Influence of cracks on the carbonation resistance of concrete structures

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ABSTRACT

Carbonation-induced corrosion of steel rebar embedded in concrete is one of the major issues influencing durability of reinforced concrete structures. It has been acknowledged that structural cracks in concrete influence the carbon dioxide (CO₂) diffusivity and accelerates the carbonation-induced reinforcement corrosion, however most of the previous studies on the carbonation induced corrosion have concentrated on the un-cracked / unloaded concrete. This study investigates the impact of cracks caused by loading on the depth of carbonation into concrete. Concrete prisms (100x100x500 mm) were subjected to four different crack widths (0, 0.05-0.15 mm, 0.15-0.25 mm and 0.25-0.35 mm) and the carbonation depth was determined using an accelerated environment test programme based on the CEN/TS 12390-10:2007 and XRD analysis. The impact of replacing OPC cement by pulverized fuel ash (PFA) and ground granulated blast furnace slag (GGBS) on the carbonation depth in cracked concrete was also investigated. The results show a considerable influence of crack width on the depth of carbonation and the X-ray powder diffraction analysis (XRD) confirms these results. The penetration of carbon dioxide and accumulation of carbonation compound (CaCO₃) were found to be concentrated at crack locations, whereas the carbonation depths at other locations were found to be less than the carbonation depth in un-cracked concrete. The results also demonstrate a significant increase in the penetration of carbonation due to the addition of supplementary materials in the samples when compared to the reference mixes.

Keywords: Carbonation, Deterioration, XRD analysis and Cracked concrete.

INTRODUCTION

Carbonation is the chemical reaction between carbonic acid (H₂CO₃), resulting from a combination of atmospheric carbon dioxide (CO₂) with water, and calcium ion (Ca²⁺) 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 results in the formation of calcium carbonate (CaCO₃), as shown in Eqs. 1 to 4 (Neville, 2011; Tarun and Rakesh, 2010).

\[
\begin{align*}
\text{CO}_2(gas) + H_2O &= H_2CO_3(aq) \quad (1) \\
Ca(OH)_2 + H_2CO_3 &= Ca_2CO_3 + H_2O \quad (2) \\
3CaO.2SiO_2.3H_2O + 3H_2CO_3 &= 3CaCO_3 + 2SiO_2 + 3H_2O \quad (3) \\
4CaO.Al_2O_3.13H_2O + 3H_2CO_3 &= 4CaCO_3 + 2Al(OH)_3 + 10H_2O \quad (4)
\end{align*}
\]

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 predictable in reinforced concrete members due to the weakness of tension capacity in concrete. Cracks maybe either non-structural or structural. 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 cracks, early-age thermal shrinkage, drying shrinkage and external chemical attack or carbonation shrinkage (Neville, 2011). The carbon dioxide penetration and reaction with hydrated cement-based products often leads to carbonation.
shrinkage in concrete structures. It is a physiochemical 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 (Neville and Brooks, 2010).

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 (Pacheco and Polder, 2010). 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 (Neville, 2011), which is a considerable factor accelerating the chloride penetration as well as the corrosion of reinforced concrete structures (Dyer, 2014; Broomfield, 2007).

Some studies have examined diffusion of deleterious substances through cracked concrete (Song et al., 2006 and Jang et al., 2011). 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 CO₂ or carbonation front based on the penetration of CO₂ through un-cracked and cracked concrete is proposed in this study. The CO₂ first penetrates the cracks within concrete, and then diffuses outwards into the sound un-cracked concrete in all directions. The focus of this paper is to examine the effect of size of cracks in reinforced concrete samples on the penetration depth of carbonation. The impact of replacing OPC cement by pulverized fly ash (PFA) and ground granulated blast furnace slag (GGBS) on the carbonation depth in cracked concrete has also been investigated.

**EXPERIMENTAL WORK**

**Materials**

Portland Limestone cement (CEM II/A-LL 32,5R) was used in this project which has specific gravity of 3.05. Chemical and physical properties of the cement satisfies the BS EN 197-part 1: 2011. Ground granulated blast furnace slag (GGBS) used in this study was produced by Hanson Cement, that satisfies the chemical and physical property requirements of BS EN 15167-part 1: 2006. Pulverized fuel ash (PFA) was obtained from CEMEX UK, that satisfies the requirements of BS EN 450-part 1: 2012.

Natural sand was used and coarse aggregate was crushed gravel with size range of 5-14 mm. The grain size analysis, chloride and sulphate content satisfies BS 882:1983. Deformed or ribbed steel (B500A) (8mm) used to reinforce the concrete prisms to achieve the crack in samples and investigate the corrosion condition. Mechanical properties of steel are compliance with BS 4449:2005+A2:2009.

**Concrete Mix Designs**

In order to achieve various properties of concrete, different water to cement ratio and different cementitious materials such as ground granulated blast furnace slag (GGBS) and pulverized fly ash (PFA) were used. The GGBS and PFA have the ability to change micro-structure and strength of concrete (Neville, 2011). Building Research Establishment method was employed to design the mixes used in this study as shown in Table 1. Mixing method is important to obtain the required workability and homogeneity of concrete mix by mechanical mixing.

Flexural method was used to induce the cracks, reinforced concrete prisms were used by fixing reinforcement in moulds with concrete cover 2 cm. 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 in a sink filled up with tap water until the time of testing or exposure to CO₂ environment condition at the age of 28 days.

Finally, 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 part-2:2009.

**METHODOLOGY**

The main objective of the study is to investigate the effect of the crack width on the carbonation in concrete structures. Therefore, cracked concrete prisms were designed and exposed to these parameters of carbonation environment. In this case, flexural method was employed to induce the cracks in concrete samples as shown in Fig.1. Four different crack width ranges, (0, 0.05-0.15mm, 0.15-0.25mm and 0.25-0.35mm) were applied to 100*100*500 mm concrete prisms.

**Fig.1. Flexural method was used to create the crack in concrete sample**
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 transfer of pulse velocity using the ultrasonic device according to the Eq.5 (Al-Samaraai & Raouf -1999).

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

Fig. 2 and 3 are illustrated the methods for crack width and crack depth measurement respectively.

In this study, the specimens were exposed to accelerated environment conditions in carbon dioxide incubator. In particular, the surface of prisms was exposed to environment with CO$_2$ concentration of 5%, temperature of 45°C and relative humidity of 65% for 8 weeks. These samples were split into two parts using compression testing machine as designated by Al-Amoudi et al. (1991). The first part was sprayed using 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) to indicate the carbonation depth. Whilst, the second face of sample was drilled at the crack location in order to collect a concrete powder at different depth to find peak intensities for Ca(OH)$_2$ and CaCO$_3$ using XRD. Three samples were tested for every case, and average values are reported in this paper.

The concrete powder was collected from the exposed face at eight depth intervals; 0-6 mm, 6-12 mm, 12-18 mm, 18-24 mm, 24-30 mm, 30-36 mm and 36-42 mm and non-carbonation sample powder at depth 42-48 mm, using dry drilling equipment. The concrete powder was filtered using 150 micro meter sieve to reduce the amount of coarse grains resulted from the aggregate, then dried in oven at 50°C for 24 hours, and then kept in sealed plastic bags till tested.

### TESTS FOR CONCRETE SAMPLES

The compressive strength, ultra-sonic pulse velocity test, porosity and carbonation depth test by phenolphthalein indicator and XRD method are carried out for concrete under investigation. The porosity and compressive strength test were performed in accordance with ASTM C642:2013 and BS EN 12390, part 3:2000 respectively. The test procedure given in CEN/TS 12390-10:2007 was used to determine the carbonation depth by phenolphthalein indicator. Method proposed by Chang and Chen (2006) to measure the change in intensity of peaks for Ca(OH)$_2$ and CaCO$_3$ by XRD due to carbonation action is used on concrete powder samples.

### RESULTS AND DISCUSSION

In this section, the results of the experimental work are presented and discussed. These results and
their discussions are mainly focused on three aspects; the impact of water to cement ratio (representing strength of concrete), crack width, and supplementary cement materials on carbonation depth.

**Carbonation Depth in Concrete Test**

The Carbonation depth is a measure of diffusivity of carbon dioxide in concrete and reduction of alkalinity of pore water solution in concrete.

**Carbonation Depth by Phenolphthalein Indicator**

The carbonation depths as a function of crack widths for the mixes used in this study are presented in Figs. 4, 7 and 8. The results illustrate that the penetration of carbonation depth from the exposed surface increases significantly with the increase in crack width in concrete samples. The percentage increases in carbonation depth for samples having a crack with respect to the control concrete samples are presented in the Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Increase percentage in carbonation depth in samples with crack width (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05-0.15 mm</td>
</tr>
<tr>
<td>M 0.4</td>
<td>87</td>
</tr>
<tr>
<td>M 0.5</td>
<td>125</td>
</tr>
<tr>
<td>M 0.6</td>
<td>76</td>
</tr>
<tr>
<td>M 0.5 + GGBS</td>
<td>226</td>
</tr>
<tr>
<td>M 0.5 + PFA</td>
<td>54</td>
</tr>
</tbody>
</table>

The carbonation depth also increases with the increase in w/c ratio. The percentage increase in carbonation depth for mix with w/c 0.5 (M 0.5) and mix with w/c ratio 0.6 (M 0.6) in comparison to mix with w/c 0.4 (M 0.4) were (60%, 93%, 35% and 17%) and (127%, 114%, 43% and 31%) respectively for samples having crack width (0, 0.05-0.15mm, 0.15-0.25mm and 0.25-0.35mm).

The effect of compressive strength (which is a function of w/c ratio) on the carbonation depth is depicted in Fig. 8. The increase in carbonation depth for control concrete mixes with the increase in compressive strength is due to the increase in the volume of permeable voids that help CO₂ penetration. Furthermore, key factor 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 (Neville, 2011).

The rate of carbonation is inversely proportional to the strength for concrete without supplementary materials (Roy et al., 1999). The porosity and compressive strength of concrete have significant impact on carbonation depth as shown in Fig. 8 and 9. From these figures, a relationship is proposed between the carbonation depth in concrete vs the compressive strength and porosity (also shown in Eq. 6 and 7);

\[
x = -31.6 \ln f_{cu} + 133.7 \quad R^2 = 0.98 \quad (6)
\]

\[
x = 0.034e^{0.535\varepsilon} \quad R^2 = 0.97 \quad (7)
\]

where: \( x \) = carbonation depth in mm; \( f_{cu} \) = compressive strength in MPa and \( \varepsilon \) = porosity in %.

![Fig. 5. Effect of compressive strength on carbonation depth for sample exposure to (CO2= 5%, RH=65% and T=45 °C)](image-url)
The results also show that the carbonation depth of these mixes is higher than the carbonation depth for mix without these materials. This can be linked to the reduction of Ca(OH)₂ that is consumed by the supplementary cementing material to produce C–H–S gel and CaCO₃ (Roy and Indorn, 1982) as shown by Eqs. 1 to 4. This reduction is accompanied by the reduction of pH, as picked up by phenolphthalein indicator used for these experiments. Hence, the carbonation depth in M 0.5+PFA is the highest due to more consumption of Ca(OH)₂ as can be seen by XRD analysis results in the next section.

Finally, it is observed from the results (Fig. 8a and Fig. 9a) that the carbonation depth within un-cracked areas of concrete (away from the discrete cracks) is considerably less than the carbonation depth in un-cracked control samples. This have not been reported in previous literature and the reasons for this are being investigated in detail.

### Table 3. Effect of compressive strength and porosity and carbonation depth for mixes used in study

<table>
<thead>
<tr>
<th>Sample</th>
<th>w/c</th>
<th>Comp. strength MPa</th>
<th>Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 0.4</td>
<td>0.4</td>
<td>7.5</td>
<td>53.2</td>
</tr>
<tr>
<td>M 0.5</td>
<td>0.5</td>
<td>12</td>
<td>48.1</td>
</tr>
<tr>
<td>M 0.6</td>
<td>0.6</td>
<td>17</td>
<td>39.7</td>
</tr>
<tr>
<td>M 0.5+ GGBS</td>
<td>0.5</td>
<td>15</td>
<td>47.2</td>
</tr>
<tr>
<td>M 0.5+ PFA</td>
<td>0.5</td>
<td>26</td>
<td>31.6</td>
</tr>
</tbody>
</table>

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Finally, it is observed from the results (Fig. 8a and Fig. 9a) that the carbonation depth within un-cracked areas of concrete (away from the discrete cracks) is considerably less than the carbonation depth in un-cracked control samples. This have not been reported in previous literature and the reasons for this are being investigated in detail.

![Fig. 6. Effect of porosity on carbonation depth for sample exposure to (CO₂= 5%, RH=65% and T=45 °C)](image)

![Fig. 7. Effect of crack width on carbonation depth for sample exposure to (CO₂= 5%, RH=65% and T=45 °C)](image)

### Fig. 8 Carbonation depth of mixes used in study
Finally, Fig. 10 illustrates the corrosion of rebars focused at the crack location. The cracks encourage deeper penetration of CO\textsubscript{2}, which reacts with calcium hydroxide in the hydrated cement matrix to form calcium carbonate and decreases the pH of concrete surrounding the rebars (Tarun and Rakesh, 2010). This also provides an easy path to transport moisture and oxygen hence accelerates corrosion at the crack locations.

**Carbonation Front by X-Ray Diffraction**

As mentioned previously, the carbonation process consumes the Ca(OH)\textsubscript{2} by converting to CaCO\textsubscript{3}. In order to identify the impact of CO\textsubscript{2} diffusivity on the change in mineralogical composition, X-ray diffraction analysis (XRD) was employed. The concrete powder was collected from the exposed face at seven depth depths. The results of control specimen and cracked concrete samples are shown in Fig. 11; some changes in relative intensities of crystalline phases (peaks) with depth of carbonated concrete have been detected. The change in peak intensity would be attributed either to a change in degree of crystallization of the specified phase and/or a change in its quantity. The noticeable change in mineralogical composition due to carbonation might have an impact on the physical and chemical properties of carbonated concrete (Dyer 2014). The relative intensity or main peaks of Ca(OH)\textsubscript{2} are noticed at angles of diffraction (2\theta) 18.1° and 34.1° (International Center for Diffraction Data, ICDD). It reduces or disappears as the degree of carbonation increases in the samples. On the other hand, the intensity of CaCO\textsubscript{3} phase for main peak can be detected at angle of diffraction (2\theta) 29.39°, which increases in the samples with the increase in carbonation depth.

The depth of carbonation is represented in literature using two distinct parameters, \(X_0\) and \(X_i\). The depth of carbonation, \(X_0\) relates to the depth where concrete is considered fully carbonated and the pH of pore water in concrete is about 9 (Neville, 2011). The depth of carbonation \(X_i\) relates to the depth beyond which concrete is yet unaffected by the carbonation. At this depth, the pH of pore water of concrete maintains an original pH of concrete, which is around 13. The zone between \(X_0\) and \(X_i\) can be considered partially carbonated with pH value varying between 9 and 13.
$X_p$ have been obtained from Fig. 4 and 5, using phenolphthalein indicator whereas $X_f$ can be taken as the point on the graphs of the relative intensity X-Ray Diffraction curve where the curve of for Ca(OH)$_2$ becomes horizontal (i.e. no further change in Ca(OH)$_2$ beyond this depth is expected). The $X_p$ and $X_f$ depth for concrete samples are presented in Fig. 12 and Table 4.

Both cracked and un-cracked samples are presented in Fig. 12 and Table 4. In most cases of un-cracked concrete samples, the carbonation front depth, $X_f$ is approximately twice of depth of fully carbonation depth, $X_p$, which confirms the results of Chang and Chen (2006). In cracked concrete samples, on the other hand, the above relation do not hold true and the difference between $X_p$ and $X_f$ is considerably smaller than the case of un-cracked concrete, which agrees with the results of Park (2008) for uncracked concrete samples.

![Fig. 11. Carbonation depth investigated by XRD. (a) Sample of 0.6-0.25 mm is taken from the surface (b) sample is taken from depth 40mm (un-carbonated), Q=Quartz, F= feldspar, CH=Ca(OH)$_2$.](image)

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

<table>
<thead>
<tr>
<th>Crack width</th>
<th>Carbonation depth and front (mm)</th>
<th>0</th>
<th>0.05-0.15 mm</th>
<th>0.15-0.25 mm</th>
<th>0.25-0.35 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>$X_p$</td>
<td>$X_f$</td>
<td>$X_p$</td>
<td>$X_f$</td>
<td>$X_p$</td>
</tr>
<tr>
<td>M 0.4</td>
<td>16</td>
<td>32</td>
<td>14</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>M 0.5</td>
<td>14</td>
<td>28</td>
<td>27</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>M 0.6</td>
<td>17</td>
<td>34</td>
<td>30</td>
<td>35</td>
<td>33</td>
</tr>
<tr>
<td>M 0.5+GGBS</td>
<td>15</td>
<td>30</td>
<td>31</td>
<td>38</td>
<td>36</td>
</tr>
<tr>
<td>M 0.5+PFA</td>
<td>20</td>
<td>40</td>
<td>40</td>
<td>45</td>
<td>47</td>
</tr>
</tbody>
</table>

**CONCLUSION**

This study investigates the effect of cracks caused by loading on the carbonation depth. Carbonation depth was determined using an accelerated environment test programme by Phenolphthalein Indicator and XRD analysis. Carbonation depth $X_p$ and $X_f$ depth has been determined by Phenolphthalein Indicator, while the carbonation front has been measured by XRD analysis. The effect of replacing OPC cement by (PFA) (GGBS) on the carbonation depth in cracked concrete was also investigated. The following conclusions can be drawn from the results.
**Fig. 12.** Relative intensity of XRD analysis for CaCO$_3$ and Ca(OH)$_2$ in concrete sample (un-cracked and cracked 0.25-0.35 mm) exposure to CO$_2$ for 8 weeks.
1- The crack width significantly increases the carbonation depth for all mixes used in the study.

2- Carbonation rates 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- XRD investigation made it possible to gain better understanding of the mineral-structural changes induced due to exposure to CO\textsubscript{2} environment. Results from the XRD investigation also 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 has vital role on carbonation depth, whereby the replacement of OPC by supplementary cementing materials such as PFA and GGBS have significant increase in the penetration of carbonation in concrete.

5- The carbonation depths, $X_0$ and front $X_f$, are affected by the material behaviours such as porosity, compressive strength and due to impact of diffusivity of CO\textsubscript{2}.

REFERENCES


ASTM C642:2013, Density, Absorption, and Voids in Hardened Concrete.


