EFFECT OF CRACKS ON ALKALINITY LEVEL OF CONCRETE STRUCTURES EXPOSED TO CARBON DIOXIDE ENVIRONMENT CONDITION

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ABSTRACT:
Reduction of alkalinity of concrete due to the diffusivity of carbon dioxide (CO₂) and concrete carbonation is one of the major issues influencing the durability of reinforced concrete structures. Most of the previous studies have concentrated on the un-cracked / unloaded concrete although it has been acknowledged that structural cracks in concrete have an impact on the CO₂ diffusivity and carbonation - induced reinforcement corrosion as well as service life of concrete structures. Hence, this article aims to investigate the effect of cracks (produced by loading) in concrete exposed to the CO₂ environment condition, on the alkalinity level (apparent pH) and carbonation depth in concrete. Accelerated environmental test programme has been used on concrete prisms with four different crack widths. The depth of carbonation (DoC), apparent pH, and consumption of alkalinity (OH⁻) is investigated in accordance with the BS EN13295:2004 [1] and the method proposed by McPolin et al. [2]. The influence of replacing ordinary Portland cement (OPC) by pulverized fuel ash (PFA) and ground granulated blast furnace slag (GGBS) on the CO₂ diffusivity in cracked concrete, is also analyzed and presented in this paper. The results have shown a strong relationship between DoC and the alkalinity level (consumed OH⁻) and pH of concrete structures. There is a considerable impact of crack width on the reduction in concrete alkalinity. The results also demonstrate a significant increase in consumption of OH⁻ and reduction in pH owing to the addition of supplementary materials in the samples.

Keywords: Carbonation, Phenolphthalein indicator, pH and consumed of OH⁻ and Crack width.

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INTRODUCTION

Carbonation is the chemical reaction between carbonic acid (H$_2$CO$_3$), resulting from a combination of atmospheric carbon dioxide (CO$_2$) with water, and calcium ion (Ca$^{2+}$) from dissolution of hydrated cement products such as calcium hydroxyl Ca(OH)$_2$, calcium silicate hydrates (C-S-H) and calcium aluminates hydrates (C-A-H). This reaction results in the formation of calcium carbonate (CaCO$_3$), as shown in Equations 1 to 4 [3,4].

\[
\begin{align*}
\text{CO}_2(gas) + H_2O & = H_2CO_3(aq) \quad (1) \\
\text{Ca(OH)}_2 + H_2CO_3(aq) & = Ca_2CO_3 + H_2O \quad (2) \\
3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{CO}_3(aq) & = 3\text{CaCO}_3 + 2\text{SiO}_2 + 3\text{H}_2\text{O} \quad (3) \\
4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O} + 3\text{H}_2\text{CO}_3(aq) & = 4\text{CaCO}_3 + 2\text{Al(OH)}_3 + 10\text{H}_2\text{O} \quad (4)
\end{align*}
\]

The durability of concrete structures is controlled by their capacity to delay ion and fluid transport inside concrete. The transport properties of concrete are represented through permeability of concrete, which is likely to be significantly affected by the formation of cracks. Cracks in concrete structures are common due to its weakness in tension. Cracks maybe either non-structural or structural. Structural cracks have a tendency to be wider (> 0.1 mm), while, non-structural cracks are commonly finer.

Structural cracks, or cracks due to stress, are typically produced due to excessive loading, low strength of concrete, inadequate reinforcement, impact loading, or movement of foundations, or a combination of these factors. On the other hand, non-structural cracks may occur due to plastic shrinkage, early-age thermal shrinkage, drying shrinkage and external chemical attack or carbonation shrinkage [3]. The carbon dioxide penetration and reaction with hydrated cement-based products often leads to carbonation shrinkage in concrete structures. It is a physio-chemical change in concrete that causes increment in weight and shrinking in volume (increment in density). This type of shrinkage is likely to generate shallow cracks on the concrete surface [5].

The cracks in concrete influence the diffusivity of aggressive species affecting durability. However, current modelling methods for durability assessment often exclude the effect of cracks, voids and defects in concrete, such as corrosion initiation, thereby reducing their effectiveness in predicting durability of concrete structures [6]. Therefore, it is important to study and consider how the presence of cracks may affect the rate of carbonation in concrete structures. Moreover, carbonation negatively affects the concrete alkalinity and reduces the pH of concrete pores solution from 13 to 9 [3], which is a considerable factor accelerating the chloride penetration as well as the corrosion of reinforced concrete structures [7,8].

Some studies have examined diffusion of deleterious substances through cracked concrete [9,10]. All of these studies have concluded that cracks increase the total molar flux of gases/fluids through concrete. However, there is no agreement on how to model the movement of the carbonation front in cracked concrete.

The concept of effective diffusion of CO$_2$ or carbonation front based on the penetration of CO$_2$ through un-cracked and cracked concrete is proposed in this study. The CO$_2$ first penetrates the cracks within concrete, and then diffuses outwards into the sound un-cracked concrete perpendicular to the face of cracked surface. The focus of this paper is to examine the effect of size of cracks in reinforced concrete samples on the penetration depth of carbonation and the alkalinity level in concrete. The impact of replacing OPC cement by PFA and GGBS on the DoC in cracked concrete has also been investigated.
EXPERIMENTAL WORK

Materials and Concrete Mix Design

Portland Limestone cement (CEM II/A-LL 32.5R) with specific gravity of 3.05 was used in this project. Chemical and physical properties of the cement are according to the BS EN 197-1:2011 [11]. GGBS used in this study was produced by Hanson Cement, satisfying the chemical and physical property requirements of BS EN 15167-1:2006 [12]. PFA was obtained from CEMEX UK, satisfying the requirements of BS EN 450-1:2012 [13]. Natural sand (particle size < 5mm) was used, and coarse aggregate was crushed gravel with size range of 5-14 mm. The grain size analysis, chloride and sulphate content satisfy BS 882:1983 [14].

Building Research Establishment (BRE) method [15] was employed to design the mixes used in this study as shown in Table 1. Different water to binder ratios, and GGBS and PFA were used as supplementary cementitious materials, to investigate their effect on DoC.

Table 1: Concrete mixes design using BRE (1988) [15]

<table>
<thead>
<tr>
<th>Mix symbol</th>
<th>w/(c+b)</th>
<th>Cementitious materials kg/m³</th>
<th>Water kg/m³</th>
<th>Sand kg/m³</th>
<th>Gravel kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cement</td>
<td>PFA</td>
<td>GGBS</td>
<td></td>
</tr>
<tr>
<td>M 0.4</td>
<td>0.4</td>
<td>513</td>
<td>-</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td>M 0.5</td>
<td>0.5</td>
<td>410</td>
<td>-</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td>M 0.6</td>
<td>0.6</td>
<td>350</td>
<td>-</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td>M 0.5 + 0.35 PFA</td>
<td>0.5</td>
<td>266</td>
<td>144</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td>M 0.5 + 0.30 GGBS</td>
<td>0.5</td>
<td>287</td>
<td>-</td>
<td>123</td>
<td>205</td>
</tr>
</tbody>
</table>

Specimen Geometry

Three cube specimens, 100mm were cast to establish the compressive strength of concrete and porosity measurements. Reinforced concrete prisms of 100 x 100 x 500 mm were casted to measure the DoC in cracked specimen. Deformed steel (B500A) bars (8mm diameter) at a cover depth of 2cm was used to reinforce the concrete prisms to achieve the controlled crack sizes within the samples. The method of filling and preparation of moulds, compaction and levelling the surface of concrete, curing and transporting of samples were according to BS EN 12390-2:2009 [16]. Samples were cast in two layers. Each layer was vibrated using an electrical vibrating device to achieve the homogenous concrete and avoid the segregation of concrete. The specimens were demoulded and cured using tap water until the time of testing, or exposure to CO₂ environment condition at the age of 28 days.

Specimen Conditioning

The main objective of the study is to investigate the effect of the crack width on the DoC in concrete structures. Therefore, cracks of various sizes were produced in the concrete prisms, which were then exposed to accelerated carbonation environmental conditions. In this study, flexural method was used to induce the cracks in concrete samples as shown in Figure 1. Four different crack width ranges, (0, 0.05-0.15mm, 0.15-0.25mm and 0.25-0.35mm) were achieved in the concrete prisms.
The crack width was measured by microscope meter with accuracy 0.01 mm. The crack depth, $D_{\text{crack}}$, was computed by measuring the time of pulse transfer using the ultrasonic pulse velocity device according to the Eq.5 [17]. Figures 2 and 3 illustrate the methods for crack width and crack depth measurement respectively.

$$D_{\text{crack}} = x \sqrt{\frac{T_c^2}{T_s^2} - 1} \quad (5)$$

where: $x$ is specific distance, $T_c$ is the transfer time through cracked concrete distance ($x$) and $T_s$ is transfer time through sound concrete distance ($x$).

In this study, the one face of the specimens was exposed to accelerated environment conditions (by sealing all other faces using isolated materials) in carbon dioxide incubator oven with CO$_2$ concentration of 5%, temperature of 35 ºC and relative humidity of 65%, for 8 weeks [18].

**Testing Methodologies**

Porosity and compressive strength test were performed on 100mm cube specimen in accordance with ASTM C642:2013 [19] and BS EN 12390-3:2000 [20] respectively. The test procedure given in BS EN13295:2004 [1] was used to determine the DoC using phenolphthalein indicator on the conditioned prism samples.

The conditioned samples were split open into two parts as designated by Al-Amoudi *et al.* [21]. The first part was sprayed by phenolphthalein solution with one gram of phenolphthalein powder dissolved into a solution of 70 ml and 30 ml of ethanol and deionized water respectively according to CEN/TS 12390-10:2007 [22] to establish the DoC. The second part of sample was drilled (at the crack location) in order to collect concrete powder samples at eight different depths form the exposed surface, namely 0-6 mm, 6-12 mm, 12-18 mm, 18-24
mm, 24-30 mm, 30-36 mm, 36-42 mm and 42-48 mm using drying drilling equipment. The powder was sieved by a 150 micro-meter sieve to reduce the amount of coarse grain particles resulted from aggregate, then dried in oven at 50°C for 24 hours, and kept in sealed plastic bags till tested.

Apparent pH of concrete was measured by dissolving 1g of the concrete powder in deionized water. This mixture (powder and water) was rotated about 30 second and stood about 24 hours [2,23]. Then, the apparent pH of concrete was measured using pH meter according to BS EN ISO 10523:2012 [24]. The apparent pH can be used to compute the concentration of $[OH^-]$ for carbonated and uncarbonated sample (control) using Equation 6 [25,26].

$$pH = 14 - \log \log[OH^-]$$

(6)

Method proposed in [2,23] was used to establish the consume of $[OH^-]$ (mole/kg of concrete) due to carbonation to uncarbonated powder. A typical profile of consumed $[OH^-]$ ions concentration with the depth of concrete is shown in Figure 4. This profile can be divided into three zones based on the consumption of $[OH^-]$ ions: fully carbonated, partially carbonated and non-carbonated zone. Where, $X_p$ is the boundary between full carbonated and partially carbonated zone, and $X_f$ is the boundary between partially carbonated and non-carbonated zone (indicating the carbonation front).

![Figure 4 Analysis of the profile of consumed OH⁻ [23]](image)

RESULTS AND DISCUSSION OF TESTS

In this section, the results of the experimental work are presented and discussed. These results are mainly focused on three aspects; the impact of water to cement ratio (representing strength of concrete), crack width, and supplementary cement materials on DoC by two methods. The Carbonation depth, DoC, is a measure of diffusivity of carbon dioxide in concrete and reduction of alkalinity of pore water solution in concrete.

Carbonation Depth in Concrete Using Phenolphthalein Indicator

The carbonation depths as a function of crack widths for the mixes used in this study are presented in Figures 5 and 6. The results illustrate that the penetration of CO₂ from the exposed surface, reacts to form CaCO₃, increases significantly with the increase in w/c ratio in concrete.
samples as shown in Figure 7. And the DoC is grown considerably with increasing crack width in concrete samples as shown in Figure 8. The percentage increases in DoC for samples having a crack with respect to the control concrete samples are presented in the Table 2.

![Figure 2 Effect of w/c on Carbonation depth](image1)

![Figure 3 Effect supplementary cementitious material on Carbonation depth](image2)

On the other hand, partial replacement of OPC cement with the supplementary cementitious materials (PFA and GGBS) increases the DoC when compared to concrete samples without any replacement (Figure 6).

Table 2. Percentage increase in carbonation depth for cracked samples with respect to uncracked samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Increase in carbonation depth (%) in samples with crack width of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05 -0.15 mm</td>
</tr>
<tr>
<td>M 0.4</td>
<td>167</td>
</tr>
<tr>
<td>M 0.5</td>
<td>100</td>
</tr>
<tr>
<td>M 0.6</td>
<td>92</td>
</tr>
<tr>
<td>M 0.5 + 30% GGBS</td>
<td>109</td>
</tr>
<tr>
<td>M 0.5 + 35% PFA</td>
<td>114</td>
</tr>
</tbody>
</table>

The increase in DoC in the control concrete samples (i.e. uncracked samples) with the increase in the w/c ratio can be attributed to the increase in porosity of the concrete (as can be seen in Table 3) since the volume of permeable voids assist the CO₂ to penetrate relatively deeper inside the exposed surface. Furthermore, the fundamental influence controlling carbonation rate is the diffusivity of the hardened cement paste, which is a function of the pore system of the hardened cement paste during the period when the diffusion of CO₂ takes place [3].

![Images 1 to 6](image3)
The increase of crack width was found to be an important factor for the CO₂ penetration in concrete samples [27]. The increase in w/c ratio leads also to the decrease in compressive strength of concrete and the rate of carbonation is inversely proportional to the strength [28]. The porosity and compressive strength of concrete significantly impacts the DoC as shown in Table 3. A relationship between the DoC, compressive strength ($f_{cu}$), and porosity ($\varepsilon$) is established using non-linear regression analysis and is shown in Equation 7.

$$DoC = 0.021232 \times \varepsilon^{0.198} \exp(-0.0284f_{cu})$$  \hspace{1cm} (7)

<table>
<thead>
<tr>
<th>Sample</th>
<th>w/(c+b)</th>
<th>Carbonation depth (mm)</th>
<th>Compressive strength ($f_{cu}$, MPa)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 0.4</td>
<td>0.4</td>
<td>8</td>
<td>53.2</td>
<td>10.1</td>
</tr>
<tr>
<td>M 0.5</td>
<td>0.5</td>
<td>11.5</td>
<td>48.1</td>
<td>11.1</td>
</tr>
<tr>
<td>M 0.6</td>
<td>0.6</td>
<td>15</td>
<td>39.7</td>
<td>11.5</td>
</tr>
<tr>
<td>M 0.5+ GGBS</td>
<td>0.5</td>
<td>12</td>
<td>47.2</td>
<td>10.1</td>
</tr>
<tr>
<td>M 0.5+ PFA</td>
<td>0.5</td>
<td>20</td>
<td>31.6</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Ca(OH)$_2$ is the main source of the alkalinity of pore water solution [29] as measured using the phenolphthalein indicator. This rate of carbonation is controlled by the availability of Ca(OH)$_2$ within the pore water solution. The mixes incorporating supplementary cementitious materials utilised the Ca(OH)$_2$ to form secondary hydration product, but in return reduces the quantity of Ca(OH)$_2$ [30]. This can explain an increase in the DoC in samples with PFA and GGBS, as was also observed in [31].

**Carbonation depth by apparent pH and consumed OH⁻ ion method**

The formation of CaCO$_3$ and CaMg(CO$_3$)$_2$ in concrete sample and consumption of Ca(OH)$_2$, are significantly influenced by the pH of pore water in concrete, where pH can reduce
to 9 at the full carbonated samples. The results of measured apparent pH of the concrete powder samples are presented in Figure 9 (a, b, c, d and e).

The results clearly depict the reduction in apparent pH value near the exposed surface for all samples but rises to over 12 at a depth of about 50mm. This can be used as (control sample) to establish the consume $[\text{OH}^-]$ and the carbonation front. It is also worth noting that for the cracked samples, the apparent pH value converges to the value of uncracked samples at a depth of about 50mm, which relates to the depth of cracks within the samples. The results also illustrate the effect of supplementary cementitious materials on pH level in pore water solution of concrete, where the replacing cement by these material leads to reduction in the pH values.

The main reason of reduction in the pH is due to the reaction of the $\text{CO}_3^{2-}$ and consumption the major contribution of alkalinity in concrete, $\text{Ca(OH)}_2$, as well as C-S-H and formation CaCO$_3$ [3,7]. The consumed OH$^-$ values (mol/kg) due to carbonation process for all
samples are illustrated in Figure 10. Where, X_p is the boundary between the full carbonated and partially carbonated zone, and X_f is the boundary between partially carbonated and no-carbonated zones (that indicates the carbonation front). At the carbonation front, X_f, the OH^- is at the verge to react with CO_3^{2-} dissolved in pore water solution to form CaCO_3.

![Figure 6 Analysis of the profile of consumed OH^- for concrete sample exposure](image)

The depth of X_p and X_f are summarized in Table 4. The results of consumed OH^- shows a significant influence of w/c ratio, crack width and supplementary cementitious materials on consumption of OH^- and reduce the alkalinity level in concrete. The increase in w/c ratio lead to increase of consumption of OH^- and increase the depth of carbonation front.

The results also indicates the carbonation front measured in the cracked specimen is always deeper than the carbonation front obtained in un-cracked specimens for all mixes. The reduction in pH level (and increase in the consumed OH^- ) with increase in w/b ratio and replacement of supplementary cementitious materials can be attributed to increased porosity and decrease the compressive strength (as previous discussed in relation to data presented in Table 3). Hence, the reduction in apparent pH (and increase the consumption OH^-) in samples with PFA and GGBS are higher than OPC based concrete samples.
Finally, the reduction in alkalinity level of concrete surrounding the rebars was observed in cracked concrete since the crack opening initially helps to transport the CO\textsubscript{2} deeper inside exposed surface at the crack locations from where the CO\textsubscript{2} diffuses inside the cracked surface \cite{27} orthogonal to the surface of cracks as can be seen in Figure 8.

Table 4. Carbonation depth and front according to intensities of XRD for samples

<table>
<thead>
<tr>
<th>Crack width</th>
<th>DoC (X\textsubscript{p}) ; Carbonation front (X\textsubscript{f}) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncracked</td>
</tr>
<tr>
<td>Sample</td>
<td>X\textsubscript{p}</td>
</tr>
<tr>
<td>M 0.4</td>
<td>6</td>
</tr>
<tr>
<td>M 0.5</td>
<td>10</td>
</tr>
<tr>
<td>M 0.6</td>
<td>12</td>
</tr>
<tr>
<td>M 0.5+GGBS</td>
<td>11</td>
</tr>
<tr>
<td>M 0.5+PFA</td>
<td>14</td>
</tr>
</tbody>
</table>

CONCLUSION

The influence of cracks caused by loading on the DoC was investigated in this study. Concrete samples were subjected to an accelerated environment test programme. DoC (X\textsubscript{p} and X\textsubscript{f}) has been obtained using Phenolphthalein Indicator, whilst the carbonation front has been obtained through apparent pH and consumed OH\textsuperscript{-} technique. The effect of partially replacing OPC cement by the PFA and GGBS on the carbonation depth in cracked concrete was also investigated. The following conclusions can be drawn from the results:

1- The crack width significantly increases the DoC and reduce alkalinity of concrete by consuming the OH\textsuperscript{-} ions, and reduces the pH level for all mixes used in the study.

2- DoC in the vicinity of the cracks are considerably higher due to relatively faster penetration of CO\textsubscript{2} into the crack followed by orthogonal outward diffusion into the un-cracked concrete surrounding the crack.

3- Results from the apparent pH and consumed OH\textsuperscript{-} technique helps in identifying areas of fully carbonated and un-carbonated concrete in greater detail including the partially carbonated zones.

4- The type of binding materials have vital role on the carbonation penetration depth, whereby the replacement of OPC cement by supplementary cementitious materials such as PFA and GGBS have significant increase in the DoC and reduce pH level and consumed alkalinity compounds in concrete.

5- The DoC, X\textsubscript{p} and front X\textsubscript{f} are influenced by the material behaviours such as porosity, compressive strength and due to their impact of diffusivity of CO\textsubscript{2}.

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