PREDICTING DEPTH OF CARBONATION OF CONCRETE - A PERFORMANCE-BASED APPROACH

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Abstract

The deterioration of concrete structures by environmental actions has become a great concern for engineering design and maintenance. In most cases, corrosion of the reinforcing steel in the concrete is the main cause of deterioration affecting the durability performance of the structures. The alkaline environment of the concrete protects the reinforcing steel by maintaining it in a passive state. However, the protection is compromised by carbonation of concrete which may be followed by corrosion in the presence of sufficient oxygen and moisture. Hence there is a need to understand the mechanism of carbonation and adequately model it to be useful in service life design. The main aim of the study reported here is to develop or modify an existing carbonation model for natural exposure conditions, with the South African Oxygen permeability Index (OPI) test parameter as the key variable. For the experimental work, twelve different concrete mixes were produced by varying the water:binder ratio (w/b), curing conditions, and by using fly ash. The specimens were exposed to four different sites for natural carbonation, with the depth of carbonation measured periodically. The carbonation model developed is validated based on the experimental results and the limitations are pointed out.

1. INTRODUCTION

The durability of reinforced concrete (RC) structure depends strongly on its interaction with the service environment. The main cause of deterioration of RC elements or structures is identified as the ingress of various ions, liquids and gases from the environment (especially chlorides or carbon dioxide) resulting in depassivation of steel in concrete, followed by corrosion. Carbonation-induced corrosion occurs mainly in concrete structures which are exposed to carbon dioxide-rich environments (bridges, parking infrastructure etc.) where the carbon dioxide from the atmosphere diffuses into the capillary pores of concrete and reacts with the products of cement hydration to form calcium carbonates. This process of carbonation results in the pH of the pore solution of concrete reducing from between 12.5 - 13.5, to a value of about 8.3 in fully carbonated zones. This reduction in the alkalinity destabilises the protective oxide layer and renders the steel susceptible to corrosion [1-2].

The current South African service life prediction model for carbonation induced-corrosion is an empirical model based on a power relationship between permeability and
measured carbonation depths in concretes with certain binders [3]. Apart from the influence of diffusivity and permeability of the concrete on carbonation, concrete chemistry also plays an important role in carbonation and hence needs to be considered in the model. In addition, the durability of reinforced concrete in terms of carbonation also depends on the aggressiveness of the environment. Therefore, it is important to quantify the exposure conditions accurately, rather than expressing them merely as qualitative categories. A model that accounts for the cement chemistry, quantifies environmental exposure, and relates the permeability to the microstructure of the concrete will give a more accurate and updatable model.

The performance-based South African concrete durability design method requires the penetrability and quality of the concrete matrix to be evaluated. Durability indexes (DIs) have been adopted as engineering measures of the potential resistance of concrete cover to the transport mechanisms of gaseous diffusion, water absorption and chloride diffusion [4]. The DI derived from the Oxygen Permeability Index (OPI) test is used to establish the carbonation resistance of concrete. With these indexes, together with service life prediction models, a performance specification can be established. The advantages of the South African Durability Index approach, as opposed to a prescriptive approach which is still used primarily in concrete design, is that it incorporates the properties of the constituent materials of the concrete and accounts for concrete construction variables such as mixing, placing, compaction, finishing and curing [5].

A carbonation model based on oxygen permeability coefficient as the key material variable and taking into account the effect of relative humidity (RH) on diffusion and carbonation was developed by Salvoldi using accelerated carbonation test data [6]. In the present work, a carbonation model is being developed adopting the modelling framework by Salvoldi for natural carbonation [6]. The model is being ‘calibrated’ using experimental results of carbonation tests conducted under natural conditions for different exposures and for concretes with different binders. Finally the influence of drying and wetting cycles on the carbonation rate is also emphasised.

2. EXPERIMENTAL INVESTIGATION

2.1 Materials and Curing Regime Used

Concrete mixes with a combination of cement (CEM I 52.5 N), and fly ash (at 30% replacement) and a range of w/b were used. The fine aggregate was a blend of dune sand and granite crusher sand at a ratio of 40:60, whereas the coarse aggregate was 13 mm granite. Details of the mix constituents and proportions are shown in Table 1. Superplasticiser was added to the concrete mix with the aim of achieving a target slump in the range of 90-120 mm. Two different curing regimes were adopted:

- Curing –A: Water bath maintained at a temperature of 23 - 25°C (till 28 days after casting)
- Curing –B: 1 day in moulds, then inside lab (20-22°C and 60-70% RH), till 28 days after casting)
Table 1: Concrete mix proportions

<table>
<thead>
<tr>
<th>Mix Designation</th>
<th>CEM I 52.5</th>
<th>Flyash (30%)</th>
<th>Crusher Sand</th>
<th>Dune sand</th>
<th>13mm Granite</th>
<th>w/b</th>
<th>Permeability coefficient (kL from OPI test (m/s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 PC</td>
<td>377</td>
<td>0</td>
<td>512</td>
<td>341</td>
<td></td>
<td>0.45</td>
<td>4.23E-11</td>
</tr>
<tr>
<td>0.55 PC</td>
<td>309</td>
<td>0</td>
<td>553</td>
<td>368</td>
<td></td>
<td>0.55</td>
<td>4.89E-11 1.01E-10</td>
</tr>
<tr>
<td>0.65 PC</td>
<td>262</td>
<td>0</td>
<td>581</td>
<td>387</td>
<td></td>
<td>0.65</td>
<td>5.77E-11 2.92E-10</td>
</tr>
<tr>
<td>0.45 FA</td>
<td>264</td>
<td>113</td>
<td>512</td>
<td>341</td>
<td></td>
<td>0.45</td>
<td>3.59E-11 1.13E-10</td>
</tr>
<tr>
<td>0.55 FA</td>
<td>216</td>
<td>93</td>
<td>553</td>
<td>368</td>
<td></td>
<td>0.55</td>
<td>5.84E-11 2.87E-10</td>
</tr>
<tr>
<td>0.65 FA</td>
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<td>79</td>
<td>581</td>
<td>387</td>
<td></td>
<td>0.65</td>
<td>9.86E-11 6.06E-10</td>
</tr>
</tbody>
</table>

2.2 Oxygen Permeability Index Test

For the oxygen permeability test, specimens consist of a 70 ± 2 mm diameter, 30 ± 2 mm thick concrete discs acquired by coring concrete cubes perpendicular to the casting direction at the age of 28 days. 5 mm slices on either end of the core are cut off and discarded to avoid any wall effect. From the remaining core, two concrete discs of required thickness (30 ± 2 mm) are cut, one from each end, and the rest of the core discarded. A total of four specimens are needed.

Directly after cutting, the specimens were conditioned by placing in an oven at 50 ± 2°C for 7 days ± 4 hours. This was followed by cooling the specimens to 23 ± 2 °C in the desiccator for a period of 2 - 4 hours. Each specimen was then sealed into a falling head permeameter as shown in Figure 1. Details of the test method are given in UCT (2010).

The test permits evaluation of the D’Arcy coefficient of permeability. The oxygen permeability index (OPI) is expressed as the negative log of the average of the coefficients of permeability of the four specimens.

2.3 Test for Carbonation

The carbonation test was conducted on concrete prism of dimensions 100x100x200 mm. At the end of the curing period, the specimens were coated with epoxy except the two opposite faces perpendicular to the casting direction, and then exposed to the natural environment without any preconditioning. Two different exposure sites were selected: one in Cape Town (-33.958662, 18.460060) and the second one in Johannesburg (-26.192209, 28.029418). At each site, one set of sample is sheltered and the other exposed such that it can be wetted by rain.

Carbonation depth was measured using a 1% solution of Phenolphthalein applied on a freshly cut surface, depth readings being measured using a Vernier Calliper. A minimum of six readings were taken on each side and the depth of carbonation to obtain an average. The cut surface was then resealed with epoxy and allowed to dry for a day inside the lab, and thereafter returned to their respective location and the process was repeated.
3. CARBONATION MODELLING

The rate of carbonation is governed mainly by the diffusion of CO₂ from the atmosphere through the pore system in concrete; hence Fick’s first law of diffusion can be applied to model carbonation with the depth of carbonation being related to time as per Kropp [7] as follows:

\[
\sqrt{\frac{2Dc}{a}} \times \sqrt{t}
\]

Where \(x\) is the depth of carbonation (mm); \(c\) is the ambient carbon dioxide concentration (mol/m³); \(a\) is the amount of carbonatable material in the concrete matrix (mol/m³), \(t\) is the effective time of carbonation over the service life of the concrete (days); \(D\) is the effective diffusion coefficient (mm/days).

In the derivation of the above relation, Kropp (1995) made the following assumptions: the diffusion coefficient is taken as a constant [7]; the carbonation depth is given by a reaction front which separates the carbonated and non-carbonated zone (whereas in reality there exist a transition zone where the carbonatable materials are partially carbonated [8-9]); and the amount of carbonatable material is considered to be constant throughout the concrete matrix.

3.1 Carbonatable Material

Most carbonation models estimate the amount of carbonatable material as a function of total molar concentration of calcium oxide in cement and the degree of cement hydration [10-11]. Steffens et al. [2] considered the concentration of calcium hydroxide (CH) as the total carbonatable material considering that the carbonation reaction of other compounds such as calcium silicate hydrate (C-S-H) does not contribute to the reduction of pH. A similar approach was adopted by Thiery et al. [9] and Salvoldi [6]. The method used for the calculation of CH by Salvoldi [6] is adopted in the present work and is as follows.

\[
\text{CH} = 1.5[C_3S]F_{C_3S} + 0.5[C_2S]F_{C_2S} - 4[C_4AF]F_{C_4AF} + [C_3A]F_{C_3A} + [C_{SH_2}] + [C]P_{C} - 1.5[S]P_{S} - 4[A]P_{A}
\]

Where [i] indicates the molar concentration (mol/m³), \(F_i\) indicates the degree of hydration and \(P_i\) indicates the degree of pozzolanic activity of the species i.

3.2 Diffusion Coefficient

Diffusion is the driving mechanism which controls the rate of carbonation. Diffusion coefficient is a material property whose experimental measurement is usually difficult and hence in most of the models, it is expressed in terms of porosity [9,11]. However, this is not always the best approach as the same porosity can be associated with different carbonation rates [13]. Permeability is another transport mechanism which is driven by pressure head and can be relatively easily measured both on site and in the laboratory. In South Africa, the OPI test is used to measure the permeability coefficient of concrete. The permeability coefficient and the diffusion coefficient can be related to each other as the flow process take place in the same pore system with similar moisture conditions, as shown below [14]

\[
D_c = m k^n
\]
where, $D_c$ is the diffusion coefficient, $k$ is the permeability coefficient, $m$ and $n$ are empirical constants.

Carbonation is a reaction-diffusion process and the relative humidity (RH) is a key parameter in carbonation. The most favourable exposure condition for carbonation is between 50 to 70% relative humidity. At higher RH conditions the CO$_2$ cannot diffuse into the concrete as the pores are filled with condensed water, and at low RH conditions there is insufficient water in the pores for the carbonation reaction to take place [1]. Taking into account the influence of relative humidity on carbonation, Salvoldi proposed a humidity factor ‘$H_s$’ [6], which is a function of RH as shown in equation 4 and is adopted in the present study.

$$H_s = 23.32 \left(1-\frac{[\text{RH}]/100}{100}\right)^2 \left(\frac{[\text{RH}]/100}{100}\right)^{2.6}$$  \hspace{1cm} (4)

The OPI test is carried on dry concrete specimens and hence the diffusion coefficient $D_c$ calculated using equation 3 will be the dry diffusion coefficient. The effective diffusion coefficient ‘$D$’ in equation 1 for a given RH will therefore be a function of $D_c$ and $H_s$ as shown in equation 5

$$D = m k^n H_s$$  \hspace{1cm} (5)

where, $m$=126 and $n$= 0.96 are empirical factors which were calibrated in this work, based on the data of the OPI test and natural carbonation test results on PC and FA samples as shown in Figure 3.

3.3 Time of Exposure

The process of carbonation ceases when the concrete is saturated with water, and hence the wetting period is not taken into account in the time of carbonation. This mainly happens in the case of concrete exposed to rain. fib-Model Code [15] defines the ‘time of wetness’ ($t_w$) as the number of days with rainfall above 2.5 mm. The effective time of carbonation ‘$t$’ in equation 1 is then given by:

$$t = t_e - t_w$$  \hspace{1cm} (6)

where, $t_e$ is the total exposure time and $t_w$ is the time of wetness. When the concrete is sheltered from rain, $t_w = 0$ and hence the effective time of carbonation is equal to the total exposure time.

4. RESULTS AND DISCUSSIONS

4.1 Oxygen Permeability Index

The OPI test results of the concrete mixes after 28 days curing is shown in Figure 2. (The OPI values are the negative logarithm of the k values in Table 1). All mixes with Curing –A show higher OPI values (which imply lower permeability) than mixes with Curing –B. This can be attributed to the denser microstructure development for water cured concrete. The test results also reflect the influence of w/b; the OPI values decrease as the w/b increases. Such an effect is expected since increase in w/b makes the concrete more permeable thereby reducing the OPI value. Similar conclusions to the above were also reported in literature [16]. Figure 2 also shows that the fly ash mixes are more sensitive to curing than the PC mixes.
4.2 Natural Carbonation and Model Validation

The carbonation test results of samples exposed to natural environment, exposed and sheltered from rain in Cape Town and Johannesburg, are shown in Figures 4 (a) & (b) respectively.

In general the result shows that the carbonation is lower for samples which are exposed to rain. This can be attributed to the resistance to CO₂ diffusion caused by the pore saturation due to rain. Similar experimental results are also reported in literature (e.g., [8]). Curing also has a profound influence on the rate of carbonation, as can be observed from Figures 4 (a) & (b), with samples with Curing –A showing better carbonation resistance for the same w/b. Such a trend is due to the dense microstructure achieved through water curing as reflected in the OPI test results discussed earlier. Similarly the increase in w/b gives a decrease in the carbonation resistance which can be related to the variation in the microstructure. For the same w/b fly ash concrete shows an increase in carbonation [17]; confirmed by the results in Figures 4 (a) & (b). Such an effect is due to the reduction in the carbonatable material and to an extent due to the poor microstructure.
The carbonation model developed as shown in equation 1 was validated using the present experimental results, as shown in Figures 5 (a) & (b) respectively.

![Figure 5: Depth of carbonation: Prediction model vs. experimental results for (a) samples sheltered from rain (b) samples exposed to rain.](image)

The model seems to be able to predict carbonation depth of samples which are sheltered from rain with more precision than exposed ones. Though the model takes into account the influence of rainfall as per equation 6, it overestimates the carbonation depth. Hence it is necessary to consider the effect of drying and wetting cycles. This can probably be related to the fact that, although the wetting period is accounted for, the model does not take into consideration the time required for the concrete to dry, after a wetting period, to the depth of previous carbonation, since there will be no carbonation till the concrete is ‘dry’ at the carbonation front. Hence an approach followed by Thiery et al. in calculating the time of drying along with the time of wetting concept needs to be adopted (since the approach based on RH alone will not distinguish between samples exposed to and sheltered from rain) [18]. This is the subject of on-going study.

5. CONCLUSIONS
   
   - The South African OPI test reflects relevant concrete material properties and hence can be used as a powerful tool for performance-based service life design of reinforced concrete structures.
   
   - The model developed in the present work gives a good estimation of the carbonation depth of samples sheltered from rain, whereas it overestimates the carbonation depth for samples exposed to rain. The influence of drying-wetting cycles needs to be considered and the current model updated in on-going research so as to better predict carbonation depth.

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