INFLUENCE OF CHLORIDE IONS ON PROGRESS OF CARBONATION IN CONCRETES

Yaocheng Wang
School of Civil Engineering, Shenzhen University;
Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen, P.R.China

P.A.M. Basheer
School of Civil Engineering, University of Leeds, England, the UK

Sreejith Nanukuttan
School of Planning, Architecture and Civil Engineering, Queen's University Belfast, Northern Ireland, the UK

Yun Bai
Department of Civil, Environmental and Geomatic Engineering, University College London, London, UK

ABSTRACT: Concretes used in marine environment are generally under the cyclic effect of CO_2 and chloride ions (Cl^-). To date, knowledge on influence of Cl^- in concrete on the progress of carbonation has not been fully established. During the study, concretes of well-cured and previously exposed to NaCl solution were exposed to high CO_2 concentration environment for three months. Profiles of apparent pH and chloride concentration were used to indicate the progress of carbonation and ingress of Cl^- in concretes. Results show that carbonation was significantly slowed down due to the existence of Cl^-, *viz.* the profile of consumed OH^- became modest. For the well-cured concretes, the carbonation generated microcracks on concrete surface and increased permeation properties; for the chloride contaminated concretes, due to the limited extent of carbonation, permeation properties did not present obvious difference.
Keywords: alkalinity, carbonation, chloride, combined mechanism, permeation properties.

INTRODUCTION

Durability of concrete structures is a world-wide important studying topic and it significantly

influences the service life of a structure. Regarding all the aspects of the durability issues, corrosion of embedded reinforcement is one of the most detrimental concerns for engineers, which may be initiated by carbonation and chloride ingress. For certain structures, such as those constructed in marine environment[1-5], their reinforcement might be simultaneously influenced by the carbonation and chloride ions (Cl^-). Similar aggressive environment is also found for structures that are constructed in cold regions[6], where rock salt is usually used in winter to melt ice and contains significant amount of Cl^-. Study from scholars has proved that the corrosion of reinforcement will be accelerated when it is under the effect of carbonation and chloride ions simultaneously[7-9]; the difficulty for initiation of the corrosion relates to alkalinity (is decreased due to the carbonation) and content of chloride ions in its vicinity concrete[7,8]. Therefore, ingress of Cl^- and carbonation in cover concretes under the combined mechanism of exposure needs to be studied.

In the case of a combined carbonation and chloride ingress, chemical reactions taken place are very complicate, including the CO_2 or Cl^- with cement hydration products and their further reactions with products of previous carbonation and chloride ingress. The findings from the independent carbonation and chloride ingress cannot describe the progress of carbonation and chloride ingress in the concretes under the combined effect of CO_2 and Cl^-. Therefore, study on development of alkalinity and distribution of chloride ions in concrete under the combined effects is significantly needed, which are still limited.

In this paper, a systematic study on progress of carbonation in well-cured and chloride contaminated concretes is reported. By comparing the consumption of OH^- and change in permeation properties of concretes that exposed to independent carbonation and combined chloride ingress and carbonation regimes, the influence of Cl^- on progress of carbonation is established.

EXPERIMENTAL PROGRAMME

Details of the experimental programme of this study are summarised below:
1. Table 1 gives detailed mix proportions of the different concrete mixes used in this study. The mixes had a w/b of 0.55 and a total binder content of 320kg/m^3, which were selected according to BS EN 206[9] for concrete exposed to XC2, XD2 and XS2 environments and for an expected service life of 50 years[10]. Three types of binders were used, *viz.* Portland cement (PC), Pulverised Fuel Ash (PFA) and microsilica (MS). The mixes are denoted as 0.55PC, 0.55PFA and 0.55PFA+MS. A polycarboxylate based superplasticiser was used to achieve a slump of 50 to 90 mm (S2 class in BS EN 206[9]).
2. Three types of block samples were manufactured: 150×150×80mm blocks were cast for monitoring the relative humidity (RH) of concrete during conditioning and carbonation; 500×500×80mm blocks were cast for coring 75mm diameter×80mm long cylindrical specimens; 230×230×80mm blocks were cast for detecting permeation properties of the concretes under the effects from different exposure regimes.
3. After cast, samples were placed in a room at a temperature of 20(±2)°C for 24 hours and subjected to another period of 55 days of curing after demould, which included a period of water curing of the hardened concrete for 6 days and storage in a room at 20(±1)^{0}C and 60(±5)% RH for 49 days.

Table 5. *Mix proportions of the concretes*

Mixes	w/b	Type of binder and their content (%)	Quantities (kg/m3)							
			PC	PFA	MS	Sand	10mm Agg	20mm Agg	Super plasticiser	Water
0.55PC	0.55	PC(100)	338	0	0	683	663	663	1.6	176
0.55PFA	0.55	PC(70)+PFA(30)	234	100	0	677	658	658	1.68	176
0.55PFA +MS	0.55	PC(85)+PFA(10) +MS(5)	285	34	17	679	659	659	2.18	176

4. Conditioning of samples for different exposure regimes. The independent and combined carbonation and chloride ingress regimes are denoted as xCl^-, yCO_2, yCO_2+xCl^- and xCl^-+yCO_2. 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. In the carbonation stage of the regimes, samples were all conditioned to a consistent RH of 65 (±2)% in ovens before exposing to 20 (±1)°C, 5 (±0.1)% CO_2 and 65 (±2)% RH environment. Prior to the chloride immersion stage, samples were water saturated and then exposed to 165g/l NaCl solution at 20 (±1)°C. In both the independent and combined regimes, maximum duration for the carbonation and chloride ingress processes was three months.

5. During the experimental analysis, following tests were carried out:

Apparent pH[11] was determined using drilled dust samples and this is used to indicate the alkalinity of concrete[12]. By further analysis of the results, the amount of consumed OH^- at different depths of the samples was ascertained using Equation 1, where the pH_0 and the pH_x are the apparent pH results measured before and after the exposure. The relationship between apparent pH and remaining and consumed OH- is presented in **Error! Reference source not found.**.

Acid soluble chloride content of the powder samples extracted from the different depths of the sample was analysed according RILEM TC 178- TMC[24].

Concrete permeability was measured by using the Autoclam permeability system[13] and the 'Permit' chloride ion migration test[14] on three 230×230×80mm blocks.

$$Consumed\ OH^- = Initial\ OH^- - Remained\ OH^- = 10^{pH_o-14} - 10^{pH_x-14} \quad (1)$$
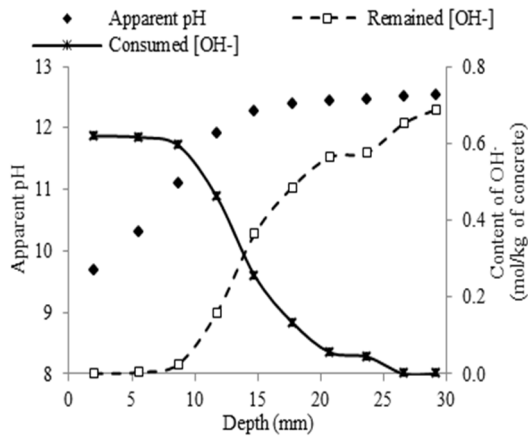
Fig. 1: *Relationship between apparent pH and remaining and consumed OH⁻*

PRESENTATION AND DISCUSSION OF RESULTS

Progress of carbonation in well-cured and chloride contaminated concretes

Fig. 1 presents the consumed OH^- in the yCO_2 concretes. During the 'yCO_2' regime, alkalinity of concrete was studied every two weeks. However, the profile of consumed OH^- was presented in a monthly basis to keep the clarity of figures.

Before carbonation, the OH^- concentration of the three concretes was 0.62, 0.32 and 0.39mol/kg of concrete, respectively. The relatively lower values in the 0.55PFA and the 0.55PFA+MS should be due to the use of PFA and MS, which consumed OH^- during their pozzolanic reaction. A higher OH^- content in the 0.55PFA+MS than that in the 0.55PFA should be mainly due to the lower substitution of cement in the 0.55PFA+MS (15%) than in the 0.55PFA (30%). in the profiles Fig. 1, clearly show the progress of carbonation in concretes, which was the most obvious during the 1st month. The progress of carbonation, viz. the location where the consumed OH^- was no longer zero, was similar is 0.55PC and 0.55PFA+MS, while the 0.55PFA was the highest. Similar results on concrete alkalinity during carbonation were reported in other studies[15,16].

Fig. 3 presents the progress of the consumed OH^- and the carbonation depths for concretes during the yCO_2 stage of the $3Cl^-+yCO_2$ regime. It indicates that the consumption of OH^- at the surface layer mainly took place during the early stage of carbonation; at the later stage of carbonation, it mostly took place at deeper depths. Compared to the 0.55PC, the other two mixes, especially for the 0.55PFA, had a stabilised consumed OH^- area (around 0-3mm), which should be due to their relatively lower anti-carbonation property.
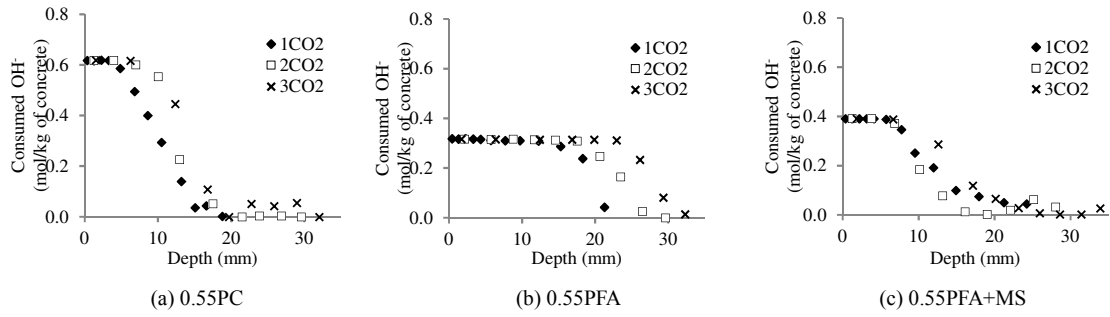
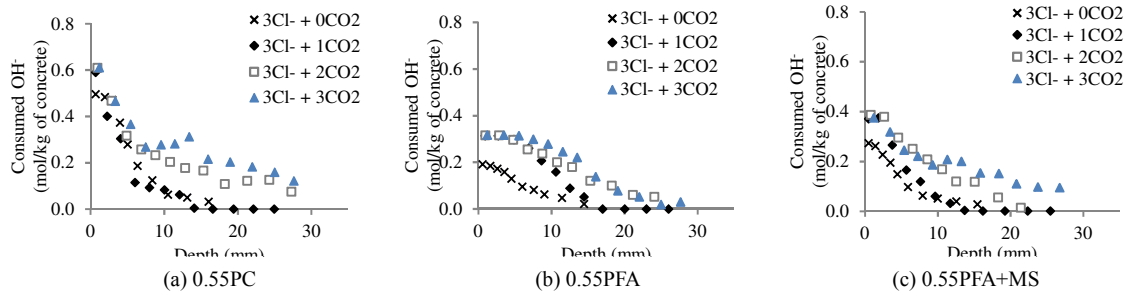**Fig. 1** *Progress of carbonation in concretes during the yCO₂ regime*

Fig. 2 *Variation of consumed OH⁻ in the concretes subjected to the 3Cl⁻+yCO₂ regime*

Change in permeation properties of concretes

Air permeability index

Fig. 3 presents change in the Air permeation Index (API) during the three months of carbonation and there was a general increase in the results for the mixes studied. In theory, the change in the API results during carbonation is related to a few parameters, including content of water, densification of concrete due to formation of $CaCO_3$ and formation of microcracks on concrete surface.
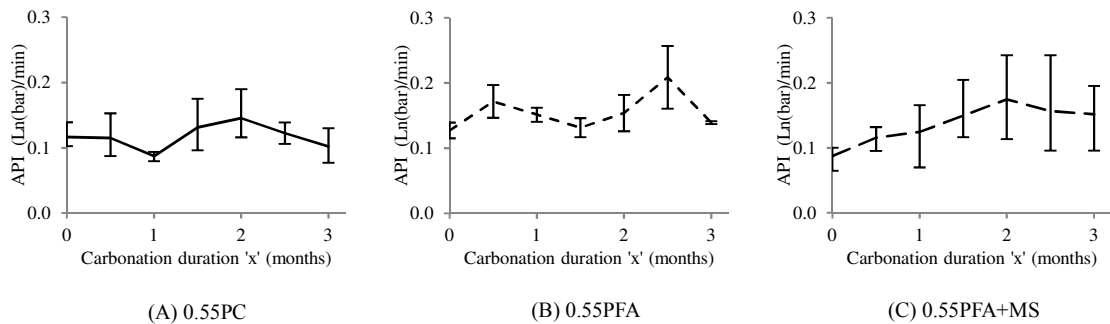

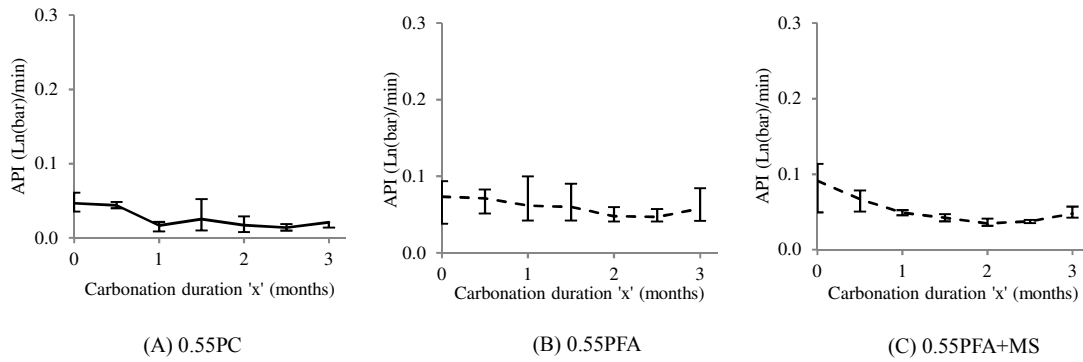**Fig. 3** *Change in API during the 3CO₂ regime*

Theoretically, the content of water, which will be generated during carbonation, influences the permeation properties of concrete. During the $3CO_2$ stage, the water content, in term of RH, at different depths of concrete was in a range of 50% to 70%, which have been proved lead to negligible influence on air permeability of concrete[17,18]. Therefore, the change in the API in **Fig. 3** could be regarded as completely due to microstructure variation of concrete under carbonation. Based on existing knowledge, regarding to the effect of carbonation, a decrease in API should be caused by formation of $CaCO_3$ from hydration products, which is a volume expansion process and densified the microstructure; an increase in values should be caused by the formation of cracks on concrete surface. The observed increase in API for the three mixes is in consistent with findings reported in other studies on influence of carbonation on concretes: under the effect of carbonation, concretes with relatively higher w/b ratios are easily to get crack comparing with those with low w/b ratios[19]; higher dosage of PFA increases the potential of cracking for concretes[20].

Fig. 5 presents the change in API during the $3CO_2$ stage of the $3Cl^-+3CO_2$ regime, which decreased continuously. The RH of the concrete at the surface was tested during the study and was in the range of 65-70%, which has negligible influence on the API results[17,18]. Therefore, the decrease in API can deduce that the pore structure is densified.

Chloride migration coefficient

Error! Reference source not found. shows the steady state chloride migration coefficient (D_{SSM}) of concretes before and after the three months of carbonation stage in the two regimes. After the 56 days of curing, the D_{SSM} of the three mixes was in the range of 0.8 to $2.3 \times 10^{-12} m^2/s$ and the values increased to about 12 to 15 times of their original values after the three months of carbonation. This is inconsistence with the increase in API results and indicates the formation of cracks. In the $3Cl^-+3CO_2$ regime, after the $3Cl^-$ stage, the D_{SSM} results presented an noticeable increase, which should be because calcium hydroxide crystals leached out of the concrete and led to an increase in porosity at the surface layer. During the latter $3CO_2$ period, the change in the D_{SSM} was negligible comparing with that in the independent $3CO_2$ regime.
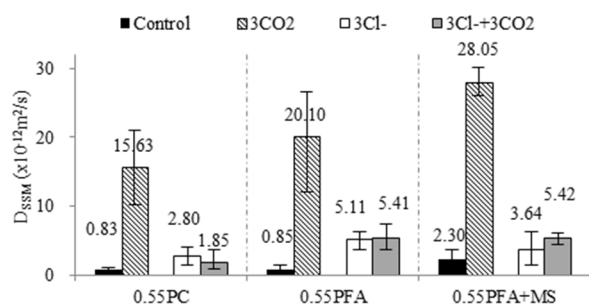
120

Fig. 6: *Change in D_{SSM} of the concretes*

CONCLUSION

In this paper, experimental work carried out in comparison progress of carbonation in well-cured and chloride contaminated concretes was reported. As can be concluded from the results, immersion of concretes in NaCl solution can slow down the consumption of OH^-. Detailed evidences those support this conclusion can be summarised as follows.

1. In the previous chloride contaminated concrete, amount of OH^- consumed during carbonation was lower than those exposed to individual carbonation regime. Also, in the consumed OH^- profile, the gradient of the curve was relative modest and the carbonation front decreased significantly. The noticeable consumption of OH^- at deeper depths of the $3Cl^-+yCO_2$ concretes was likely to be due to the ionic exchange between Cl^- and OH^- during the previous chloride immersion stage.

2. Comprehensive results from the air pereability and the chloride migration tests proved the increase in permeation properties in well cured concretes after carbonation, which might be due to formation of microcracks. For the carbonation after the chloride immersion stage, air permeability decreased and the chloride migration did not present obvious variation, which proved the densification of concrete that is generally taken place at initial stage of carbonation.

REFERENCE

[1] Castro, P., Moreno, E.I. and Genesca, J., 2000. Influence of marine micro-climates on carbonation of reinforced concrete building. *Cement and Concrete Research*, 30(10), pp. 1565-1571.

[2] Mohammed, T.U., Hamada, H. and Yamaji, T., 2004. Concrete after 30 years of exposure - Part II: Chloride ingress and corrosion of steel bars. *ACI Materials Journal*, 101(1), pp. 13-18.

[3] Moradian, M., Shekarchi, M., Aabdollah, M. and Alidadi, R., 2012. Assessment of long-term performance of a 50-year-old jetty in the south of Iran. *Journal of Performance of Constructed Facilities*, 26(5), pp. 633-643.

[4]   Zhao, H., Zhang, Y.M. and Ming, J., 2013. Tests and evaluation of structural concrete durability at Ningbo Marine wharf. *Hydro-Science and Engineering*, 5, pp. 54-60.

[5]   Song, Y.D., Liu, J.H., Yi, F.X., Xu, B. and Ge, P., 2013. Research on the Concrete Performance in the Marine Environment. *Applied Mechanics and Materials*, 345, pp. 184-188.

[6]   Aveldano, R.R. and Ortega, N.F., 2011. Characterization of concrete cracking due to corrosion of reinforcement in different environments. *Construction and Building Materials,* 25(2), pp. 630-637.

[7]   Moreno, M., Morris, W., Alvarez, M. and Duffó,G., 2004. Corrosion of reinforcing steel in simulated concrete pore solutions: Effect of carbonation and chloride content. *Corrosion Science,* 46(11), pp. 2681-2699.

[8]   Pakawat, S. and Uomoto, T., 2005. Effect of cyclic exposure of carbonation and chloride on corrosion of reinforcing steel in concrete. *Seisan Kenkyu,* 57(2), pp. 29-32.

[9]   British Standard EN 206, 2000. *Concrete- Part 1: Specification, performance, production and conformity.* British Standard Institution, London.

[10]   British Standard BS 8500, 2006. *Concrete - Part 1: Complementary British Standard to BS EN 206 - Part 1: Method of specifying and guidance for the specifier.* British Standard Institution, London.

[11]   McPolin, D., Basheer, P.A.M., Long, A.E., Grattan, K. and Sun, T., 2007. New test method to obtain pH profiles due to carbonation of concretes containing supplementary cementitious materials. *Journal of Materials in Civil Engineering,* 19(11), pp. 936-946.

[12]   Li, L., Sagüés, A.A. and Poor, N., 1999. In situ leaching investigation of pH and nitrite concentration in concrete pore solution. *Cement and Concrete Research,* 29(3), pp. 315-321.

[13]   Basheer, P.A.M., 1994. The Autoclam-a new test for permeability. *Concrete,* 28(4), pp. 27-29.

[14]   Nanukuttan, S. V., Basheer, P. A. M., Russell, M. I. and Robinson, D. J., Recent developments in in-situ chloride migration test: Permit ion migration test; 2008; MEDACHS 2008: Conference on Construction Heritage in Coastal and Marine Environments, January 2008, Lisbon, Portugal. CD-Rom 1-9.

[15]   McPolin, D., Basheer, P.A.M., Long, A.E., Grattan, K. and Sun, T., 2007. New test method to obtain pH profiles due to carbonation of concretes containing supplementary cementitious materials, *Journal of Materials in Civil Engineering,* 19(11), pp. 936-946.

[16]   Sisomphon, K., and Franke, L., 2007. Carbonation rates of concretes containing high volume of pozzolanic materials, *Cement and Concrete Research,* 37(12), pp. 1647-1653.

[17]   Parrott, L.J., 1991. Measurement of air permeability and relative humidity in cover concrete*, British Cement Association Report,* pp. 12*.*

[18]   Nolan, E., 1996. *Influence of near surface moisture gradients in concrete on Autoclam permeation measurements*, Queen's University Belfast.

[19]   Ngala, V.T. and Page, C.L., 1997. Effects of carbonation on pore structure and diffusional properties of hydrated cement pastes. *Cement and Concrete Research*, 27(7), pp. 995-1007.

[20]   Hobbs, D., 1994. Carbonation of concrete containing pfa. *Magazine of concrete research,* 40(143), pp. 69-78.