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**Influence of combined carbonation and chloride ingress regimes on rate of ingress and redistribution of chlorides in concretes**

Y. Wang<sup>1</sup>, S. Nanukuttan<sup>2</sup>, Y. Bai<sup>3</sup>, P.A.M. Basheer<sup>4\*</sup>

<sup>1</sup> School of Civil Engineering, Shenzhen University; Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen, P.R.China

<sup>2</sup> School of Planning, Architecture and Civil Engineering, Queen's University Belfast, Northern Ireland, the UK

<sup>3</sup> Department of Civil, Environmental and Geomatic Engineering, University College London, London, the UK

<sup>4</sup> School of Civil Engineering, University of Leeds, England, the UK

\* Corresponding Author Contact Details

Professor P.A. Muhammed Basheer

Head of School of Civil Engineering

University of Leeds

Leeds

England

LS2 9JT

United Kingdom

Ph: +44 113 343 2272

E-mail: [p.a.m.basheer@leeds.ac.uk](mailto:p.a.m.basheer@leeds.ac.uk)

## HIGHLIGHTS

- Discusses the ingress and distribution of chloride ions in concretes subjected to carbonation.
- Influence of carbonation and its extent on both the ingress and redistribution of chlorides.
- Interactions between carbonation and chloride ingress for different types of binders.
- Relevance of combined effects of carbonation and chloride ingress to service life prediction.

## **Abstract:**

In majority of exposure environments for concrete structures, there is a high probability of the cyclic occurrence of both chloride ingress and carbonation. This paper reports a detailed investigation on the influence of carbonation on both the ingress and distribution of chlorides in three different types of concretes, by comparing results from exposure to chlorides, chlorides before carbonation and chlorides after carbonation. Concretes studied were of 0.55 water-binder ratio with 100% Portland Cement (PC), 70% PC + 30% pulverized fuel ash (PFA) and 85% PC + 10% PFA + 5% microsilica (MS) as binders. Chloride profiles were compared to assess the effects of all variables studied in this research. The effect of carbonation was quantified by measuring the consumption of hydroxyl ions ( $\text{OH}^-$ ), air permeability and chloride migration coefficient. The results indicated that carbonation of concrete increases chloride transport, but the precise nature of this is dependent on the combined regime as well as the type of binder. In general, it was found that carbonation of chloride contaminated concretes results in a decrease of their chloride binding capacity, that is it releases the bound  $\text{Cl}^-$  in concretes and pushes chlorides inwards, [as has been established previously by other researchers](#). [However, it is established](#)

in this research that the combined regimes detrimentally affect the service life of concrete structures, particularly when chloride induced corrosion is a concern.

**Key words:**

Air Permeability, Carbonation, Chloride Profile, Chloride Migration, pH Profile, Combined Exposures

**1. Introduction**

Corrosion of steel in reinforced concrete structures is initiated either by carbonation of the cover concrete or chloride ingress, both of which are known to depassivate the carbon steel and make it susceptible to electrochemical corrosion. For certain types of structures, such as those exposed to the atmospheric zone in marine environments<sup>[1-5]</sup> both carbonation and chloride ingress may occur either simultaneously or in succession. Costa and Appleton<sup>[6]</sup> have reported that concrete in tidal zone, where the internal moisture content could be relative high, also suffer from severe carbonation and chloride penetration. Carbonation and chloride ingress in succession can also occur in abutments of bridges<sup>[7]</sup> or concrete tunnel linings which are constructed in cold regions, where rock salt is usually used in winter to melt ice and contains significant amount of chloride ions (Cl<sup>-</sup>). There is some evidence that the corrosion of reinforcement is accelerated when it is under the simultaneous effect of carbonation and Cl<sup>-</sup><sup>[8-10]</sup>. [Although sulphate also is present in both seawater and rock salt, the combined effect of chlorides, sulphates and carbonation is considered to be beyond the scope of the current study. Nevertheless, the combined effects of chlorides and sulphates with or without carbonation need to be studied in order to understand fully the durability behaviour of concretes in marine environments. Some related publications exist in the literature<sup>[11,12]</sup> but these are not sufficient to propose changes to

practice for designing concrete structures in these combined exposure environments.]

During the carbonation of concrete,  $\text{CO}_2$  reacts with cement hydration products and leads to a decrease in alkalinity (pH), which is responsible for the initiation of corrosion. At the same time, as the products of carbonation (primarily calcium carbonate) occupy more space than that of the cement hydration products that are affected by the carbonation, there is a reported decrease of permeation properties of concretes<sup>[13,14]</sup>. On the other hand, carbonation may cause shrinkage of hydrated cement paste (hcp) in concrete<sup>[15]</sup>, which is likely to increase the permeation properties. As a result of both these effects, further ingress of  $\text{CO}_2$  into concrete is changed and the rate of  $\text{CO}_2$  ingress becomes not a simple function of initial permeation properties of the concrete. For the chloride ingress in concrete, the main physical effect is a reduction in porosity and permeation properties due to the pore filling effect of newly formed calcium chloro-aluminate, or Friedel Salt, when  $\text{Cl}^-$  reacts with the aluminate phase in hcp<sup>[16]</sup>. It is also known that carbonation can release the bound chlorides, leading to a redistribution of chlorides in the concrete<sup>[17,18]</sup>. Therefore, when there is the simultaneous or successive carbonation and chloride ingress, their combined effects on initiation of corrosion is less than clear due to the complex interactions between chemical and physical effects of carbonation and chloride ingress.

Studies on the ingress of  $\text{CO}_2$  and  $\text{Cl}^-$  into concretes in the past have been primarily based on their independent effects and most of them introduced a time-dependent factor to describe the changes in the rate of carbonation or chloride ingress<sup>[16,19,20]</sup>. In the case of combined carbonation and chloride ingress, for both situations when they act in succession or simultaneously, reactions of  $\text{CO}_2$  or  $\text{Cl}^-$  with cement hydration products and their further reactions with previously formed products of carbonation and chloride ingress are complicated. It is considered that a study on the distribution of pH and  $\text{Cl}^-$  in concrete under the combined effects is a necessary first step to understand this complex mechanism

and such studies are relatively limited.

Previous investigations on the combined ingress of CO<sub>2</sub> and Cl<sup>-</sup> into concrete have primarily focused on obtaining relationships between the exposure duration and the depth of carbonation and chloride ingress<sup>[9,17]</sup>. Furthermore, some researchers<sup>[18,21]</sup> reported chemical reactions in the hcp during the combined process. However, these results are not sufficient to establish the physical and chemical effects of the combined processes, particularly the changes in alkalinity and ingress of chlorides in concretes. Therefore, an investigation was carried out to determine the effect of the combined regimes of carbonation and chloride ingress on the distribution of chlorides in different types of concrete as a first step to understand the implications of this on the service life of reinforced concrete structures.

## 2. Experimental programme

Details of the experimental programme of this study are summarised below:

- a) Table 1 gives detailed mix proportions of the different concrete mixes used in this study. All the mixes were selected according to BS EN 206<sup>[22]</sup> for concrete exposed to XC2, XD2 and XS2 environments and for an expected service life of 50 years<sup>[23]</sup>. Therefore, they had a w/b of 0.55 and a total binder content of 320kg/m<sup>3</sup>. Three types of binders were used, viz. Portland cement (PC), Pulverised Fuel Ash (PFA) and microsilica (MS). Based on the w/b and type of binder used, the three mixes are denoted as 0.55PC, 0.55PFA and 0.55PFA+MS. The mix proportions are reported in Table 1, which take account of the changes in specific gravity of the cementitious materials while calculating the aggregate content. A polycarboxylate based superplasticiser was used to achieve a slump of 50 to 90 mm (S2 class in BS EN 206<sup>[22]</sup>). Before mixing, all the aggregates were dried in an oven at 105 (±5)°C for 24 hours and allowed to cool down to the room temperature

( $20 \pm 2^\circ\text{C}$ ) for at least another 24 hours. The water needed for the aggregate to attain the saturated surface dry (SSD) state from the totally dry state was taken into account in the total amount of water used during the manufacture of the concrete (reported in Table 1).

b) Three types of concrete blocks were cast:

(i) Blocks of size 150x150x80mm with four embedded PVC tubes of different lengths (10, 20, 30 and 40mm) were cast (Fig. 1) for monitoring the relative humidity (RH) of concrete during conditioning and carbonation, as described by Russell et al.<sup>[24]</sup>;



**Fig. 1.** Concrete blocks of size 150x150x80mm along with PVC inserts and various attachments used to create holes for monitoring the internal RH values

(ii) Blocks of size 500x500x80mm were cast for coring 75mm diameterx80mm long cylindrical specimens. After each exposure regime, two replicate cylinders were used to determine the extent of carbonation and degree of chloride ingress by using methods described in steps (g) and (h) below, and their average values are presented in the paper;

(iii) Blocks of size 230x230x80mm were cast for detecting permeation properties of the concretes under the effects from different exposure regimes.

Table 1. Mix proportions of the concretes

Mixes	w/b	Type of binder and their content (%)	Quantities (kg/m <sup>3</sup> )							
			PC	PFA	MS	Sand	10mm-Agg	20mm-Agg	Super-plasticiser	Water
0.55PC	0.55	PC(100)	320	0	0	683	663	663	1.60	176
0.55PFA	0.55	PC(70)+PFA(30)	224	96	0	677	658	658	1.68	176
0.55PFA+MS	0.55	PC(85)+PFA(10)+MS(5)	272	32	16	679	659	659	2.18	176

c) All types of specimens were cast in marine plywood moulds, and then they were covered with polythene sheet and placed in a room at a temperature of 20 ( $\pm 2$ )<sup>o</sup>C for 24 hours. The samples were then demoulded and were subjected to another period of 55 days of curing, which included a period of water curing of the hardened concrete for 6 days and storage in a room at 20 ( $\pm 1$ )<sup>o</sup>C and 60 ( $\pm 5$ )% RH for 49 days. Before the specimens were subjected to carbonation or chloride ingress as per the procedure described in step (f) below, they were cured and conditioned for a duration of approximately 4 months. Figure 2 presents the flowchart of the experimental process applied in this study.

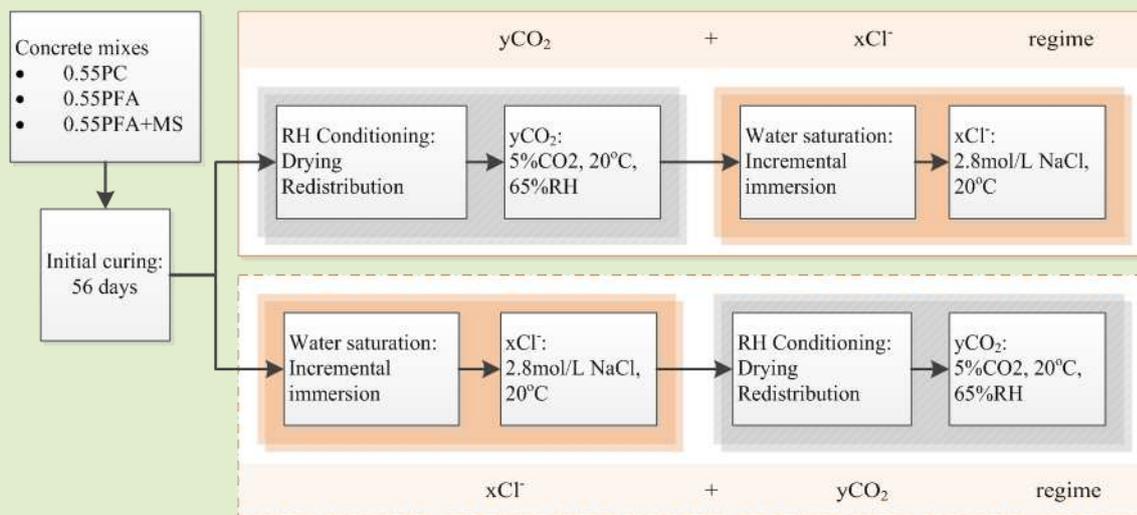


Fig. 2. Flowchart of the experimental processes

- d) The independent and combined carbonation and chloride ingress regimes are denoted as  $xCl^-$ ,  $yCO_2$ ,  $yCO_2+xCl^-$  and  $xCl^-+yCO_2$ , where  $x$  and  $y$  indicate respectively the duration of exposure of the samples to chlorides and carbon dioxide. For example,  $yCO_2+xCl^-$  indicates that the concretes were exposed to a combined carbonation and chloride ingress exposure regime, starting with 'y' months of carbonation and a subsequent immersion in chloride solution for 'x' months.  $xCl^-$  indicates that these samples were exposed to 'x' months of chloride ingress.
- e) Samples which were subjected to carbonation first (i.e.,  $yCO_2$  and  $yCO_2 + xCl^-$ ) were all conditioned to a consistent RH of 65 ( $\pm 2$ )% before exposing to a  $CO_2$  environment by following the procedure described by Russell et al.<sup>[24]</sup>. As per this procedure, the 150x150x80mm test specimens (Fig. 1) were firstly dried in an oven at 40 ( $\pm 2$ )°C to let the moisture evaporate from the exposed surface. The internal RH value was measured at 10mm, 20mm, 30mm and 40mm depths by inserting a capacitance based RH probe in the cavities made using the PVC inserts (Fig. 1). Once the average RH value in the 0-40mm deep concrete reached a value of 60-70%, all the samples were taken out of the oven and each one was sealed air tight using polythene sheet and parcel tape. Subsequently, the sealed blocks were transferred to a 50 ( $\pm 2$ )°C oven for redistributing their inner RH until a consistent RH of 65 ( $\pm 2$ )% was reached at the four depths of 10, 20, 30 and 40mm. After the samples were carbonated by using the procedure described in section (f) below, those for the  $yCO_2 + xCl^-$  study were water saturated by incrementally immersing them over a period of 9 days, which were subsequently immersed in the chloride solution. Similarly,  $xCl^- + yCO_2$  samples were water saturated first prior to the chloride exposure and after  $x$  months of chloride exposure the samples were removed and conditioned to an RH of 65 ( $\pm 2$ )% before starting the carbonation exposure, which lasted for  $y$  months.

- f) For carbonation, the exposure environment was kept at 20 ( $\pm 1$ ) $^{\circ}$ C, 5 ( $\pm 0.1$ )% CO<sub>2</sub> and 65 ( $\pm 2$ )% RH; for chloride ingress, the chloride exposure solution was 165g/l NaCl (2.8mol/L), as identified in NT Build 443<sup>[25]</sup>, and, controlled at a temperature of 20 ( $\pm 1$ ) $^{\circ}$ C. In both the independent and combined regimes, maximum duration for the carbonation and chloride ingress processes was three months. After each designated test regime, two cylindrical samples of each mix were taken out from the exposure environment. Subsequently, powder samples were extracted by progressively profile grinding from the exposure surface in layers up to a depth of approximately 30mm. In the region that was close to the exposure surface (0-5mm), the degree of carbonation and the chloride concentration were relatively high. Therefore, powder samples were extracted from a depth of every 1mm to determine the extent of change. At the inner depths (beyond 5mm), the degree of carbonation as well as the chloride concentration were relevantly small and hence dust samples were collected from 2 to 3mm deep layer of concrete. The exact location of the depth at which the powder samples were collected was measured by using the vernier callipers.
- g) The pH of the solution that was obtained by digesting the drilled powder samples in deionised water was determined. It indicates the alkalinity of concrete<sup>[26]</sup>, which is referred to as apparent pH<sup>[27]</sup> in this paper. For this purpose, 1( $\pm 0.001$ )g of powder sample from each layer was digested with 20ml of deionised water. By further analysis of the results, the amount of consumed OH<sup>-</sup> at different depths of the samples were ascertained using Equation 1, where the pH<sub>0</sub> and the pH<sub>x</sub> are the apparent pH results measured before and after the exposure.

$$\text{Consumed OH}^{-} = \text{Initial OH}^{-} - \text{Remained OH}^{-} = 10^{pH_0-14} - 10^{pH_x-14} \quad (\text{Eq. 1})$$

- (h) Acid soluble chloride content of the powder samples extracted from the different depths of the test

specimens was analysed in accordance with RILEM TC 178-TMC recommendations<sup>[28]</sup>.

- (i) During the exposure, concrete permeability was measured by using the Autoclam permeability system<sup>[29]</sup> and the 'Permit' chloride ion migration test<sup>[30]</sup> on three of the 230x230x80mm blocks.

### **3. Presentation and discussion of results**

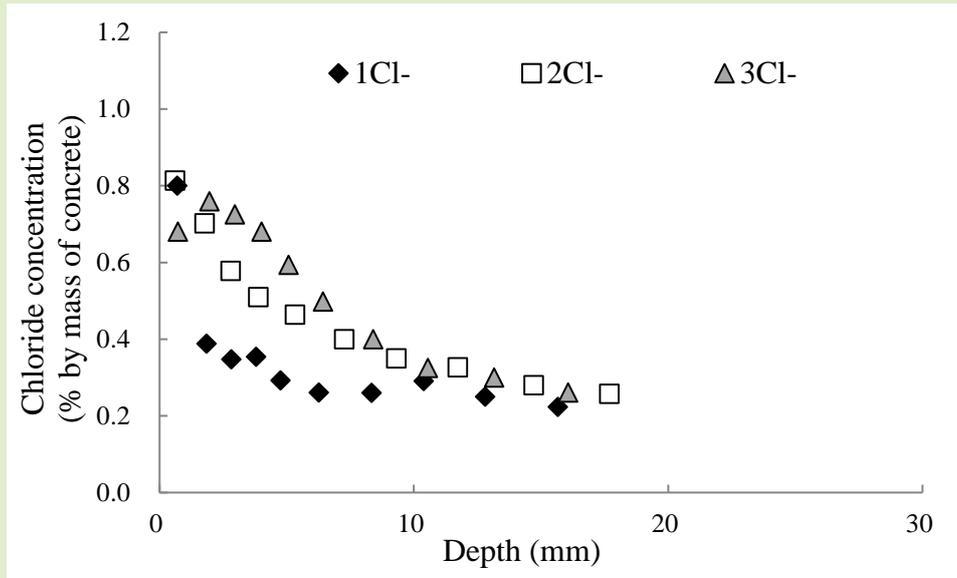
#### **3.1 Concretes exposed to the chloride immersion followed by carbonation regime ( $x\text{Cl}^- + y\text{CO}_2$ )**

As samples used in the study were exposed to the two aggressive environments successively. In this regime, the progress of carbonation in concretes is influenced not only by properties of the concretes but also by the  $\text{Cl}^-$  in them. Therefore, in this section, results from the independent chloride ingress regime are discussed first, followed by those from the carbonation stage.

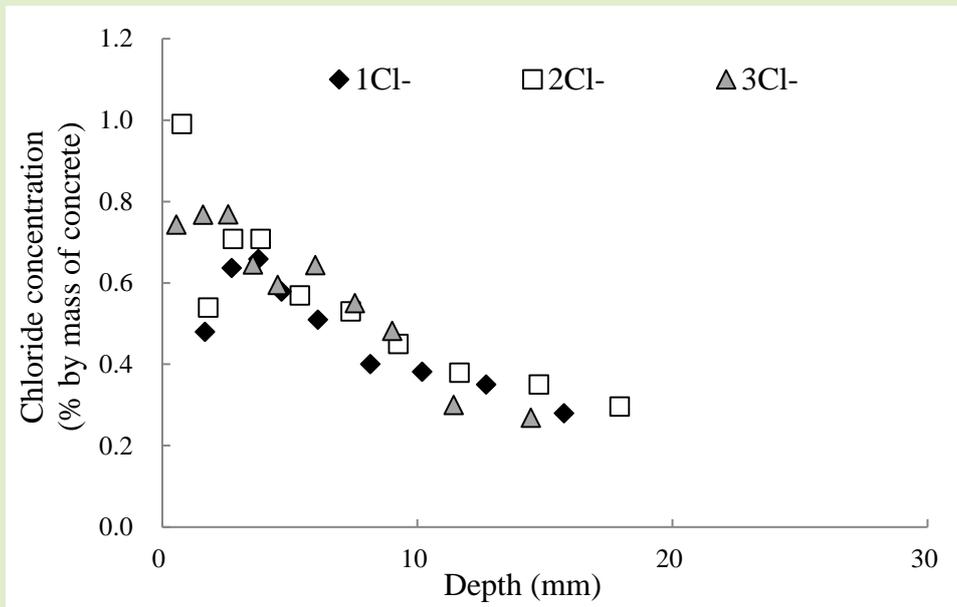
##### **3.1.1 Influence of initial independent exposure to chlorides on chloride distribution ( $x\text{Cl}^-$ )**

Distribution of  $\text{Cl}^-$  in concretes during the initial  $x\text{Cl}^-$  exposure regime is presented in Fig. 3. Results in Fig. 3(a) shows that at any given depth, the chloride concentration increased from 1 month to 3 months, which indicates that  $\text{Cl}^-$  continuously penetrated into the 0.55PC during the three months of immersion. In contrast, the ingress of  $\text{Cl}^-$  mainly took place in the first month in both 0.55PFA (Fig. 3(b)) and 0.55PFA+MS samples (Fig. 3(c)) and prolonging the duration of immersion did not lead to any obvious increase in the chloride ingress. Additionally, the results in Table 2 show that for the three concretes the chloride content at the surface layer of 0-1mm (referred to in this paper as  $C_s$ ) did not change at any large extent with increased duration of immersion and the values for the three concretes were close (about 0.8% by mass of concrete). These  $C_s$  data somewhat contradict some other published data (obtained from the regression analysis of chloride profiles) for concretes containing

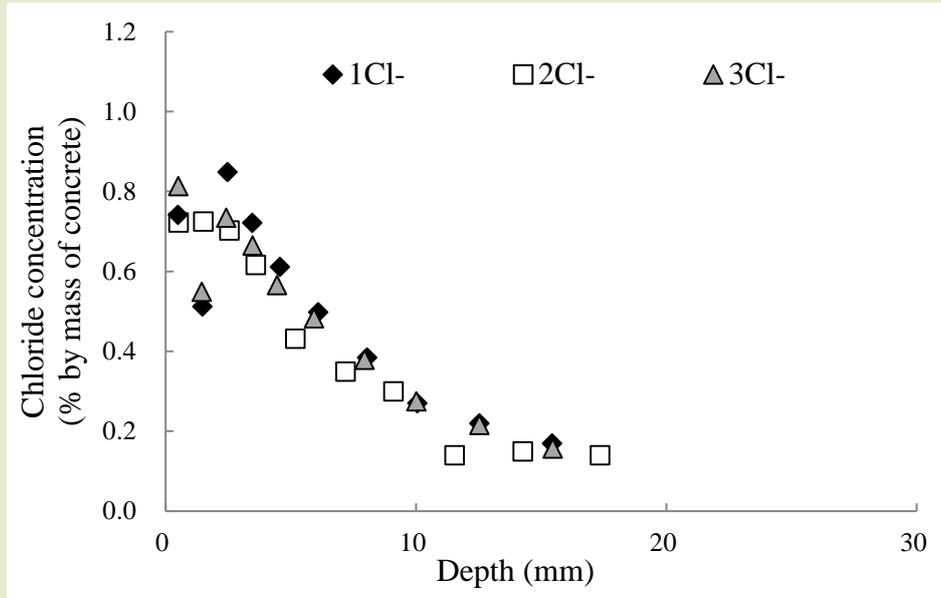
supplementary cementitious materials<sup>[31]</sup>, in which it is reported that the  $C_s$  value increases with time, but the values for different mixes in that study were very close after a period of 18 months of immersion in the chloride solution (concentration 0.51 mol/L NaCl solution; w/b ratio of concretes = 0.5).



(a) 0.55PC



(b) 0.55PFA



(c) 0.55PFA+MS

Fig. 3. Distribution of Cl<sup>-</sup> in concretes during the xCl<sup>-</sup> regime

Table 2. Development of C<sub>s</sub> during the xCl<sup>-</sup> regime\*

	1Cl <sup>-</sup>	2Cl <sup>-</sup>	3Cl <sup>-</sup>
<b>0.55PC</b>	0.81 (0.01)	0.75 (0.09)	0.67 (0.01)
<b>0.55PFA</b>	0.47 (0.02)	0.78 (0.30)	0.75 (0.01)
<b>0.55PFA+MS</b>	0.63 (0.16)	0.73 (0.01)	0.82 (0.01)

\*Values in bracket indicate standard deviation of tested results from two individual cylindrical samples.

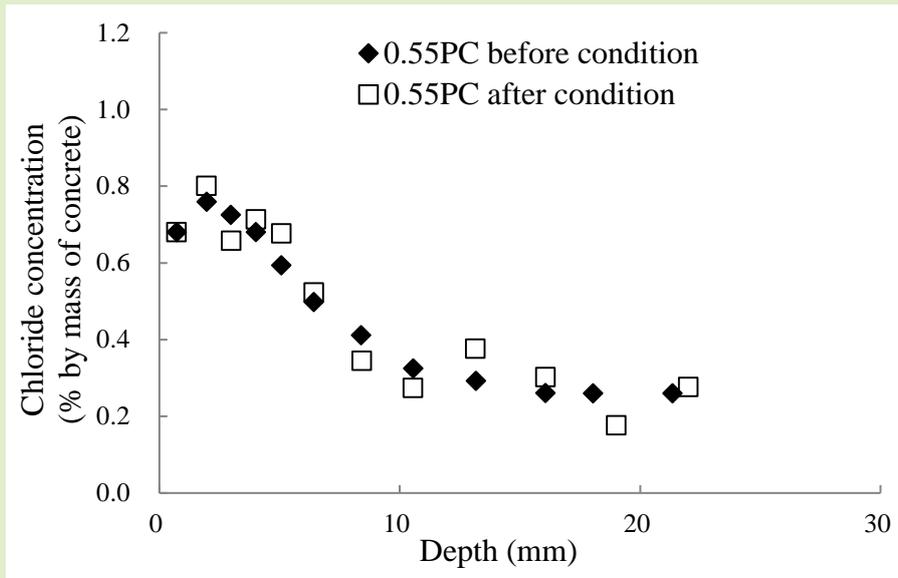
Compared to PC concretes, pores in PFA and MS concretes are known to have relatively smaller diameter due to their continued hydration, which would lead to a slower diffusion of Cl<sup>-</sup>[32,33]. Further, it is reported that some cement hydration products, such as aluminate phases and CSH gel, which are enriched in PFA and MS concretes respectively, can bind Cl<sup>-</sup> and the binding process can further decrease the pore diameter[10,34,20]. Thus, negligible ingress of Cl<sup>-</sup> in the two types of concrete containing supplementary cementitious materials (SCMs) after the first month of immersion is seen in Figs. 3(b) and 3(c). In contrast, such an effect was less obvious for the PC concrete in Fig. 3(a).

The accumulation of Cl<sup>-</sup> on concrete surface is a complex process and is governed by many factors,

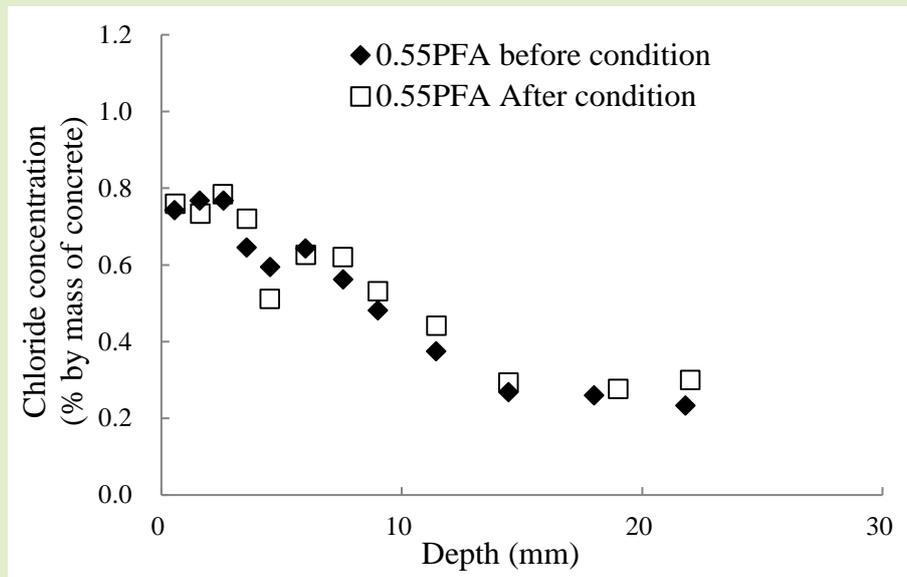
including the chloride binding capacity of cement hydration products<sup>[35]</sup>, ionic exchange between  $\text{Cl}^-$  and other ions that exists in concretes, e.g.  $\text{OH}^-$ <sup>[36,37]</sup>, and diffusion of  $\text{Cl}^-$  in pore solution due to the concentration gradient. These processes relate to physical characteristics of capillary pores and chemical properties of the hydrated binders, viz. the CH content and the chloride binding capacity. Bai et al.<sup>[31]</sup> have indicated that the type of binder has limited influence on the  $C_s$  value when the chloride ingress is stabilised at the surface layer (exposed to  $0.51\text{mol/L}$  NaCl). This normally takes more than a year in concretes containing SCMs. It is somewhat surprising to observe in this research that the surface chloride content stabilised very fast, almost within a month of starting the immersion in the  $2.82\text{mol/L}$  NaCl solution. As the exposure was not continued beyond 3 months in this research, it is not appropriate to make any further remarks on this observation.

### **3.1.2 Influence of carbonation of chloride exposed samples on chloride distribution ( $3\text{Cl}^- + y\text{CO}_2$ )**

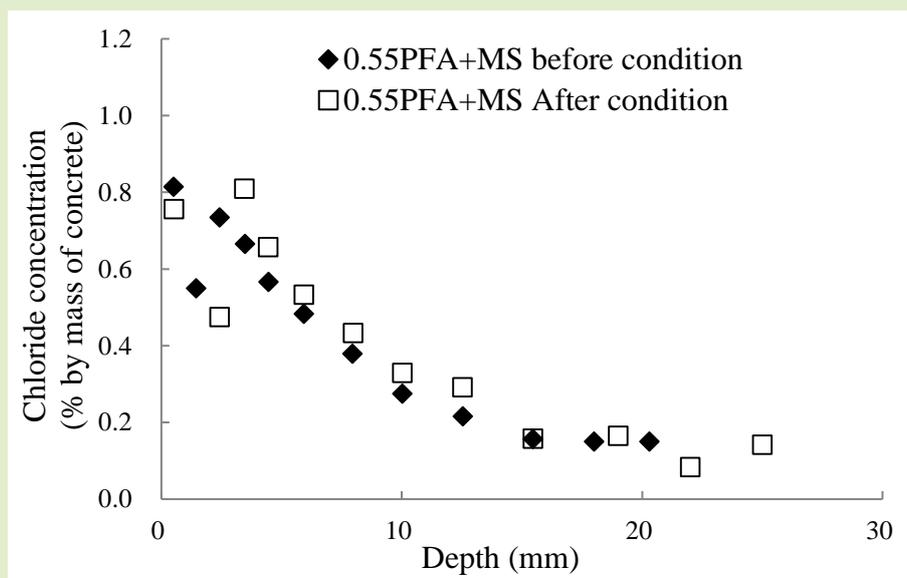
In the  $3\text{Cl}^- + y\text{CO}_2$  regime, before the chloride exposed samples were subjected to accelerated carbonation, they were conditioned in an oven to achieve a uniform RH of  $65 (\pm 2)\%$ . As the movement of moisture during this preconditioning stage may lead to movement of  $\text{Cl}^-$  that existed in concretes, distribution of  $\text{Cl}^-$  in the three concretes before and after the RH conditioning process was tested and the results are presented in Fig. 4. As can be seen in this figure, the difference in the  $\text{Cl}^-$  distributions due to aforementioned preconditioning is negligible. Therefore, it can be inferred that the RH conditioning regime used in this study did not lead to any noticeable redistribution of  $\text{Cl}^-$  in the samples.



(a) 0.55PC



(b) 0.55PFA

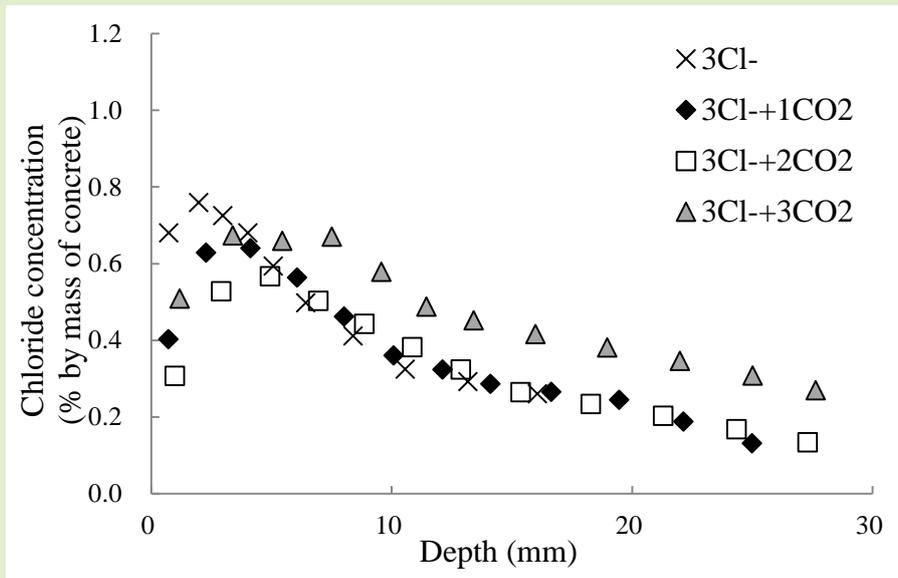


(c) 0.55PFA+MS

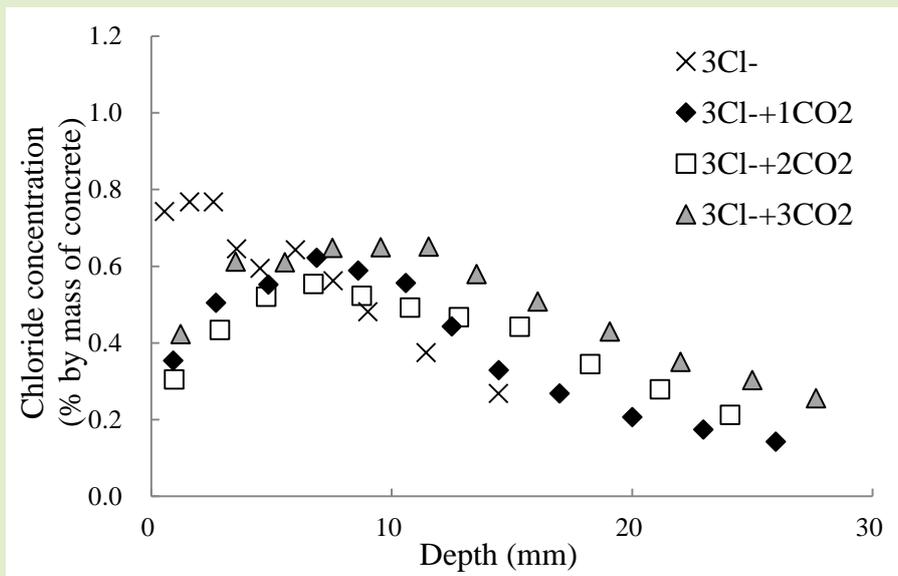
**Fig. 4.** Distribution of  $\text{Cl}^-$  before and after the condition of RH

The distribution of  $\text{Cl}^-$  after subjecting to  $3\text{Cl}^- + y\text{CO}_2$  regime (i.e. 3 months in chloride solution followed by up to 3 months of carbonation) is presented in Fig. 5. The  $C_s$  values obtained are summarised in Table 3. The following observations can be made from the results: (i) the  $C_s$  value decreased due to carbonation; (ii) carbonation resulted in redistribution of chlorides to greater depths;

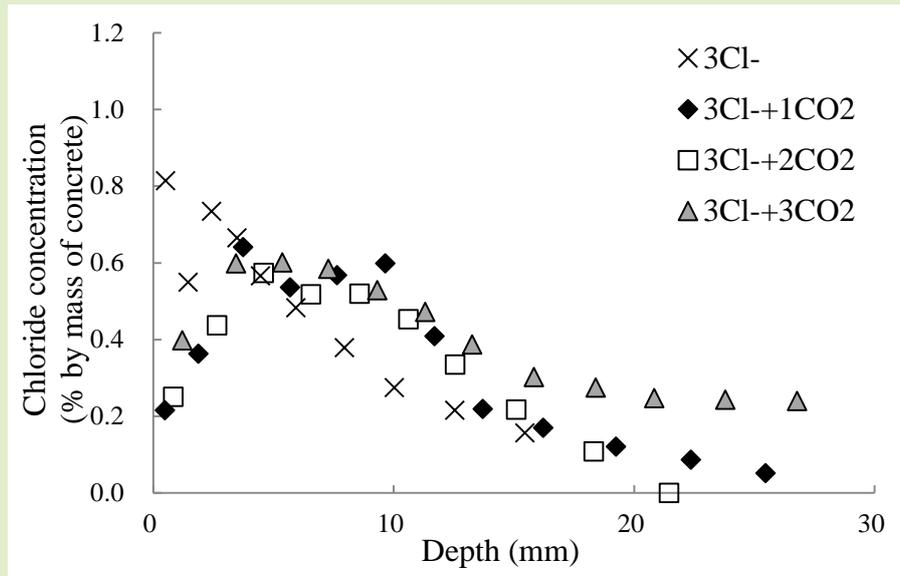
and (iii) the location of the peak chloride content [appeared to have moved inward](#).



(a) 0.55PC



(b) 0.55PFA



(c) 0.55PFA+MS

Fig. 5. Distribution of Cl<sup>-</sup> in concretes exposed to the 3Cl<sup>-</sup>+yCO<sub>2</sub> regime

Table 3. C<sub>s</sub> of the concretes under the 3Cl<sup>-</sup>+yCO<sub>2</sub> regime\*

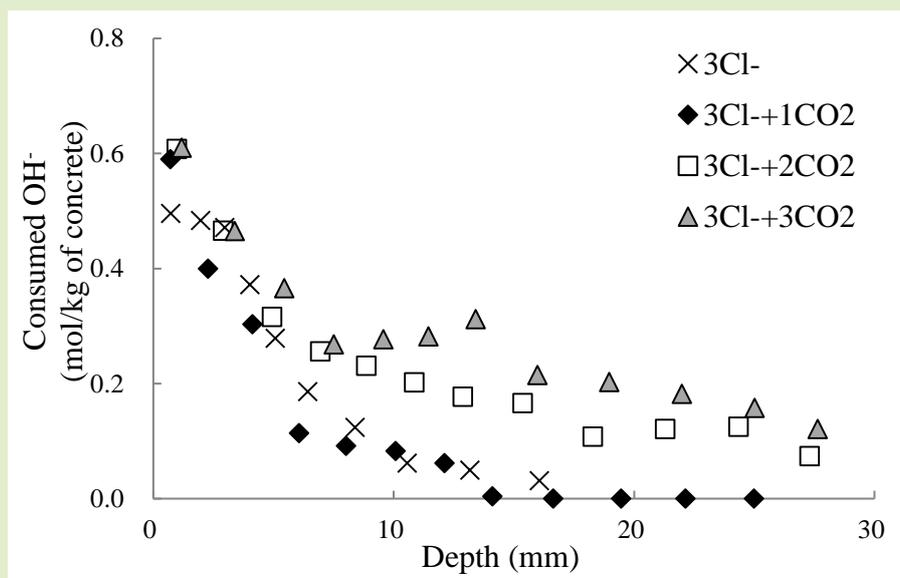
	3Cl <sup>-</sup>	3Cl <sup>-</sup> +1CO <sub>2</sub>	3Cl <sup>-</sup> +2CO <sub>2</sub>	3Cl <sup>-</sup> +3CO <sub>2</sub>
<b>0.55PC</b>	0.67 (0.01)	0.43 (0.04)	0.32 (0.01)	0.50 (0.02)
<b>0.55PFA</b>	0.75 (0.01)	0.39 (0.05)	0.36 (0.06)	0.44 (0.02)
<b>0.55PFA+MS</b>	0.82 (0.01)	0.25 (0.04)	0.24 (0.01)	0.43 (0.04)

\*Values in bracket indicate standard deviation of tested results from two individual cylindrical samples.

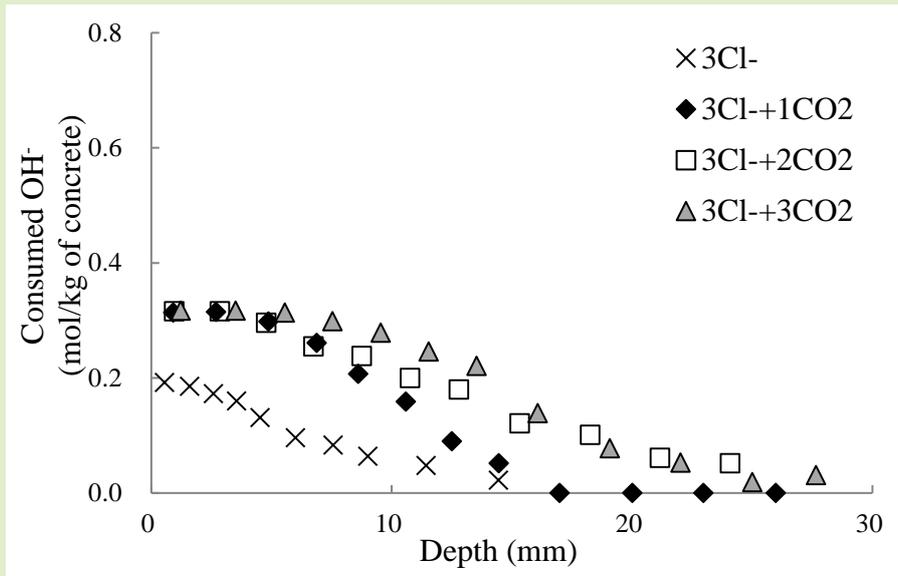
The redistribution of Cl<sup>-</sup> due to carbonation of chloride contaminated concrete is considered to be due to the release of Cl<sup>-</sup> that was previously bound in hydration products and the changes to concrete microstructure, as has already been reported by Tang and Nilsson<sup>[38]</sup> and Neville<sup>[10]</sup>. The movement of the released Cl<sup>-</sup> to greater depths can be considered to be due to the following reasons: (i) to maintain the equilibrium of free Cl<sup>-</sup> at different depths (i.e. diffusion process) of the concretes; (ii) to maintain the **electrical charge** balance between cations and anions, more specifically the balance between OH<sup>-</sup> and Cl<sup>-</sup>; (iii) carbonation leads to a densification of microstructure for the surface concretes and forces the released Cl<sup>-</sup> moving inward; and (iv) water generated during the carbonation and the subsequent

redistribution of moisture carry free chlorides to a new location inward.

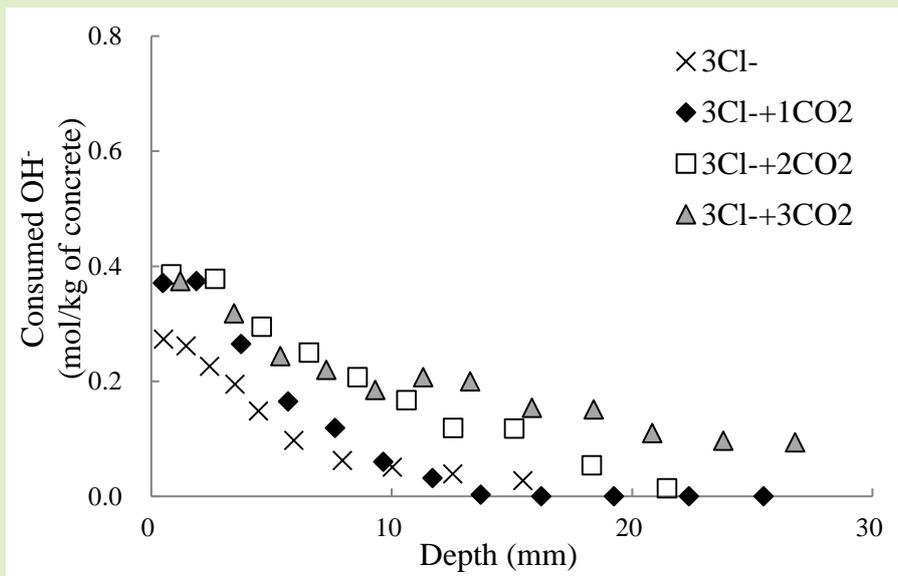
As can be seen from Fig. 5 and Table 3, the decrease in the  $C_s$  value occurred during the first month of carbonation and further continued carbonation did not have any similar effect. To explain this, the profile of the consumed  $\text{OH}^-$  is presented in Fig. 6. The results in this figure show that during the latter two months of carbonation the amount of consumed  $\text{OH}^-$  at the near-surface zone (0-3mm) of each mix did not have any noticeable increase. As the chloride binding capacity is pH related<sup>[39]</sup>, it can be stated also that concretes in this region did not have any obvious change in their chloride binding capacity. The previously bound chloride ions in the near-surface region were released by the carbonation (during the first month) and these  $\text{Cl}^-$  were free to move inwards, leading to a decrease of the total  $\text{Cl}^-$  in the near-surface region and the increase at greater depths. During the latter two months of carbonation, further decrease in pH occurred at inner depths (>3mm) which resulted in a continuous release of the bound  $\text{Cl}^-$  in this region. Therefore, the location of the maximum chloride content continuously moved inwards.



(a) 0.55PC



(b) 0.55PFA



(c) 0.55PFA+MS

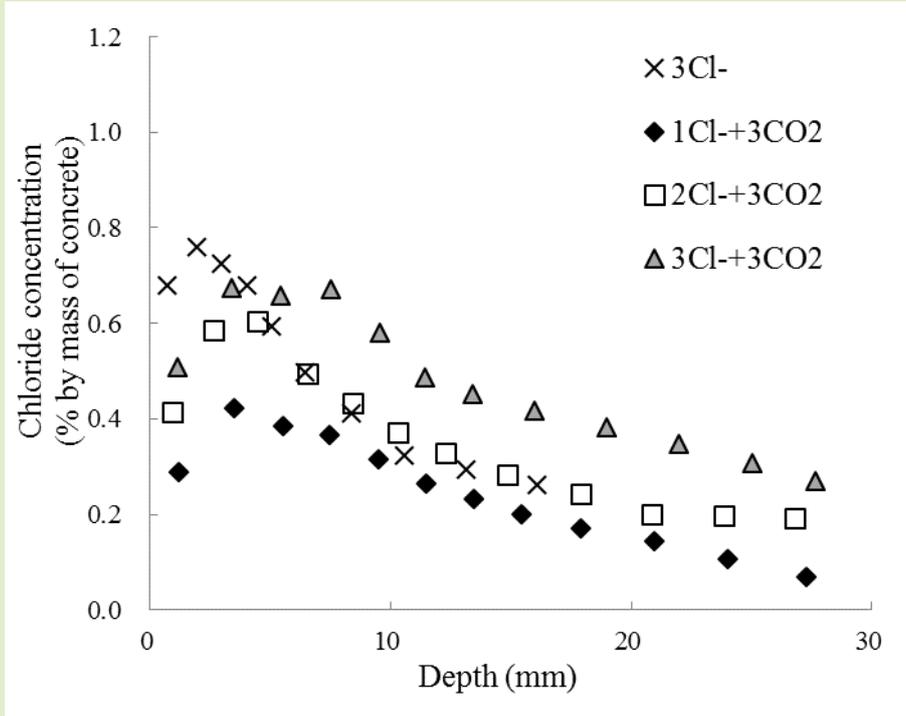
Fig. 6. Consumed OH<sup>-</sup> in concretes exposed to the 3Cl<sup>-</sup>+yCO<sub>2</sub> regime

**3.1.3 Effect of different duration of chloride immersion followed by 3 months of carbonation on chloride distribution (xCl<sup>-</sup>+3CO<sub>2</sub>)**

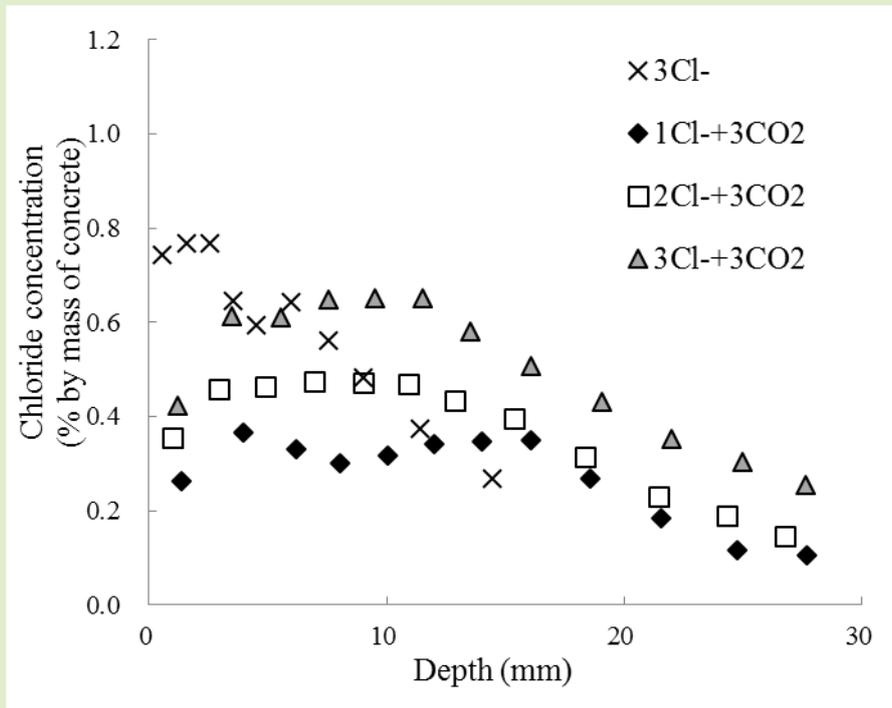
The distribution of Cl<sup>-</sup> in concretes exposed to three different durations of chloride exposure followed by three months of accelerated carbonation (xCl<sup>-</sup>+3CO<sub>2</sub> regime) is presented in Fig. 7. For

demonstrating the effect of carbonation on chloride profiles, the  $3\text{Cl}^-$  chloride profile (i.e. chloride profile after 3 months of immersion in chloride solution without subjecting to any carbonation) is also plotted in the figures. For each of the three mixes, similar findings have been observed, viz: (i) for each type of concrete, carbonation for three months after immersing in chlorides resulted in further inward penetration of chlorides; (ii) whilst comparing with the data in Fig. 3 for the three different durations of immersion in chloride solution, there was an increase in concentration of  $\text{Cl}^-$  at most inner depths in Fig. 7 when the concretes were subjected carbonation after the three different duration of immersion in chloride solution; (iii) the  $C_s$  value for the three mixes was relatively close and the values are comparable to  $3\text{Cl}^- + 3\text{CO}_2$  regime; (iv) the peak values of the chloride content and their locations were different for the three mixes.

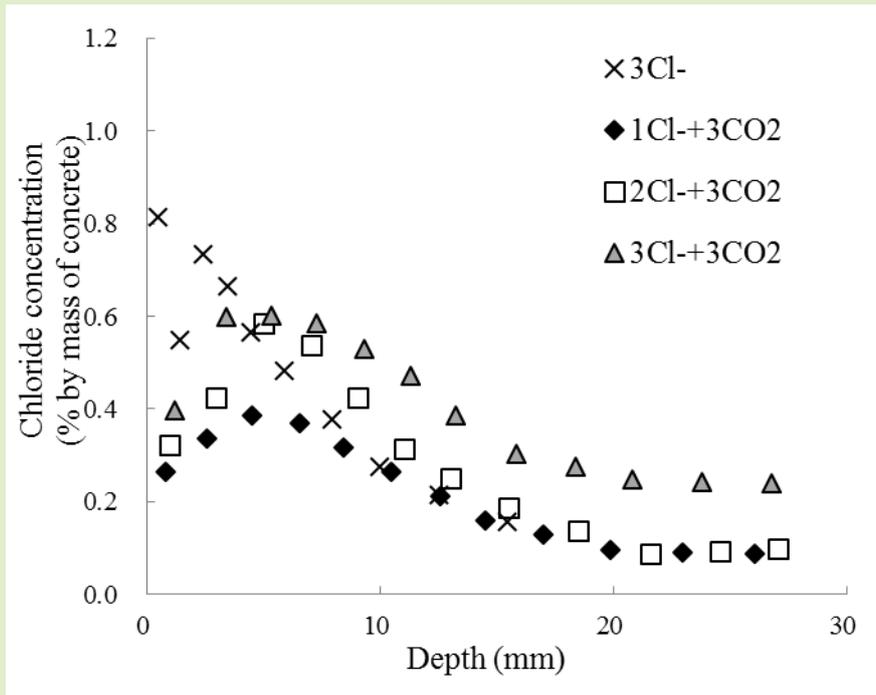
Given that there was not much of a difference between the three profiles for both 0.55PFA and 0.55PFA+MS mixes in Fig. 3, the data in Fig. 7 showing further penetration of chlorides in these concretes due to the 3 months of carbonation is unexpected. This could be an artifact of the experimental procedures or a chemical behaviour that cannot be explained without carrying out further microstructural analysis. Therefore, further investigation is solicited.



(a) 0.55PC



(b) 0.55PFA



(c) 0.55PFA+MS

**Fig. 7.** Distribution of  $\text{Cl}^-$  in concrete exposed to the  $x\text{Cl}^-+3\text{CO}_2$  regime

As in the case of  $3\text{Cl}^-+y\text{CO}_2$  regime presented in Fig. 5, there was a decrease in  $C_s$  values compared to the  $\text{Cl}^-$  concentrations within the concretes in these cases as well. As before, this is considered to be due to the release of bound  $\text{Cl}^-$  from binders as a result of carbonation and consequential physico-chemical changes, as explained previously.

A comparison of the location of the peak chloride concentration between the three concretes would indicate that the peak is at a greater depth for 0.55PFA compared to the other two concretes. This is indicative of a comparatively faster progress of carbonation in the chloride contaminated 0.55PFA concrete, which has been reported by Dhir et al.<sup>[40]</sup>, resulting in chlorides being pushed inward more rapidly than the other two concretes.

### **3.1.4 General discussion on exposure of concretes to chlorides first and then carbonation**

In reality, for most types of concretes carbonation is slower compared to chloride penetration. Therefore, the experimental data reported in this section are relevant to most concretes exposed to service environments. The data indicated that if there was no carbonation, chlorides would continually penetrate into concretes at different rates of ingress depending on the type of binder. In contrast, when these concretes are subjected to carbonation after a period of chloride exposure, the effects on chloride distribution within the concretes are obviously dependent on both the duration of CO<sub>2</sub> and chloride exposures and the type of binder. In general, carbonation of chloride contaminated concretes results in the release of bound chlorides, which pushes chlorides inwards and, hence, could be detrimental to the corrosion of steel reinforcement. Further, as the degree of carbonation could be different for different types of binders, the above effect could be more severe in some types of concretes, such as PFA, when compared to others. Therefore, it is essential to consider the combined effects of chlorides and carbonation in the design of concrete structures in marine and similar exposure conditions.

### **3.2 Concretes exposed to carbonation followed by chloride immersion (yCO<sub>2</sub>+xCl<sup>-</sup>)**

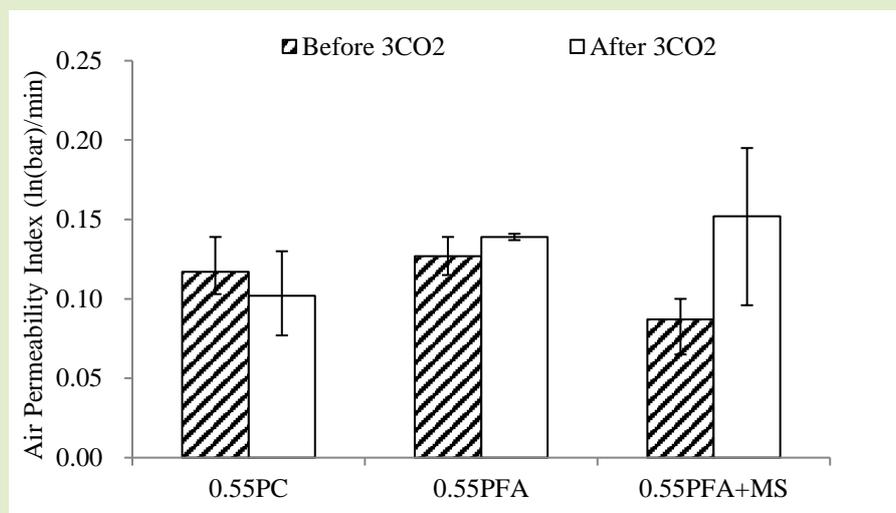
In the previous section, the effect of carbonation of chloride contaminated concretes was established. In this section, the influence of carbonation on subsequent ingress of Cl<sup>-</sup> is discussed based on the results obtained from the yCO<sub>2</sub>+xCl<sup>-</sup> regimes.

#### **3.2.1 Influence of carbonation on consumed OH<sup>-</sup>**

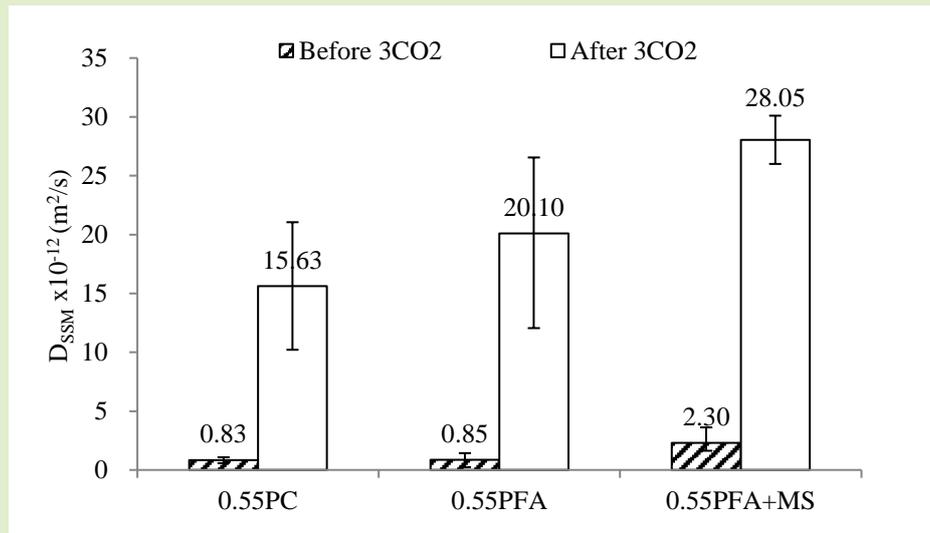
Before discussing the effect of chloride immersion of carbonated concretes on the distribution of chlorides within the concretes, the effect of different durations of carbonation itself is discussed. This

is done by comparing the effect of duration of carbonation on air permeability, chloride migration coefficient and the consumed  $\text{OH}^-$ .

To quantify the influence of carbonation on permeation properties of the near-surface region, *in situ* air and chloride permeability tests were carried out and the results are presented in Fig. 8. There was a significant increase in the chloride migration coefficient **due to prolonged carbonation** whereas the influence was rather subdued on air permeability, except for the microsilica concrete. **These differences in behaviour between air permeability and chloride migration depend on the nature and extent of influence of the changes to the pore structure due to carbonation in the near surface region of these concretes.** For the carbonation process, conventional understanding is that it causes calcite precipitation in the pores and therefore should densify the microstructure. However, carbonation is also known to induce cracking due to shrinkage, particularly when accelerated carbonation of CSH occurs<sup>[41-42]</sup>. This can explain the prominent increase in the air permeability for the microsilica concrete. The results in Fig. 8, particularly the chloride migration coefficients, would **suggest** the presence of carbonation-induced cracks in all the three concretes **as well**.



**(a) Air Permeability Index**



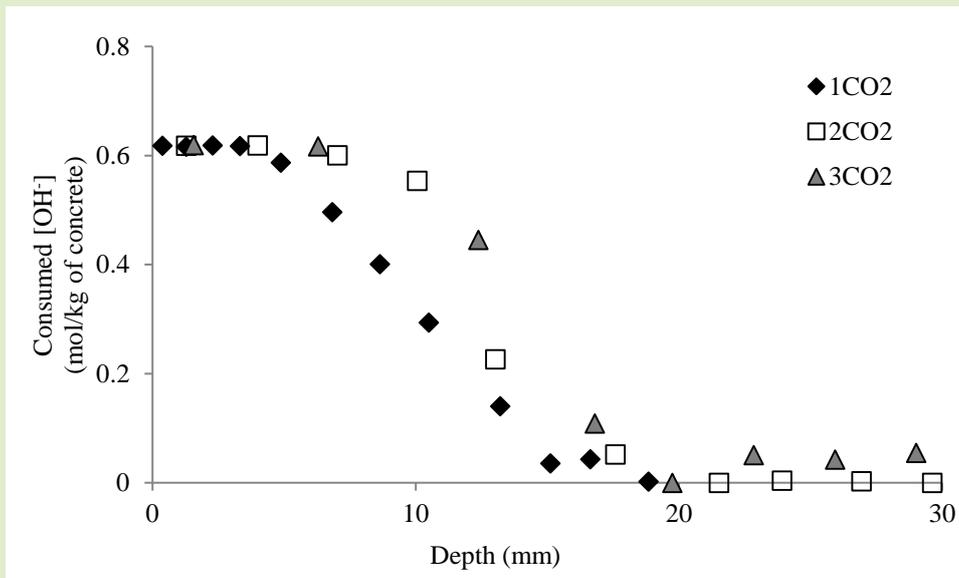
**(b) Chloride Migration Coefficient**

**Fig. 8.** Influence of carbonation on permeation properties of concretes

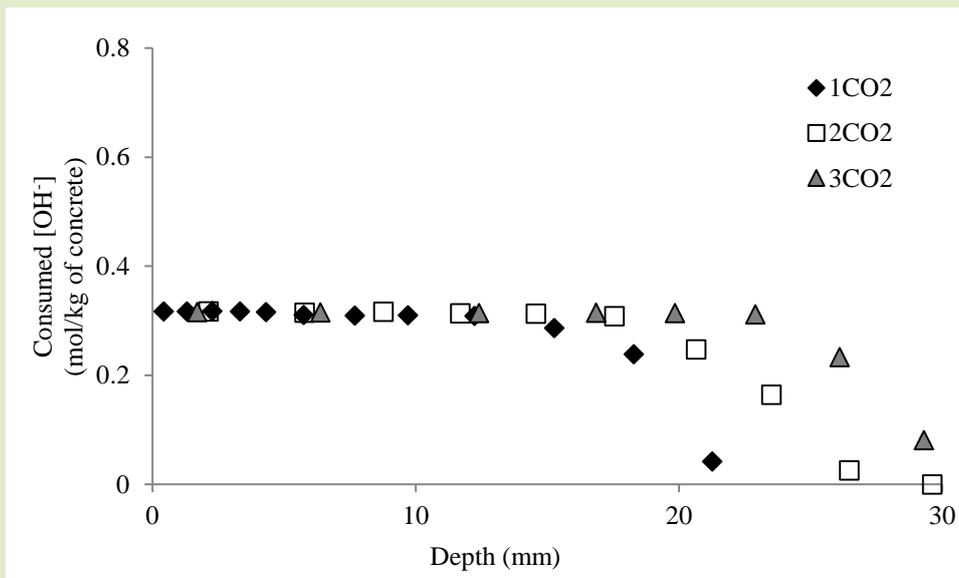
The amount of consumed  $\text{OH}^-$  calculated using Eq. 1 is plotted in Fig. 9, as an indicator of the pH change due to carbonation rather than using the traditional phenolphthalein test due to its limitation in distinguishing pH variations at different degrees of carbonation of concretes containing supplementary cementitious materials<sup>[43]</sup>. For the three types of concretes the change in consumed  $\text{OH}^-$  is obviously slowed down after 1 month of carbonation, indicating that microstructural changes during the first month of carbonation had retarded further penetration of carbon dioxide into the concrete. This may appear to contradict the permeation results reported in Fig. 8, which shows an increase in permeability due to carbonation, presumably due to the formation of microcracks during the carbonation process.

The highest consumption of  $\text{OH}^-$  due to carbonation was found for PC concretes, presumably due to the availability of sufficient quantities of  $\text{Ca}(\text{OH})_2$  to buffer the pH reduction due to carbonation. Due to the low PC content in 0.55PFA concretes, there was relatively a lower consumption of  $\text{OH}^-$  at all depths. However, the consumption of  $\text{OH}^-$  was almost constant up to 20-30mm for the 0.55PFA

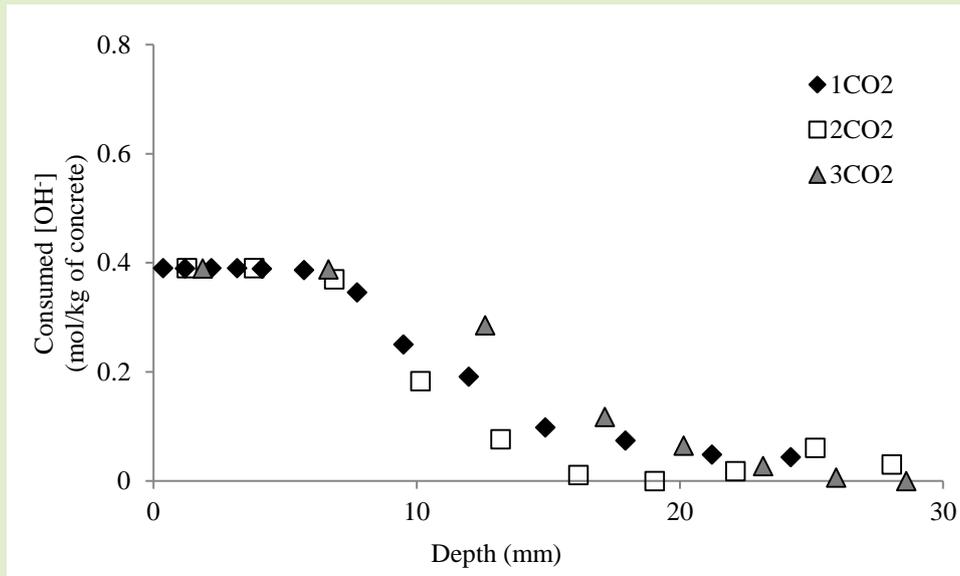
concretes, indicating that these concretes carbonated much deeper than their PC counterparts. The results in Fig. 9c shows that for 0.55PFA+MS concretes, there is a sudden decrease in the consumption of  $\text{OH}^-$  at a depth of around 7mm. This concrete has only 85% PC and consequently it has a lower availability of  $\text{OH}^-$  to carbonate compared to the PC counterpart. This was reflected in the rather low value of  $\text{OH}^-$  consumption nearer to the surface.



(a) 0.55PC



(b) 0.55PFA

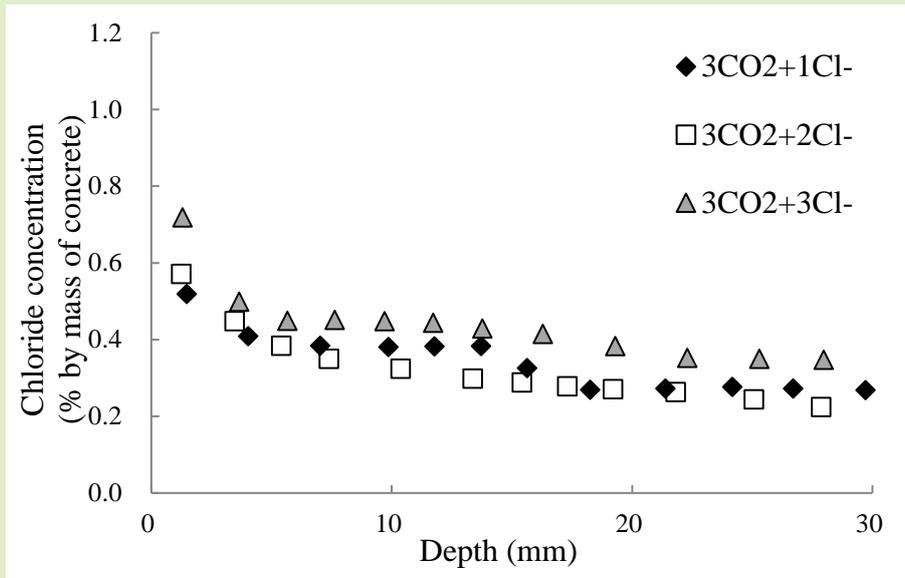


(c) 0.55PFA+MS

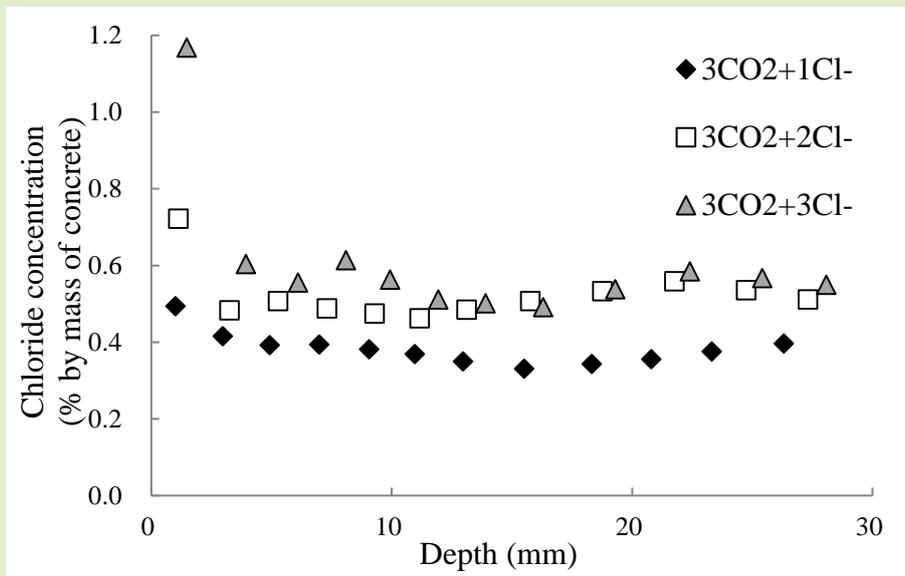
Fig. 9. Consumed  $\text{OH}^-$  during the three months of carbonation

### 3.2.2 Ingress of chloride ions in carbonated concretes ( $3\text{CO}_2+x\text{Cl}^-$ )

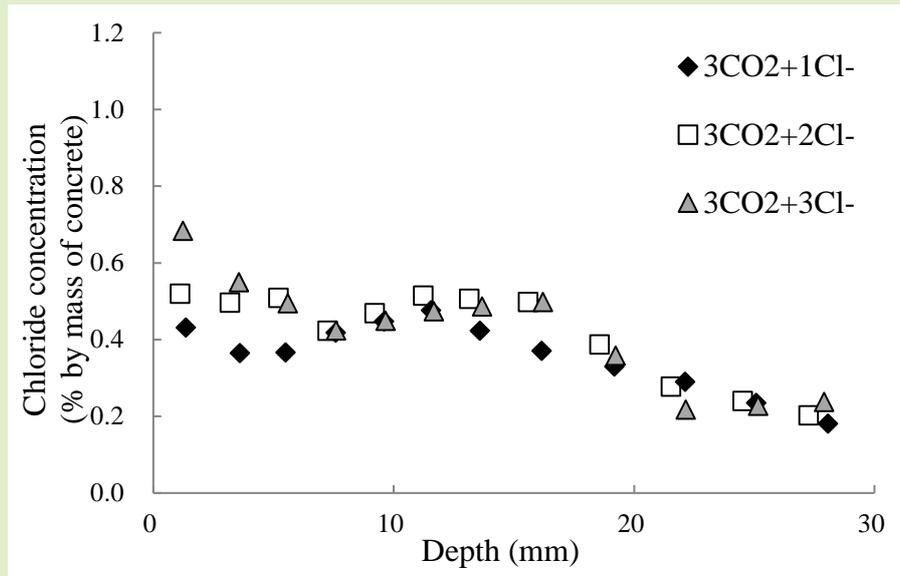
Figure 10 shows that 3 months of carbonation had severely affected the subsequent ingress of chlorides, so much that the chloride profile is more or less flat in all cases. These results confirm that carbonation had detrimental effect on chloride transport in all the three concretes, as concluded in the previous section. It may also be noted that prolonging the duration of exposure have negligible effect on the chloride profile for the first 30mm. The reduction in pH due to carbonation also affects the flow of chlorides as well as the binding capacity to an extent. Unlike the previous cases, there is no Friedel's salt that can decompose during carbonation. As the pH is low in carbonated concrete, Friedel's salt is not expected to have been formed during the chloride immersion after the carbonation. **Therefore, the relatively higher chloride concentration at the near-surface layer than that of the inner depths might be due to an increased quantity of chloride salts deposited in the carbonation induced cracks in the near surface region.**



(a) 0.55PC



(b) 0.55PFA

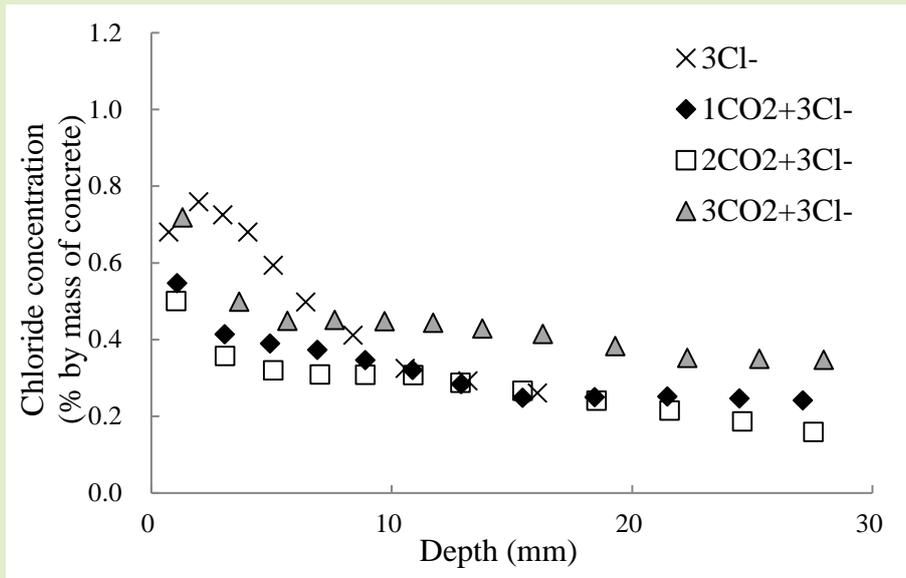


(c) 0.55PFA+MS

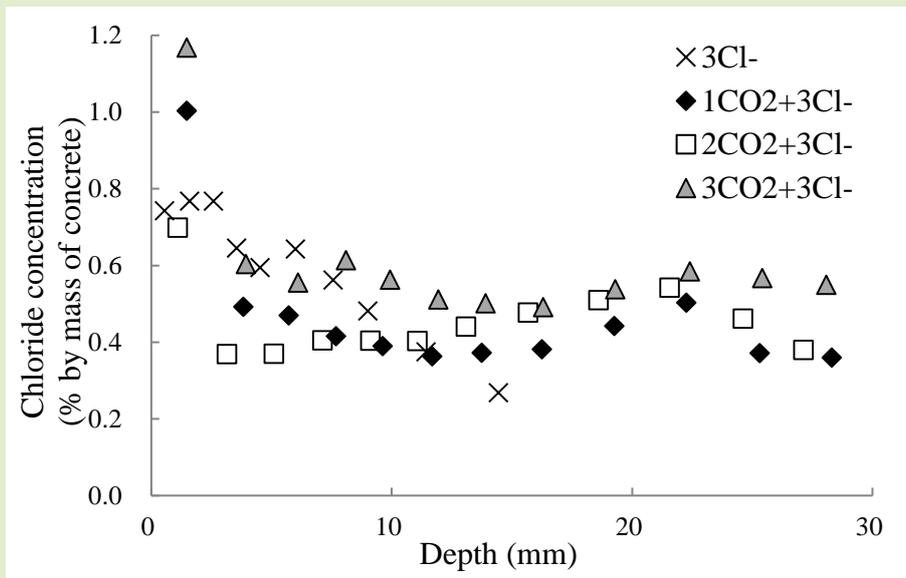
Fig. 10. Distribution of Cl<sup>-</sup> for the 3CO<sub>2</sub>+xCl<sup>-</sup> regime

### 3.2.3 Influence of carbonation duration on distribution of chloride ions (yCO<sub>2</sub>+3Cl<sup>-</sup>)

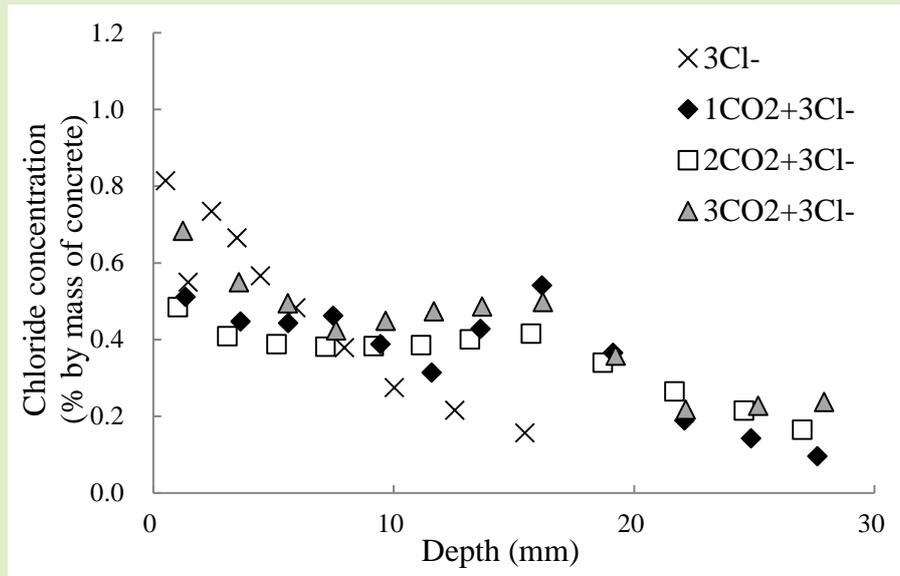
Figure 11 presents the distribution of Cl<sup>-</sup> in concretes subjected to the yCO<sub>2</sub>+3Cl<sup>-</sup> regime. These results show that compared to non-carbonated samples exposed to chlorides for three months, immersion of carbonated concretes in the chloride solution led to a decrease in chloride concentration at the near-surface area (but did not have an associated decrease in the C<sub>s</sub> values in all cases) and an increase at greater depths. For all carbonated specimens subjected to three months of chloride immersion, a flat-shaped chloride profile can be seen. As discussed in the previous section, this shape indicates a highly diffusive chloride flow. That is, the chloride profiles in Fig. 11 would suggest that chlorides could reach the level of reinforcement in carbonated concretes much faster than that in uncarbonated concretes. It can also be noted that prolonging the carbonation duration beyond a month has led to only a slight increase in the Cl<sup>-</sup> concentration across the samples.



(a) 0.55PC



(b) 0.55PFA



(c) 0.55PFA+MS

Fig. 11. Distribution of  $\text{Cl}^-$  in concretes exposed to  $\text{yCO}_2+3\text{Cl}^-$  regime

### 3.2.4 General discussion on exposure of concretes to chlorides after carbonation

The discussion in this section is relevant to concretes which are in sheltered environment (such as bridge abutment or bridge deck) or protected with surface treatments. In the former case, carbonation may proceed initially and then leaking of expansion joints may well admit chlorides into the concrete. In the latter case, the surface treatment would prevent chloride ingress but allow breathing of concrete. In such cases, carbonation may well progress initially, but with continuous influence of ultraviolet radiation, the protective properties of surface treatments against chloride penetration may diminish with time. In both these cases, there is a serious issue because chlorides can penetrate deep and at higher quantities due to the presence of carbonation induced shrinkage cracks in the near surface region. This combination, as seen in this section, could be much more severe than the previous more realistic situation, particularly for certain types of concretes.

Finally, the results in both combination regimes studied in this research would indicate that service

life models which do not take account of these interactive effects on different types of binders are likely to underestimate the life of concrete structures in such environments, e.g. [tunnel linings](#).

#### **4. Conclusion**

Based on the experimental results presented in this paper, the following conclusions have been drawn:

1. During the immersion of concretes in chloride solution for three months, the ingress of  $\text{Cl}^-$  in the PC concrete took place during the entire duration. However, for the two concretes containing PFA and MS, the ingress of  $\text{Cl}^-$  was mainly in the first month, confirming the already established benefits of these cementitious materials to reduce the chloride penetration in concretes.
2. Chloride content at the near-surface layer of concrete is sensitive to the exposure regime. After immersion in chloride solution for three months, the  $C_s$  value for the three concretes was about 0.8% by mass of concrete. When exposed to the subsequent carbonation process, the  $C_s$  value decreased to values in the range 0.2-0.5%.
3. The influence of carbonation on chloride ingress is found to be dependent on their sequence of occurrence. When concretes are subjected to chloride exposure followed by carbonation,  $\text{Cl}^-$  are redistributed during the carbonation stage and the extent of this redistribution is related to the degree of carbonation of the samples. However, when carbonated concretes are exposed to chlorides, there is an increased penetration of chlorides much deeper into the concrete due to possible presence of carbonation induced microcracking in the near-surface region.
4. The results reported and discussed in this paper illustrates the complex interactions that could upset any service life model which does not take account of these interactive effects and the differing

nature of them for different types of concretes.

## **Acknowledgement**

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