CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Carbonation is a major cause for deterioration of concrete structures. Rate and depth of carbonation depends on various parameters curing, porosity, cover, relative humidity, temperature and concentration of carbon dioxide etc. as well as factors like type of cement, constituents of concrete mix, W/C or W/B, curing regimes, addition of admixtures, curing compounds, super plasticizer. It has also been found that the depth of carbonation decreases with increasing compressive strength for all types of concrete, however these relations also depend on the type of cement and curing [Fattuuhi, 1986 and Wierig, 1984]. The natural process of carbonation being very slow, experimental methodologies have been adopted over the years to accelerate the speed of carbonation for the purpose of determination of carbonation depths in concrete. While conventional methods yield satisfactory results, advanced methodologies have also been developed for obtaining accurate results.

This chapter deliberates the summary of research findings of authors over the years. Research studies summarized below incorporate development of Indian and international standards of cement, properties of OPC and PPC concrete, durability of concrete, compressive strength of concrete, process of carbonation and factors influencing carbonation, impact of various combinations of the constituents of concrete mix i.e. variable mix proportions of FA, Fine aggregate, Micro silica and GGBS.

2.2 Development of Indian and International Cement Standards with respect to OPC and PPC

The earliest use of cement concrete can be related to the ancient romans who applied hydraulic cement to construction works i.e. a material which hardened immediately on application of water. This property of hardening on application of water prevented it from undergoing any chemical changes in later life and made it the most preferable construction material. However, the immediate hardening of cement was also a major drawback for construction purpose. Much later in the year 1824, Portland cement was introduced. Calcareous and argillaceous or other silica-alumina and iron oxide bearing minerals were added to erstwhile cement and the mixture was heated to form clinkers. Commercial Portland cement, widely used in construction, is industrially produced by mixing fixed proportions of powdered raw materials including calcareous materials (such as limestone or chalk), silica and alumina (mostly found in the state of clay or shale) and heating the resultant mixture in a large rotary kiln at a high temperature of 1400^0C to form clinkers which are grinded to fine powder on cooling and mixed with very small quantity of gypsum. Cement can be produced by both wet and dry processes. After burning the mixture to form clinkers no material can be added other than gypsum, water and grinding aids. The development of cement standards of early British origin and new European as well as American standards are all based on the above principles. The raw materials in the kiln undergo numerous reactions to produce a nearly equilibrium mix of the following compounds which are the major constituents of Portland cement:

Tricalcium Silicate	$3CaO. SiO_2$	C_3S
Dicalcium silicate	$2CaO. SiO_2$	C_2S
Tricalcium aluminate	$3CaO. Al_2O_3$	C_3A
Tetra calcium aluminoferriate	$4CaO.Al_2O_3. Fe_2O_3$	C_4AF

Besides, some other compounds also constitute cement, but their quantity is relatively very small. As per BS EN 197-1, OPC is made of nearly 95-100% of Portland cement clinker, while the balance percentage is a minor constituent, either cementitious in nature or a filler. The ratio of CaO to SiO_2 should be less than 2 in OPC and MgO content should not exceed 5%. ASTMC 150-05 specifies no ceiling for lime content in OPC. The characteristics of OPC used in modern construction work have undergone considerable changes and found to have higher C_3S content and more fineness. While OPC has excellent performance and is most widely used, the use of PPC is also gaining much popularity. PPC is a blended product of Portland cement and pozzolana. As per ASTM-C 618-06, a pozzolan is a siliceous or siliceous and aluminous material which in itself possesses no binding properties but reacts with the lime content of cement in presence of moisture to yield products with binding properties. ASTM C 595-05 recommends standards for general construction when high strengths at early ages are not required. The pozzolana content should be limited to 1-40 % of total mass of cementitious material. The process of gaining strength of PPC is slow. As such, PPC requires more curing. However, the long term strength gain is high. The use of PPC is not only economic, but also advantageous due to its slow process of hydration which results in lower rate of heat development which increases the durability of concrete.

As per various international standards, cement can be categorised into the following types based on their constituents and resultant properties.

Table 2.1 Classification of Cement as per Indian and International Standards

Traditional Classification		European Classification [BS 8500-1: 2006]	
British	**American**		
Ordinary Portland [BS 12]	Type I [ASTM C 150]	CEM I	Portland
Rapid-hardening Portland [BS 12]	Type III [ASTM C 150]	CEM II/A	Portland with 6 to 20% fly ash, GGBS, limestone or 6 to 10% silica fume
Low heat Portland [BS 1370]	Type IV [ASTM C 150]	CEM II/B-S	Portland with 21 to 5% GGBS
Modified cement	Type II [ASTM C 150]	CEM II/B-V	Portland with 21 to 5% fly ash
Sulphate resisting Portland (SRPC) [BS 4027]	Type V [ASTM C 150]	CEM II/B+SR	Portland with 25 to 35 % fly ash with enhanced sulphate resistance
Portland blast furnace (slag cement) [BS 146]	Type IS Type S Type I (SM) [ASTM C 595]	CEM III/A	Portland with 36 to 65 % GGBS
High slag blast furnace [BS 4246]		CEM III/A+SR	Portland with 36 to 65 % GGBS with enhanced sulphate resistance
White Portland [BS 12]		CEM III/B	Portland with 66 to 80 % GGBS
Portland pozzolan [BS 6588; BS 3892]	Type IP Type P Type I(PM) [ASTM C 595]	CEM III/B+SR	Portland with 66 to 80 % GGBS with enhanced sulphate resistance
		CEM III/C	Portland with 81 to 95 % GGBS
		CEM IV/B-V	Portland with 36 to 55 % Fly ash

The specifications of cement for use in construction in India are covered under the following Indian standards:

IS 269 – Indian Standard Specification for OPC

IS 455 - Indian Standard Specification for Portland Slag Cement (PSC),

IS 1489 - Indian Standard Specification for PPC.

2.3 Physical and Chemical Characteristics of OPC and PPC and Components

Since the composition and features of cement are of vital importance in determining the properties of concrete, a number of characteristics can be tested experimentally to ensure that the cement in use confirms to national standards as desired for concrete in construction. Some of the measurable characteristics of cement are defined as follows:

The fineness of cement is a measure of the size of particles of cement and is expressed in terms of the specific surface area of cement.

The consistency of cement paste is defined as the viscosity at which cement particles hold each other for ease of construction. The standard consistency of a cement paste is defined as that consistency which will permit the standard vicat plunger (IS 5513-1976) to penetrate to a point 5 to 7 mm from the bottom of the vicat mould.

Initial setting time is the time when the paste starts losing its plasticity. Final setting time is the time when the paste completely loses its plasticity.
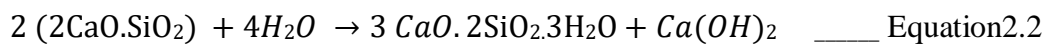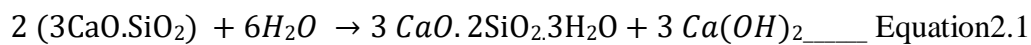
The soundness of cement refers to the stability of the volume change in the process of setting and hardening.

Strength is the most important property of cement and tests for the same are carried out on cement sand mortar instead of neat cement. While strength of cement can be compressive, tensile and flexural, the most important property of cement is its compressive strength.

2.4 Hydration of Cement

Hydration of OPC

Concrete is made of cement which consists of various phases including Tri-calcium silicate ($3CaO.SiO_2$) or C_3S and Di-calcium silicate ($2CaO.SiO_2$) or C_2S. Hydration is the process of reaction of water with the different constituents of cement. Cement constituents in concrete undergo hydration reaction in presence of water to produce calcium silicate hydrate ($CaO.2SiO_2.3H_2O$) or CSH gel and calcium hydroxide. The latter dissociates into calcium and hydroxyl ions, thus increasing the pH of the pores. The chemistry of hydration of Portland cement has been reviewed thoroughly by Bensted, 1983; Brunauer and Copeland, 1964; Frigione, 1983 and Taylor, 1986. Hydration reaction in OPC may be represented by Eqn 1.3 & 1.4 below:

$$2\ (3CaO.SiO_2)\ + 6H_2O\ \rightarrow 3\ CaO.2SiO_2.3H_2O + 3\ Ca(OH)_2 \_\_\_\_\ \text{Equation2.1}$$

$$2\ (2CaO.SiO_2)\ + 4H_2O\ \rightarrow 3\ CaO.2SiO_2.3H_2O + Ca(OH)_2\ \_\_\_\_\ \text{Equation2.2}$$

Hydration of Blended Cement

Blended cements are a mixture of plain cement and supplementary cementitious materials (SCM). Cement blended with fly ash (FA) and condensed silica fume (CSF) both of which are pozzolanic in nature and ground granulated blast furnace slag (GGBS) which is a latent hydraulic material shall be analysed in this study with a view to investigate the durability of blended cement concrete. FA and CSF are pozzolanic in nature and contain aluminous compounds but have low calcium content. They do not have binding properties of their own, but develop the same in the presence of $Ca(OH)_2$, resulting in hydration products as in case of plain cement, unlike GGBS which forms

hydration products on its own when mixed with water. However, the hydration reactions in case of GGBS are very slow since the amount of $Ca(OH)_2$ released by GGBS in the reaction is extremely low and does not facilitate rapid dissolution of the glass phase. Thus, GGBS often uses the $Ca(OH)_2$ from cement to go into reaction. The reaction between SCM, $Ca(OH)_2$ and water is known as pozzolanic reaction (Bertolini et al., 2013).

The reaction of pozzolanic material with calcium hydroxide can be represented as follows:

$$Ca(OH)_2 + H_2O + pozzolana \rightarrow C-S-H \_\_\_\_Equation2.3$$

$$Ca(OH)_2 + H_4SiO_4 \rightarrow CaH_2SiO_4 + 2H_2O \_\_\_\_Equation2.4$$

The hydration of the above blended cement results in consumption of $Ca(OH)_2$, as a result of which $Ca(OH)_2$ content of blended cement is low. This also results in reduction of clinker in cement.

2.5 Fresh Concrete Properties

It is learnt that compaction has a conspicuous impact in the long term characteristics of hardened concrete i.e. its strength, volume and durability. Thus workability of fresh concrete is an important tool to monitor its compaction to yield best results in the long term. Workability can be defined as the magnitude of useful internal work required to ensure complete compaction of fresh concrete. In practical condition it is also measured by consistence of fresh concrete which reflects the ease with which concrete can flow.

Since it is not possible to detect workability experimentally, following tests have been designed to indicate extent of workability of fresh concrete: Slum test, Compacting factor test and compatibility test.

2.6 Strength Development of Concrete

One of the most important properties of concrete is its strength, besides others such as durability and impermeability. Strength of concrete is almost directly related to the physical structure of hardened cement paste. Concrete may fairly be considered as a brittle material although it exhibits very small amount of plasticity and performs very well under compressive loads. The compressive strength of concrete is its resistance to failure under compressive forces.

2.7 Effect of Various Factors on Depth of Carbonation in Concrete:

   Carbonation Resistance of Concrete

Much research has been dedicated to the identification of the influence of various factors on carbonation which thereby results in reinforcement corrosion [RILEM, 1976 and 1984; CANMET/ACI, 1991]. Neville (2011) stated that the pH value of normal concrete which ranges from 12.6 to 13.5 is mainly attributed to the presence of CH in the cement paste. Jiang et al (2000) stated that the reaction of the diffused CO_2 and water in the pores of cement paste forms a weak carbonic acid, which dissolves CH and CSH. Jiang et al (2000) and Bertolini et al (2000) observed that The reaction progresses from the surface of the concrete inwards, the rate of which depends on several factors.

A detailed review of the literature on such factors is elaborated hereunder.

2.7.1   Water/Binder (W/B) Ratio

Author	Observation
Henry and Kurtz (1963)	The fluid transport potential increases with the increase of W/C

Khaiat and Fattuhi (2002)	The rate of flow of water through the pore system increases with an increase in W/C due to a change in pore structure under both carbonated and non-carbonated conditions
Uomoto and Takada (1993), Roy et al (1999) and Sulapha et al (2003)	An increase in the W/B reduces the carbonation resistance of concrete.
Fattuhi (1986)	A proportional relationship exists between W/C and carbonation depth in Normally Vibrated Concrete (NVC) mixes
Loo et al (1994), Mackechnie & Alexander (1999), Atiş (2003), Sisomphon & Franke (2007), Mohammed Rabehi et al (2013)	Rate of carbonation is found to be higher when W/C is increased.
Lo & Lee (2003)	The increase in W/C ratio results in an increase of carbonation depth and with the age of NVC as well. 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.
Ho & Lewis (1987)	Carbonation depth is directly proportional to W/C with curing period of seven days.
Balayssac, Dériché,. Grandet (1995)	Experiments were conducted on four different mixes by varying curing period andW/C ratio andit was concluded that with the increase in the cement content and curing period from 1 to 28 days durability increases from 10-30%. Experiments also revealed that carbonation depth decreases with decreasing W/C and increases with the period of exposure.
S K Roy et al (1999)	Carbonation depth increased with increasing W/C ratio and with period of exposure to Carbon dioxide at a

	given W/C.
Witmann et al (2002)	The effect of W/C was negligible when the same is less than 0.4.
Ha-Won Song, Lee and Ann (2008)	Carbonation process is faster with higher W/C and has larger crack width. 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.
T. Y. Lo, Tang and Abid Nadeem (2008)	W/C ratio has a conspicuous effect on carbonation irrespective of the mix design.
Badaoui, Badaoui and Kharchi (2015)	W/C has random effect on Concrete Carbonation.
Fattuhi (1988), Balayssac et al (1995) and Parrott (1996)	The rate of concrete carbonation decreases when the water-curing period is extended. Curing depends on W/C ratio. The lower the latter the shorter the curing period (Comite Euro-International du Beton, 1984).
Van Balen K.,Van Gemert D (1994)	The carbonation rate can only be determined experimentally.
Arandigoyen M., Álvarez J.I. and Lange (2006)	The constant K is proportional to the W/B. W/B ratio at lower levels does not influence carbonation depth but higher ratios influence other properties.
Khaiat and Fattuhi (2002) and Sulapha et al. (2003)	A decrease in the water to total binder ratio enhances the carbonation resistance of concrete.
Dinakar, Babu and Manu Santham (2007)	At lower W/B, 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, FA replacements significantly affects all other properties.

Lo et al (2008)	Carbonation depth for concrete mixes increased with the increase in W/B ratio. The decrease in W/B in NVC mixes replaced with FA is due to the refinement of pores which results in reducing the carbonation coefficient. Carbonation increases with the increase of W/B ratio and the decrease of binder content. Also it was found that with increase in W/B ratio, value of slump of NVC increases with considerable increase in carbonation depths in concrete mixes.
Shi et al (2009)	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.

2.7.2   Mineral Admixture

(a) Silica Fume

Author	Observation
Kulakowski et al (2009)	Compressive strength is not the only parameter for estimating the service life of concrete structures and that its durability is also dependent on many other factors one of which is the impact of addition of SF in concrete mixes.
Khan and Siddique (2011)	Silica fume is very effective in the development of high strength and high performance concrete. It has been found that SF helps to enhance compressive strength, bond strength, and abrasion resistance, while it reduces the permeability of concrete and therefore helps in protecting reinforcing steel from corrosion.
Skjolsvold (1986)	For a given compressive strength, Silica fume (SF) based

	NVC manifested higher rates of carbonation than NVC made without SF. When SF replaces cement, the porosity increases proportionally with the amount replaced.
Lo et al (2008)	Addition of SF in the concrete mixes increases the carbonation depth. Upon addition of SF in concrete increase in compressive strength results but simultaneously carbonation depth is also found to increase. Silica fume reacts with the calcium hydroxide and reduces the pH of the pore solution thus facilitating the carbonation process. SF replacement up to 10 % was found to have no influence on carbonation of concrete but as the percentage replacement increases beyond 10%, effect of SF begins to become significant. Beyond this, it not only increases carbonation depth but also increases the variation in the intensity of carbonation-induced corrosion.
Goldman and Bentur (1989)	SF concretes with the same W/C and different SF-content have the same total porosity, although they have different strengths. However, despite having almost same porosity, SF mortars presented different density, with an increase in micro-pore volume as compared to the control.
M. Hamada (1969)	Above may be attributed to pore refinement (conversion of larger pores to smaller ones) and grain refinement (conversion of larger crystals to smaller ones)
Grimaldi et al (1989)	Carbonation depth was greater in mortars containing SF as compared to controlled NVC which may be attributed to the reduction of pH caused by the pozzolanic reaction. In case of binary blends with high percentage of replacements of FA and lower amount of other blends like SF it was found that carbonation depth decreases linearly.

(b) Fly Ash

Author	Observation
Dhir et al (1988); Dhir et al (1993)	The use of fly ash (FA) with Portland cement (PC) to produce structural concrete is a growing practice in construction over the last 20 years. FA when used as a component of cement has shown several technical benefits to concrete.
Hwang, Noguchi, Tomosawa, (1998)	When significant quantity of FA replaces portion of the fine aggregates, the carbonation depth reduces.
Manmohan and Mehta (1981)	The addition of Fly Ash to Portland cement resulted in conversion of larger pores of concrete to finer pores.
Mehta (1983)	There is a reduction in concrete permeability on account of addition of FA.
Sasatani, Torii and Kawamura (1995)	When concrete is tested after 5-year period of exposure in natural conditions, depth of carbonation increases when fly ash or GGBS substitute cement.
Berry and Malhotra, 1987; Papadakis et al (1992)	Blended cement concrete carbonates much more rapidly than normal Portland cement concrete.
Ho and Lewis (1987)	Concrete carbonation increases when fly-ash (FA) is used.
Ogha and Nagataki (1987)	Carbonation increases with the replacement ratio of cement by fly-ash.
Ho and Lewis (1987) and Hobbs (1988)	Fly ash replacement for Portland cement in concrete results in an increase in the rate of carbonation.
Ho and Lewis (1987) and Byfors (1985)	Higher rate of carbonation has been found in concrete containing fly ash with respect to PC concrete.
Ogha and Nagataki (1989)	Increase in the replacement ratio of fly ash and air content resulted in an increase of the carbonation coefficient.
Cabrera and Woolley	It was found that a25-year-old fly ash concrete specimens

(1985)	remained non- carbonated.
Wesche (1991)	There were discrepancies in results of carbonation of concrete made with fly ash. The above reports were on the basis of similar fly ashes.
Malhotra et al (2000)	After 10 years of outdoor exposure, similar and small (in the range of less than 1–5 mm) values of carbonation depths were observed for plain concrete (water to total cementitious material ratios of 0.27–0.29) and concrete with 28–35% slag, 57% fly ash, or 7–12% silica fume.
Schubert and Vom Berg (1979) and Mathews (1984)	The rates of carbonation in concrete with and without fly ash were nearly equal.
Lin and Fu (1987)	Experiments revealed that 20, 30, and 40% fly ash mortar specimens were less permeable after 28 days of curing but more permeable after carbonation with respect to plain cement mortar.
Nagataki et al (1989) and Osborne (1999)	Carbonation rate increased with an increased slag replacement level of 30–70% in mortar and 50–80% in concrete. There exists few publications that report the effect of type of fly ash on carbonation, especially in the natural environment.
Papadakis et al (1992), Ho and Lewis(1987), Uomoto and Takada (1993), Sulaha et al (2003)	With the replacement of cement with fly ash, the rate of carbonation increases significantly.
Papadakis et al (2000)	If fly ash is replaced with fine aggregate, the carbonation rate decreases.
Ho & Lewis (1987)	Carbonation depth increased with increase in the percentage replacement of FA varying from 0-40 %. Specific percentage of replacement of FA helps in increasing the compressive

	strength but decreases carbonation.
Ogha and Nagataki (1989)	The replacement of cement by FA resulted in an increase in carbonation depth.
Alexander, Skalny and Mindess (1989)	The rate of carbonation might not as well be more in FA concrete.
Thomas et al (1990)	Carbonation depths in FA concrete and OPC concrete were comparable under similar conditions.
Alonso et al (1990)	Blended cement is more prone to carbonation than OPC.
Papadakis (2000)	Slight replacement of cement with SCM results in increased rate of carbonation.
Jiang et al (2000)	Carbonation depth of high volume fly ash (HVFA) NVC at a curing period of 90 days was comparable with that of PC concrete.
Bakharev et al (2001)	Alkali activated slag concrete is more vulnerable to carbonation than OPC concrete.
Sulapha et al (2003) and Shi et al (2012)	Pozzolanic material reacts with calcium hydroxide of concrete there increasing the vulnerability to carbonation.
Khan and Lynsdale (2002)	Carbonation depth increases with the increase of fly ash percentage as a partial replacement of cement.
Atis (2003)	Fly ash concrete made with 70% replacement ratio showed higher carbonation than that of 50% fly ash replacement concrete and Normal Portland Cement concrete for both moist and dry curing conditions. While Fly ash concrete with 50% replacement ratio showed lower or comparable carbonation with respect to that of Normal Portland Cement concrete under both moist and dry curing conditions.
Khunthongkeaw et al (2006)	Carbonation depth of concrete and mortar specimens tested up to 24 months were equivalent to the cement-only samples. The increment was considerably huge when the fly ash content was

	more than 30%. At fly ash content of 50%, the carbonation coefficient was approximately twice or thrice the value of that of cement-only mixture.
Ruixia HE (2010)	Carbonation depth of concrete samples reaches 13.8 mm, 15.6 mm, 17.9 mm and 18.2 mm, with the FA content respectively, 0, 10, 20 and 25%, maintaining the upward trend. However, carbonation rate tends to be stable with the increase of FA and carbonation age.
Jian Geng & Jia ying Sun (2013)	Analysis of the effect of cement replacement ratio by fly ash on the carbonation depth was done 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%.
Eehab Ahmed Badreldin Khalil & Mohamed Anwar (2015)	It was observed that for mixes with 0% FA and 0% SF, the carbonation rate was found to be 60% and 390% for a W/C of 0.5 and 0.6 respectively with respect to the W/C 0.4. For the set with 25% FA and 5% SF, the carbonation rate was found to be 108% and 285% for W/C 0.5 and 0.6 respectively with respect to the W/C 0.4. For the set with 25% FA and 10% SF, it was found to be 129% and 251% for W/C 0.5 and 0.6 with respect to the W-C 0.4, respectively. Finally, it was concluded that the variation in the SF does not affect the increase in the carbonation rate much, while the percentage of FA increased the carbonation rate considerably.
Salvoldi et al (2015)	Plain cement concrete carbonated the least, closely followed by the SF mixes. The FA and GGBS mixes performed similarly, both carbonated more than the PC concrete and SF mixes.
Kokubu and Nagataki (1989)	Carbonation depths of fly-ash concrete decreased significantly with increasing strength grades of concrete.

(c) GGBS

GGBS performed far better than FA as GGBFS has more fineness which results in denser mix which subsequently reduces carbonation depth. GGBS is proved to be more active than FA, which is also confirmed from the higher compressive strength development rate of Portland cement with GGBS when compared to that of PC against FA at the same W/B ratio.

Author	Observation
Borges et al (2010)	Rate of carbonation increased with the increasing amount of blast furnace slag in the concrete mix.
Monkman et al (2010)	Concrete specimens having GGBS as replacements were superior to normal hydrated concrete.
Dinakar et al (2007)	Higher depth of carbonation in blast furnace slag concrete might probably be due to the small amount of $Ca(OH)_2$ in the concrete paste and so smaller amount of carbon dioxide is required to carbonate all the $Ca(OH)_2$ by producing $CaCO_3$.
Bouikni et al. (2009)	65% blast furnace slag replacement showed much higher depth of carbonation than concrete with 50% replacement. It was concluded that incorporation of GGBFS reduced the carbonation depths but only at particular replacement levels.
McPolin et al (2009)	Depth of carbonation of blast furnace slag concrete is higher than the OPC mortar mix.
Nagataki et al. (1987)and Osborne (1999)	Carbonation rate increases as the slag replacement level increased from 30–70% in the mortar and 50–80% in concrete.
Collepardi et al. (2004)	Addition of mineral admixture had increased the carbonation rate, except when the amount of cement replacement was as low as 15%.

Divsholi et al. (2014)	30% and 50 % blast furnace slag replacement in concrete increased the rate of carbonation, but longer period of pond curing for blast furnace slag cement concrete reduced the rate of carbonation.
Li et al (2016)	Replacement of pozzolanic materials, such as fly ash or blast furnace slag decreased concrete carbonation resistance in both normal temperature curing and under high-temperature curing.

2.7.3 CO_2 Concentration

Author	Observation
Gonen and Yazicioglu (2007)	Carbonation in high concentration of CO_2 develops more rapidly in comparison to that in normal atmosphere.
EN 13295:2004	The standard establishes that accelerated carbonation tests should be conducted in a 1% CO_2 environment. The concentration of 1% CO_2 in air facilitates similar reaction products with hydrated cement as in normal atmosphere at 0.03% CO_2.
Ngala and C. L Page (1997)	The carbonation rate increases with an increase in CO_2 concentration, particularly for concrete with higher w/b, the transport of CO_2 being instrumental through the pore system in hardened cement paste.
Wittmann et al. (2002)	Carbonation depth is related to the rate of diffusion of CO_2, external pressure and carbon dioxide concentration.
Sanjuan and Olmo (2001)	The influence of three CO_2 levels: 5, 20, and 100% was studied in concretes. Carbonation at 5% and 20% CO_2 showed a more homogeneous carbonation against plain concrete than at 100% CO_2. The results observed at 100% CO_2 were quite different and were apparently much different from those in natural conditions. Firstly, carbon dioxide diffusion coefficient

	was found 48.8×10^{-12} cm^2/s which was not practical. Secondly, the calcium carbonate formed as the main product of the reaction at 100% CO_2 had a crystalline structure, unlike that produced under natural carbonation process. That is, smaller $CaCO_3$ crystals are formed when the process is accelerated.
Hongzhi Cui et al (2015)	Accelerated carbonation test was conducted at five different CO_2 concentration levels of 2, 10, 20, 50 and 100% by volume, at a fixed temperature of 20°C and RH of 70%. It was found that the concrete carbonation depth increased with increased CO_2 concentration but the significance is reduced when the CO_2 concentration is higher than 20%. Generally, in non-ventilated laboratory, the concentration of CO_2 may rise to above 0.1%. In large cities, it is about 0.3% and in some exceptional cases, it can increase to 1%.
But Limbachiya et al (2012)	Accelerated carbonation tests (3.5% CO_2) was adopted stating that ''1 week-time exposure of concrete specimen in the carbonation chamber is some-what equivalent to12 months exposition under natural environment''.

2.7.4 Relative Humidity

Author	Observation
Wierig, 1984	Relative humidity is identified as an important factor affecting carbonation where a value of 65% is optimal for carbonation.
Morinaga (1988) and Idem (1990)	For relative humidity more than 50% but less than 100%, as soon as carbonation depth crosses the concrete cover and advances towards the reinforcing bars, corrosion of the latter may start. In such case, experimental results for diverse parameters indicate that the rate of steel corrosion in carbonated concrete is much higher than that of carbonation.

Idem (1995)	Experimental investigations, observations and mathematical analysis show that carbonation is maximum at relative humidity around 50%.
Roy et al. (1999)	There is a significant increase of the carbonation depth when the relative humidity increases from 84 to 92%.
Bijen (1989)	Pour water is also important for corrosion of steel, since it blocks oxygen diffusion and also provides the electrolyte for the corrosion process. Corrosion in carbonated concrete is highest for relative humidity of 90%, while it is much slower for relative humidity below 50%. In completely saturated concrete the blocking of gas diffusion in turn blocks both carbonation and corrosion. The degree of pore saturation is variable with time and location within the concrete, since the surrounding relative humidity is variable and the external concrete surface may get exposed to rain and snow.
Papadakis et al, 1991	Water may ingress through the capillary suction and vapour diffusion-condensation on the pore walls, and evaporate subsequently, with a certain hysteresis once relative humidity drops again.
Atis (2003)	Carbonation depths at 65 % RH were greater than those at 100 % RH.
Li (2004)	With the increase of ambient temperature, carbonation depth increased, while carbonation depth was found to decrease when the RH increased from 45% to 95%.
Ruixia HE (2010)	The carbonation rate increases when the ambient temperature is around 10°C to 30°C and RH falls from 70% to 50% simultaneously.
Gu et al (2011)	Increase in temperature results in enhanced rate of CO_2 diffusion as well as reduced moisture content, thus providing more space for diffusion of gas.

Scholz and Wierig (1984)	If concrete mixes were prepared for equal strengths, the water requirements of concrete containing mineral admixtures would result in reduced carbonation rates.
Russell et al (2001)	Maximum carbonation occurred at 55% RH while carbonation depth was found to decrease when RH increased from 55 to 75%.

2.7.5   Curing Period

Author	Observation
Loo etal (1994)	Increase in curing periods reduces the rate of carbonation, but beyond 14 days of water-curing the reduction is slower.
Dhir et al (1989)	Extending the water curing period beyond 14 days has reduced effect on the carbonation rate than curing in initial period.
Fattuhi (1986)	Results obtained from 1 day, 7 days, 21 days and 28 days clearly justified the above statement. It was found that when the curing periods were increased from 1-28 days, the depth of carbonation was reduced to the extent of 61, 43, 25 and 17%.
Fattuhi [1988] and Nagataki et al (1989).	Concrete carbonation rates decreased with an increase in water curing period. Delay in water curing period resulted in higher rates of concrete carbonation. 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.
Gowripalan et al (1990)	Effects of curing on carbonation depend on type of cement. Changing curing period was found to exhibit different effect, for the same cement content, on a concrete of Portland cement and on a concrete of slag cement. Curing is more significant for a concrete with slag cement, as has been demonstrated by others.
Balayssac et al	Curing time has a huge effect on the durability of commonly

(1995)	used NVC and one-day curing is not sufficient irrespective of 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.
Atis (2003)	Carbonation depth has been lower in case of longer initial curing period.
Sulapha et al (2003)	To improve carbonation resistance, sufficient water curing of at least seven days is necessary for Portland cement based concrete, whereas, an extended curing period is required for ground granulated blast furnace slag (GGBS), Fly ash and Silica Fume concretes.
Sisomphon and Franke (2007)	Depth of carbonation decreased with the increase of curing period in FA concrete.
Qingxin Zhao et al (2016) and Ki-Bong Park (2016)	Longer periods of curing decrease the carbonation depth.
Lo and Lee (2003)	Huge differences were observed in carbonation depth of water cured and air-cured samples but the difference was less significant with time. After 1 month of exposure in an accelerated carbonation chamber, the depth was 3 mm in air-cured concrete and 1.5 mm in water-cured concrete. The depth under air and water curing after 3 months increased to 10 and 8.5 mm, respectively.
Nagataki et al(1989)	After 15 years of outdoor exposure, the depth of carbonation was greater for concrete initially cured for 1 day, while the

	result for 7 and 91 days were similar. However, for the fly ash mixes slight increases in carbonation resistance were observed when curing was extended from 7 days to 1 year.

2.7.6 Porosity

Author	Observation
Muntean and Bohm, 2009	Carbonation is principally dependent on the degree of porosity.
Wang and Lee, 2009	Porosity paves way for carbon dioxide and water to transport in concrete, and the content of calcium hydroxide which reacts with carbon dioxide and water to cause carbonation of concrete.
Rozirreet al (2009)	Pore structure is one of the major influencing factors concerning durability. The decrease of the capillary porosity resulting from reduced water content decreases the carbonation rate. For durability of concrete structures proper compaction is a must. A linear relationship exists between accelerated carbonation and porosity. However, porosity is only a mild indicator of carbonation since it primarily indicates the compactness of the concrete.
Neville (2011)	Depths of carbonation were affected considerably by the amount of compacted pores, moisture content of the concrete and the relative humidity.
Thomas and Matthews (1992) and Koulumbi et al (1994)	Pozzolanic materials, such as pulverised fuel ash and GGBS, have been used to refine the pore structure, but they adversely accelerated the rate of carbonation.
Kulakowski et al (2009)	Only silica fume was advantageous in lowering the rate of carbonation by minimising the pore network.
Atis (2004)	Carbonation depth of concrete decreases, when the compressive

	strength and porosity increases.
Atis (2004)	Carbonation depth increases with increase in porosity of concrete and a linear relationship exists between the two.
Audenaert et al (2007)	As porosity increases, carbonation depth also increases.
Tragardh (1999)	Aggregate-paste and steel-paste interfacial transition zones are denser, stronger and stiffer in SCC than in NVC of the same W/C ratio.

2.7.7 Super Plasticizers

Author	Observation
Villain et al (2007)	Incorporation of super plasticizers has been of great interest and is gradually applied to concrete in practical projects. Their utilization changes carbonation phenomenon of ordinary concrete.
He et al (2012)	Super plasticizers can change the size, amount and orientation of hydrations induced in concretes thus improves anti-carbonation ability.
Fattuhi (1988)	In some cases, addition of super plasticizer did not show much influence on the carbonation depths; but appropriate dosages can bear significant 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.
Atis (2003)	The type of admixtures also influences the compressive strength and permeability of NVC. 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. Experimental 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.

2.7.8 Concrete Cover, Surface Coating and Period of Exposure

Author	Observation
Fattuhi (1986)	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%.
Bakharev (2001)	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 the incidence of carbonation from 89 to 8% and the average carbonation depth from 22 to 2 mm.
Sisomphon et al (2007)	A cover thickness of 35-40 mm is considered necessary for reinforced NVC made of special kind of cements with FA replacement up to 50%. A minimum cover depth of 25 mm is a must and for cements, with up to 50% FA replacement, the cover thickness of 30 mm is sufficient to provide the passivity of steel rebar in 50 year service life.
Roy et al, 1999	Experiments reveal that the carbonation depth increases in proportion to the square root of exposure time.

2.8 Literature Review on Effect of Carbonation on Compressive Strength

Author	Observation
Roy et al (1999)	A linear relationship was experimentally observed between depth of carbonation and compressive strength as carbonation depth was found to be inversely proportional to strength. Lower grades of NVC show larger carbonation depths than the higher grades.
Shi et al (2009)	Compressive strengths at both 28 and 90 days were marginally higher in case of high performance concrete made with PC and Blast Furnace Slag Cement compared to corresponding concretes.
Bakharev et al (2001)	Alkali activated slag concrete of Grade 40 has lower resistance to carbonation than that of OPC concrete.

2.9 Test Methods for Determination of Carbonation

Carbonation in concrete materials in service has been identified as a critical problem, particularly where the environment is warm and relatively humid. There have been several experimental studies of concrete carbonation both for outdoor conditions [Schiessl, 1976; Nagataki, Ogha and Kim, 1986] and for controlled indoor conditions [Tuutti, 1982; Nagataki and Mansur, 1988; Nagataki, Ogha and Kim, 1986; Ying Yu and Qui-dong, 1987]. A practical problem faced by most previous workers was the very long time needed to perform the experiments under normal exposure conditions, which contain 0.03-0.05% CO_2. The evolution of carbonation depth with time is very slow and, typically, samples are studied over periods of 5-10 years [Nagataki, Ogha and Kim, 1986; Litvan and Meyer, 1986]. An accelerated carbonation chamber was used where concrete samples were exposed to 50% CO_2 under controlled temperature and RH conditions. While the natural process of Carbonation of concrete structures in our surroundings is very slow, accelerated carbonation effect on the concrete simulates the actual behaviour of effect of carbonation on the concrete. Studies developed by Ho and

Lewis, 1987 showed a good correlation between the natural carbonation test with the accelerated test, using a 4% CO_2, 50% relative humidity (RH), and temperature of 23°C. However, it is observed that a large part of the available studies reported in the literature adopt higher CO_2 concentrations than 4% [Sanjuan, DelOlmo, 2001; Van Gerven, 2003; Nepomuceno and Andrade, 2006; Thiery, Villain, Dangla and Platret, 2007]. In order to predict carbonation in a short period of time, accelerated carbonation is widely applied for the study of both Portland cement [Papadakis, Vayenas and Fardis, 1989; Ho and Lewis, 1987; Ho and Lewis, 1983; Castellote and Andrade, 2008 da Silva, Helene, Castro-Borges and Liborio, 2009] and alkali-activated [Bakharev, Sanjayan and Cheng, 2001; Criado, Palomo and Fernandez-Jimenez, 2005; Deja, 2002; Bernal, Mejia de Gutierrez, Rose and Provis, 2010; Puertas, Palacios and Vazquez, 2006; Bernal, Mejia de Guitterez, Pedraza, Provis, Rodriguez and Delvasto, 2011; Bernal and Provis, 2012] binders.

The process of carbonation in concrete demands prime concern since it is a major deteriorating factor in concrete structures in our surroundings. The accurate determination of impact of carbonation in concrete is still a challenge. In this study, Carbonation effect on concrete has been simulated in controlled carbonation chamber in short duration of time and experiments have been conducted on concrete cubes by varying multiple parameters such as type of cement, W/C, super plasticizer, CO_2 concentration, replacement of cement and fine aggregate with FA, SF and GGBS and variation of curing period in order to assess the depth of carbonation. Initially Phenolphthalein indicator has been used to assess the depth of carbonation by varying factors. The experimental results have been graphically analysed to conclude the effect of various factors and overcome the discrepancies observed in previous studies.

The Phenolphthalein indicator method is by far the most conventional method of determination of depth of carbonation in concrete, being most economic and quick. However, it does not provide accurate results with respect to carbonation depth. Past evidence has shown that carbon dioxide could react at depths greater than those indicated by a phenolphthalein indicator [Parrot, 1987]. Thus an experimental study of carbonation effect of concrete by advanced methods such as X-Ray Diffraction Analysis (XRDA), Fourier Transform Infra-red Spectroscopy (FTIR) & Scanning Electron Microscope (SEM) methods was also conducted. Visual examination, optical microscopy, and SEM have been extensively used in microstructure research of hardened cement paste and concrete, providing additional understanding of macroscopic properties [Brunauer and Copeland, 1964; Mehta, 1983; Neville, 1995; Jennings, 1983; Johansen and Thoulow, 1996]. The process of Carbonation has been carried out in an accelerated carbonation chamber under controlled environmental conditions using OPC

concrete at W/C ratio 0.4, 0.45 and 0.5. Study shows that carbonation depth obtained from advanced methods is greater than that obtained from conventional method and that the carbonation depth increases with the increase of W/C.

2.10 Conclusions

It can be seen from the above literature that there exists difference in opinions and conclusions drawn by various researchers. For example, many researchers opined that replacement of cement with Micro silica bears no impact on carbonation, while others concluded that carbonation in concrete reduces till some percentage replacement of cement with micro silica. Similarly, for cement replacement with Fly ash or fine aggregate replacement with Fly ash, different school of opinions exist. While some

concluded that decrease in carbonation is observed with increasing percentage of replacement, some stated that replacement is effective in carbonation resistance only till specific percentages. Conclusions with respect to GGBS replacement are also variable. Similarly, various researchers have indicated various impacts of relative humidity percentages on carbonation. While some opined that carbonation is maximum at peak RH of 50 %, some observed that carbonation consistently increases when RH increases from 45 to 90 %. Other researchers observed the change in carbonation pattern at 70 % RH. Also past researches have been done by both conventional and advanced methods and differences in test results have been found.

Having gone through the above literature review, the following points were identified for need for further research:

- Need for a detailed study on the relation between strength of concrete and carbonation resistance.

- Need for the accurate study of influence of mineral admixtures with various water binder ratios on rate of carbonation Though the concept of the durability of concrete with mineral admixtures has been well established, as mentioned in this chapter previously, there have been many contradictions regarding the carbonation resistance of concrete mix with cement and fine aggregates partially replaced by mineral admixtures. The optimum dosage of these mineral admixtures, if intended for the use in the concrete mix, in terms of durability should be clarified.

- Need to compare the test results by various advanced and conventional methods of determination of carbonation depths.