

MECHANISM OF CARBONATION IN CONCRETE AND ITS PREDICTION - A REVIEW

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Abstract. This paper examines the process of carbonation in concrete as well as factors that influence carbonation progression in concrete. Quantification of carbonation process in an inland environment and basis for the derivation of the carbonation progression rate in concrete were also reviewed. The paper then reviewed extensively existing carbonation prediction models and finally it proposed an approach for the development of carbonation prediction model for reinforced concrete structures located in an inland environment.

Keywords: Durability Performance; Service Life; Carbonation; Prediction; Inland Environment; Concrete.

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INTRODUCTION

The durability performance and service life of reinforced concrete structures situated in an inland environment is often principally affected by the ingress of carbon dioxide (CO₂). When atmospheric air penetrates reinforced or

unreinforced concrete, carbon dioxide in the air dissolves in the pore water of the concrete to form carbonic acid which then chemically reacts with alkalis (hydroxide) in the cement paste that are produced from the hydration reaction of cement to form

carbonate with the release of water. This reaction is commonly referred to as “carbonation” and it moves as a “front” into the concrete as

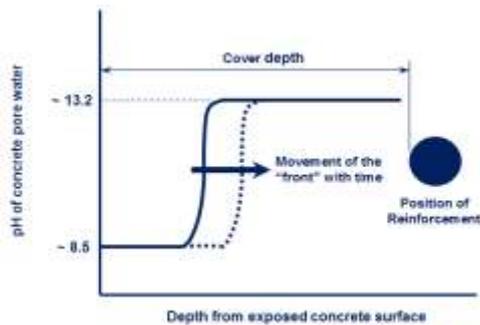


Figure 1: pH reduction due to carbonation moving as a “front” from the concrete surface (Ballim et al., 2009).

The rate of movement of the carbonation front depends on the concrete characteristics as well as the environmental exposure condition and this follows a square-root of time law (Bertolini et al., 2013). In unreinforced concrete, carbonation has beneficial implications for both strength and durability by the reduction of concrete pore volume and permeability (Neville, 1981). However, in reinforced concrete, carbonation has an important effect in initiating the corrosion of reinforcing steel, therefore reducing the durability performance and service life of reinforced concrete

schematically shown in Figure 1 (Ballim et al., 2009; Beckett, 1986; Neville, 1981; Roberts, 1981).

members/elements and structures. Some of the reasons for attention on concrete carbonation problems are the high cost of maintenance and repair of existing infrastructure; the need for improvement in current design specifications for concrete structures since design approaches of the past do not account for the increasing sophistication of modern materials; the increasing aggressiveness of the environment due to industrialization and; the need to prolong the service life of concrete structures. Thus, the main objective of the paper is to propose an approach for the development of a model for the prediction of the

rate of carbonation in reinforced concrete located in an inland

Mechanism of Carbonation in Concrete

Carbonation is a reaction between carbonic acid and hydroxides in cement paste that form carbonates. Carbonic acid can be introduced in the pore structure of *hardened cement paste (hcp)* by dissolution of gaseous atmospheric carbon dioxide (CO_2) in pore water or by direct penetration of rain water with dissolved CO_2 . Cementitious pastes are basic (pH as high as 13.5) and the carbonation reaction reduces the pH of the paste to less than 8.5 when fully carbonated (Glass et al., 1991). Carbonates formed in the carbonation reaction are larger molecules and of lower solubility than the hydroxides, thereby increasing the density of the cement pastes of the concrete and locally, the strength (Neville, 1997). Reduction of the pH of the cement paste is a concern for reinforcing steel embedded in

environment.

concrete because steel is more susceptible to corrosion at lower pH level. As a result, carbonation studies most often concern themselves with this potential corrosion and the rate at which carbonation progresses from the exposed concrete face towards the reinforcing steel. As stated above, carbonation has positive effect on mass concrete while for reinforced concrete, it depassivate the reinforcing steel making it susceptible to corrosion.

Factors that Influence Carbonation Progression in Concrete

Carbonation rate in concrete is greatly affected by both external and internal factors to the concrete. Thus, the factors that encourages the process of carbonation in concrete can be classified into two distinct categories: environmental factors (extrinsic) and concrete properties (intrinsic).

Environmental Factors

The relative humidity (RH) at the concrete exposure site determines the drying rate of the concrete and thus the concrete internal humidity or the saturation degree of pores in the concrete. Concrete under low humidity does not react with CO_2 because there is insufficient water for the CO_2 to dissolve and form carbonic acid. On the other hand, penetration of CO_2 into saturated concrete under a condition of high humidity is difficult. The most favourable exposure condition for carbonation to progress is between 50 to 70 % of relative humidity (Verbeck, 1958; Richardson, 2002; Neville, 1997; Fernandez et al., 2004). The rate of carbonation in concrete can be significantly reduced under cyclic wetting and drying conditions, when compared with constant RH conditions (Bakker, 1994). For instance, when a concrete surface becomes saturated with water as a result of rain period, diffusion of CO_2 into the concrete becomes negligible and the advance of the carbonation

front is halted. The concrete has to dry out to the depth to which the carbonation front had reached just before the wetting period, in order for the carbonation front to advance. Periodic rewetting significantly reduces carbonation due to the slower rate of CO_2 diffusion through the partially saturated pores of the cement paste matrix. The penetration of CO_2 in concrete is given by the diffusion mechanism, according to Fick's first law, where the gas penetration is proportional to the difference of CO_2 concentration between the two environments. Thus, the higher the concentration between the external and internal environment of concrete, the higher the CO_2 penetration will be and, consequently, the higher the carbonation depths observed in a period of time (Da Silva et al., 2009; Nischer, 1984; Hamada, 1969; Fukushi, 1985). Since diffusion is a concentration gradient-driven transport of gas, the partial pressure of CO_2 affects the rate of diffusion and the rate of the carbonation

reaction. Temperature is another environmental factor that affects the reaction rate of the carbonation process. Depending on the temperature to which the concrete is exposed, there is a tendency to accelerate hydration reactions of cement, thus improving the micro-structural conditions or increasing the carbonation reaction. However, if temperature is high, it can cause micro-cracking of the material. Micro-cracking is the preferential way for aggressive agent – to penetrate into concrete. Similarly, depending on the temperature, the dissolution and saturation degrees of different species with water change. At lower temperatures, less calcium hydroxide and more carbon dioxide will dissolve in the pore water, but the reaction rate will generally be reduced (Balen & Gemert, 1994). The diffusivity of CO_2 is increased due to increase in activation energy with an increase in temperature.

Concrete Properties

The carbonation process in concrete depends also on the microstructure and chemical composition of the cover concrete. Factors that affect the concrete pore structure and chemical composition influence the rate of carbonation in concrete as well. The concrete microstructure largely depends upon the w/b ratio, the paste content, cement content, binder type, aggregate type, aggregate content, water content, quality of mix constituents as well as all the concrete processing practice such as mixing, transportation, placing, compacting, curing etc. While the chemical composition of the concrete is a function of the cement and/or the binder type and content as well as the degree of hydration. The discussion below focuses on both these aspects in considering the influence of the material and processing properties on carbonation rate in concrete. The effects of concrete microstructure and chemical composition on

carbonation rate are influenced by the following factors as explained.

1. Cement type affects CO_2 buffering capacity and the physical parameters of the concrete. Finely ground Portland cement decreases the permeability of cement paste hence the rate of carbonation. Similarly, Portland cement has high hydroxide content thus high buffering capacity against CO_2 ingress. However, the effect of blended cement concretes on the rate of carbonation depends on the interplay of the effects of the supplementary cementing materials (*SCM*) on the concrete permeability as well as its hydroxide content. Manmohan and Mehta (1981) have shown that a significant effect of the addition of fly ash (*FA*) to Portland cement was that it effected a refinement of the pore structure upon hydration, by transforming

large pores into fine pores. As a result of this effect, Mehta (1983) noted a decrease in cement paste permeability after the addition of *FA*. Although, the addition of *FA* decreases the fluid transport properties of concrete (Alhassan, 2014), the influence in such concrete regarding the rate of carbonation is uncertain since the carbonation process is a function of the hydroxide (*CH*) content of the concrete too. The pozzolanic reaction consumes *CH* leaving less active materials to resist CO_2 ingress. This led Alexander et al. (1989) to conclude that: "Fly ash concrete may or may not carbonate faster than comparable plain cement concrete under similar conditions depending on such interlinked factors as permeability and *CH* content". In a survey of the literature on the effects of *FA* on concrete carbonation, Thomas et al. (1990) conclude that for equal strength grade of concrete,

depths of carbonation were similar for *FA* and plain cement concretes while Alonso et al. (1990) note that blended cements are not as effective as plain cement in passivating reinforcing steel and therefore, increases the probability of corrosion. For ground granulated blast furnace slag (*GGBS*) blended concretes, research appears to indicate that *PC/GGBS* paste cured for 28 days have similar total porosity values as plain *PC* paste at the same w/c ratio (Pigeon & Regourd, 1983). However, the *GGBS* pastes have more gel pores and fewer capillary pores than corresponding *PC* paste. This does not appear to have a significant effect on the permeation properties of the material in concrete as water permeability of a 70/30 *GGBS/PC* concrete is slightly higher than that of a plain concrete. Similarly, research

conducted by Osborne (1999) shows that the replacement of *PC* with *GGBS* increases the rate of carbonation as well as the permeability of the concrete. Osborne also noted increased carbonation and permeability with increasing *GGBS* replacement. However, the extent of increase in the carbonation rate decreases as the total binder content of the concrete increases. Condensed silica fume (*CSF*) on the other hand causes pore blocking in the hydrating cement, densifying the hydrating gel structure (Mehta & Gorve, 1982). This is as a result of its high reactivity (Roy, 1997) and its ability to form nucleation sites for cement hydration (Mitchell et al., 1998). These effects give *CSF* blended concrete reduced rate of carbonation, despite the fact that its *CH* content is low in comparison to plain cement concrete.

2. Water binder ratio (w/b) affects the physical parameters of concrete and may influence the amount of hydrated cement present and hence buffering capacity of the concrete. Permeability of concrete generally decreases with w/b and hence, the rate of carbonation is reduced, other factors being held constant. The positive influence of w/b on the rate of carbonation of concrete is as a result of the increasing volume and degree of interconnectivity of the capillary pores. Similarly, since permeability increases with w/b, the rate of ingress of CO_2 also increases. A study by Henry and Kurtz (1963) shows increasing fluid transport ability with increasing w/b. This largely explains the noted increases in concrete carbonation rate by numerous researchers as w/b increases (Atiş 2003; Ho & Lewis, 1987; Loo et al., 1994; Mackechnie & Alexander, 2002; Sisomphon & Franke, 2007; Sulapha et al., 2003, Alhassan, 2014).
3. Cement content in concrete affects its buffering capacity. While cement content is not a basic parameter in determining the permeability of concrete (Addis, 1986), it does have an influence on the carbonation progression in concrete. For instance, the rate of carbonation in concrete is influenced by the amount of hydration products available for reaction. Hence, for the same permeability a concrete with more cement will show a slower rate of carbonation progression.
4. Although aggregate type has no direct effect on concrete carbonation, it may lead to "through-aggregate" carbonation (BRE, 2001). However, the size of the aggregate and its content has

effect on concrete permeability because of the role of the *Interfacial Transition Zone (ITZ)*. Thus, the rate of carbonation increases with an increase in aggregate size and content as a result of increased volume of the *ITZ*.

5. Curing is a process aimed at encouraging the hydration of cement during the early period of casting, hence, ensuring that the engineering properties of concrete develop to their required potential. Curing has very significant effect on the permeability of concrete. Continued hydration of concrete decreases both the size and continuity of the pores in *hcp* as well as its composition. Thus, curing may either increase or decrease the rate of carbonation in concrete depending on the type of binder used. While curing has positive effect on rate of carbonation in plain cement

concrete, the effect depends on the inter-play between permeability and hydroxide content in blended cement concrete (Alexander, et al, 1989). The chemical composition of the cover concrete depends on the mix constituents, especially the binder type and content, and the chemical composition of the binder. Additionally, the chemical composition of concrete also depends on the degree of hydration and degree of pozzolanic activity in the case of blended binders. Curing influences the degree of hydration and pozzolanic activity thus the chemical composition of the concrete. With the use of *SCM*, hydroxide components in the cement paste are reduced due to its consumption. With this reduction, carbonation rates would tend to increase, as there is less material to react with the CO_2 . However, *SCM*

have the effect of decreasing permeability of the cement paste which tends to decrease the diffusivity of the ingress of CO_2 . If the reduction in permeability has a higher impact than the reduction in hydroxide components, then the overall carbonation is reduced. The chemical parameter of importance to carbonation is the amount of carbonatable material (hydroxides) that is available in the concrete matrix. It has been observed that, given a sufficiently high CO_2 concentration, unhydrated products (C_2S , C_3S) as well as the CSH gel and other hydration products such as ettringite will carbonate. While at ambient CO_2 concentration, only the CH will mainly carbonate. Thus, the rate of carbonation is slow at low CO_2 concentration.

Measurement of Carbonation in Concrete

No standard method to measure concrete carbonation exists, although several publications do discuss methods of analysis, e.g. Rilem Recommendation CPC 18, ASTM C 856, etc. (Neville, 1997). Carbonation of concrete can be measured using either of the following methods: phenolphthalein solution, rainbow indicator, measuring the pH of pore solutions, thin-section examination with petrographic microscope, x-ray diffraction, infra-red absorption. While some of the methods require a significant amount of time and often expensive equipment, the phenolphthalein solution and rainbow indicator methods are quick and economical. Although the phenolphthalein solution and rainbow indicator methods do not identify areas of partial carbonation, the rainbow indicator requires subjective analysis in determining the location of the colour change which is not as vivid as the phenolphthalein solution.

Thus, the phenolphthalein solution was considered as sufficient for carbonation measurement and it is often used in its measurement. The phenolphthalein method involves spraying freshly broken concrete surfaces with 1 or 2% phenolphthalein solution (Wierig, 1984). The surface where the pH is greater than 9 turns magenta and a gradually lightening shades of pink for pH of 8 – 9. The location where the surface is colourless represents the depth to which full or nearly full carbonation has been achieved and the *pH* of the cement is at or below 8. Phenolphthalein testing can be sufficient to determine the extent of carbonation, but it is critical to understand what is actually being measured. The test does not indicate the level of carbonation in the cement paste, but only the location where the *pH* is above or below 9. A *pH* of 9 or lower is generally accepted as ‘fully carbonated’. A *pH* greater than 9, however, is not an indicator that no carbonation has occurred. However,

the “frontal” nature of the progress of the reaction means that the point of colour change is sufficiently close to the zone of uncarbonated concrete (or something similar).

Derivation of the Basic Carbonation Progression Rate Equation

Carbonation progression into concrete follows a square-root of time law which is based on a few assumptions (Tutti, 1982). Derivation of the square-root of time equation is necessary if it is to be used appropriately and modelled in line with the governing assumptions. The carbonation rate in concrete is controlled by the ingress of CO_2 into the concrete pore system by diffusion, with a concentration gradient of CO_2 acting as the driving force. Therefore, the CO_2 always has to pass through concrete sections that have already undergone carbonation in order to participate in a reaction at some depth into the concrete. Thus, applying Fick’s first law of diffusion, the amount, - (*m*)

of CO_2 diffusing through a concrete layer is given by:

$$m = -DA \frac{C_1 - C_2}{x} t \dots\dots\dots 1$$

x = thickness of the penetrated concrete layer (m)

t = time (s)

Where,

m = mass of CO_2 (g)

D = diffusion coefficient of CO_2 through carbonated concrete (m^2/s)

A = area through which the transport is taking place (m^2)

C_1 = CO_2 concentration at the concrete surface (g/m^3)

C_2 = CO_2 concentration at the carbonation front (g/m^3)

It is assumed that the carbonation front cannot move on except when all carbonatable matter, (a , in g/m^3 -) has reacted within a reference volume, $A dx$. The total mass of CO_2 , m that has to be transported to the carbonation front to transform this matter, a thereby progressing the carbonation front by, dx is given by:

$$m = a.A.dx \dots\dots\dots 2$$

Since this is similar to the flux that goes through this reference volume in a reference time, dt to move a

distance dx forward, substituting Equation 2 in the simplified form of Fick's first law gives:

$$-DA \frac{(C_1 - C_2)}{x} t = aAdx \dots\dots\dots 3$$

The boundary condition for the CO_2 concentration C_2 at the carbonation front is that it is zero. Using this

boundary condition and solving Equation 3 by integration results in:

$$x^2 = \frac{2D}{a}(C_1)t \dots\dots\dots 4$$

If all constant parameters of Equation 4 (diffusion coefficient, CO_2 concentration difference and the amount of carbonatable material) are combined into one

single constant K , Equation 4 will result in the well-known equation, Equation 5, the square root of time equation:

$$x = K\sqrt{t} \dots\dots\dots 5$$

Where,

x = depth of carbonation

t = time

K = carbonation rate, dependent on the surrounding concentration of CO_2 , the possible absorption of CO_2 in the concrete and the permeability of the material.

The assumptions inherent in the derivation of Equation 5 are that:

depth from the surface of the concrete inwards;

1. The pore structure of the cement paste in concrete (pore size distribution and degree of interconnection of the pores) remains uniform with depth into concrete;

3. The degree of hydration and the amount of carbonatable material remains constant with depth.

2. The value and quality of the pore structure remains constant with

Note that these assumptions are rarely true in practice, especially under conditions of limited curing of the surface zone.

The assumptions in the derivation of the square-root of time equation, demonstrate that the application of Fick's law of diffusion using constant parameters is subject to many limitations. However, numerous prediction models for the development of the depth of carbonation with time exist based on this theory. For higher concrete ages, the depth of carbonation observed is often less than expected according to a \sqrt{t} relation. In controlled climates such as laboratory, satisfactory results may be obtained. However correlation

with actual carbonation rates is often poor, especially for outdoor exposure with changing temperature and humidity conditions. Although Equation 5 is the commonly accepted form of the carbonation rate equation, numerous researchers (Bentur and Jaegerman, 1991; Wierig, 1984; Meyer, 1968; Smolczyk, 1980; Nischer, 1984) have proposed the following alternative equation, claiming that this form gives better correlation with the measured results:

$$x = Kt^n \dots\dots\dots 6$$

Where, $n < 0.5$ and the terms are as described for Equation 5.

Based on long term observations of the carbonation rate of concrete subjected to natural weather conditions, Wierig (1984) concluded that a \sqrt{t} approach is sufficiently accurate to describe the progress of carbonation as long as the concretes are sheltered from rain. Similarly, a study on existing

concrete structures in South Africa by Yam (2004) and Alexander et al. (2007) observed a \sqrt{t} relationship for carbonation progression in inland concrete structures while deviations from the \sqrt{t} relationship was noted for concrete structures in the marine environment. Furthermore, Lampacher (2000) in

a study of the durability performance of inland concrete structures in South Africa ranging in age between 19 and 70 years, used the \sqrt{t} relationship for the ingress of CO_2 . Since the shortest conceivable initiation time is used when assessing the service life of the concrete structure (Tutti, 1982), the square-root of time equation can be utilized in most cases. The square-root of time relationship is therefore an upper limit value for the penetration of the carbonation front. For reliable modelling of the mechanism or process of carbonation in concrete, the local environmental exposure condition of the concrete is vital in the determination of a time function for the rate of carbonation. However, the derivation of the rate of carbonation from the square-root of time law is influenced by numerous factors which can be grouped into concrete characterisation (concrete making materials and processing) and the

environmental exposure condition of the concrete as explained above.

Existing Models for the Prediction of Carbonation Depth/Rate in Concrete

Reinforced concrete structures are expected to carbonate in their natural environmental exposure condition. Surprisingly, the majority of articles on concrete carbonation modelling have been focused on laboratory concrete specimens that were carbonated under controlled or accelerated exposure. Following an intense literature review, only four unique publications on experimental modelling of concrete carbonation in the inland environment by Dhir et al. (1989), Watkins and Jones (1993), Parrott (1994) and BRE (2001) were found. These works will be discussed in detail later in the section. Since environmental exposure conditions affect the rate of carbonation in concrete, it is questionable if the numerous experiments (and hence the models) that were and continue

to be conducted in the absence of a natural environmental exposure conditions are truly representative of the behaviour of in-service structures. One of the criteria that is often used to define the end-of-service life of carbonation-affected reinforced concrete structures, is the time it takes the carbonation front to reach the level of the reinforcing steel (Initiation Limit State – *ILS*) (Bertolini, et al., 2013). Considerable experimental works have been done on the time it takes the CO_2 to move from the concrete surface to the reinforcing steel level. The main intent of the majority of the research work is to correlate the properties of concrete to the depth or rate of carbonation in the

companion concrete. Review of experimental work and the corresponding results from various researchers in their attempt to model the advance of carbonation is presented. Similar to findings from Kikuchi et al. (1988), Osborne (1999) and Hilsdorf (1989), Dhir et al. (1989) proposed an empirical equation (Equation 7) to predict the depth of carbonation in concrete. The equation represents a model based on the relationship between the intrinsic permeability of plain and blended concrete and the carbonation depth of companion concrete. Equation 7 was derived by regression analysis between the depth of carbonation in concrete and its permeability values.

$$D = (t/20)^\gamma (22.8 \log K - 6.9) \dots\dots\dots 7$$

Where,

D = depth of carbonation (mm) after t year normal exposure

t = design life of the concrete structures (years)

K = intrinsic permeability of the concrete (10^{-17} m^2)

γ = time exponent ($\gamma = 0.5$, if $w/c \leq 0.6$ and $\gamma = 0.4$ if $w/c > 0.6$)

Dhir et al. (1989) study represents a notable contribution to understanding the relationship between concrete microstructure, its environmental exposure conditions and the carbonation process in concrete. The variable time exponent accounts for the carbonation process for the different concrete types. In addition, the concept of employing the intrinsic permeability in a prediction model is appealing as test specimens for a variety of concretes can be made and the permeability measurements obtained after 28 days. Furthermore, the principle of using the inherent characteristics of the concrete, in the absence of site environmental conditions, to obtain estimates for carbonation performance of concretes appears to be reasonable, provided the intrinsic values are compared to actual site specific data to validate the model. Whilst the Dhir et al. modelling attempt was based on a study of the natural

environmentally exposed concretes and the consideration of the time exponent as well as the concrete fluid transport properties in the model, the chemical composition of the concrete was however, not given specific consideration in the model. Additionally, the environmental exposure conditions considered were those of the UK, which will definitely be different from conditions elsewhere both in its weather and its concrete materials and technology. Clearly, the Dhir et al. model, even though comprehensive, cannot be used by other countries building owners and design engineers in the design of concrete structures as it can be expected to give inaccurate predictions. Watkins and Jones (1993), in an assessment of over 800 buildings in Hong Kong in the late 1980's in terms of depth of carbonation, strength, cement content, density, permeability, porosity and age, developed a prediction model that is similar to the general carbonation prediction

model presented in Equation 6. However, the time exponent n , varied between 0.5 and 1, while the rate of carbonation K , varies in accordance to the strength of the concrete. Table 1 gives the K and n exponent, based on Honk Kong's concrete making materials and

environmental conditions respectively. The authors gave the climatic condition in Hong Kong in terms of the CO_2 , RH and temperature variation as ranging between 0.03 - 0.1%, 70 - 84% and 15 - 28°C respectively.

Table 1. Coefficients for Carbonation Prediction Model (Watkins and Jones, 1993)

| Strength of concrete (MPa) | K | n |
|----------------------------|------|-------|
| 15 - 24.99 | 6.43 | 0.570 |
| 25 - 34.99 | 4.28 | 0.592 |
| 35 - 44.99 | 3.07 | 0.614 |

The correspondence of the data with theoretical models appears to be reasonable and it enables the depths of carbonation to be predicted under a number of varying conditions with some precision. This leads directly to an ability to predict the initiation period for concrete of varying grades. The Watkins and Jones model (1993), although applicable to a variety of concrete grades and exposures, has similar shortcomings as the Dhir et al. model.

Additionally, since this model was developed based on study on existing structures, it is not applicable to proposed concrete structures as early-age concrete characterisation results were not used. In a more thorough research, Parrott (1994) proposed a carbonation prediction model that is potentially quite broad in application, taking into account variations in cement types (through calcium oxide content), w/c, strength and curing through

permeability. Parrot's model although based on UK exposure condition is applicable for a variety of RH conditions. The Parrott model is similar in concept to the generally accepted empirical carbonation

prediction model and it explicitly considers the permeability of the concrete, thereby allowing for a broader application. Parrott's model is given in Equation 8.

$$d = \frac{aK^{0.4}}{C^{0.5}} t^n \dots\dots\dots 8$$

Where,

d = carbonation depth (mm)

t = exposure time (years)

k = air permeability of cover concrete (10^{-16} m^2)

n = the time exponent

a = calibration coefficient for a particular environmental effect

C = calcium oxide content in the hydrated cement matrix which can react with CO_2 , expressed in kg/m^3 of cement matrix. C depends on the cement type, RH and proportion of cement which has reacted.

Despite the fact that Parrott model is comprehensive in terms of its coverage of the factors that influences concrete carbonation rate, it is unlikely to accurately predict the carbonation process of concrete structures in other part of the world. This is because it was developed under an environmental exposure conditions peculiar to the

UK, in terms of temperature and relative humidity condition. Additionally, different concrete making materials and technology were used in the production of the concrete used. Another attempt to develop prediction model for the carbonation depth in concrete was conducted in the UK by the Building Research Establishment (*BRE*). The

BRE (2001) model was similar to Parrott's model and was developed using carbonation depth over time for concrete made using different cement types, cement contents, w/c ratios and different curing regimes.

Equation 9 present the BRE model developed based on regression analysis between the response (carbonation depth) and predictor (concrete permeability and cement content) variables.

$$d = (3.165t^{0.49} \times k^{0.5} + 1.47t^{0.59})/C \dots\dots\dots 9$$

Where,

d = depth of carbonation (mm)

K = oxygen permeability values of the concrete at 28 days

C = is the normalized cement content

t = time of exposure (years)

The *BRE* model has similar shortcomings as the Parrott model suffered in terms of its applicability in other part of the world. It is evident from the above discussion that despite the sophistication of the various prediction models for the estimation of rate of carbonation in concrete, the accuracy of the prediction will be questionable when used under environmental exposure conditions order than the one developed for in the model. This is mainly attributed to as stated above - the differences in the

concrete making materials and concrete technology as well as the environmental exposure condition. For instance in Equation 8, "a" is determined to be 64 for the "European" climate. Clearly the climate in Africa will differ greatly from that of Europe. Ballim (1994) made the foremost attempt in the development of prediction model for carbonation of concrete in South Africa using the fluid transport properties of concrete. Concretes were cast using plain and blended binders and were treated to varying

degree of initial moist curing. The oxygen permeability and water sorptivity of the concrete were measured at 28 days after casting while the depth of carbonation of companion concretes exposed to a controlled laboratory environment

were measured at 10 and 20 months. Plots of the early-age permeation properties of the concretes against equivalent carbonation depth shown in Figures 2 and 3, taken from Ballim (1994) shows good correlation.

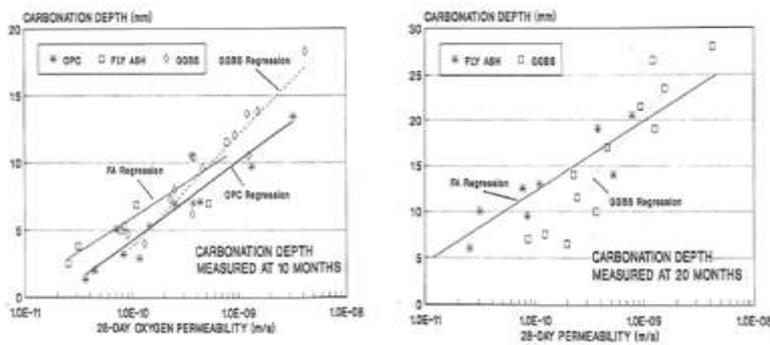


Figure 2: 28 day oxygen permeability vs carbonation depth (Ballim, 1994)

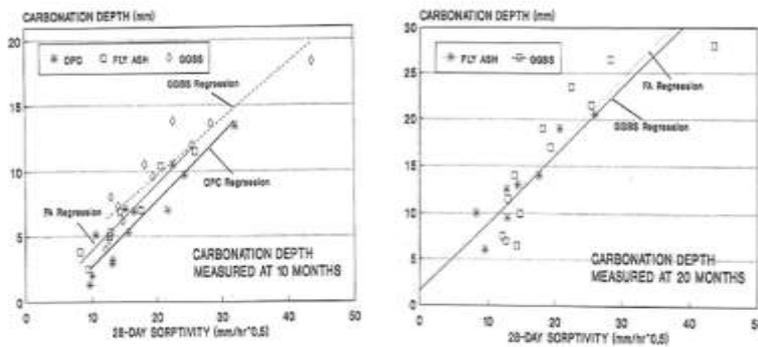


Figure 3: 28 day water sorptivity vs. carbonation depth (Ballim, 1994)

The relationships shown in Figures 2 and 3 were presented in Equations 10 and 11, between the

concrete carbonation depth and the oxygen permeability index and water sorptivity respectively.

$$X = \lambda_9 \cdot \ln(K) + \lambda_{10} \quad \dots\dots\dots 10$$

$$X = \lambda_{11} \cdot S + \lambda_{12} \dots\dots\dots 11$$

Where,

X = carbonation depth (mm)

K = oxygen permeability

S = water sorptivity

$\lambda_{9 \text{ to } 12}$ = are coefficients dependent on the binder type

In a similar study, Mackechnie (1996) related the 28-day oxygen permeability values for both plain and blended concretes to the 12-months carbonation depth after exposure to the marine

environment. Good correlations were also obtained over a wide range of concretes as shown in Figure 4. Mackechnie however did not present this relationship in the form of an equation.

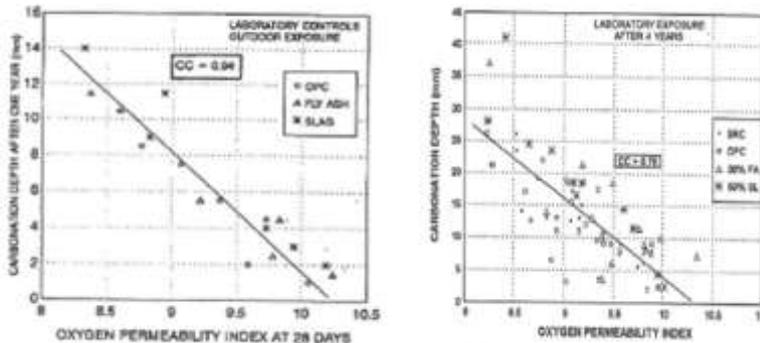


Figure 4: 28 day oxygen permeability vs carbonation depth (Mackechnie, 1996)

Mackechnie and Alexander (2002) proposed an empirical relationship that was similar to the general carbonation model, for the

prediction of the depth of carbonation in concrete. In their study, Plain and blended concretes of different grade were exposed to

the marine environment of South Africa for up to 6 years, and the carbonation depth measured at intervals of 1, 4 and 6 years, using the phenolphthalein method. The pore structures of the companion concretes were characterized using the oxygen permeability test at 28

days after casting. Figure 5 shows the correlation between the oxygen permeability values recorded at 28 days and the carbonation depths, which shows good correlation. This relationship was presented in Equation 12.

$$X = K_c t^{0.4} \dots\dots\dots 12$$

Where,

X = carbonation depth (mm)

K_c = material coefficient

t = time (years)

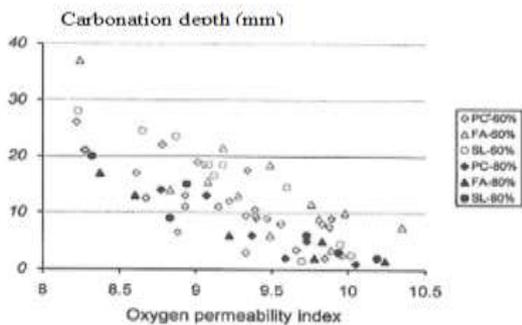


Figure 5: 28 day oxygen permeability vs carbonation depth (Mackechnie and Alexander, 2002)

The studies by Ballim (1994), Mackechnie (1996) and Mackechnie and Alexander (2002) represent a notable contribution to

understanding the relationship between concrete early-age permeation properties and the carbonation rate in concrete. The

models or relationship developed by these authors will however not allow for the prediction of the performance of concrete not represented in the data set as small samples sizes were used. In addition, these authors attempts at predicting the carbonation depths in concrete, did not consider the chemistry of carbonation in terms of the concrete chemical composition. Furthermore, the Mackechnie (1996) and Mackechnie and Alexander (2002) models are not applicable to the inland environment since samples were exposed to the marine environmental exposure conditions.

In a more thorough research, Bruno (2010) assessed the oxygen permeability of plain and blended concretes, as well as the accelerated carbonation depths of the companion concretes. His intention was to develop a model for predicting the depth of carbonation in concrete. Using the Oxygen Permeability Index (*OPI*) values of the concrete, exposure condition effects and the quantification of the chemical composition of the concrete, Bruno proposed a regression model shown in Equation 13, for the prediction of carbonation depth in concrete.

$$X = \sqrt{\frac{2D_{dry}C\beta}{a}} * \sqrt{t_e} \dots\dots\dots 13$$

Where,

X = depth of carbonation

D_{dry} = effective diffusion coefficient and is calculated from the oxygen permeability, k

C = ambient carbon dioxide concentration (mol/m^3)

β = relative humidity factor

a = the amount of carbonatable material in the concrete matrix (mol/m^3)

t_e = effective time of carbonation over the service life of the concrete.

Bruno's model, although comprehensive in the coverage of the factors that influence the process of carbonation and also has the advantage of differentiating exposure conditions and concrete types, is based on an accelerated carbonation process. In addition, the amount of carbonatable materials in the concrete and the environmental conditions parameters were obtained theoretically. This limits the applicability and usefulness of the model in natural exposure conditions. Ballim and Lampacher (1996) in a study of the durability performance of existing concrete structures aged between 19 and 30 years and located in the inland environment of South Africa propose an average rate of carbonation of $3.67 \text{ mm}/\sqrt{\text{years}}$. A lack of relationship between the depth of carbonation and either the oxygen permeability index or water sorptivity at later age was noted by the authors. The poorly known

variations in mix constituents, the degree of initial curing received and the subsequent environmental exposure history of these structures are the possible reasons given by the authors for the lack of correlation. Lampacher (2000) in a more detailed study of the durability performance of existing concrete structures in the inland environment of South Africa presented the average rate of carbonation to be $3.16 \text{ mm}/\sqrt{\text{year}}$. In his study, carbonation depths of existing concrete structures, ranging in age between 19 and 70 years, were measured. Also measured were the concretes permeation properties (in terms of oxygen permeability index and water sorptivity), compressive strength, CaO and cement contents and the modulus of elasticity. Lampacher did not however relate the concrete carbonation depth to any of these concrete properties measured.

The study by Ballim and Lampacher (1996) and Lampacher (2000) represent a contribution to understanding the relationship between concrete permeation properties at later ages, exposure condition and carbonation depth of existing concrete structures. The coefficients obtained by these authors for these concrete structures are functions of the variability in material properties and exposure conditions on the carbonation process. Although the outcomes of their study cannot be directly applicable to proposed concrete structures, it can be used for maintenance and repair scheduling for inland structures. Similarly, their study also buttress the point that the rate of carbonation in concrete decreases at an increasing time of exposure. Hence, the reduced average rate of carbonation from 3.67 to 3.16 mm/ $\sqrt{\text{year}}$ when the exposure duration increases from 19–30 years to 19–70 years. Alexander et al. (2007) drawing data from Yam (2004) presented similar studies to

that of Watkins and Jones (1987), Ballim and Lampacher (1996) and Lampacher (2000), in which the depths of carbonation were obtained for 90 in-service reinforced concrete bridges that are between the ages of 11 and 76 years. The structures investigated were drawn from three South African localities – Cape Peninsula, Durban and Johannesburg. The depths of carbonation for the different structures were obtained and the general square-root of time equations applied in order to derive the various rate of carbonation. In the study, prediction models that were similar to the general carbonation model were developed, except for the variables K and n in Equation 6 which were different. The differences in the values of the variables were attributed to the variable concrete strength and exposure conditions of the bridges. Table 2 gives the values of K and n for the different localities and concrete strength grades, while Table 3 presented the weather conditions in the three localities.

The CO_2 concentrations for these localities are similar - about 0.035%.

Table 2: 90th Percentile Carbonation Prediction Model Parameters in Equation 2.25 for Exposed Conditions in the Three Localities in South Africa (Alexander et al, 2007; Yam, 2004)

| Localities | Strength grade | K | n |
|----------------|----------------|------|-----|
| Cape Peninsula | Grade 20 | 5.94 | 0.4 |
| | Grade 30 | 3.48 | 0.4 |
| | Grade 40 | 2.95 | 0.4 |
| Durban | Grade 25 | 7.01 | 0.4 |
| | Grade 35 | 5.53 | 0.4 |
| | Grade 45 | 4.38 | 0.4 |
| Johannesburg | Grade 25 | 5.00 | 0.5 |
| | Grade 30 | 4.65 | 0.5 |

Table 3: Weather Conditions in the Three Localities in South Africa (Alexander et al, 2007; Yam, 2004)

| Rainfall seasons | Cape Peninsula | | Durban | | Johannesburg | |
|-----------------------------|----------------|-----------|------------|-----------|--------------|-----------|
| | Av. RH (%) | Temp (°C) | Av. RH (%) | Temp (°C) | Av. RH (%) | Temp (°C) |
| Wet March - September | 78 | 14 | 79 | 23 | 68 | 19 |
| Dry Oct - April | 71 | 19 | 73 | 18 | 51 | 13 |

The study by Yam (2004) and Alexander et al. (2007) represents a notable contribution to understanding the relationship between strength, exposure condition and carbonation depth of

existing structures. The different coefficients obtained by these authors for the variable K and n for different localities and strength grades of concrete are as a result of the variability in material and

exposure conditions on the carbonation process. The models developed will not allow prediction of the performance of proposed concrete structures since the effects of construction variability in terms of curing were not captured. Furthermore, this model cannot be used during the design stage of proposed concrete structure since they lack early-age parameters. Relationships have been developed for predicting the carbonation depth/rate from material and environmental factors. However, some of these relationships or models require too many parameters to be practical. For instance, Bruno's model require measurement of diffusion masses of CO_2 concentration inside and outside the samples, and diffusion constant that varies as relative humidity changes. While most of the models do not consider all factors that affect carbonation depth/rate, for example, the equations developed by Ballim (1994), Mackechnie and Alexander (2002), are not dependent upon

environmental conditions. The fluid transport properties of the concrete may help capture some of the material properties and curing effects, the effect of the concrete chemistry and varying curing periods are often not considered.

Approach for the Development of Carbonation Depth/Rate Prediction Model for Concrete

Justification is drawn from the process of carbonation and the factors that influences carbonation in concrete as presented above, for the choice of input variables in an improved model. In principle, the rate of penetration of the carbonation reaction front depends upon the atmospheric concentration of CO_2 , the CO_2 binding capacity of cover concrete and the gas diffusion coefficient of the carbonated surface layer (Dhir et al., 1989; Hilsdorf, 1989; Tutti, 1982; Papadaki et al., 1989). Thus, for a prediction model of CO_2 ingress into concrete to be reliable and useful, provision must be made for different cementitious materials

used in making concrete, construction effects and conditions of exposure. Existing prediction models reviewed generally fail to address all of these issues adequately. It is therefore necessary that this review be conducted in order to propose an improved model for concrete durability performance and service life predictions. From the findings of the review on both foreign and local models, there appear to be sufficient reason to believe that a more reliable and quantitative model may be devised which could have sufficiently broad application to be practical for specifications and predictions.

The use of the square-root of time equation for the prediction of carbonation rate is limited by:

- The variations with depth from the exposed surface of the moisture content.
- The degree of cement and carbonation reactions.

- The pore structure of the concrete.
- The CO_2 binding capacity.
- The CO_2 diffusion coefficient.

The above-mentioned variables are as a result of curing effect, cement composition and moisture history. In the formulation of the CO_2 ingress into concrete, it is assumed that:

- The coefficient of CO_2 diffusion can be represented by the permeation properties of the cover concrete.
- The binding capacity is related to the CH and CaO content and degree of reaction of the cement.
- Variation of atmospheric concentration of CO_2 can be ignored.
- Under wetter exposure conditions there is progressive departure from the square-root of time function predicted by simple diffusion theory.

In the literatures reviewed, the oxygen permeability and water sorptivity tests on concrete at early-age is known to correlate with the resistance of the concrete pore structure to CO_2 ingress (Ballim, 1994; Bruno, 2010; Lampacher, 2000; Mackechnie, 1996). These tests are sensitive to both material and construction effects and can be used on laboratory and site concretes. The chemical composition of concrete that is of importance to the ingress of CO_2 is the hydroxide content which can be quantified by either the *TGA* or wet chemical analysis technique (Midgley, 1997). It was noted from the review on factors that influence CO_2 ingress that the exposure conditions surrounding concretes, the curing duration of the concrete and the binder types used in making concretes affects its buffering of the CO_2 ingress (BRE, 2001; Dhir et al., 1989; Parrott, 1994). Similarly, relationships exist between concrete early-age characterisation parameters and the depth of carbonation (Ballim, 1994;

Mackechnie, 1996; Basheer et al., 2001; Dhir et al., 1994). Further, the rate of carbonation can be obtained from the depth of carbonation using the square-root of time law (Tutti, 1982; Alexander et al., 2007; Lampacher, 2000, Ballim and Lampacher, 1996). Thus, with the above information, prediction models can be developed by relating the rates of carbonation to the numerous factors known to influence or affect it, using a computational regression approach on measured data.

CONCLUSION

This paper has placed carbonation of concrete into context by reviewing the process of carbonation in concretes, its measurement, factors that influence the rate of CO_2 ingress as well as existing models for the prediction of carbonation in concrete. Attempts by African researchers to develop models to improve the predictive ability for the carbonation process under African environmental condition were also reviewed. Based

on the shortcomings of existing models, an approach was formulated for the development of

models for the prediction of carbonation depth/rate in concrete.

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