studies that higher grades of concretes generally have lower values of carbonation depths. Due to different properties/structures of admixtures these have different kind of impacts on the performance concrete.

3.5.1 Effect of fly ash (FA)

Use of FA in NVC was found to have notorious impact on carbonation resistance. The depth of carbonation increased with an increase in the replacement of FA. Particular amount of replacement of FA helps in increasing the compressive strength but it has simultaneously some negative effect in resisting the carbonation of concretes. Studies were done by correlating the ratios of 7 and 28 compressive strengths with different replacements varying from 0-40% [4]. Replacement of FA beyond 60% could not benefit much as a sharp increase in carbonation depth was observed & 0-30% replacements were proved to be better than other higher replacements of FA [11]. The above statement is clearly understood by Fig.-7a & Fig.-7b in which four different mixes (F21-F24) having replacement level of 15%, 30%, 45% and 60% of FA. Carbonation depth of high volume fly ash (HVFA) NVC at the curing period of 90 days were close to concrete made with PC only. Carbonation depth increases with the use of FA but in HVFA mixes curing of 90 days gives comparable depth values close to PC made concrete [17].
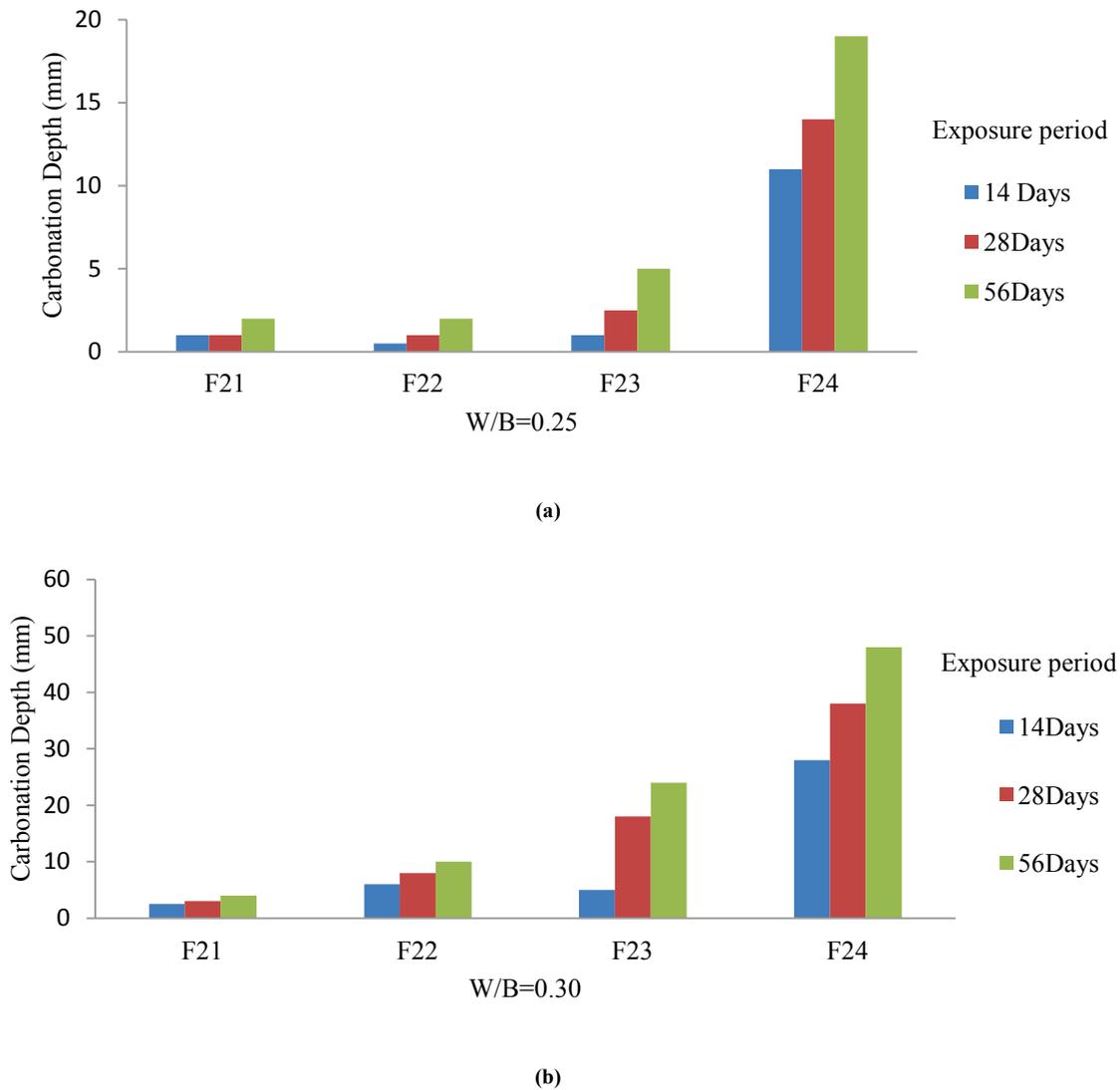
(a)

(b)

Fig.-7 (a & b) Influence of fly ash on carbonation depths of HPC at various w/b ratios with different exposure periods [15].

3.5.2   *Effect of ground granulated blast furnace slag (GGBFS)*

Concretes having GGBFS as replacements were found much comparable or superior to normal hydrated concrete. It was confirmed that incorporation of GGBFS certainly helped in decreasing the carbonation depths but only with particular replacement levels. It was found that carbonated slag cement based NVC with 15 and 25% slag had higher strength than other hydrated NVC at ages of 28 and 120 days hence it helps in reducing carbonation depths [18]. In case of high performance concrete (HPC) made with PC and Blast Furnace Slag Cement (BFSC), the compressive strengths at both 28 and 90 days were marginally higher than the corresponding concretes. GGBFS performed much well as compared to FA as GGBFS has more fineness which results in denser matrix which ultimately helps in reducing carbonation depth, the fact becomes more clear from the (Fig.-8a & Fig.-8b). GGBFS is proved to be more active than FA, which is also confirmed from the higher compressive strength development rate of PC with GGBFS when compared with that of PC against FA at the same w/b ratio [15-16].
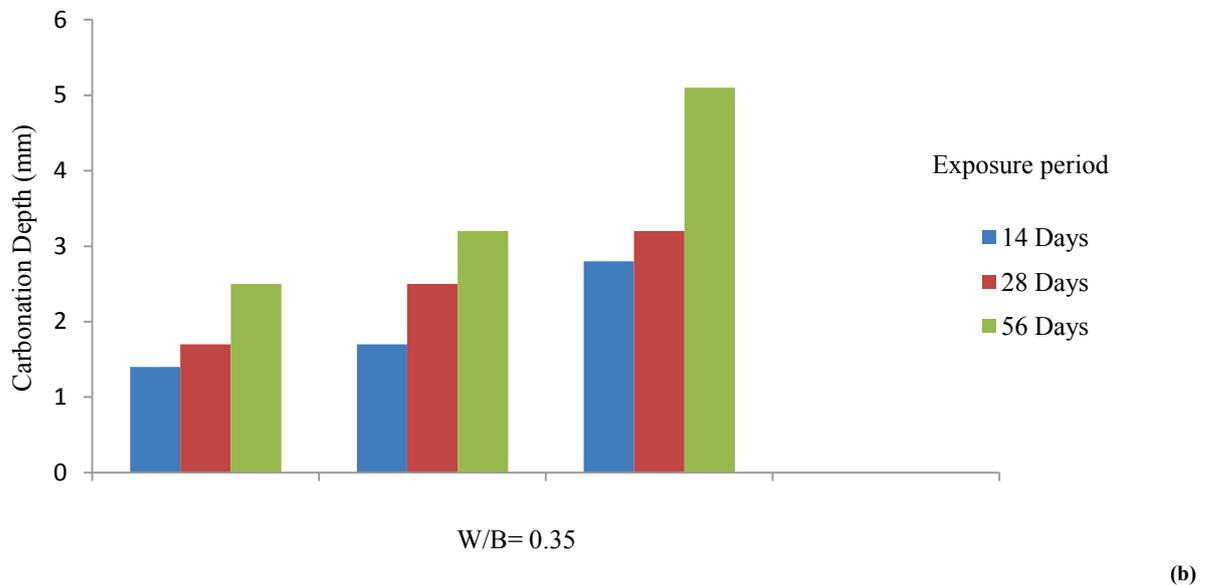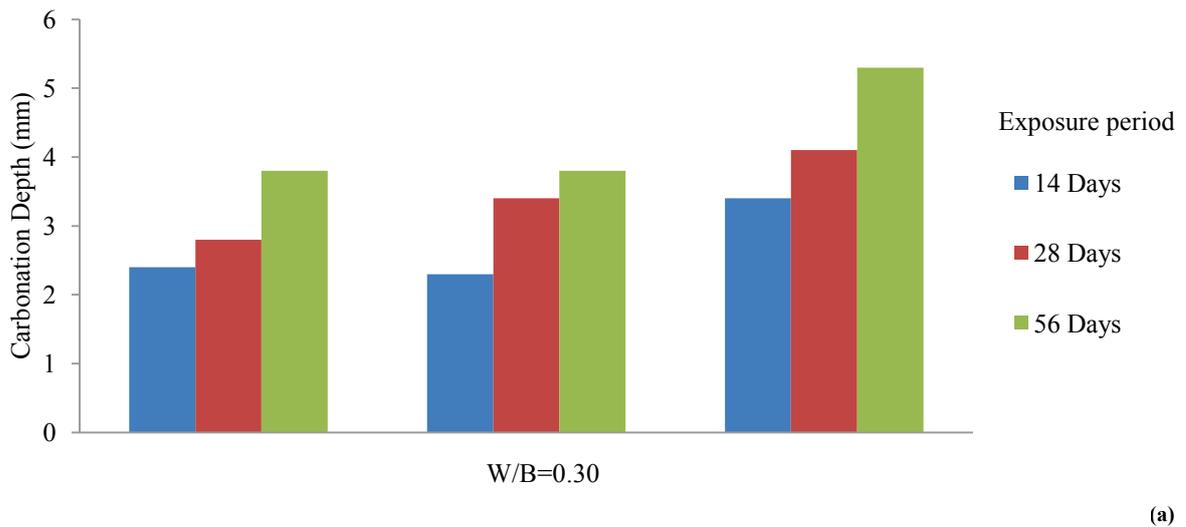
(a)

(b)

Fig. 8 (a & b) Influence of GGBFS on carbonation depths of HPC at various w/b ratios with different exposure periods [15].

3.5.3   Effect of silica fume (SF)

Silica fume is very effective in the development of high strength and high performance concrete. It has been found that SF improves compressive strength, bond strength, and abrasion resistance, reduces permeability and therefore helps in protecting reinforcing steel from corrosion [19]. Addition of SF in the concrete mixes increases the carbonation depth. When SF is added in concrete mix then increase in compressive strength is observed but simultaneously increase in carbonation depth is also observed. Silica fume can react with $Ca(OH)_2$ and lower the pH of the pore solution, facilitating the carbonation process. It was found that up to 10% replacement of SF doesn't influence on carbonation phenomena of the concrete but as the limit increases beyond 10% effect of SF start coming in to picture (Fig.-9). Beyond this limit it not only increases carbonation depth but it also increases the variation in the intensity of carbonation-induced corrosion (Fig.-10) [20]. So it was concluded from the study that compressive strength is not the only parameter for estimating the service life of concrete structures [21]. Some studies showed that for a given compressive strength, SF based NVC had greater carbonation rates than NVC made without SF [22]. Also carbonation depth was greater in mortars containing SF in comparison to control NVC which is due to the reduction of pH caused by the pozzolanic reaction [23]. In case of binary

blends with high levels of replacements of FA and less amount of other blend like SF it was found that carbonation depth decreases linearly (Fig.-10) [20].
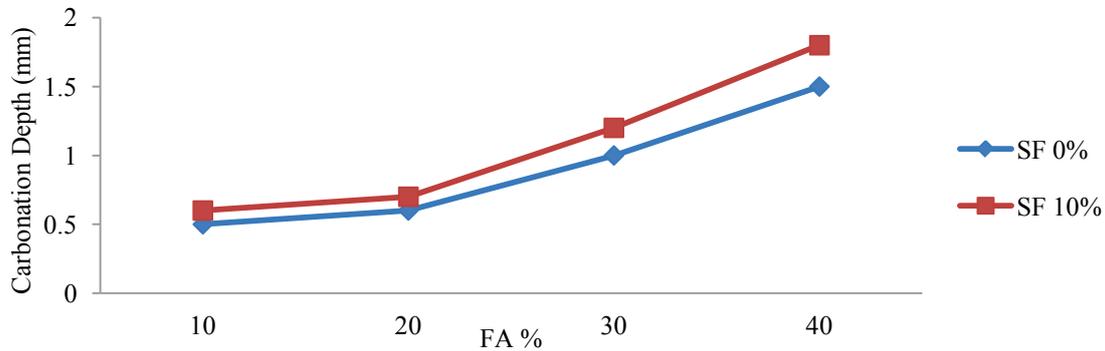

Fig. 9 Carbonation depth of concrete at age of 2 years of natural exposure having w/b ratio of 0.27 with varying percentages of fly ash and silica fume [19].
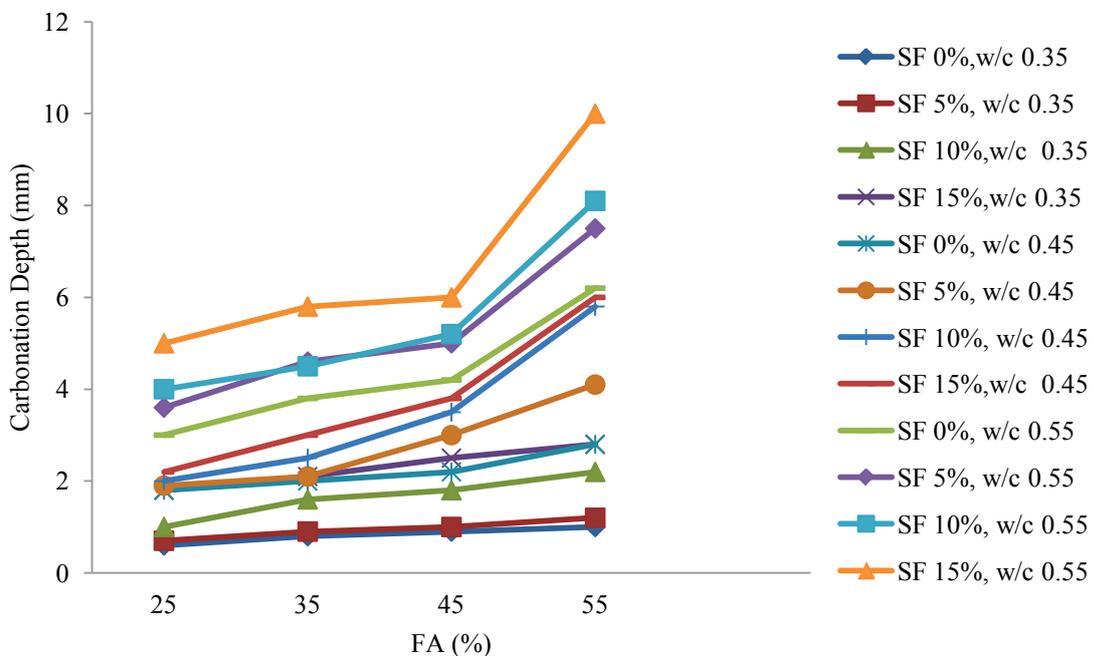

Fig. 10 Carbonation depths for 28 days of exposure with varying levels of fly ash and silica fume at different w/c ratios [20].

Adding limestone fines produces better particle packing hence reduces the carbonation [24]. Increasing replacement of PC with FA in PC-FA air cured NVC increases carbonation depths on the other hand; systematically replacing the FA with MK helps in reduces carbonation depth [13]. If ternary blends (FA, GGBFS, SF) are used as replacements it is observed that the carbonation depth directly increases up to 2.5 times than NVC mixes. In ternary blends it was also observed that after considerable exposure of 12-28 weeks the rise in depth of carbonation varied from 30-215% in comparison to control NVC. No particular amount of ternary blends was decided for controlling such a huge margin of the occurred carbonation [25].

3.6 Effect of porosity

As porosity increases, carbonation depth also increases. Pore structure is one of the major influencing factors concerning durability. The decrease of the capillary porosity, obtained by lowering water content decreases the carbonation rate [26]. A linear relationship exists between accelerated carbonation and porosity. In some cases porosity is found to be

unreliable indicator for prediction of carbonation as it only tells the compactness of the concrete [27] but in another research it was found that with increase in porosity of concrete carbonation depths increases and a linear relationship exists between two [28]. Carbonation in CO_2 enriched environment has rapidly developed in comparison to in normal atmosphere. For durability of concrete structures proper compaction is must [29]. It was found that the depths of carbonation were affected significantly by the amount of compacted pores, moisture content of the concrete and the relative humidity [30].

3.7 Effect of super plasticizers

Incorporation of super plasticizers has been of great interest and is gradually applied to concrete practical projects. Their utilization changes carbonation phenomenon of ordinary concrete [31]. In some cases addition of super plasticizer did not show much influence on the carbonation depths; but appropriate dosages can effect on the performance of concrete against carbonation resistance. Addition of a phosphate based retarding admixture resulted in a decrease in the depth of carbonation [6]. Super plasticizers can change the size, amount and orientation of hydrations induced in concretes thus improves anti-carbonation ability [32]. Type of admixtures also influences on the compressive strength and permeability of NVC. It was found from the Table -1. values which are obtained from the mixes M0, M1, M2 M3 and M4 in which mix M0 is a conventional concrete (NVC) with no replacement and addition, mixes M1 and M3 have replacement of cement with FA but no addition of super plasticizer and finally mix M2 and M4 made with both replacement of FA and addition of super plasticizers. The carbonation depth values were found as shown in Tables 2. & Table 3. which confirmed that there was no significant influence on the mixes M1 and M3 which contain super plasticizer and in the mixes M2 and M4 which do not contain super plasticizer [10].

Studies revealed that super plasticizers like poly carboxylic acid (PA), naphthalene sulphonated (NS) and amino sulfonic acid based super-plasticizer can improve the ability of resistance to carbonation of tri calcium silicate (C_3S) and tri calcium aluminate (C_3A) hydration products. Experiment analysis was done by thermal gravimetric analysis (TGA) method and it was found that PA has the most significant effect of improvement among all others [32].

Table 2- Accelerated carbonation depths (mm) of concretes cured at 65% RH with 20º C for exposure period of 2 weeks [10].

Mix Name	3 Days curing	7 Days curing	28 Days curing	90 Days curing
M0	9.6	8.5	6.5	5
M1	14.1	12.8	10.4	8.4
M2	14.9	13.4	11.3	8.9
M3	10.3	9.8	6.3	4.5
M4	9.8	9.3	5.7	3.8

Table 3- Accelerated carbonation depths (mm) of concretes cured at 100% RH with 20º C for exposure period of 2 weeks [10].

Mix Name	3 Days curing	7 Days curing	28 Days curing	3 Months curing
M0	9.1	7.4	4.5	3.3
M1	13.3	10.9	6.5	4.6
M2	13.8	11.7	7.3	5
M3	8.7	8.4	3.2	1.8
M4	9.6	7.5	2.1	1.6

3.8 Effect of cover

Rendering or plastering with proper cover provision helps in reducing carbonation depths. Studies also revealed that the surface protected concretes presented generally lower carbonation diffusion coefficients than the non-protected concretes. Carbonation of the concrete can be retarded by the application of surface finishing materials. Studies have shown that plastering helps in reducing (cement-sand render) the incidence of carbonation from 89 to 8% and the average carbonation depth from 22 to 2 mm [33]. The use of surface coatings reduced the depth of carbonation considerably. Single and double layers of protective coatings were applied to the concrete specimens and it was found that depth of carbonation was reduced by approximately 9 and 25%; hence the use of surface coatings considerably reduced the rate of carbonation [6]. A cover thickness of 35-40 mm is considered necessary for reinforced NVC made of special kind of cements (CEM II or CEM III) with FA replacement up to 50%. A minimum cover depth of 25 mm is must and for cements, with up to 50% FA replacement, the cover thickness of 30 mm is sufficient to for providing the passivity of steel rebar in 50 year service life [34].

3.9 Others parameters

Carbonation and chloride penetration depends on the concrete micro structural evolution due to mechanical bending. In fact, contamination by aggressive ions is more important in the tensile zone of bent reinforced concrete beams than in other zones. Presence of contaminants effects negatively on performance against carbonation process [35]. Carbonation is greatly accelerated by migration of pore solution and increase in alkali content of cement. Alkali content in cement is another major factor for enhancing the carbonation process and this depends on migration of pores solution in the mixes [36]. The increased carbonation in the contaminated specimens is attributed to changes in pore structure of cement due to the inclusion of contaminants. Chances of increasing carbonation in contaminated concretes are higher as pore structure becomes disturb due to inclusion of contaminants in cement mortar [37].

Electrochemical re-alkalisation helps in stopping the damage due to carbonation. For preventing important /historical structures from damaging due to carbonation, electrochemical re-alkalisation process is used. Movement of ions through pore structures due to current application helps in reducing carbonation [38]. A particular linear relationship is observed between depth of carbonation and compressive strength as carbonation depth is being proportional to inverse of strength. Lower grades of NVC show larger carbonation depths than the higher grades. The fact was justified by measuring CC for different grades. Due to higher concentration of CO_2 in laboratory it was concluded that the carbonation rate constant (K) measured in the accelerated laboratory tests was considerably higher than those measured in normal atmospheric conditions; the results confirmed from the values which are shown in Table 4. [39].

Table 4 - Compressive strengths, carbonation depths and carbonation rate constants (K) with different exposure periods [39]

Water/Cement Ratio	Compressive Strength (MPa)	Carbonation Depth (mm)						Carbonation Rate Constant K, (mm/year½)
		Exposure to Carbon Dioxide						
		7d	14d	21d	28d	35d	42d	
0.55	27	0	1	2.2	3	3.7	5.3	10.89
0.6	26.5	0	1	2.8	3.3	4.5	5.5	11.9
0.65	23.5	0	1	3.3	3.8	5.1	7.1	13.7
0.7	20.5	0	1	3.9	4.3	6.1	7.5	15.5
0.75	18.5	0	1	4.1	4.7	6.3	8.5	16.9

d = days

Carbonation process obeys Fick's second law i.e. the rate of carbonation (an increase of the carbonation depth with time) follows a square-root-time law. It was found that after carbonation, concrete pore structure became denser and pH

value decreased in pore solution which results in the decrements in rapid chloride permeability test (RCPT) charges, sorptivity and water absorption as well as an increment in resistivity was observed. These tests are not only solely used to judge concrete durability for the carbonated concrete. It was also observed that the RILEM CPC-18 method sometimes might underestimate carbonation induced corrosion risk [40-41]. Carbonation coefficient is not influenced by type of FA. Admixtures used in excess as replacement (greater than equal to 50%) results in increase in carbonation coefficient approximately two to three times but the same is not true for small quantities, this due to pozzolanic reactions and pore refinement properties. From the relationship between carbonation coefficient and 28-day compressive strength, it was observed that when compared with the cement-only NVC, the carbonation coefficient increases with an increase in FA content, but is not influenced by type of FA [42] also type of cement had no significant influence on carbonation of NVC. As stated earlier, type of cement had no significant influence on carbonation of concrete. White cement based NVC exhibited the least carbonation followed by sulphate resisting cement and PC [7]. The workability of fresh NVC has a significant influence on long-term behaviour and durability [14].

Compaction of concrete also influences on the carbonation depth as maximum carbonation was observed on non-compacted specimens. The minimum carbonation and sorptivity coefficient were obtained on specimens compacted by vibration. Proper compaction reduces the porosity in concrete. Increase of porosities (9%, 12% and 17%) causes increases the carbonation depth. It is cleared from Fig.-11 that the carbonation rate increases with an increase of porosity [29]. A strong relationship between gas permeability and carbonation of HPC was confirmed [13]. Air diffusing into concrete can cause carbonation i.e. more the penetration of air higher will be the chances of degradation [43]. The concentration of CO_2 has a considerable effect on estimating the carbonation resistance of high volume low quality FA concrete [44].
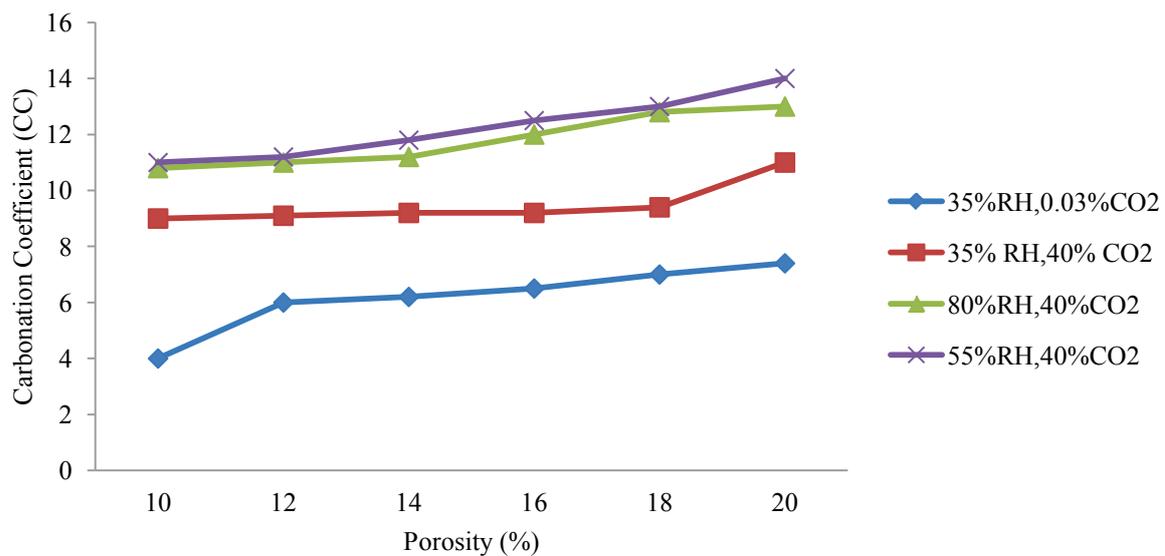

Fig. 11 Carbonation coefficient vs porosity for natural and CO_2 enriched environment with different levels of relative humidity (RH) [29].

The pH profile is inexpensive, simple and reliable method to establish the effect of carbonation on concrete. The rate of carbonation derived from pH profiles could be utilized to estimate the service life of structures when the deterioration is caused by carbonation induced corrosion of steel in concrete. Information regarding advancement of carbonation and critical pH levels can be obtained more reliably by method of pH profiling rather from traditional phenolphthalein test. Such method is a new method in which the resistance ratio can be used to identify regions of concrete which are non-carbonated, partly carbonated and fully carbonated [45]. Gamma-ray measurement method is a non-destructive method and is suited for samples submitted to laboratory tests, TGA can also be used on laboratory samples as well as on core samples taken from concrete structures. For most of the times an accelerated carbonation test is proposed as a performance test as it is sensitive enough and results were found consistent with natural carbonation exposure conditions. It has been observed in the study that carbonation rate in real environment is approximately 10 times slower than the accelerated carbonation tests [34]. Therefore, carbonation depth from accelerated carbonation test may be used as an indicator to show equivalent performance [27].

Curing compounds based on resin and emulsions were as effective as six days of water-curing in reducing carbonation. Curing compounds/aids were twice as effective when used or tested during the winter rather than the summer. There are strong relations between the carbonation depth of NVC tested in natural environments and that in the accelerated carbonation chamber. A linear relation is proposed to predict the carbonation depth in the natural environments based on the results obtained from the accelerated carbonation test and the square root-t-law. Carbonation coefficient is inversely proportional to the carbonation resistance of concrete and was estimated by the regression analysis using the empirical relation $X_c = K(t)^{0.5}$, where X_c is the carbonation depth in mm, t is the period of exposure in months, K is the CC (mm/month$^{0.5}$). Carbonation coefficient of NVC increased with increase in FA, w/b ratio and CO_2 concentration [42]. It was found for all supplementary cementitious materials (SCM) tested that the carbonation depth decreases as aggregate i.e. sand replacement by SCM increases, and increases as cement replacement as SCMs increases [46].

4   Carbonation of Normally Vibrated Concrete made with Recycled Concrete Aggregates

Construction and demolition waste has been dramatically increased in the last decade. Social and environmental concerns on the recycling have consequently been increased. Recycled aggregate concrete (RAC) is being used more frequently as a NA replacement and from ten years ago to now, the number of investigations about this topic has been increased significantly [47]. In general it was concluded that the carbonation depths were found to be increased with an increase in the replacement ratio of NA by recycled concrete aggregates (RCA) [48] and a reliable linear relationship between CC and RCA and time of exposure as well as between the CC and compressive strength was observed [49].

4.1 Effect of water/cement (w/c) ratio

Durability of the NVC mix increases if w/c ratio for water penetration test and porosity test is decreased by 0.1 and 0.05 for carbonation test respectively. It was found that there is a significant increase in the rate of carbonation with the RCA incorporation and the durability of RCA mixes cast with the same w/c ratio is less than that of the conventional concrete and this only due to the higher porosity of RCA. The influence of the RCA is worse for higher w/c ratios [50]. There is a significant increase in the rate of carbonation with the RCA incorporation as w/c ratio increases; the fact becomes clear from Fig.-12. It was noted that for similar compressive strength concretes, the carbonation rate of RCA is slightly lower than that from normal concrete which is obtained in terms of carbonation coefficient. Fig.-13 justifies the above statement.
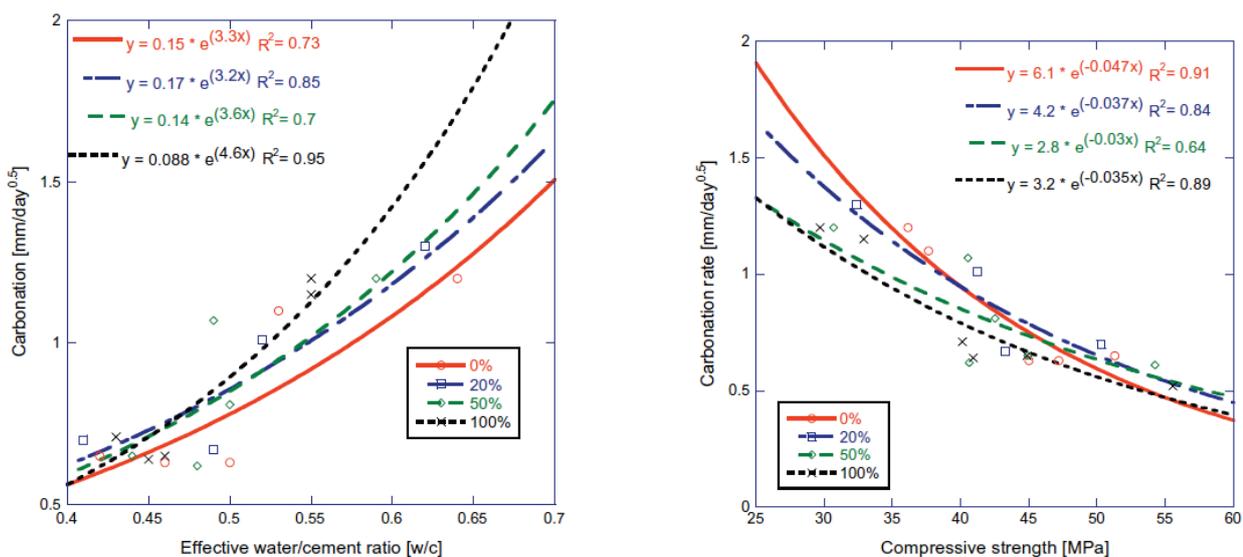

Fig. 12 Carbonation rate vs the w/c ratio for different levels of substitution of RCA [50].
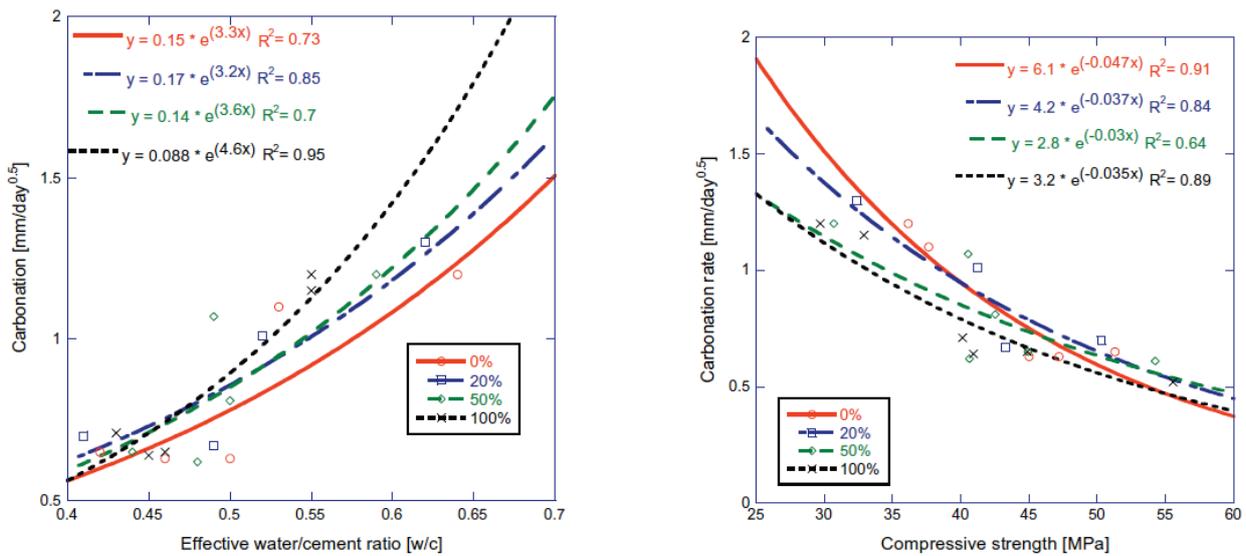
Fig. 13 Relationship between the rate of carbonation and compressive strength with different levels of RCA [50]

4.2 Effect of admixtures

The carbonation coefficient of NVC increased FA content [51]. Combining FA with coarse RCA in NVC may help in enhancing the long term resistance to carbonation. The use of limestone filler with a finer grading curve does not influence the carbonation behaviour. The use of FA as filler material decreases the porosity and decreases the amount of carbonic material [26]. Recycled concrete aggregates and SCM such as FA and SF were used to produce durable and environmentally friendly concrete. RCA with adhered mortar and SCM (by pozzolanic reaction) can provide increase and decrease, respectively in the alkaline reserve and porosity. The negative effect of 100% RCA on carbonation depth is evident from Fig.-14. Although SF has greater reactivity than FA and therefore, during the pozzolanic reaction more CH is consumed with the higher speed, NVC formed with RCA having 10% replacement with SF presented very minor advances of carbonation front than that of mixture of RCA having 30% replacement with FA, this is again due to porous system refinement that dominated in spite of the greater consumption of CH [47]. Using an equivalent mortar volume method, RCA mixes have higher resistance to freeze–thaw action, chloride penetration and carbonation than those designed with the conventional method; also the negative effect of RCA can be nullified by incorporating a certain amount mineral additives such as FA, SF, and MK etc. The use of FA as a partial replacement of cement with RCA inclusion increases the carbonation depth of the NVC in early ages [48]. The results of carbonation depth of the outdoor exposed NVC at the ages of up to 10 years were observed which clearly showed that the use of RCA in NVC decreased the resistance against carbonation at all test ages. After 10 years of outdoor exposure, when compared with the NVC prepared without FA and with FA content of 55% it was found that the CC was approximately 1.68 times for the concrete made with NA and 1.89 times for concrete made with RCA (Fig.-15) [51,52]. It is also confirmed that low carbonation resistance particularly at early age is compensated with maturity and better microstructure by adding pozzolanic additives [53]. In addition, the measured carbonation depth of the concrete made with NA was ranged from 3 to 11 mm after 28 days of the accelerated carbonation exposure [54]. Hence the addition of mineral admixtures proved to be effective up to some extent in reducing carbonation in concrete made with RCA. Its use can be beneficial in increasing the service life of RCA structures if provided in proper amount as it increases the initiation period for reinforcement corrosion [55].
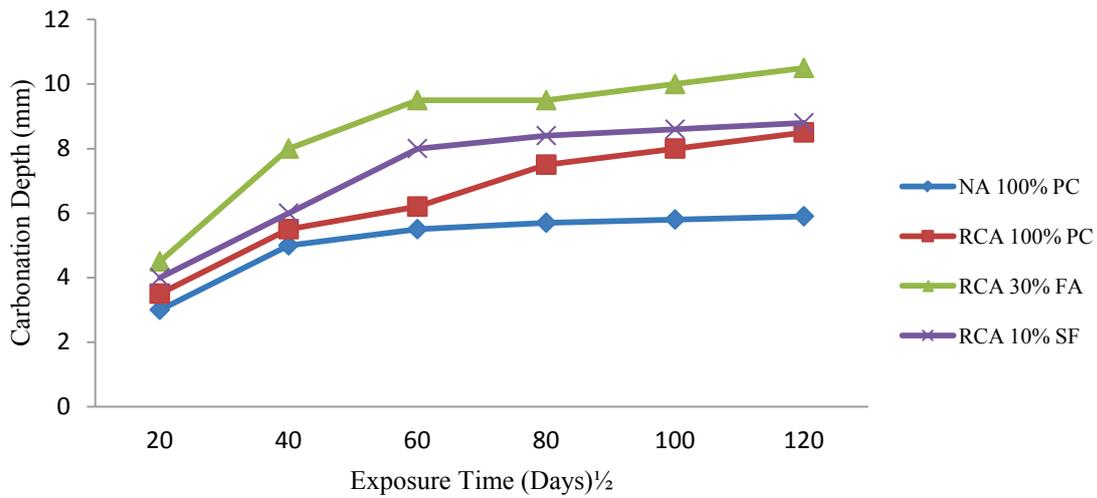
Fig. 14 Carbonation depth vs exposure time for different levels of RCA substitution with addition of fly ash and silica fume [47]
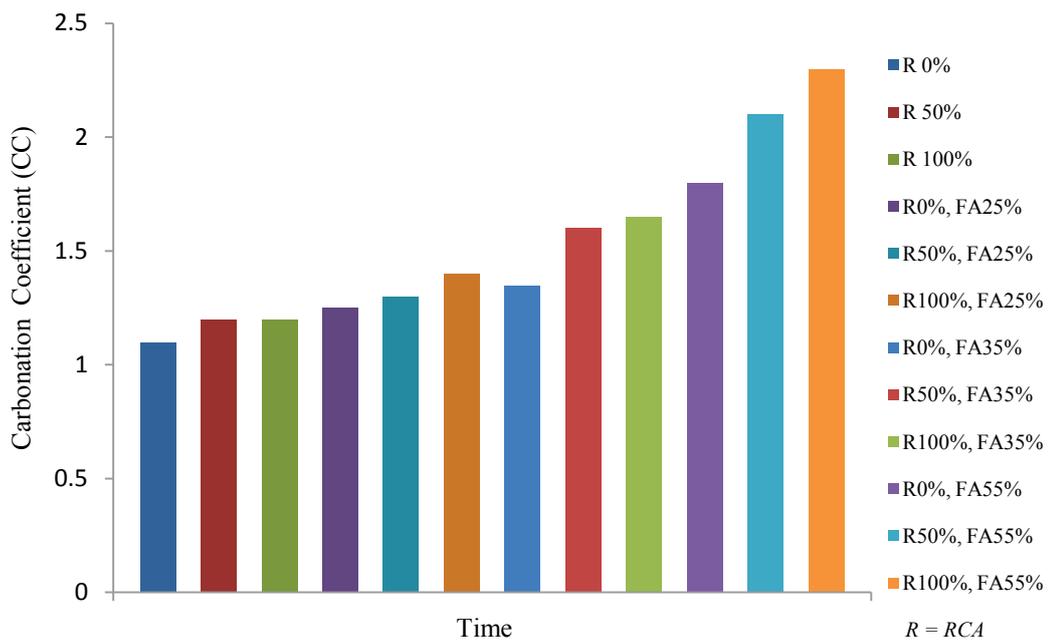

Fig. 15 Carbonation coefficient after 10 years of natural exposure for altered percentages of RCA with different levels of fly ash [51].

4.3 Effect of cover

Recycled concrete aggregate is significantly more permeable than NA. A more permeable concrete presents a higher depth of carbonation. The replacement of NA by RCA affects the quality of the concrete cover. As the carbonation rate of RCA is faster so this limits the use of RCA in the production of reinforced concrete elements. Hence the provision of proper cover is must to increase resistance against carbonation in case of RCA made concretes [43].

4.4 Effect of porosity

The durability of the concrete made with RCA is worse due to the intrinsic porosity, as the compressive strength and modulus of elasticity are relatively lower than that of the parent concrete hence risk of reinforcement corrosion is higher. A clear relationship was not obtained for the replacements of RCA ratio but sufficient carbonation resistance was attained. It was found that long term carbonation depths were lower at 60% and 100% replacements than at 0% and 30% replacements. Hence use of low replacement level of RCA does not harm the overall performance but higher level completely deteriorates the mechanical and durability properties of concrete. The fact is confirmed from the Fig.-16 [52].
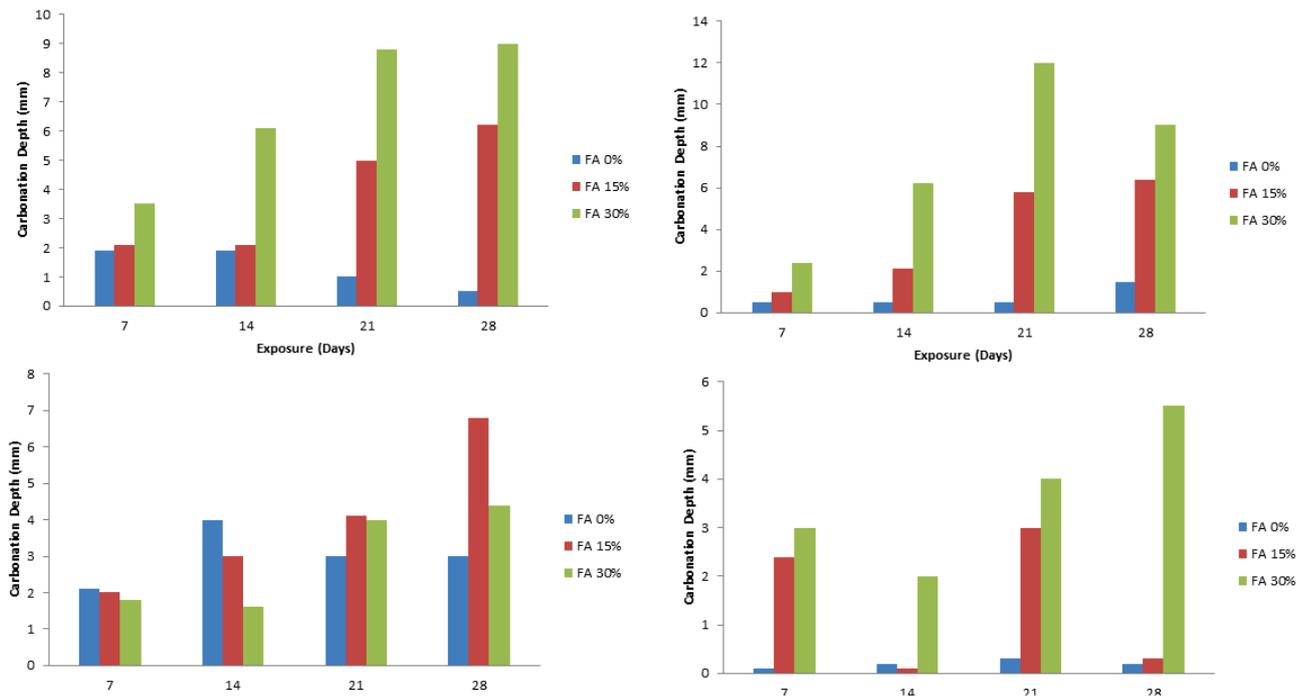

Fig. 16 Carbonation depth measured at different exposure period for 21 day curing with varying levels of levels of RCA; (a) 0% (b) 30% (c) 60% (d) 100% with low levels of fly ash [52].

4.5 Effect of exposure and grade of concrete

The depth of carbonation is proportional to the duration of exposure. The higher the exposure period, the higher will be the depth of carbonation. It is well known that the water stored in the pore system of the RCA released throughout hydration process and contributes in the carbonation process. The results showed that the carbonation depth of all the FA based NVC mixes were quite greater than the one of the PC based NVC mixes as discussed earlier. Results from the literature revealed that in low strength/grade concretes, carbonation is much more rapid as CO_2 can permeate the cement matrix more easily and for relatively dense concretes with higher compressive strengths, the carbonation rate and depth of progress is slow throughout the pore network. Fig.-17 justify the discussed fact which shows linear relationship between the carbonation coefficients and exposure period and which proved that carbonation rates increases with increase in exposure period.
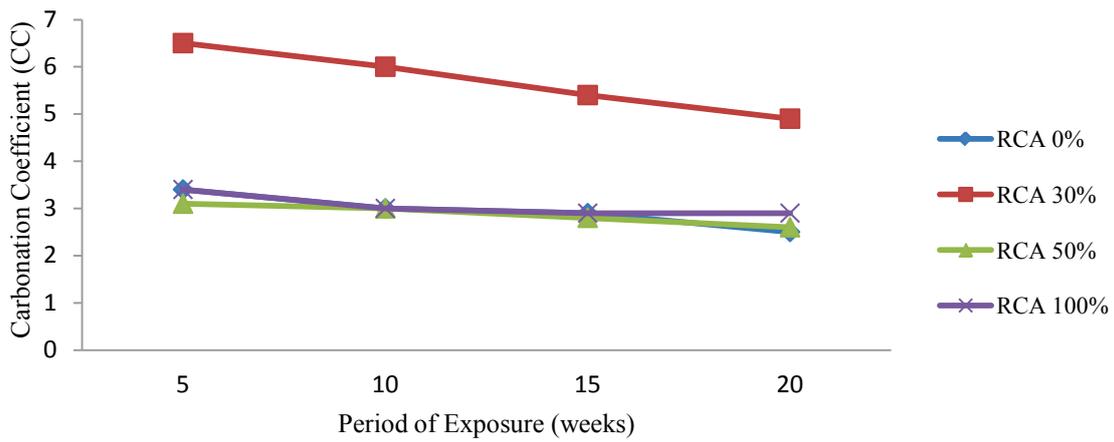
(a)
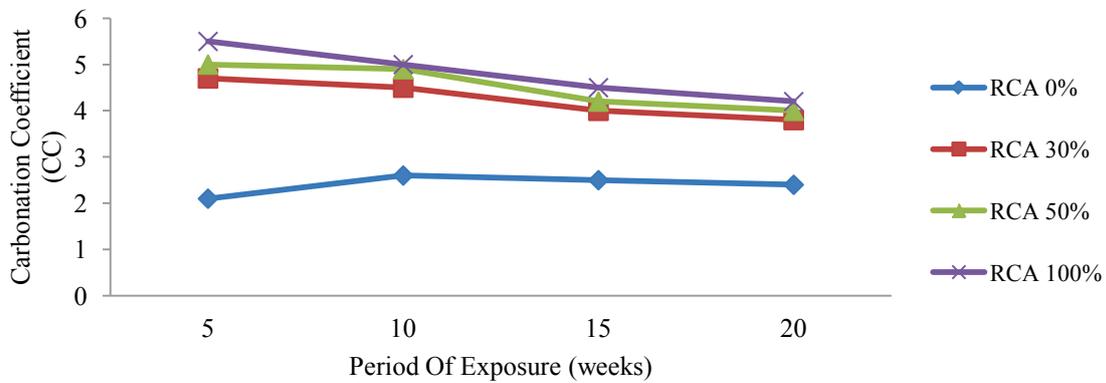
(b)

Fig. 17(a & b) Relationship showing carbonation coefficient-exposure period for concrete mix made with different levels of RCA with and without replacement of fly ash [49].

5   Carbonation of Self Compacting Concrete made with Natural Aggregates

Self-compacting concrete (SCC) has improved durability characteristics than NVC of the same strength class. Service life of reinforced concrete structures against carbonation is extended when SCC were used [56]. The amount of carbonic material depends on the type of cement, the cement content and the degree of hydration.

5.1 Effect of water/cement (w/c) ratio

A similar kind of trend regarding effect of w/c ratio has been obtained in previous researches in case of NVC and SCC. As discussed earlier the advantage of SCC over NVC w.r.t. overall performance. The durability of SCC mixtures in terms carbonation appears to be more, in low strength class of mixes with high w/c ratios. In both SCC and in NVC, as w/c ratio is decreased carbonation depth was found to be reduced (Fig.-18 & Fig.-19) [24].
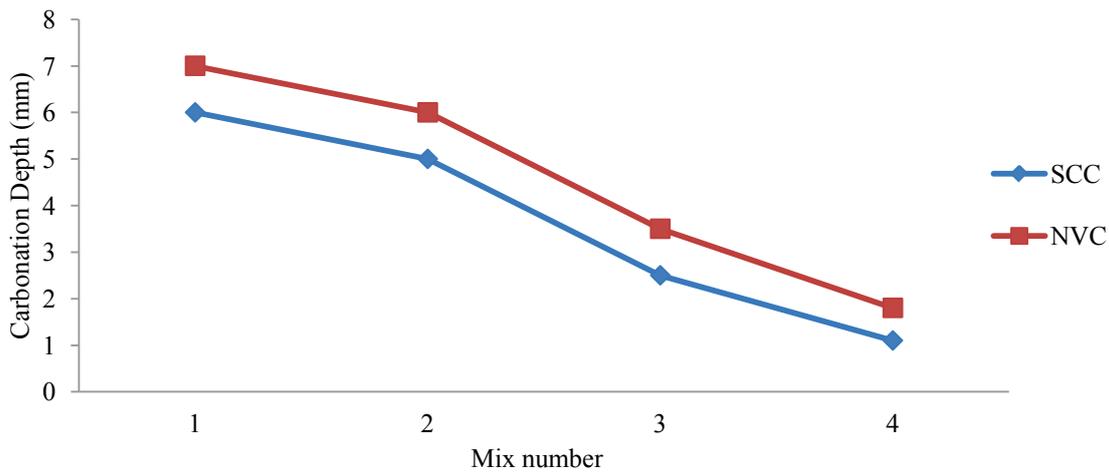
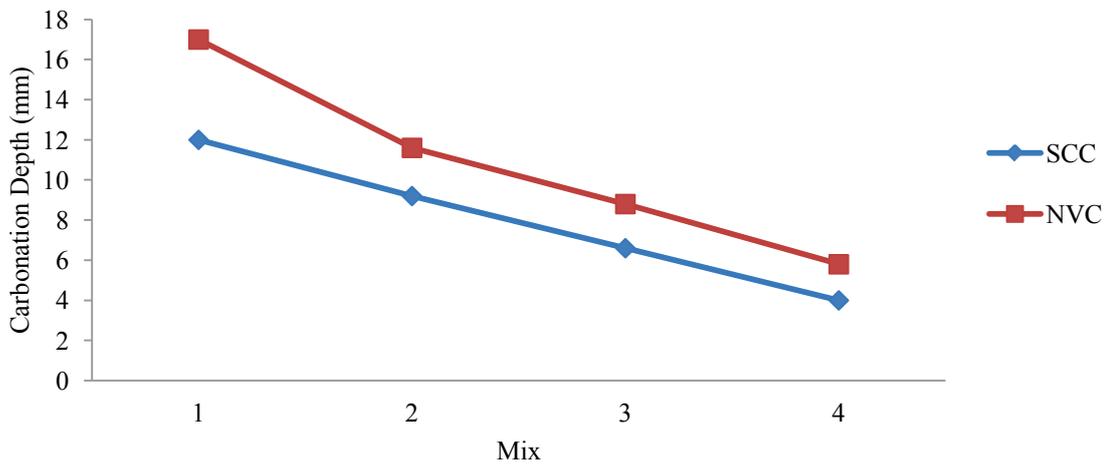**Fig. 18 Carbonation depth after 9 months of accelerated carbonation [24]**

Fig. 19 Carbonation depth after 42.5 months of accelerated carbonation [24]

5.2 Effect of admixtures

Under normal/ atmospheric pressure, in 100% CO_2 accelerated testing; the carbonation depth of Limestone Powder-Self Compacting Concrete (LP–SCC) or mortars was found to be higher than FA and FA–SF–SCC or mortars at all ages of the test. The combined results of the Mercury Intrusion Porosimetry (MIP) test and Scanning Electron Microscopy (SEM) observations suggests that the addition of SF has a positive effect in modifying the internal pore structure while it has a negative effect on the connectivity of the capillary pores after carbonation especially at the micro scale level. Results revealed that after 50 years of exposure to natural environment, the predicted carbonation depths were found to be only 5.44 mm, 4.60 mm and 3.61 mm for LP-FA and FA–SF–SCC. Hence there is no risk of carbonation-induced corrosion during the service life. Even if atmospheric CO_2 is going to increase up to 0.06% in coming next 50 years then these predictions rise to 6.7, 5.66 and 4.42 mm for LP- FA and FA–SF–SCC respectively. Therefore additions of admixtures certainly helped in increasing carbonation resistance [57].

5.3 Effect of porosity

The carbonation progression in SCC is not only chemically controlled but, instead the pore structure also plays a substantial role in determining the progression of the carbonation also change of the chemistry of the matrix due to the addition of different fillers had little impact on the actual carbonation rate. Limestone fillers produce a better particle

packing, which results in lowering porosity and a finer pore structure which ultimately makes the pore network more intricate. [58].Carbonation rate is lower in SCC than NVC due to the lower porosity and finer pore structure. It was found that total pore volume is on average 10.8% less in SCC than in NVC, also entrained air volume (pores over 100 ml) is between 43.8% and 128.6% greater in SCC than in NVC [24, 57]. Results revealed that deterioration of SCC is similar to that of NVC if accelerated carbonation test is performed and at the same level of compressive strength, SCC can be considered to be as more useful and highly durable as compared to NVC in terms of physicochemical properties (Fig.-20) [57, 58].
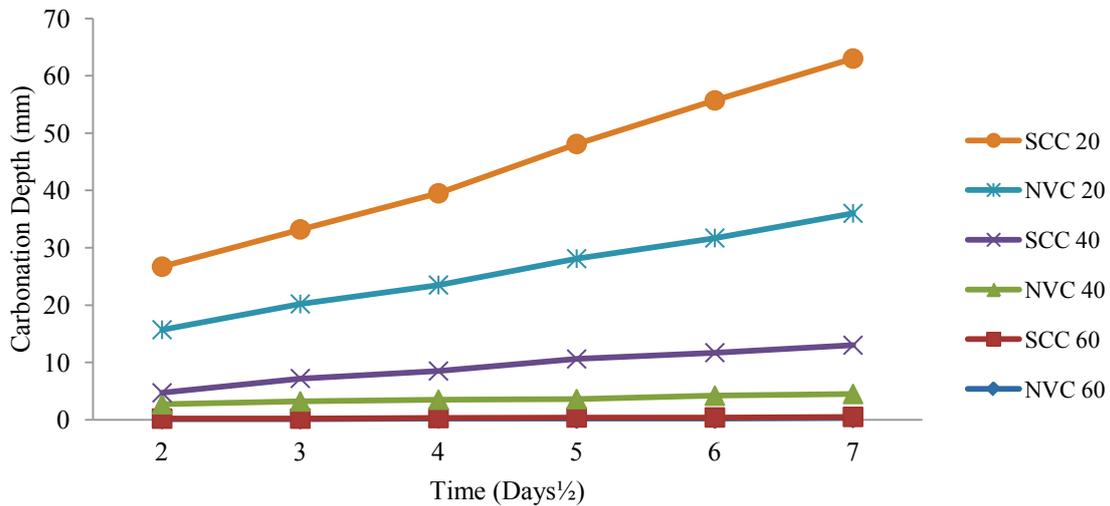

Fig. 20 Carbonated depth vs sq. root of time for SCC and NVC having different grades of strength for an exposure period of 7 days [58]

5.4 Effect of super plasticizers

Concrete with low potential for carbonation could be produced with less than 50% replacement of FA, and that the use of super plasticizer did not affect the carbonation depth. A mathematical method predicts the actual carbonation depth based on the square root time relationship. Since controlled amount of super plasticizer does not influence the long term structural performance but excessive amounts leads to change in micro structural combinations.

5.5 Other parameters

The rate of carbonation (expressed by the CC) is lower in SCC mixtures. Service life is increased by 39.5% when elements were casted with low grades of SCC produced with siliceous sand. When SCC is used instead of conventional concrete of the same grade, service life of reinforced concrete structures against carbonation induced corrosion is extended [56]. At the same w/c ratio, using more strength cements provides concretes with greater resistance to carbonation. The reduction of the CC is on average 32.7% in SCC and 27.2% in NVC. It was found that the carbonation rate is lower in SCC than NVC.

6 Conclusions

- Carbonation depends mainly on the w /c ratio. The influence of the w/c ratio is very important. The carbonation diffusion coefficients increase with the w/c ratio. Higher the w/c ratio, higher will be the carbonation depth.
- Prolonged or longer water curing period proves to be beneficial in reducing the carbonation depths. To improve carbonation resistance of concrete, sufficient water curing of at least seven days is necessary for plain PC concrete.
- Air curing helps in increasing the weight of concrete hence lesser carbonation resistance is offered by air cured concretes. Concrete mixes with certain quantity of admixtures which are undergone air curing are more prone to carbonation attack.
- Addition of super plasticizers sometimes helps in reducing the carbonation depths to some extent as these helps in improving the anti-carbonation ability of C_3S and C_3A hydrations.

- Addition of admixtures may have a positive effect on modifying the internal pore structure also it has a negative effect on the connectivity of the capillary pores during carbonation.
- Addition of SF cause considerable pore refinement i.e. transformation of bigger pores into smaller one due to their pozzolanic reaction concurrent with cement hydration. Silica fume improves the long term corrosion resistance, alkali silica expansion, but increases the carbonation depth.
- High performance concrete with GGBFS having lower CH content and denser matrix shows a better carbonation resistance than HPC with FA. As expected, carbonation depth of HPC with FA/GGBFS both increases with the increase of w/b.
- As porosity increases, carbonation depth also increases. A linear relationship exists between accelerated carbonation and porosity.
- The use of surface coatings and provision of proper cover considerably reduced the rate of carbonation. The desired services lives can only be obtained with the use of surface protection treatments.
- The carbonation depth increases with an increase in the replacement ratio of NA by RCA. Satisfactory concrete properties can be developed with recycled fine and coarse aggregates with proper selection and proportioning of the concrete materials with RAC, containing FA, can be proved to be an effective alternative to ordinary concrete for structural purposes.
- Self compacting concrete appears to have improved durability characteristics in terms of carbonation than NVC.
- Carbonation process obeys Fick's second law i.e. the rate of carbonation (an increase of the carbonation depth with time) follows a square-root-time law. Relationship between compressive strength depends on w/b ratio and mineral admixture types. In some cases lower w/b ratios affects the depth of carbonation but higher ratios completely deteriorate all other properties of concrete.

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