

The effects of carbonation on the chloride resistance of concretes with supplementary cementitious materials (SCMs)

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ABSTRACT

Concrete structures employed in de-icing and marine environment are commonly under the cyclic influence of carbon dioxide and chloride ion. Recently, the impact of chloride content on carbonation in concretes has been frequently considered; in comparison, the investigation of the influence of carbonation on the progress of chloride penetration is limited. This study is to investigate the potential influence of the carbonated concrete incorporating supplementary cementitious materials (SCMs) including GGBS and PFA on the chloride ingress in concretes. The experimental programme involves casting concrete cubes at three different water- cementitious ratios (w/cm) of 0.4, 0.5 and 0.6 with four crack widths of 0.1, 0.2, 0.3 and 0.4 mm. For concretes of 0.5% w/c ratio, the OPC was partially replaced by 30 % of GGBS and PFA. Concretes were exposed periodically to accelerated chloride- carbon dioxide (CO₂) - chloride environment. Chloride penetration and carbonation depth have been experimentally found for two types of concretes, uncracked and cracked concretes. The results have shown that the depth of carbonation (DoC) increased with the increase in the w/cm ratio and replacing OPC by GGBS and PFA. The penetration depth of chloride (d_{Cl-}) in concrete structures increased significantly owing to the influence of carbonation. The results also demonstrate a significant decrease in the penetration of chloride ions in carbonated concretes incorporating SCMs when compared to the reference concretes.

1. INTRODUCTION

The Durability of concrete structures is a common significant investigating issue, and it considerably impacts the service life of the concrete structures. Regarding all the concerns of the durability problems, chloride and carbonation diffusion are two factors that can be accelerated the corrosion of reinforcement. In some structures, such as those exposed to atmospheric zone in marine environment conditions (Castro et al., 2000) concretes suffer from both the chloride and carbonation ingress simultaneously or in series. The successional carbonation and chloride penetration process can also happen in concrete structures that built-in cold regions (Avelano & Ortega, 2011), where de-icing rock salt is usually used in winter to melt ice and contains high concentration of chloride ions (Cl⁻). Concerning the combined mechanisms of ingress of CO₃²⁻ and Cl⁻ ions in concrete, from one hand, it has been proved that carbonation affects the penetration of Cl⁻ noticeably. The process can be described as follows: at the first stage of carbonation, the formation of CaCO₃ leads to densify the concrete and slows down the penetration of Cl⁻ (Xu et al., 2011); on the other hand, the process of carbonation may reduce the chloride binding capacity of cement compounds that promotes the ingress of chloride in a certain degree (Wang et al., 2016). For the effect of replacement of

supplementary cementitious materials (SCMs), the results of the depth of carbonation (DoC) for GGBS and PFA samples are higher DoC than DoC of mixes without these materials by using phenolphthalein indicator and XRD analysis. The results of DoC for the mixes incorporating SCMs (GGBS and PFA) have less Ca(OH)₂ than the OPC mixes at a different depth. Thus, relative intensities of Ca(OH)₂ remains low at a deep depth, while the concentration of CaCO₃ remains high at that depth (AL-Ameeri et al., 2018) On the other hand, the partial replacement of OPC with SCMs, GGBS, and PFA has a higher resistance to chloride penetration in concrete and the total concentration of chloride at a shallow depth remains high, and the reduction of concentration with depth at this zone was minor, while, the decrease of chloride content in the zone beyond the first one reduced sharply. To date, knowledge on the effect of Cl⁻ in concretes on the progress of carbonation is limited and the mechanism is still unclear. Therefore, the diffusivity of Cl⁻ and carbonation in concrete cover under the combined mechanism of exposure and the effect of carbonation penetration on the chloride resistance of concretes with (SCMs) needs to the .

2. Experimental work

2.1 Materials and Concrete Mix Design

Portland limestone cement (CEM II/A-LL 32,5R) with a specific gravity of 3.05 was used in this

study. Chemical and physical properties of the cement comply with BS EN 197- 1: 2011. Natural sand was used as fine aggregate (particle size < 5mm), and the coarse aggregate used was crushed gravel with the size ranging from 5-14 mm. The properties the aggregates comply with BS 882:1983. Three different w/cm ratios (0.5,0.5,0.6) were used to investigate their effects on the penetration of carbonation and chlorides. The Building Research Establishment method was used for concrete mix designs (see Table 1).

Table1 Concrete mixes designs used in this study

Mix symbol	Content per unit volume of concrete (kg / m ³)					
	w/c	Cement	GGBS or PFA	Water	Sand	Gravel
M 0.4	0.4	510	-	204	653	980
M 0.5	0.5	408	-	204	711	1023
M 0.6	0.6	340	-	204	711	1041
M 0.5+ GGBS	0.5	285	123	204	711	1023
M 0.5+ PFA	0.5	285	123	204	711	1023

2.2 Specimen Geometry

Three 100 mm cube specimens were used to establish the compressive strength of concrete and porosity measurements. Also, the concrete cubes samples were used to measure the depth of carbonation (DoC) and chloride penetration in both the cracked and un-cracked specimens. The artificial crack(notch tip) method was used to induce the cracks in concrete samples by using steel plates (see Figure 1). In addition to the control samples (no cracks), four different crack width, (0.1mm, 2mm, 0.3 mm and 4mm) were studied. The crack depth was fixed at 20 mm. Samples were cast in two layers and each layer was vibrated to achieve homogenous concrete. The specimens were demoulded and cured using tap water until the time of testing at the age of 28 days, or exposure to Cl⁻-CO₂ -Cl⁻ environment.



Figure 1. Method for cracking in the cubic sample

2.3 Specimens Conditioning

The main objective of this study was to investigate the effect of carbonation on the chloride penetration for different properties of concrete and crack width in concrete samples. In this study, one face of the specimens was exposed to accelerated environment conditions whereas the other faces were sealed using coats of water-based alkyl polysiloxane resin. The control samples were

exposed to a chloride fog environment (with 5% NaCl) within a Cyclic Chloride Test (CCT) chamber for 17 weeks in total. The rest of the samples were taken out of the CCT chamber (see Figure 2) after 10 weeks of chloride exposure and they were exposed to CO₂ concentration of 5% within a CO₂ chamber (at a temperature of 25 °C and relative humidity of 65%) for 5 weeks before returning them back in the CCT chamber (chloride exposure) for the remaining 7 weeks.



Figure 2. CCT Chamber for accelerating chloride penetration

2.4 Testing Methodologies

The compressive strength, porosity, depth of carbonation (DoC) and chloride penetration were carried out for this study. Porosity and compressive strength tests were conducted according to BS EN 12390-3:2000 respectively. The chloride penetration depth was measured by splitting the conditioned samples into two parts and spraying 0.1% silver nitrate solution in accordance with (He et al.,2011). The silver nitrate solution reacts with chloride ions to form silver chloride, changing the colour of the concrete surface hence the depth of chloride penetration can be measured(He et al.,2011). In order to measure the depth of carbonation, CO₂ conditioned samples were split into two parts using a compression testing machine. The two parts were sprayed by a solution with one gram of phenolphthalein powder dissolved into a solution of 70 ml and 30 ml of ethanol and deionized water respectively complied with BS EN13295: 2004. The change of colour of the concrete surface was measured to find DoC.

3. Results and discussion

In this section, the results of the experimental work are presented and discussed. These are mainly focused on the impact of carbonation on d_{cl⁻} for different w/cm ratio, SCMs and crack widths.

3.1 Carbonation Depth in Concrete

The depth of carbonation was established by measuring the depth of carbonation at different points along the sample width and computing the average of these measurements as shown in Figure 3. The DoC as a function of w/cm ratio for the mixes used in this study is shown in Table 2, where M 0.4, M 0.5 and M 0.6 refers to w/cm ratio of 0.4, 0.5 and 0.6 respectively. The results illustrated that the DoC increases slightly from the

exposed surface with the increase in w/cm ratio in concrete samples. On the other hand, the results showed that the DoC for un-cracked concretes with SCMs (M0.5+GGBS and M 0.5+PFA) were a higher than the DoC for control sample (M 0.5). While, the effect of crack on the DoC was limited because the duration of exposure to CO₂ environment was a few (5 weeks).

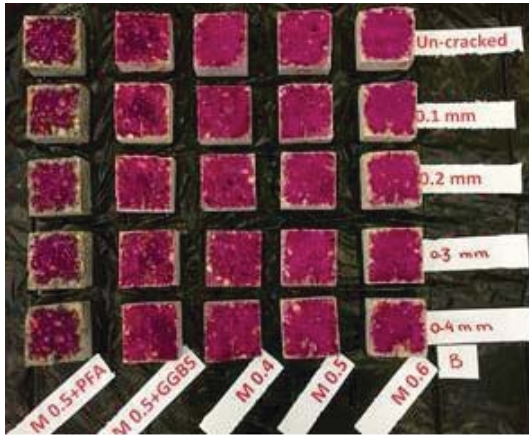


Figure 3. Carbonation depth of mixes used in the study (Series B)

Table 2 Carbonation depth of for mixes used in the study

Sample	Depth of carbonation (DoC) mm					Porosity %	Compressive strength (MPa)
	Un-cracked	Crack width 0.1 mm	Crack width 0.2 mm	Crack width 0.3 mm	Crack width 0.4 mm		
M 0.4	3	20	21	20	22	10	54
M 0.5	4	22	23	24	23	11	49
M 0.6	5	23	22	23	24	12	40
M 0.5+GGBS	5	23	22	23	24	10	48
M 0.5+ PFA	8	22	23	25	26	10	32

The increase of DoC in concrete mixes as a function of the w/cm ratio and type of cementitious materials is a result of two reason: first, the increase in porosity of concrete (see Table 2) and volume of permeable voids, i.e. the pore system of the hardened cement paste (Neville, 2011) and second, the decrease of quantity of Ca(OH)₂ due to the fact that there is a lesser quantity of Portland cement available to form Ca(OH)₂ in the blended cements as well as the pozzolanic reactions in blended cements converting calcium hydroxide to produce secondary C-S-H in the first days of hydration (Roy & Indorn, 1982), that helps CO₂ to penetrate and react with water to form CO₃²⁻, the latter then reacts with Ca(OH)₂ to form the CaCO₃.

3.2 Chloride penetration

Two sets of concrete samples were tested for chloride penetration; the first set (Series B) was exposed to a CO₂ environment in-between the exposure to the chloride fog environment, whilst the second set (Series A) was just exposed to the chloride fog (control specimen). The difference between the series is the first was exposed to an accelerated CO₂ environment, while the second was exposed to a normal CO₂ environment and exposure time to CO₂ for both was 5 weeks. The

silver nitrate colorimetric method was used to measure the d_{cl}⁻. The AgNO₃ solution spray reacts with chloride ions to form a mixture of silver oxide and silver chloride that precipitates on the concrete surface and changes colour forming a boundary corresponding to the chloride penetration within the concrete specimen. Results for the two sets for different crack widths and w/cm ratio are presented in Figures 4 & 5 and Tables 3 & 4.

Table 3 Chloride penetration depth for samples used in (Series A)

Sample	Chloride Penetration depth (d _{cl} ⁻) mm				
	Un-cracked	Crack width 0.1 mm	Crack width 0.2 mm	Crack width 0.3 mm	Crack width 0.4 mm
M 0.4	24	30	30	29	35
M 0.5	35	≥40	≥40	≥40	≥40
M 0.6	40	≥40	≥40	≥40	≥40
M 0.5+ GGBS	15	25	29	30	33
M 0.5+ PFA	14	23	22	25	27

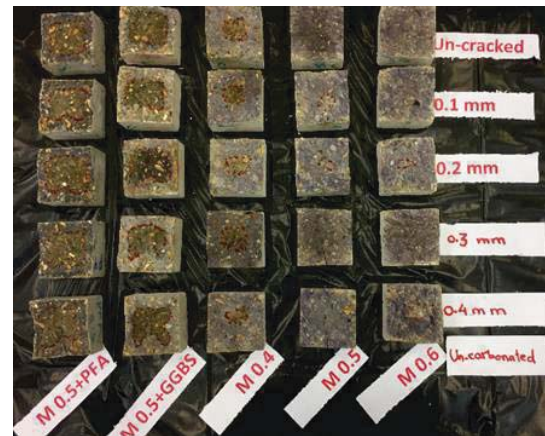


Figure 4. Penetration of chloride for uncarbonated sample with different crack width

Table 4 Chloride penetration depth for samples used in (Series B)

Sample	Chloride Penetration depth (d _{cl} ⁻) mm				
	Un-cracked	Crack width 0.1 mm	Crack width 0.2 mm	Crack width 0.3 mm	Crack width 0.4 mm
M 0.4	27	33	31	34	39
M 0.5	40	≥40	≥40	≥40	≥40
M 0.6	≥40	≥40	≥40	≥40	≥40
M 0.5+ GGBS	15	29	31	31	31
M 0.5+ PFA	20	25	26	27	30

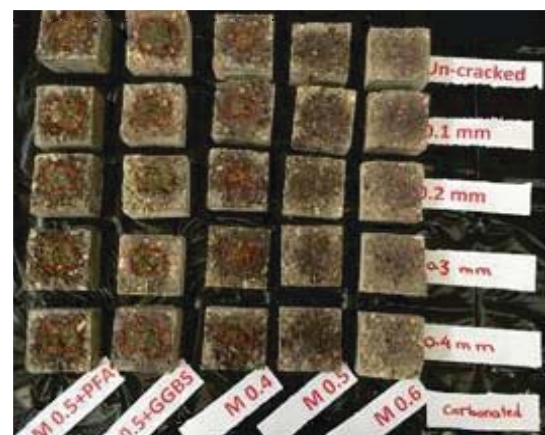


Figure 5. Penetration of chloride for carbonated sample with different crack width

Key observations from these results are:

(i) The results exhibit higher chloride penetration depths for samples exposed to CO₂ environment when compared with the control samples as shown in Figures 4 and 5 and Tables 3 and 4, particularly for the uncracked concrete samples. This can be attributed to the fact that the carbonation reduces the pH of the pore water in concrete which is a significant factor in liberation of bound chlorides (calcium chloroaluminate) in cement mortar (Wan et al., 2013) hence increases free chloride concentration and ultimately the penetration depth. The results depict an increase in chloride penetration with the increase in w/cm ratio and decrease with using SCMs for both sets of concrete samples (i.e. with and without carbonation) particularly for the un-cracked samples.

(ii) This can be explained by the fact that the w/cm ratio affects the volume of internal voids or porosity in the concrete that in turn affects the chloride ions transport mechanisms in concrete, i.e. diffusion, permeation, sorption and permeability (Basheer et al.2001). The replacement of OPC by GGBS in concrete (M 0.5+GGBS and M 0.5+PFA) may refine pore networks and improve chloride binding capacities and subsequently decrease chloride transport through concrete compared to that of M 0.5 concretes (Thomas *et al.*, 2012). Where, the pore structure of SCMs can be defined by, pore size distribution, pore specific surface area, total porosity as well as some characteristic pore sizes. The pore structure is the result of the observed hydration processes of cement and SCMs.

(iii)The chloride penetration depth increases with the crack widths for all mixes till a threshold crack width is reached, which is estimated from Figure 4 and 5 to be around 0.1 mm. The crack width and depth affect the transport mechanism of chloride ion into the crack opening since wider cracks may allow the chloride solution to penetrate in the cracks. The cracks width less than 0.1 mm appear to have contributed only through an increase in the rate of transport of chloride ions (i.e. increase in permeability and diffusion rates of concrete). However, cracks of width greater than 0.1 mm appear to have provided additional surface area (along the crack walls) for the transport of chloride ions into the concrete. Hence, an increase in chloride penetration perpendicular to the crack walls can also be observed (Figure 4&5), which is similar to the chloride penetration profile from the surface of an uncracked concrete.

4. Conclusion

This study investigates the influence of carbonation on the chloride penetration and replacing OPC by GGBS and PFA in cracked concrete samples. The d_{cl^-} and DoC were explored by using an accelerated environment test programme for (CO₂ and Cl⁻). The DoC was found by phenolphthalein Indicator, whereas the d_{cl^-} was

measured by AgNO₃ spraying. The following conclusions can be drawn from the results;

- 1- The w/cm ratio, porosity, and compressive strength, quality and properties of concrete, affects the depth of carbonation and chloride penetration depths.
- 2- The chloride penetration increases significantly within the concrete samples exposed to CO₂ environment for all mixes used in the study.
- 3- There is a significant decrease in the penetration of chloride ions in uncarbonated and carbonated concretes incorporating SCMs when compared to the reference concretes.
- 4- For concrete specimens exposed to carbonation and chlorides, crack widths affect the penetration of chloride and therefore should be taken into consideration in service life prediction models.

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