Influence of carbonation on the bound chloride concentration in different cementitious systems.

Article:

Zheng, Y, Russell, M, Davis, G et al. (4 more authors) (2021) Influence of carbonation on the bound chloride concentration in different cementitious systems. Construction and Building Materials, 302. 124171. ISSN 0950-0618

https://doi.org/10.1016/j.conbuildmat.2021.124171

Influence of carbonation on the bound chloride concentration in different cementitious systems

Yujia Zheng[1], Mark Russell[1], Geoff Davis[1], Daniel McPolin[1], Kai Yang[2], P.A.M Basheer[3] Sreejith Nanukuttan[1*]

[1]School of Natural and Built Environment, Queen's University Belfast, Northern Ireland, United Kingdom

[2]College of Materials Science and Engineering, Chongqing University, China

[3]School of Civil Engineering, University of Leeds, England, United Kingdom

Abstract

Deterioration of reinforced concrete is often studied in idealised scenarios where only one exposure environment is dominant. For example, to study concrete structures exposed to de-icing salt environments, the effect of a cyclic wetting and drying regime is considered, but deterioration by carbonation is not given any emphasis. However, some studies have shown that carbonation could result in the release of bound chlorides and this could lead to an increase in chloride content near steel in reinforced concrete. Through an investigation on the influence of carbonation on the bound chlorides in different cementitious pastes, this paper highlights the positive initial effects that carbonation has on the chloride binding behaviour and later the changes that occur in both the pH of concrete and the bound chloride content for both low and high w/b mixes. Two mathematical expressions are put forward for mapping: (i) the changes in apparent pH as a function of the duration of carbonation and mix ingredients; and (ii) the reduction in the bound chlorides with a proportional reduction in apparent pH. The latter is valuable in quantifying the changes to binding capacity in service life models due to carbonation, with the help of a simple pH measurement.

Keywords: bound chlorides; carbonation; pH, hindrance effect; pulverized fly ash; silica fume

*Corresponding author s.nanukuttan@qub.ac.uk

1. Introduction

The deterioration caused by steel corrosion is one of the major causes of failure of steel reinforced concrete structures. This is generally initiated by chlorides in structures exposed to the marine and/or de-icing salt environments [1-3]. Corrosion can also be initiated by carbonation of the concrete, in which the protective passive layer on the steel reinforcement is destroyed due to the reduction in alkalinity of the concrete [4]. Although a large volume of work exists on corrosion caused by both chlorides [5, 6] and carbonation [7, 8], the combined effects of chlorides and carbonation on corrosion of steel in concrete, the microstructural changes during the initial phase of their transport as well the physical and chemical mechanisms causing different degrees of corrosion are not clearly documented. This is discussed further in the following sections.

Carbon dioxide (CO_2) travels much faster than chloride ions in relatively dry hardened concrete. The transport of CO_2 is influenced by the relative humidity in the micro pores and the way CO_2 reacts with the mineral phases in the hydrated cement paste [9]. During the ingress of chlorides, they can chemically react with the AFm phase in hydrated Portland cement to form Friedel's salt (FS) or be physically absorbed by the C-S-H gel [10, 11]. It is considered that only the free chloride ions, which can move into the vicinity of the steel bars, can contribute to their corrosion [12]. Some researchers [13, 14] have found that carbonation could promote further chloride ingress due to two reasons: firstly, the decomposition of the hydrated phases (such as C-S-H gel and FS) containing chlorides could release the bound chlorides into the pore solution; secondly, the near surface concrete becomes less porous due to the formation of calcium carbonate, hence the released chlorides can only move inward.

The influence of carbonation on chloride ingress was found to depend on several parameters, such as w/b, type of supplementary cementitious material (SCM) and degree of carbonation. Liu et al. [15] studied the combined effects of chlorides and carbonation on normal Portland cement concrete with different w/b (0.38, 0.47, 0.53). They found that the samples with higher w/b have higher chloride binding capacity before carbonation. The chloride binding capacity of all samples with different w/b decreased with the influence of carbonation. Comparatively speaking, the degree of decrease of chloride binding capacity was greater in lower w/b (0.38). Saillio et al. [16] compared the influence of different types of SCMs, including ground granulated blast slag (GGBS), pulverised fuel ash (PFA) and metakaolin (MK) on the chloride binding capacity of concrete with the same w/b before and after carbonation. Their results showed that the carbonated concrete bound less chlorides than the non-carbonated ones. Meanwhile, Khan et al. [17] found that the chloride binding capacity of the hydrotalcite (layered double hydroxide), which occupied a significant proportion of the GGBS paste, was not impaired by the carbonation. Wang et al. [13] found that the chloride binding capacity as well as the amount of chlorides released from the bound form are influenced by the degree of carbonation. Chang et al. [18] compared the chloride binding capacity of hardened cement pastes under three different conditions: (i) carbonated first and then immersed in the chloride solution; (ii) immersed in the chloride solution first then carbonated; and (iii) carbonation of cement paste prepared with NaCl solution. The results showed that the paste prepared with NaCl solution had a higher chloride binding capacity. However, after carbonation almost all bound chloride ions were released, and no chloride binding was detected after carbonation.

From the above discussion, it is clear that, despite a global interest on the effect of carbonation on chloride binding and establishing the influence of w/b, nature of supplementary cementitious material and the extent of carbonation on the rate of chloride binding, there is no clarity on how the results of these studies could be used for specifying concrete for these combined exposures. Further, it is not clear whether it is possible to predict the influence of carbonation on chloride binding in combined exposure regimes from a knowledge of the properties of concrete. The research reported in this paper aims to address these scientific queries. Therefore, in this paper an investigation on the influence of water-to-binder (w/b) ratio and different pozzolanic materials on the bound chloride content, both before and after carbonation is reported, with an emphasis on deriving a mathematical relationship between carbonation (represented by a change in apparent pH) and the quantity of bound chlorides for different cementitious systems. It is anticipated that such a relationship will transform most chloride transport models to adopt a dynamic binding behaviour that evolves with carbonation.

2. Factorial experimental design

According to BS 8500 (BS 8500-1- Table A.4) [19] the binder for concrete structures exposed to XS1 and XS3 exposure environments should normally contain no more than 35% PFA and 10% SF. Thus, the factorial design for paste composition used in this study considered three factors, viz. PFA content (0-15%), SF content (0-15%) and w/b (0.3-0.6). Four levels were considered for each independent variable, as reported in Table 1. PFA and SF were considered at four equal levels (despite BS 8500 not recommending more than 10% SF) so that a comparison of the relative effect of these two variables could be studied. In the case of w/b, 0.3, 0.4, 0.5 and

0.6 were the four levels. As there are 3 factors, and each factor was considered at 4 different levels, there should be a total of 64 (4*4*4) treatment combinations for full factorial design. Doing this research with 64 different treatment combinations is both time-consuming and resource-intensive. Therefore, the orthogonal experimental design was used in this research. It requires a minimum number of experimental units (treatment combinations) to examine the influence of both single and combined representative factors [20, 21]. According to the number of factors and levels from Table 1, 16 experimental units obtained from $L_{16}^{(4^3)}$ were chosen in this research[22]. These 16 experimental units are shown in an imaginary cube in Figure 1 and the different treatment combinations are reported in Table 2. Each point satisfies that [23]: i) for each factor, the treatment combinations have been repeated 4 times. For example, as can be seen from Table 2 the levels 1 to 4 of PFA content, SF content and w/b occurred 4 times; ii) For each pair of factors, all combinations of factor levels occur once. i.e. the combinations of PFA content and SF content are (1,1), (1,2), (1,3), (1,4), (2,1), (2,2), (2,3), (2,4), (3,1), (3,2), (3,3), (3,4), and (4,1), (4,2), (4,3), (4,4); iii) the scalar product of each pair of factors is zero in a combinatoric sense. For example, if levels 1, 2, 3 and 4 of both PFA content and SF content are assigned value of -2, -1, 1, 2, the sum of these combinations is 0 ($i.e. -2\times-2+-2\times-1+-2\times1+-2\times2+ -1\times-2+ -1\times-1+-1\times1+-1\times2+1\times-2+1\times-1+1\times1+1\times2+2\times-2+2\times-1+2\times1+2\times2=0$). By using the orthogonal design, the parameter space is sampling uniformly[24]. .

Table 1. Factors and levels for the factorial experimental design

Factor	Level 1	Level 2	Level 3	Level 4
PFA content	0	5%	10%	15%
SF content	0	5%	10%	15%
w/b	0.3	0.4	0.5	0.6

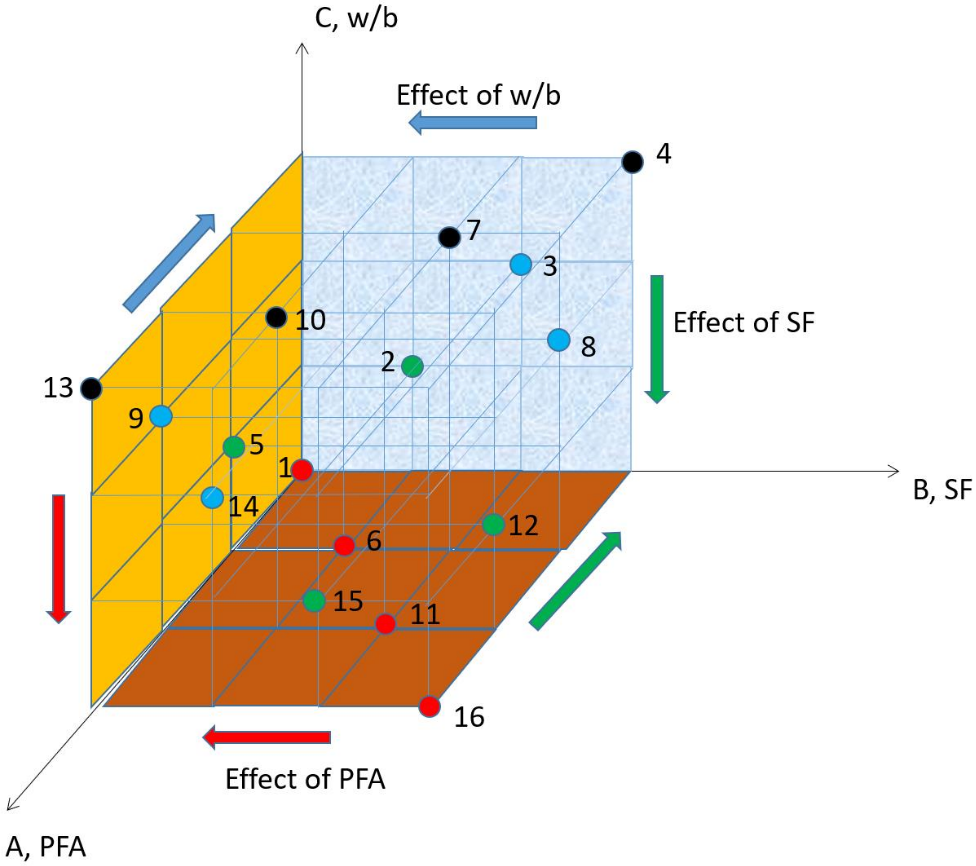


Figure 1. The mixes represented as sides of an imaginary cube.

Table 2. Mix composition of the cement pastes

Mix no.	Mixture Notations	PFA content	SF content	w/b
1	0.3 100%PC	0%	0%	0.3
2	0.4 5%SF	0%	5%	0.4
3	0.5 10%SF	0%	10%	0.5
4	0.6 15%SF	0%	15%	0.6
5	0.4 5%PFA	5%	0%	0.4
6	0.3 5%PFA5%SF	5%	5%	0.3
7	0.6 5%PFA10%SF	5%	10%	0.6
8	0.5 5%PFA15%SF	5%	15%	0.5
9	0.5 10%PFA	10%	0%	0.5
10	0.6 10%PFA5%SF	10%	5%	0.6
11	0.3 10%PFA10%SF	10%	10%	0.3
12	0.4 10%PFA15%SF	10%	15%	0.4
13	0.6 15%PFA	15%	0%	0.6
14	0.5 15%PFA5%SF	15%	5%	0.5
15	0.4 15%PFA10%SF	15%	10%	0.4
16	0.3 15%PFA15%SF	15%	15%	0.3

To examine the influence of each factor on the properties of the pastes, in addition to the analysis of variance (ANOVA), the following additional analyses were performed:

(i) The F-test [25] was used to examine the significance of these factors on the properties of binders. It is calculated by dividing the mean square of certain factor by the mean square of the error. A bigger F value indicates larger influence of the factor.

(ii) Sig. refers to the significance of a parameter on the results. A smaller Sig. value indicates larger influence of the factor.

(iii) The mean value of four values of samples with the same level was calculated. For example, the mean value of results for 0.3 w/b is obtained by averaging results of Mix 1, Mix 6, Mix 11 and Mix 16.

The inferences achieved using the statistical parameters are further elaborated in section 4.1.

3. Materials and methods

3.1 Materials

In this study, Class 52.5 CEM I Normal Portland Cement (PC), category C PFA (as defined in BS EN 450-1:2012 [26], supplied by AES Kilroot Powder Ltd), and SF slurry with a water content of 40%, supplied by Elkem company, were used as the cementitious materials. The chemical composition and physical properties of the materials are reported in Table 3. Tap water complying with BS EN 1008:2002 [27] was used to prepare the cement pastes. A reagent-grade sodium chloride (NaCl) was used as the source of the chlorides in the cement pastes.

As the chemical composition of the cementitious materials are important for the discussion on chemical changes due to carbonation and chloride ingress, the XRD spectra of the cementitious materials used in this study are presented in Figure 2. The presence of cement clinker minerals as well as calcium carbonate ($CaCO_3$) and calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) can be seen in the spectrum of PC. Mullite ($Al_6Si_2O_{13}$), magnetite (Fe_3O_4) and quartz (SiO_2) are identified on the XRD trace for PFA. There is only a wide diffused peak in the XRD trace of SF, indicating the presence of amorphous SiO_2 [28].

Table 3. Chemical composition and physical properties of the cementitious materials

Chemical oxides and physical properties	CEM I	PFA	SF
SiO_2	19.53	52.85	94.23
Al_2O_3	4.68	22.68	0.85
Fe_2O_3	2.92	6.92	0.65
CaO	64.22	3.02	0.48
MgO	2.11	1.60	0.59
K_2O	0.54	1.84	0.98
Na_2O	0.29	0.54	0.34
SO_3	1.76	0.13	0.05
L.O.I.	2.5	8.08	1.56
Specific gravity	3.18	2.22	2.1
Specific surface area (m^2/kg)	380	340	20000

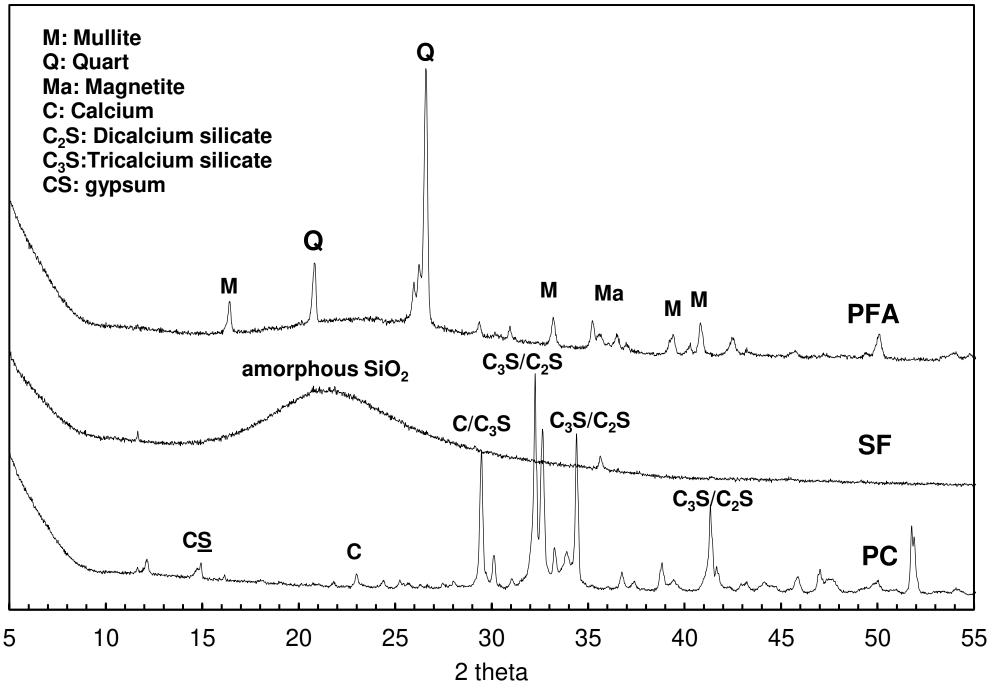


Figure 2. XRD spectra of PC, PFA and SF.

3.2 Paste composition and sample preparation

All pastes were prepared by mixing the binders with NaCl solution (NaCl content was 3.5% by the total mass of the binder) in line with previous binding capacity studies [18]. The water content was determined according to the designed w/b in **Error! Reference source not found.**. Three 50mm size cement paste cubes were cast for each treatment combination, demoulded after 24 hours and then stored for 27 days in a curing room at 20(±2) ºC [29]. The specimens were wrapped with plastic film to avoid carbonation during the curing period.

After curing, three cubes for each treatment combination were crushed and placed in an oven at 60(±1) °C for 24 hours. After this, the crushed sample without pieces from the surface was collected and ground into powder (passing through 300 μm sieve). Powder samples of mass 30(±0.01) g from each mix were then placed in a chamber filled with 4 (±0.1) % CO_2 at 65 (±1) % relative humidity and 17 (±1)°C. After 2, 5, 7, 10, 14, and 28 days of carbonation, about 5 grams of powder for each treatment were taken out for testing.

3.3 Test methods

3.3.1 Compressive strength

After curing, the compressive strength of the paste specimens ($50mm \times 50mm \times 50mm$ cube) was determined by following the guidelines set out in BS EN 12390-3:2009 [30] for concrete.

3.3.2 Apparent pH

The apparent pH is defined as the pH of the infusion solution of the powdered samples. It is reported that the apparent pH is comparable to the pH value of the pore fluid, derived through pore fluid extraction [31]. Powder of 1(±0.001)g was mixed with 20 ml of de-ionized water, then placed in a rotator for 24 hours at rate of 50 rpm. After that, the pH of the suspension was measured using a pH probe (JENWAY 4330, Conductivity & pH meter).

3.3.3 Free and bound chloride content

The free chloride content in the pastes was measured according to RILEM TC 178-TMC [32]. Powder of 1(±0.001) g was mixed with 50 ml deionized water, shaken for 3 minutes, and then filtered by manual filtration. The filtered solution was analyzed by Ion Chromatography. The free chloride content was calculated by measuring the chloride concentration in the solution and expressed as % by mass of binder. The bound chloride content in the pastes was calculated by using the total chloride content (i.e. 3.5% by mass of binder) minus the free chloride content.

3.3.4 X-Ray Diffraction test

X-Ray Diffraction (XRD) analysis was conducted on the cement powder samples using a PANalytical X'pert Pro MPD diffractometer in the 2ϴ range 5° to 70° with a step size of 0.016°.

3.3.5 Thermogravimetric analysis

Thermogravimetric (TG) analysis was conducted using a NETZSCH STA 449C to determine the phase changes in the pastes before and after the carbonation. The powder samples were tested in the temperature range from 25°C to 1000°C by heating the samples at the rate of 20°C/min in an inert N_2 environment.

4. Results and discussion

4.1 Compressive strength

The 28-day compressive strength of the paste samples is reported in Figure 3. These results are reported only for appreciating the trends in their compressive strength, as ideally the compressive strength of cementitious materials should be determined using standard mortar cubes, which was not done here.

Figure 4 shows the mean value of the four compressive strength results, for the mixes in one of sides of the imaginary cube (Figure 1). For example, the mean value of the strength results for 0.6 w/b is calculated by averaging the results of Mixes 4, 7, 10 and 13 (i.e. 0.6 15%SF, 0.6 5%PFA10%SF, 0.6 10%PFA5%SF and 0.6 15%PFA). These four mixes are represented in top face of the imaginary cube in Figure 1. The interaction effects are negated by mixing 5% PFA with 10% SF and then again with 10% PFA with 5% SF. Therefore, the mean value of strength for the four mixes adequately represents the main effect of 0.6 w/b on the compressive strength [33]. This principle has been used for all the data reported in this paper.

As shown in Figure 4, the compressive strength of the pastes was obviously influenced by the w/b. Decreasing the w/b causes a reduction in the gel/space ratio and the porosity of cement-based materials, thereby significantly increasing the compressive strength [34]

The compressive strength values are also influenced by the addition of PFA and SF. SF has a much smaller particle size (Table 1) and a faster pozzolanic reaction [35] than PFA. Further, it is known that PFA requires a longer period of curing than 28 days to benefit from its pozzolanic effect on microstructure of concrete. Therefore, any direct comparison of PFA with SF in this research should be made with caution. Nevertheless, it can be seen from Figure 4 that SF has a marginally better effect on compressive strength of paste cubes than PFA. Statistical analysis reported in Table 4 confirms this and places SF to be the next most influencing factor (higher F–value and lower Sig. value), however at a much lower level than w/b.

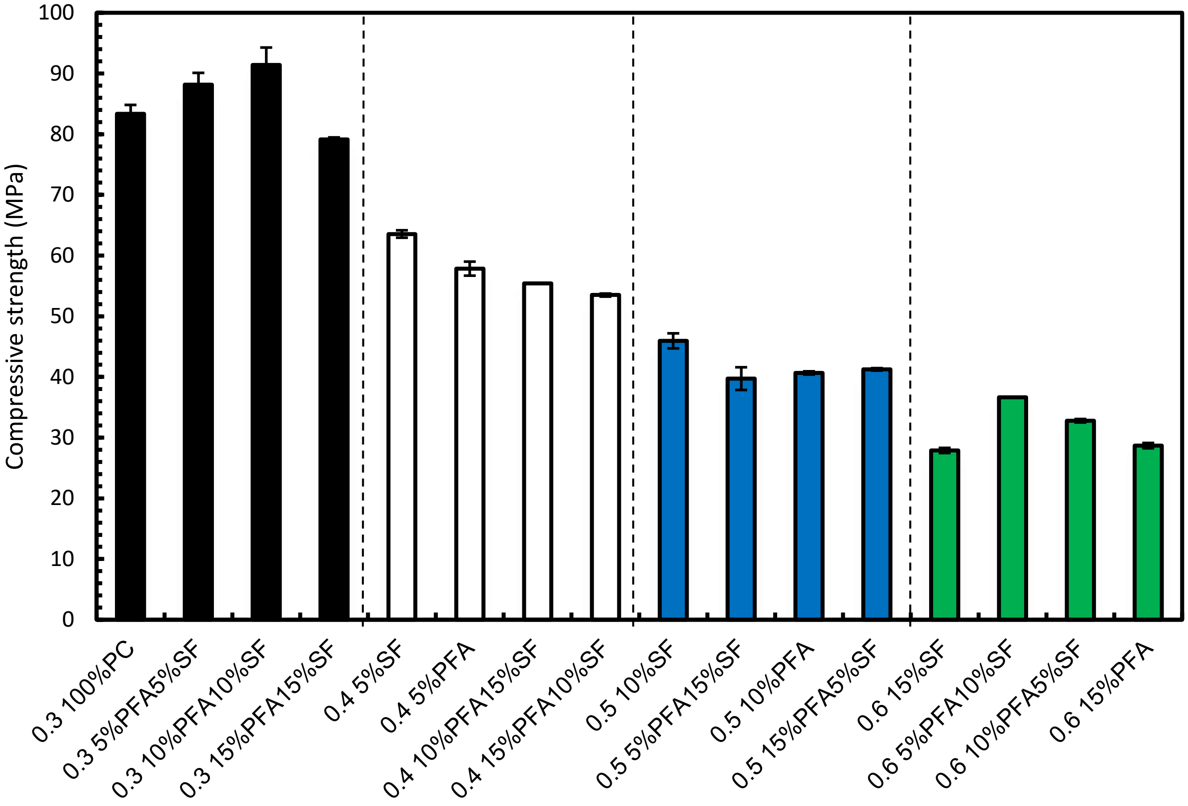


Figure 3. Effect of different parameters on compressive strength of the cement pastes at 28 days before carbonation.

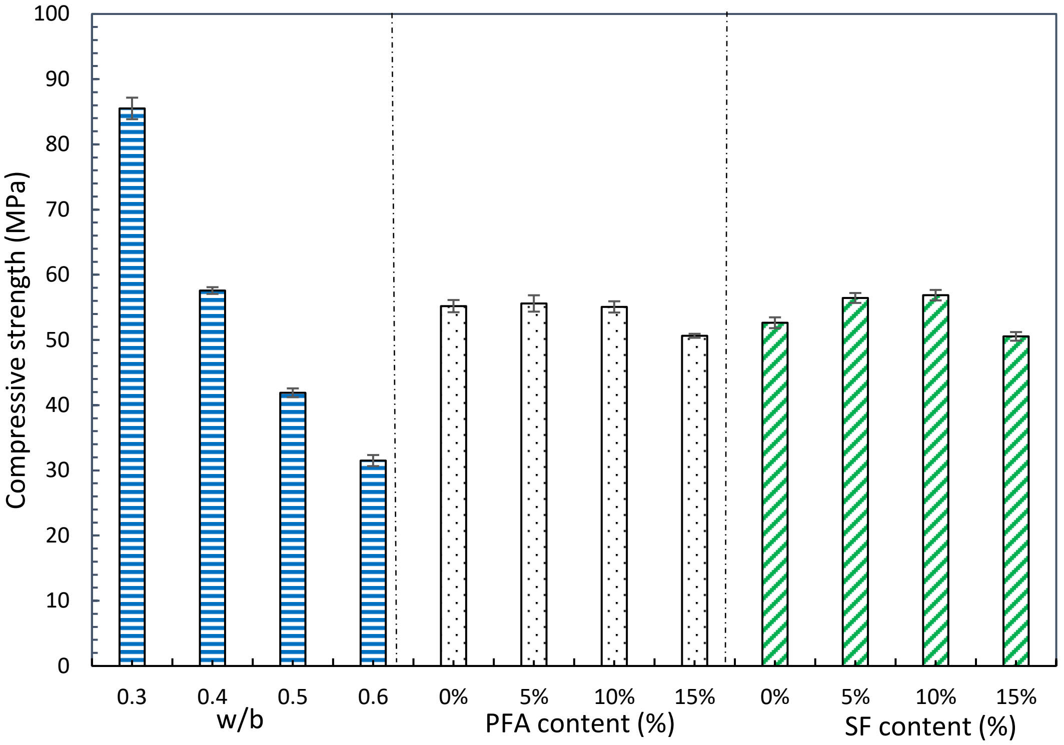


Figure 4. Main effect of different mix variables on the compressive strength of the pastes prior to carbonation.

Table 4. Parameters of the factorial analysis of the compressive strength data

Source	Sum of Squares	dof	Mean Square	F-value*	Sig*.
PFA	65.34	3	21.78	3.32	0.098
SF	111.68	3	37.23	5.67	0.035
w/b	6633.36	3	2211.12	336.00	0.000
Error	39.38	6	6.56		

* Note: Higher F-value and lower Sig. indicate the factor to be significant.

4.2 Chloride binding capacity and apparent pH value of the pastes before carbonation

The bound chloride content and apparent pH value of the non-carbonated specimens are presented in Figure . The main effects are shown in Figure and 7 and the results of the factor analysis are reported in Table 5 and 6. The data of the mineralogical analysis are shown in Figure and 9.

Influence of w/b on chloride binding: As can be seen from Figure , the bound chloride content is higher in pastes with a lower w/b. When the w/b is 0.3, the mean bound chloride content is 0.724 % by mass of the binder. When the w/b was increased to 0.6, the mean bound chloride content decreased to 0.521 % mass of the binder. However, Figure 5 shows that the effect of w/b depended on the content of both PFA and SF. The independent influence of both PFA and SF on chloride binding is discussed separately, hence the effect of w/b is discussed here. The amount of bound chlorides in the pastes is known to be related to the concentration of the total chlorides in the mixing water (hence that in the pore solution for a given degree of porosity) and the degree of hydration of the binder in the paste [5]. It is reported that the degree of hydration is better at higher w/b [35]. Further, as chlorides were added at 3.5% by the mass of the total binder, the chloride concentration in the mixing water was 11.5% and 5.8% respectively for 0.3 and 0.6 w/b. However, in this research, as the w/b was increased there was lesser quantity of binder, hence the effect of improved degree of hydration on better binding cannot be confirmed. Therefore, it is considered that higher concentration of total chlorides in the pore solution primarily contributed to the higher bound chlorides in the lower w/b cement paste [5]. In addition, the hydration products in the system with lower w/b contain less bound water, which might have also provided some locations for chloride ions to bind [36].

As expected, the parameter analysis presented in Table 5 shows a very low Sig. value of w/b is 0.004, confirming the obvious large influence of this parameter on chloride binding in comparison with that of both PFA and SF. Whilst in this research, this observation is a by-product of the experimental design, there are several other articles confirming the influence of w/b on binding capacity [37, 38].

Influence of w/b on apparent pH: As shown in Figure 5, the apparent pH for the mixes only varied slightly, between 12.6-12.7. In addition, there are no obvious differences among the four levels (for each parameter studied), as shown in Figure . The parameter analysis of the apparent pH in Table 6 shows that the F value is small, and the Sig. value is large for w/b. These results suggest that the w/b has little influence on the apparent pH. Published studies [31, 39] for pastes with w/b between 0.42 and 0.5 also demonstrated a similar behaviour before carbonation. Although $Ca(OH)_2$ is partially consumed by PFA and/or SF in some pastes, there is still enough $Ca(OH)_2$ to saturate the solution. In the meantime, alkali ions in the raw materials can also be leached into the solution to influence the apparent pH [39] and notably PFA and MS have higher proportions of Na_2O and K_2O in comparison with PC. Therefore, any reduction in pH caused by the consumption of $Ca(OH)_2$ in PFA and SF mixes are likely to have been negated by the increased contribution from the alkali ions.

Influence of PFA and SF on chloride binding: In Figure 5, for the w/b of 0.3, the bound chloride content of 0.3 5%PFA5%SF (Mix 6) is lower than that of 0.3 100%PC (Mix 1). However, with the increase of PFA and SF contents, the bound chloride content clearly increased. This phenomenon is seen for 0.4 w/b pastes as well. It is known that there is the formation of more Friedel's salt (FS) in the pastes with an increase in PFA content [40-42]. In addition, the increase of the specific surface area due to the additional C-S-H gel formed by PFA and SF may have contributed to the increase in chloride binding capacity [43]. The reduction of chloride binding in mixes with 5% replacement of both PFA and SF is possibly due to the fact that the beneficial effects of PFA and MS at this replacement level on chloride binding is not as much as that due to PC alone [44].

The XRD and TG results in Figures 8 and 9 of the selected samples also confirm this observation. As can be seen from Figure , the FS, with a characteristic peak at 11.191° 2Ө was observed in all the specimens. In Figure 9, it can be seen for the 0.3w/b cement paste samples that, in comparison to the 100%PC (Mix 1), mix with 15% of PFA and SF (Mix 16) has both higher quantities of C-S-H and FS content, which explains the higher quantity of bound chlorides for this mix (Figure 5 - 0.3 w/b).

Parameter analysis in Table 5 shows that the replacement of PC with PFA resulted in an F-value of 9.347 (the second lowest Sig. value), which is between that for the w/b and SF. As the PFA content increases from 0 to 15%, the bound chlorides in the pastes increased by 23%. However, for SF, the mean square and the F-value is 2.615 (with the highest Sig. value), which means this is the least significant factor among the three parameters in this research affecting the binding capacity of the cement pastes. This is also consistent with other published studies [45, 46].

The XRD and TG results in Figures 8 and 9 respectively for 0.6 15%SF (Mix 4) and 0.6 15%PFA (Mix 13) indicate that pastes with 15% SF contain less $Ca(OH)_2$ in comparison to the pastes with 15% PFA, which is consistent with previous studies [35, 47]. Partial replacement of cement with SF can change the chemical composition of the pore solution and decrease its alkalinity, which has an adverse effect on its chloride binding capacity [46]. Compared with SF, PFA contains higher aluminate content, as shown in Table 3, which can result in the formation of more calcium chloroferrites and FS in the paste, both of which can bind significant amounts of chloride ions [6, 48].

Influence of PFA and SF on apparent pH: In terms of the influence of PFA and SF on the apparent pH value of the pastes, there is almost no difference between them (Figure 7). From the parameter analysis (see Table 6), the PFA with an F value of 4.214 and Sig. value of 0.063

demonstrated a slightly larger influence on the apparent pH value compared to the SF with an F value of 0.777 and Sig. value of 0.548. However, the difference is very small to discuss them to be of any significance.

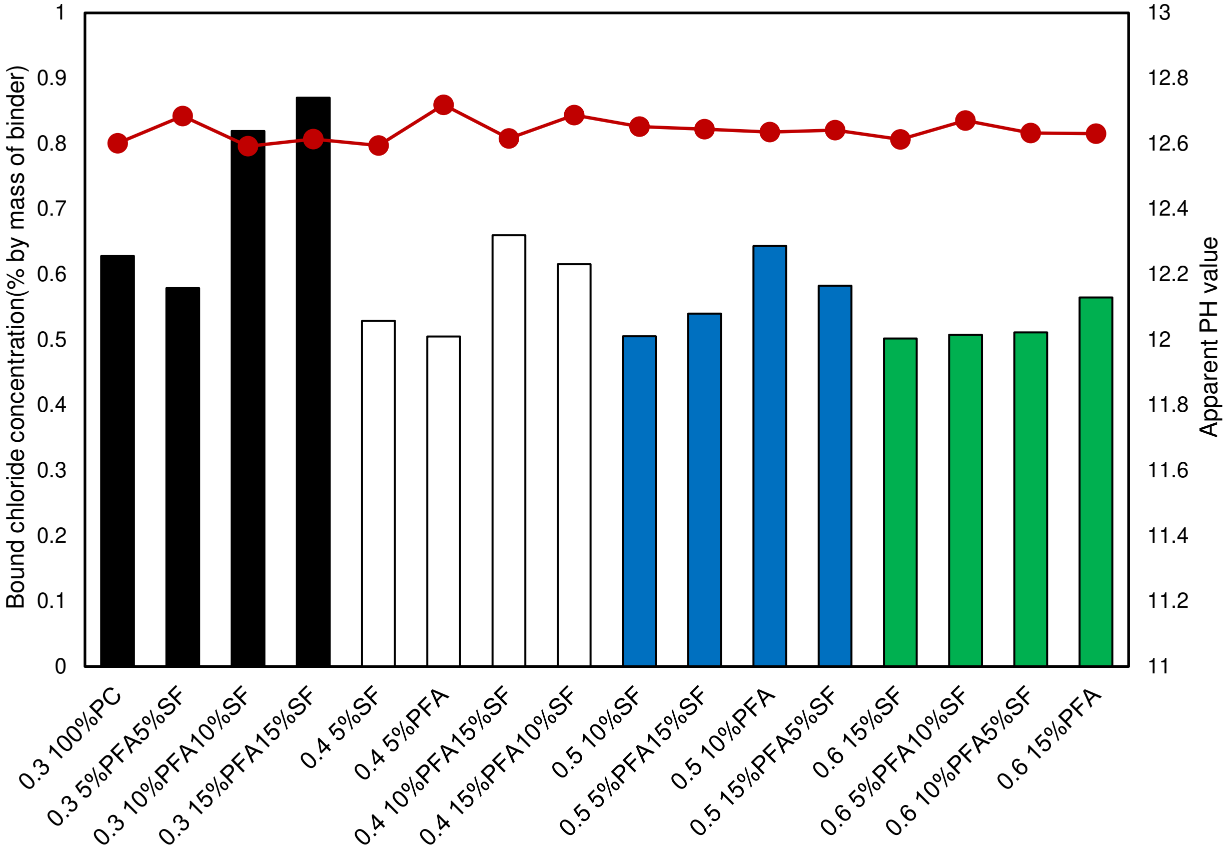


Figure 5. Effect of different parameters on bound chloride content and apparent pH of the non-carbonated pastes at the age of 28 days.

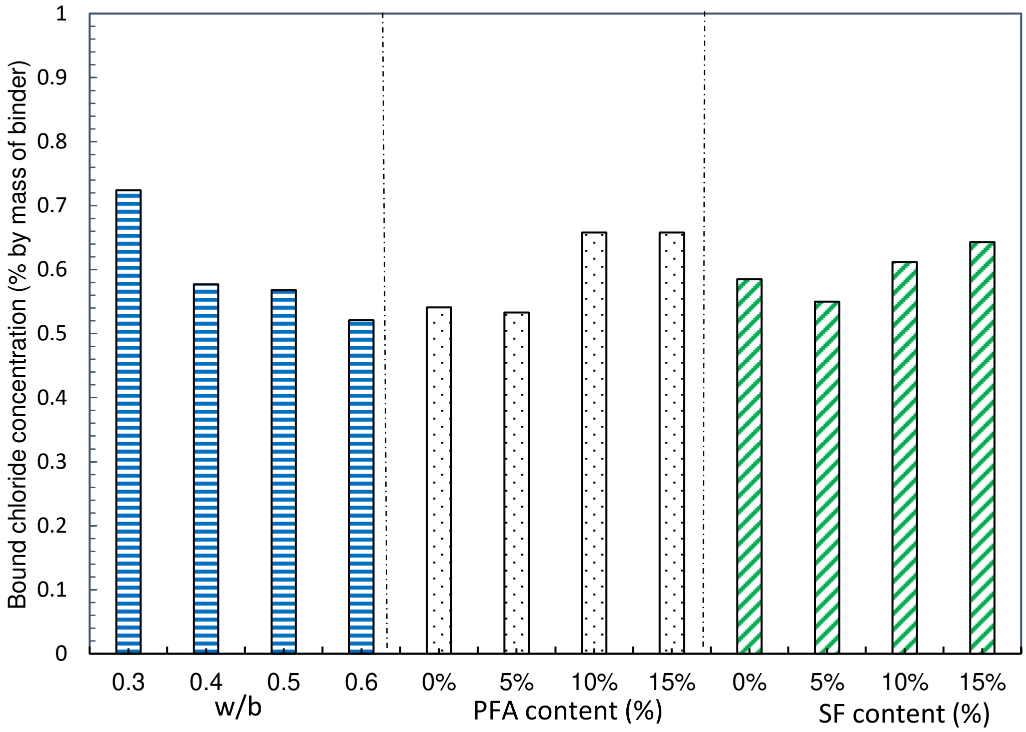


Figure 6. Main effect of different parameters on bound chloride contents of noncarbonated pastes.

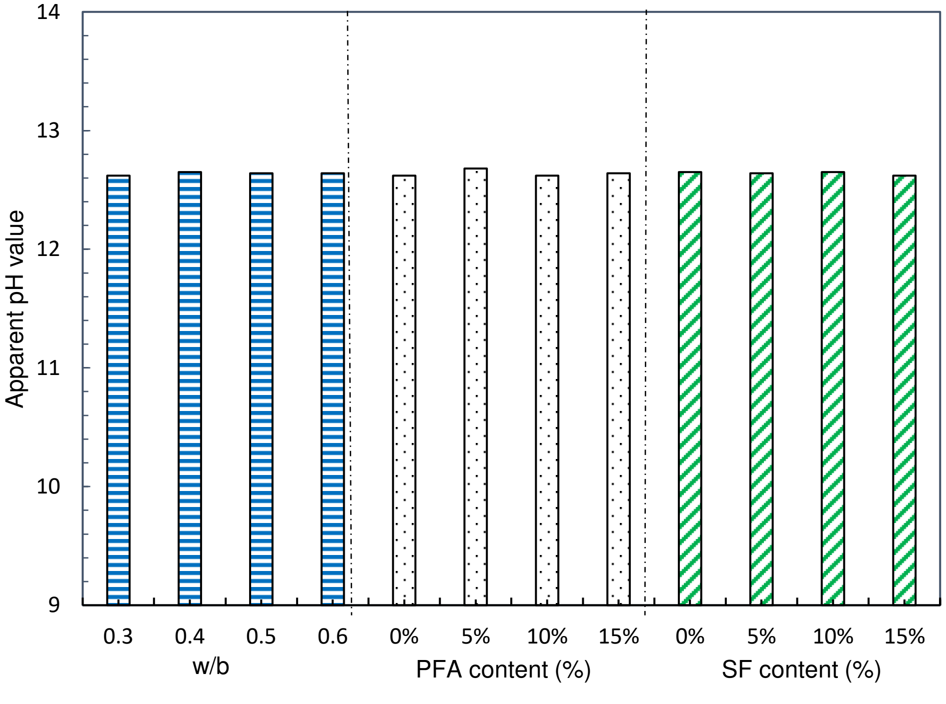


Figure 7. Main effect of different parameters on apparent pH values of noncarbonated pastes.

Table 5. Parameter analyses of the bound chloride content in noncarbonated pastes

Source	Sum of Squares	dof	Mean Square	F-value	Sig.
PFA	0.060	3	0.020	9.347	0.070
SF	0.017	3	0.006	2.615	0.470
w/b	0.093	3	0.030	14.391	0.004
Error	0.013	6	0.020		

Table 6. Parameter analysis of the apparent pH in noncarbonated pastes

Source	Sum of Squares	dof	Mean Square	F-value	Sig.
PFA	0.011	3	0.004	4.214	0.063
SF	0.002	3	0.001	0.777	0.548
w/b	0.002	3	0.001	0.813	0.532
Error	0.005	6	0.001		

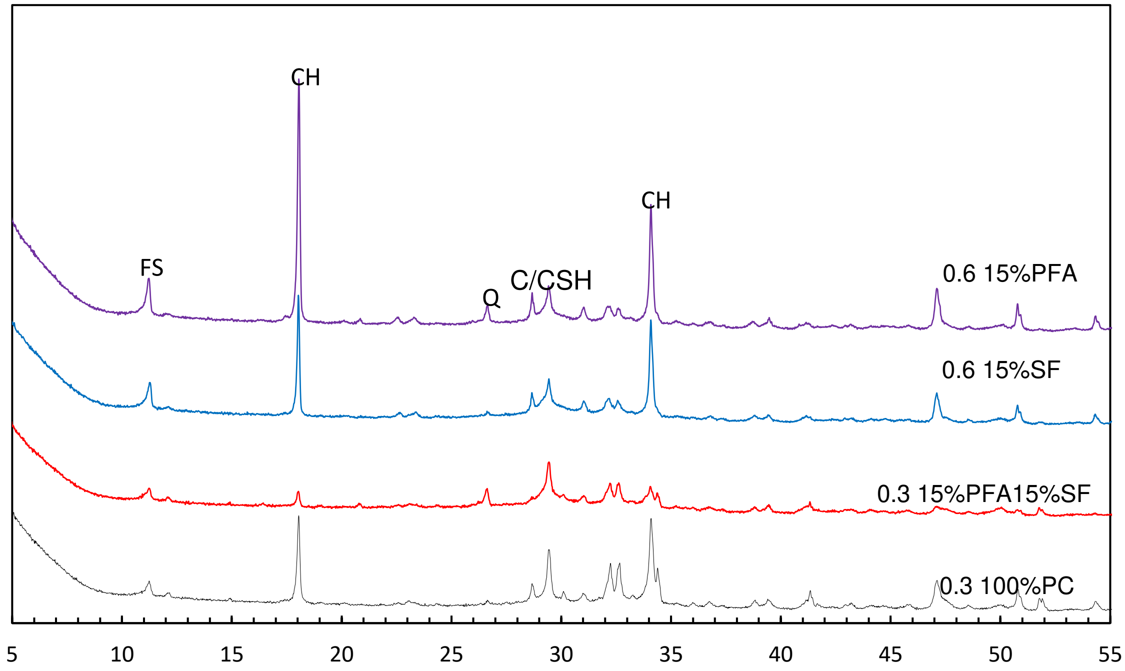


Figure 8. XRD patterns of the pastes before carbonation (FS - Friedel's salt; CH - Calcium hydroxide; Q - Quartz; C - Calcium carbonate).

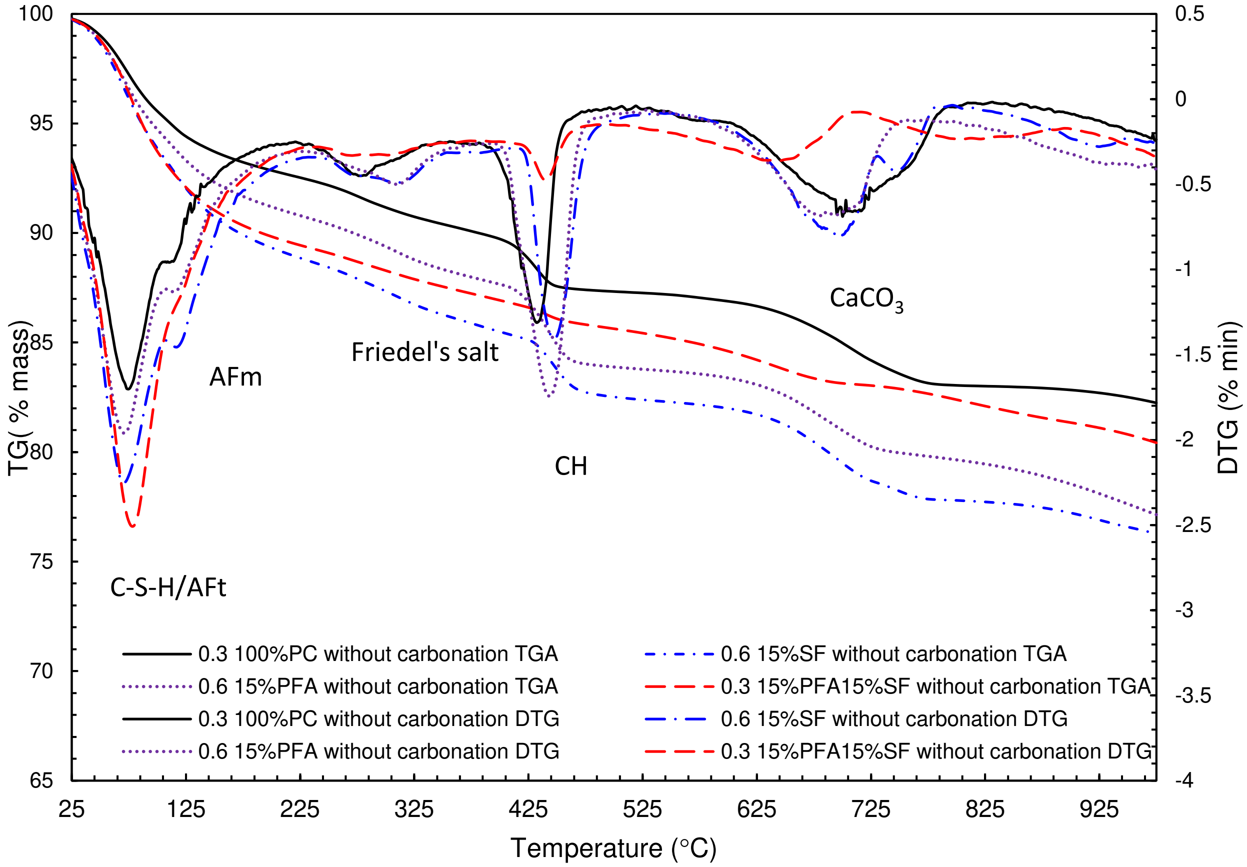


Figure 9. TGA and DTG Analyses of the pastes before carbonation.

4.3 Chloride binding capacity and apparent pH values after carbonation

The temporal changes in the quantity of bound chlorides and the apparent pH values in samples subjected to carbonation are shown in Figure and Figure respectively. The parameter analysis and mineral characterisation results are presented in Table 7 and 8 and Figure to 15 respectively.

Influence of w/b on chloride binding: It is commonly known that carbonation results in a reduction in bound chloride content. The data presented in Figure 10(c) and 10(d) for both 0.5 and 0.6 w/b mixes agree with this, but for both 0.3 and 0.4 w/b mixes there was an initial stage during which the binding increased. During the sample preparation, the mortar containing chlorides were ground and sieved to pass through a 50 microns sieve before it was subjected to carbonation. This would mean that a majority of the particles might still have its capillary pores intact, especially in lower w/b mixes where the average pore diameter is low. Non-carbonated samples, when digested in water would release chlorides from the pores readily. This will show up as free chlorides in the chemical analysis and therefore bound chlorides (which is total chlorides in the mix minus the free chlorides) would be low (at time zero for the duration of carbonation).

Carbonation can result in a number of microstructural changes:

(1) The newly formed carbonates enveloping some of the minerals that contain physically adsorbed chlorides and making the chlorides immobile. Taylor [49] reported that carbonates analogue of ettringite can form if the concentration of CO_2 is high. A similar observation was noted by Kwasny et al. [50] for samples carbonated during the hydration phase.

(2) The carbonate deposition blocks the pore entrances and thereby traps the free and physically adsorbed chlorides from moving [51].

These two phenomena (termed hereafter as hindrance effect) will reduce the free chlorides available in the digested solution, thus resulting in a higher level of bound chlorides. Such an initial increase in binding is not visible in samples of higher w/b, possibly due to large average pore diameter in comparison.

Figure 12 quantifies the changes in bound chlorides due to 28 days of carbonation and presents it across the different mix variables. Bound chloride content is shown to increase significantly from its non-carbonated counterpart for 0.3 w/b (0.34% by mass of binder), followed by a smaller increase for 0.4 w/b (0.16% by mass of binder). The figure shows a reduction in the same for 0.5 and 0.6 w/b mixes.

As can be seen from Figure , after 28 days of carbonation the $Ca(OH)_2$ peaks disappear and the intensity of the FS peak is reduced. Instead, the peaks of $CaCO_3$ are very clear. These changes in peak clearly indicate that the CO_2 reacted with the $Ca(OH)_2$ and FS and formed $CaCO_3$. As these reactions take place, they released the bound chlorides from the pastes [4, 52]. In addition, the intensity of the amorphous hump in the range of 25° to 35° 2θ, associated with amorphous C-S-H gel (in Figure 8), was reduced after carbonation (see Figure 14), implying the carbonation of C-S-H gel [4]. This process adversely affects chloride binding capacity. The TG analysis also shows that these reactions occur (Figure). It is obvious that there were $Ca(OH)_2$, AFm and FS before carbonation (Figure). However, these peaks almost completely disappeared after 28 days of carbonation. In contrast to this, the peak intensity of $CaCO_3$ increased significantly. In addition, it can be seen that the pastes with a w/b of 0.3 formed less $CaCO_3$ than those with a w/b of 0.6, which indicates that the degree of carbonation of the pastes with a w/b of 0.6 is higher than that with a w/b of 0.3.

The w/b plays a more important role on the changes in bound chloride content in carbonated pastes than the PFA and SF. As shown in Table 7, the F-value of the w/b are as high as 62.548. The Sig. value being zero indicates the strongest influence this parameter has on the results.

Influence of w/b on apparent pH: The apparent pH data presented in Figure 11 is comparable to a typical diffusion-controlled ingress/egress of ions [31]. In this case, the pH decreases from the initial value of 12.6 with the increase in the duration of carbonation. The rate of reduction is less for lower w/b mixes and high for higher w/b mixes. The specimens with high w/b will have large and connected pores so that the CO_2 can enter the pores and react with cement minerals more readily, bringing their pH down. Lower w/b mixes in this research have higher quantities of binder, leading to higher reserves of $Ca(OH)_2$. Even if some of the $Ca(OH)_2$ has been consumed, the remaining concentration is sufficient to maintain a healthy pH range.

As shown in Table 8 and Figure , the F-value of the w/b is 121.66, which is much higher than that of PFA and SF. This data analysis highlights that the w/b has a strong influence on the rate of reduction of the apparent pH due to carbonation. These data confirm that lower w/b mixes perform well in binding chlorides and maintaining the pH during the initial stages of carbonation. This, in addition to their reduced chloride and CO_2 rate of transport, makes lower w/b mixes ideal for such exposure environments.

Influence of PFA and SF on chloride binding: Figure 10(a) for all of 0.3 w/b mixes shows that both 10 and 15% of PFA/SF replacements lead to a higher quantity of bound chlorides initially and the difference with that of 100% PC and 5% PFA/SF becomes negligible as the duration of carbonation increases to 28 days. In mixes with higher PC replacement, there would be more of C-A-H (calcium aluminate hydrates) and secondary C-S-H, which would bind more chlorides. This explains the high levels of bound chlorides at time zero for these mixes [53]. Changes to the mineral phases due to carbonation were discussed earlier (and presented in Figures 14 and 15) and the destabilisation of FS would render these chlorides free. This should have been visible in Figure 10a as a reduction of bound chlorides for 10 and 15% replacement mixes, but instead what is observed is that the bound chlorides remained almost constant. It is possible that the carbonates formed might have coated the minerals and blocked the capillary pores [51], owing to the hindrance effect mentioned previously. This might have trapped the newly released free chlorides within the particle.

The parameter analysis of the change in bound chloride content (presented in Table 7) after 28 days of carbonation shows that the F-value of SF is 13.149, which is higher than the corresponding value for PFA. This means that SF has a higher influence on the bound chloride content due to carbonation than PFA. SF in comparison to PFA is likely to reduce the average pore size [54, 55] for similar w/b, so the hindrance effect is more dominant in SF mixes in comparison to PFA mixes. This may explain the sustained increase in bound chlorides in 0.4 5%SF (Mix 2) and the relatively better performance of this mix over 0.4 5%PFA (Mix 5) due to the 28 days of carbonation.

By comparison, at higher w/b (0.5 and 0.6), the average diameter of capillary pores is larger, therefore the hindrance effect is not dominant. In such high w/b mixes, PFA performs better. PFA contains more aluminate phases in comparison, so it can chemically bind more chlorides. In addition, many researchers found that the addition of SF to the pastes obviously decreases the alkalinity of the pastes [54] and therefore any further reduction of alkalinity due to carbonation affects the stability of the FS in such mixes [56, 57].

Influence of PFA and SF on apparent pH: Figure (a) shows that the apparent pH for 0.3 100%PC (Mix 1) decreased from 12.6 to 11.7 after 28-days of carbonation and the corresponding decrease for 0.3 15%PFA15%SF (Mix 16) was from 12.6 to 11. Mix 1 (0.3 100% PC) has the largest reserve of $Ca(OH)_2$ in comparison to Mix 16, which explains why the pH reduction is subdued in Mix 1. It can also be seen that as the % of PC replacement increases, the extent of pH reduction also increases as the carbonation progresses.

Across Figure 11 (a–d), all of the SF mixes have the lowest values of pH, irrespective of the duration of carbonation. As can be seen from Table 8, the F-value of the SF is 14.99, which is higher than that of PFA. It therefore confirms that SF is a more dominant parameter for apparent pH than PFA. This behaviour can be explained by the different physical and chemical properties of SF and PFA. Although the SF and PFA have similar specific density, SF has a much larger specific surface area, as shown in Table 3, suggesting that the SF can react with the $Ca(OH)_2$ faster. In addition, SF has high silica content, which is the major chemical component during the pozzolanic reaction. It also changes the Si/Ca in the cement and makes it easier to carbonate [58].

Based on the experimental results in Figure (for all 16 mixes), a mathematical relationship between apparent pH value and duration of carbonation at a 4% CO_2 exposure can be expressed by equation 1, if the apparent pH is between 8.3 to 12.6:

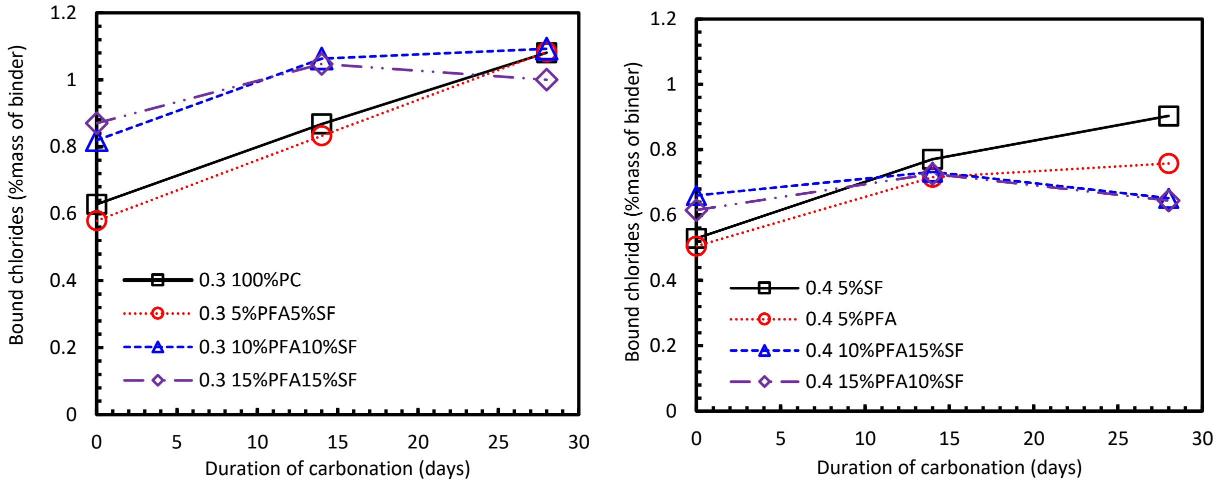
$$\mathrm{pH} = \alpha \times t^{\beta} \qquad (1)$$

where α is the parameter related to the fraction of the supplementary materials and w/b; β is the parameter which is influenced by the w/b; and t is the carbonation duration (days). The equations to calculate α and β are shown below:

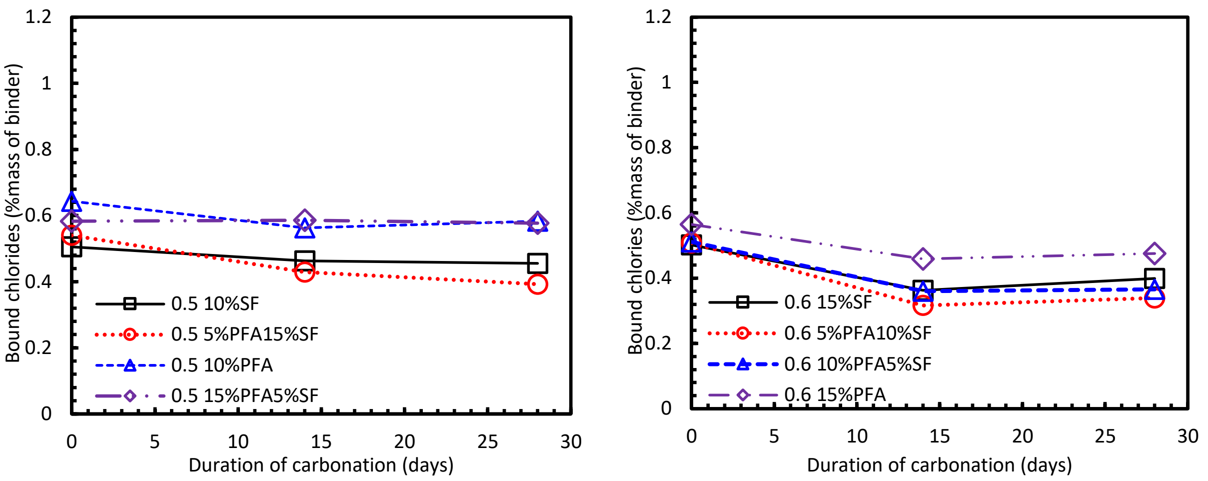
$$\alpha = 13.717 - 3.016 \times w/b - 6.231 \times SF \qquad (2)$$

$$\beta = 0.082 - 0.449 \times \mathrm{w}/b + 0.334 \times (w/b)^2 \qquad (3)$$

where w/b is the water-to-binder ratio and SF is the mass fraction of SF in the total binder. The R-square is 0.966 and the mean squared error is 0.038, which means the equations can well represent the data.



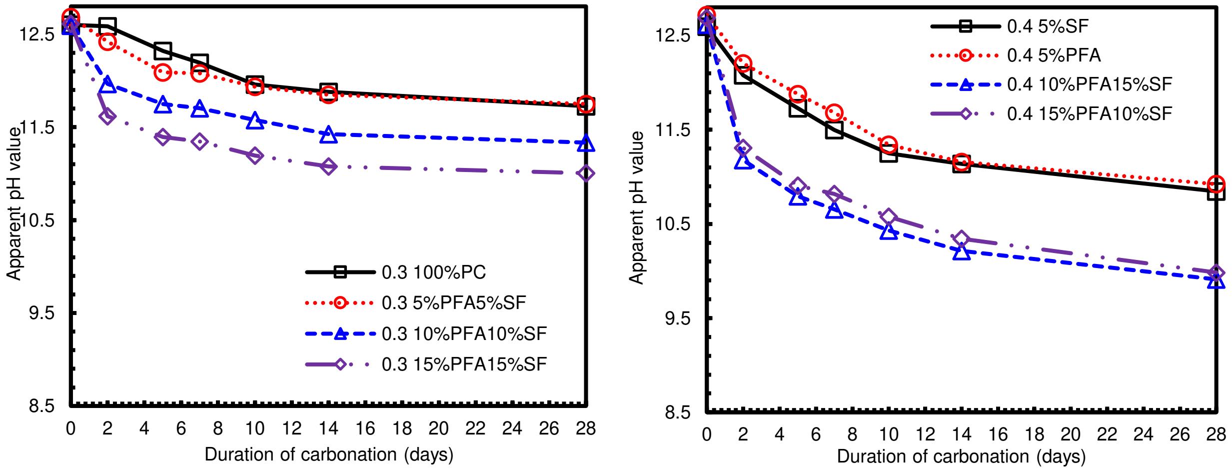
(a) (b)



(c)

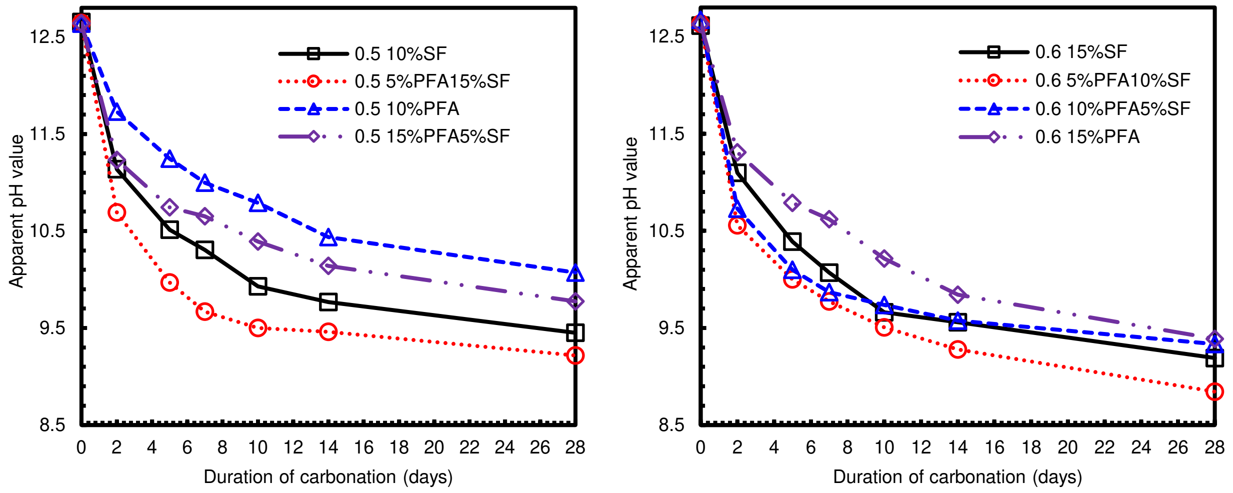
(d)

Figure 10. Relationship between bound chloride content and duration of carbonation of the pastes with w/b of (a) 0.3, (b) 0.4, (c) 0.5, and (d) 0.6.



(a)

(b)



(c) (d)

Figure 5. Effect of duration of carbonation on apparent pH values of the pastes with w/b of (a) 0.3, (b) 0.4, (c) 0.5, and (d) 0.6.

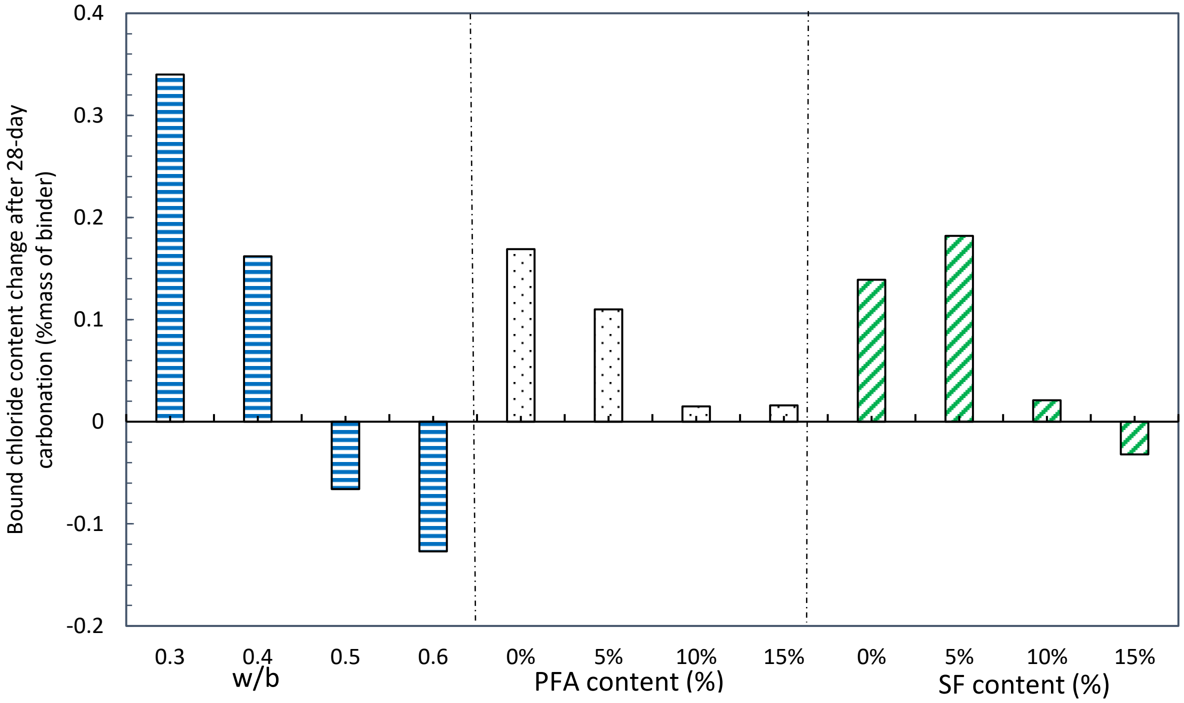


Figure 6. Effects of different parameters on bound chloride contents of the pastes after 28 days of carbonation.

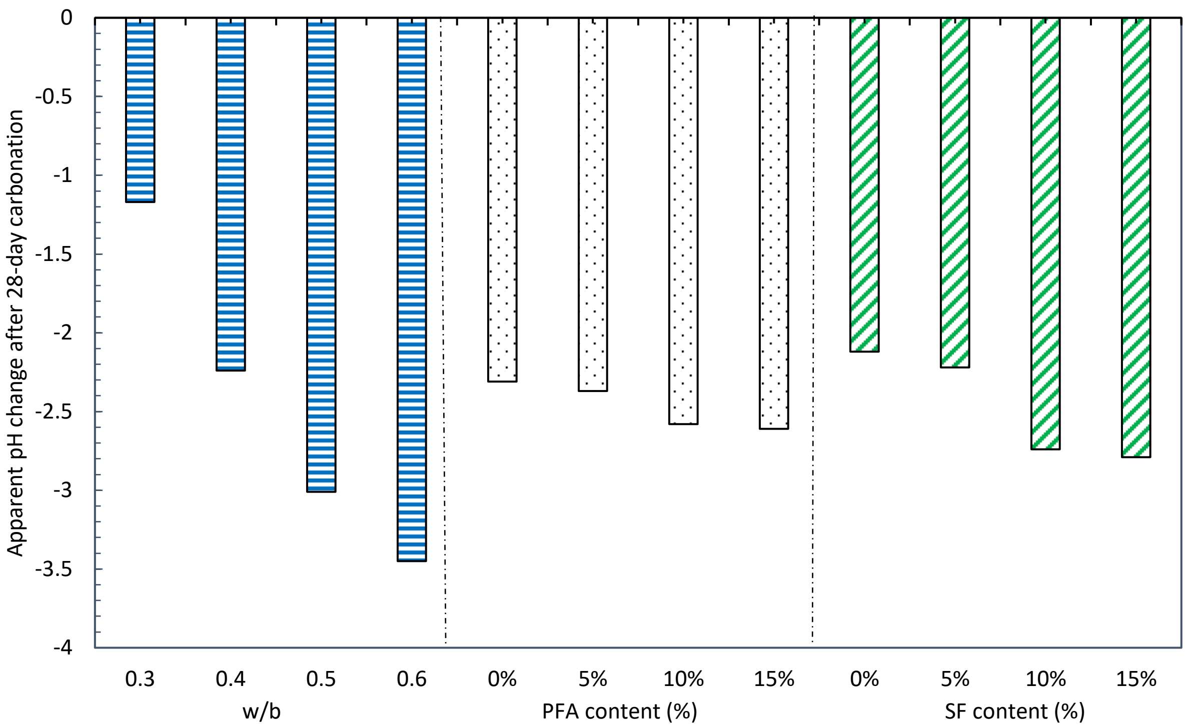


Figure 7. Changes of apparent pH classified by different parameters after 28 days of carbonation.

Table 7. Parameter analysis of the changes to bound chloride content after 28 days of carbonation

Source	Sum of Squares	dof	Mean Square	F-value	Sig.
PFA	0.069	3	0.023	7.818	0.017
SF	0.116	3	0.039	13.149	0.005
w/b	0.553	3	0.184	62.548	0.000
Error	0.018	6	0.003		

Table 8. Parameter analysis of the change to apparent pH after 28 days of carbonation

Source	Sum of Squares	dof	Mean Square	F-value	Sig.
PFA	0.117	3	0.059	1.79	0.248
SF	1.478	3	0.493	14.99	0.003
w/b	11.990	3	3.997	121.66	0.000
Error	0.197	6	0.033		

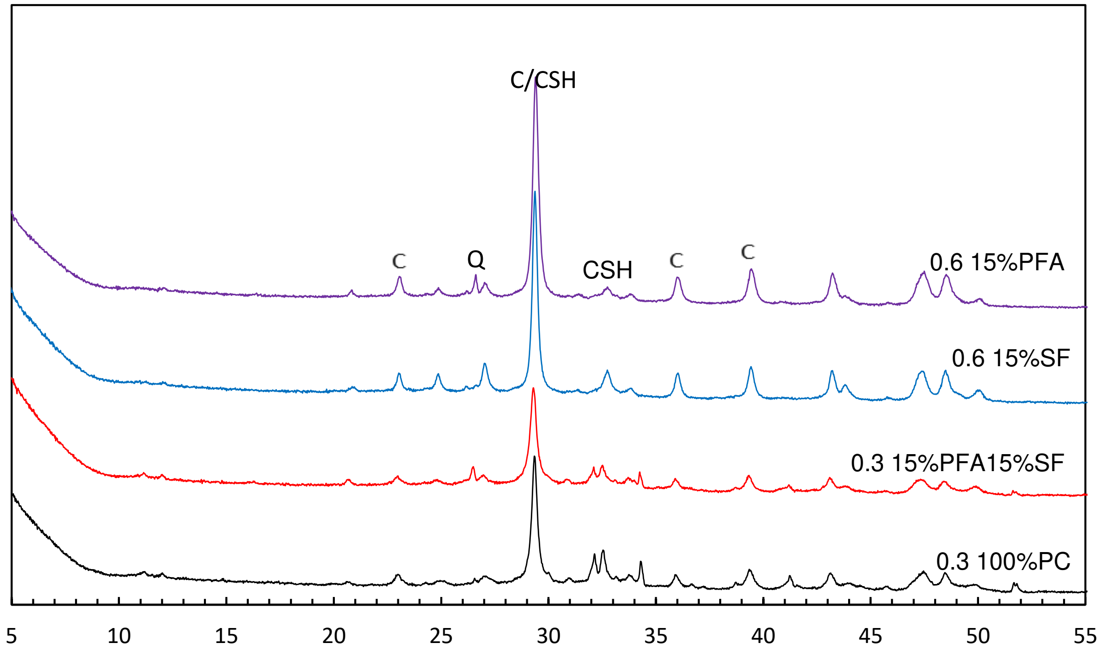


Figure 8. XRD patterns of the selected mixes after 28 days of carbonation (CH: Calcium hydroxide; Q: Quart; C: Calcium carbonate).

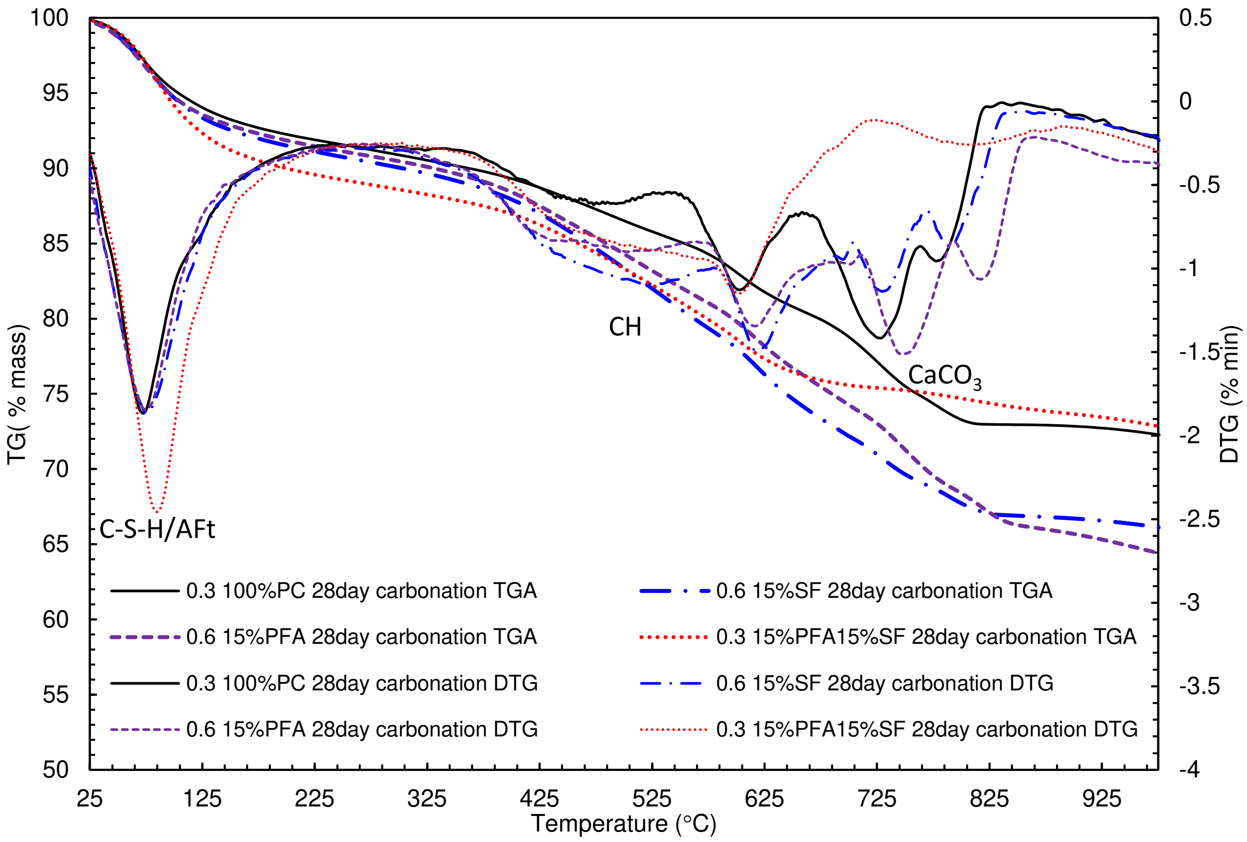


Figure 9. TGA and DTG of the specimens after 28 days of carbonation.

5. Relationship between bound chloride content and apparent pH value

Figure 16 shows that the bound chloride content increases with an increase in the apparent pH value across all the mixes studied in this research. The relationship can be described by the following linear equation:

$$C_{bind} = 2.538 \times pH - 19.565 \tag{4}$$

The coefficient of regression is 0.81; both the 95% confidence limit and prediction intervals are also shown in Figure 16. As discussed before, the equation represents the significance of apparent pH and carbonation on the bound chloride content. The unbiased selection of variables based on the factorial design in this study means this equation is representative of the range of variables considered. However, such a relationship between the chloride content and the apparent pH is not valid prior to carbonation. The individual trends for each w/b and the reasons for these trends have already been discussed in earlier sections in this paper.

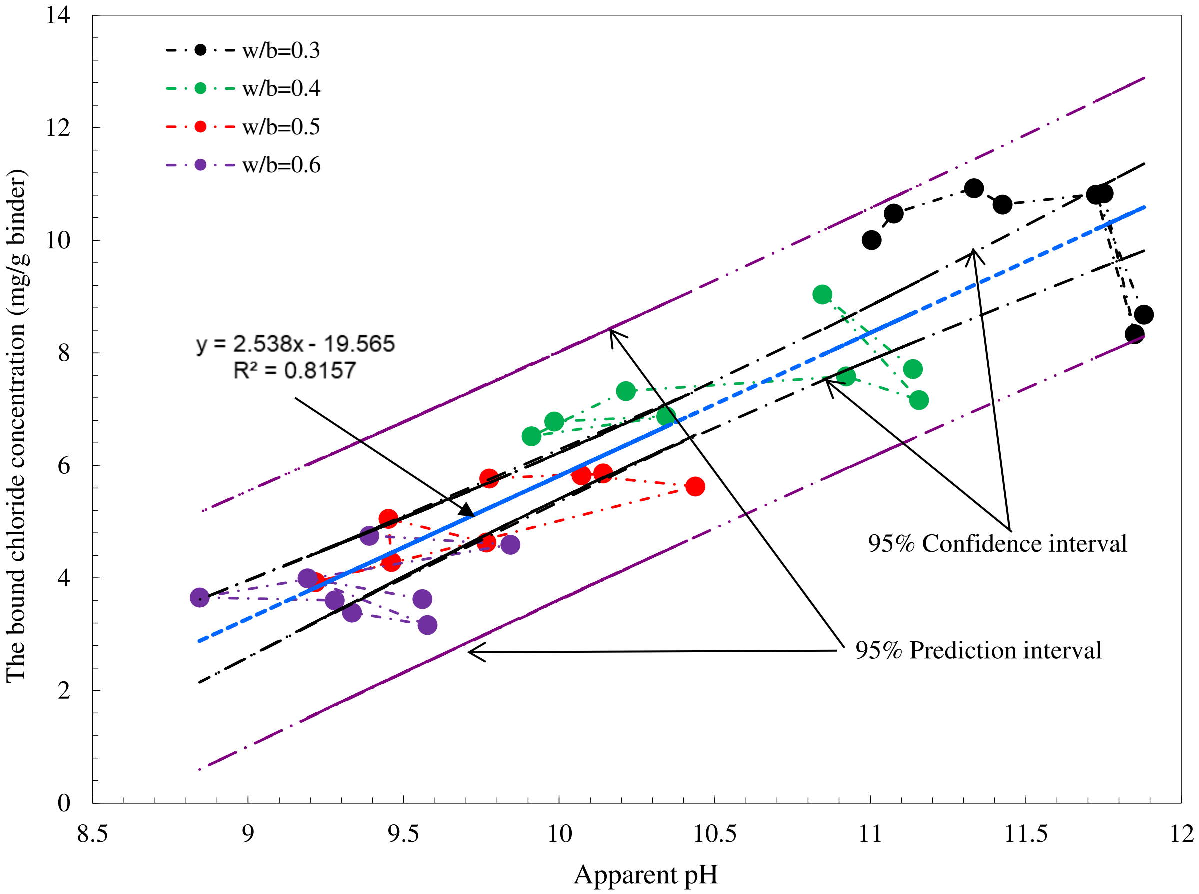


Figure 16. Relationship between bound chloride content and apparent pH after carbonation.

The phenomenon depicted in Figure 16 is illustrated schematically in Figure . Glass et al. [59] found that the bound chloride content in the paste decreased with the increasing addition of nitric acid solution, which was used to change the pH of the environment. The acid would be effective in breaking down the pores and releasing all chlorides in the region that are otherwise immobile. The approach adopted in this paper and that [16] was to expose powdered specimen to carbon dioxide environment for studying the binding as they considered this to be more representative of the real life environment. However, it should be noted that in *in situ* exposure the cement minerals and pores are unlikely to be exposed to such a high concentration of CO_2, therefore the hindrance effect could be gradual and subdued.

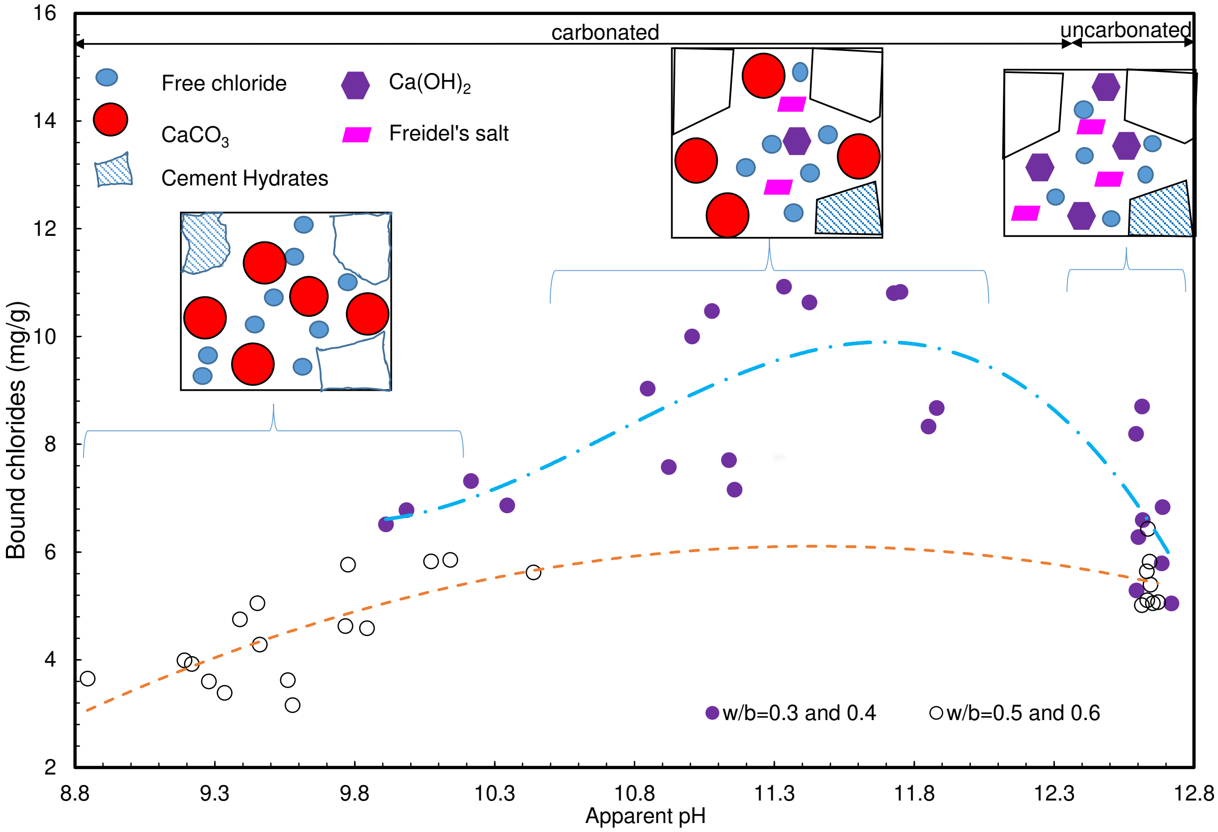


Figure 17. Relationship between bound chloride content and apparent pH value

Conclusions

Before subjecting cement pastes containing chlorides to carbonation, the 28-day compressive strength of PC, PFA and SF mixes was influenced mostly by the w/b and least by the content of PFA up to 15% by replacement of PC. All the uncarbonated pastes rendered similar apparent pH values. Amongst the three factors studied in this research (viz. w/b, SF content and PFA content), the w/b showed the most significant influence on the bound chloride content. Pastes with lower w/b had a higher binding capacity as the binder content and, therefore, the chloride concentration in the mix water was high. The partial PC replacement with PFA and SF increased the chloride binding capacity of the pastes by 10% to 30%. The introduction of PFA contributed to the formation of more FS and C-S-H gel in the paste with a higher specific surface area, while SF resulted only in more C-S-H. Thus, PFA had a more influence on the chloride binding than SF when their replacement levels were the same.

After carbonation, the apparent pH was obviously influenced by the w/b and the SF content in the pastes. The w/b influenced the change of the binding capacity of the cementitious pastes the most, followed by SF. PFA had the least effect during the 28 days of carbonation. The introduction of SF and PFA together was shown to increase chloride binding within 14 days of carbonation. However, there was no obvious difference at 28 days of carbonation.

Chloride binding was noted to increase in low w/b mixes as the carbonation progressed. This was considered due to a phenomenon termed as hindrance effect, by which the newly formed carbonates trapped the free and bound chlorides in the pores. As a consequence, the free chloride concentration decreased, which was identified as an increase in binding. Such an effect was not evident in higher w/b mixes, possibly due to their better connected and wider pore network. In most mixes, the prolonged carbonation reduced the bound chlorides with the exception of 0.3 w/b mixes where 28 days of carbonation managed to plateau the bound chloride content. There was a positive linear relationship between the bound chloride content and the apparent pH value across all the mixes studied.

It was found that there existed a linear relationship between bound chlorides and apparent pH for all of the mixes after the mixes were subjected to carbonation. Therefore, the effect of carbonation on the chloride binding capacity of the mixes could be predicted using a measurement of their apparent pH.

Acknowledgements

The authors gratefully acknowledge the financial support by both the Queen’s University Belfast and the Chinese Scholarship Council. Technical support provided by the Material Characterisation Laboratory and Concrete Research Laboratories at Queen’s University Belfast are also gratefully acknowledged.

References

[1] H. Kuosa, R.M. Ferreira, E. Holt, M. Leivo, E. Vesikari, Effect of coupled deterioration by freeze–thaw, carbonation and chlorides on concrete service life, Cem. Concr. Compos. 47 (2014) 32-40.https://doi.org/10.1016/j.cemconcomp.2013.10.008

[2] O. Poupard, V. L'Hostis, S. Catinaud, I. Petre-Lazar, Corrosion damage diagnosis of a reinforced concrete beam after 40 years natural exposure in marine environment, Cem. Concr. Res. 36(3) (2006) 504-520.https://doi.org/10.1016/j.cemconres.2005.11.004

[3] T.U. Mohammed, N. Otsuki, M. Hisada, H. Hamada, Marine Durability of 23-Year-Old Reinforced Concrete Beams, ACI Symposium Publication 192 (2000) 1071-1088.https://doi.org/10.14359/5802

[4] M.F. Montemor, M. Cunha, M.G.S. Ferreira, A.M. Simoes, Corrosion behaviour of rebars in fly ash mortar exposed to carbon dioxide and chlorides, Cement & Concrete Composites 24(1) (2002) 45-53.https://doi.org/10.1016/S0958-9465(01)00025-7

[5] R. Loser, B. Lothenbach, A. Leemann, M. Tuchschmid, Chloride resistance of concrete and its binding capacity – Comparison between experimental results and thermodynamic modeling, Cem. Concr. Compos. 32(1) (2010) 34-42.https://doi.org/10.1016/j.cemconcomp.2009.08.001

[6] W. Wongkeo, P. Thongsanitgarn, A. Ngamjarurojana, A. Chaipanich, Compressive strength and chloride resistance of self-compacting concrete containing high level fly ash and silica fume, Materials & Design 64 (2014) 261-269.https://doi.org/10.1016/j.matdes.2014.07.042

[7] W. Müllauer, R.E. Beddoe, D. Heinz, Effect of carbonation, chloride and external sulphates on the leaching behaviour of major and trace elements from concrete, Cem. Concr. Compos. 34(5) (2012) 618-626.https://doi.org/10.1016/j.cemconcomp.2012.02.002

[8] M.G. Alexander, J.R. Mackechnie, W. Yam, Carbonation of concrete bridge structures in three South African localities, Cem. Concr. Compos. 29(10) (2007) 750-759.https://doi.org/10.1016/j.cemconcomp.2007.06.005

[9] F. Pacheco Torgal, S. Miraldo, J.A. Labrincha, J. De Brito, An overview on concrete carbonation in the context of eco-efficient construction: Evaluation, use of SCMs and/or RAC, Constr. Build. Mater. 36 (2012) 141-150.https://doi.org/10.1016/j.conbuildmat.2012.04.066

[10] S.E. Hussain, S. Al-Saadoun, Effect of tricalcium aluminate content of cement on chloride binding corrosion of reinforcing steel in concrete, Materials Journal 89(1) (1993) 3-12

[11] H.G. Midgley, J.M. Illston, The penetration of chlorides into hardened cement pastes, Cem. Concr. Res. 14(4) (1984) 546-558.https://doi.org/https://doi.org/10.1016/0008-8846(84)90132-7

[12] A. Neville, Chloride attack of reinforced concrete: an overview, Mater. Struct. 28(2) (1995) 63-70

[13] Y. Wang, S. Nanukuttan, Y. Bai, P.A.M. Basheer, Influence of combined carbonation and chloride ingress regimes on rate of ingress and redistribution of chlorides in concretes, Constr. Build. Mater. 140 (2017) 173-183.https://doi.org/10.1016/j.conbuildmat.2017.02.121

[14] J. Backus, D. McPolin, Effect of Cyclic Carbonation on Chloride Ingression in GGBS Concrete, J. Mater. Civ. Eng. 28(7) (2016).https://doi.org/10.1061/(asce)mt.1943-5533.0001529

[15] J. Liu, Q. Qiu, X. Chen, F. Xing, N. Han, Y. He, Y. Ma, Understanding the interacted mechanism between carbonation and chloride aerosol attack in ordinary Portland cement concrete, Cem. Concr. Res. 95 (2017) 217-225.https://doi.org/10.1016/j.cemconres.2017.02.032

[16] M. Saillio, V. Baroghel-Bouny, F. Barberon, Chloride binding in sound and carbonated cementitious materials with various types of binder, Constr. Build. Mater. 68 (2014) 82-91.https://doi.org/10.1016/j.conbuildmat.2014.05.049

[17] M.S.H. Khan, O. Kayali, U. Troitzsch, Chloride binding capacity of hydrotalcite and the competition with carbonates in ground granulated blast furnace slag concrete, Mater. Struct. 49(11) (2016) 4609-4619.https://doi.org/10.1617/s11527-016-0810-z

[18] H. Chang, Chloride binding capacity of pastes influenced by carbonation under three conditions, Cem. Concr. Compos. 84 (2017) 1-9.https://doi.org/10.1016/j.cemconcomp.2017.08.011

[19] BS 8500-1:2015+A1:2016, Concrete - Complementary British Standard to BS EN 206 Part 1: Method of specifying and guidance for the specifier.

[20] W. Gong, Z. Cai, L. Jiang, Enhancing the performance of differential evolution using orthogonal design method, Appl. Math. Comput. 206(1) (2008) 56-69.https://doi.org/10.1016/j.amc.2008.08.053

[21] H. Hu, Application of Orthogonal Experimental Design for the Automatic Software Testing, The 2nd International Conference on Computer Science and Electronics Engineering (ICCSEE 2013), Paris, France, 2013, pp. 2298-2303.

[22] X. Hu, C. Shi, Z. Shi, L. Zhang, Compressive strength, pore structure and chloride transport properties of alkali-activated slag/fly ash mortars, Cem. Concr. Compos. 104 (2019).https://doi.org/10.1016/j.cemconcomp.2019.103392

[23] M.S. Phadke, Quality engineering using robust design, Prentice Hall PTR1995

[24] L. Franek, X. Jiang, Orthogonal design of experiments for parameter learning in image segmentation, Signal Processing 93(6) (2013) 1694-1704.https://doi.org/10.1016/j.sigpro.2012.08.016

[25] D. Hahs-Vaughn, Lomax, R., Statistical Concepts - A Second Course, Routledge, New York, 2012.https://doi.org/10.4324/9780203137802

[26] BS EN 450-1:2012, Fly ash for concrete Part 1: Definition, specifications and conformity criteria.

[27] BS EN 1008:2002, Mixing water for concrete - Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete.

[28] Q. Ye, Z.N. Zhang, D.Y. Kong, R.S. Chen, Influence of nano-SiO2 addition on properties of hardened cement paste as compared with silica fume, Constr. Build. Mater. 21(3) (2007) 539-545.https://doi.org/10.1016/j.conbuildmat.2005.09.001

[29] Y.A.V.-Z.C.J.Z.a.Á.A.D. Maio, Chloride Penetration and Binding in Recycled Concrete, J. Mater. Civ. Eng 20 (2008) 449-455.https://doi.org/10.1061/共 ASCE 兲 0899-1561 共 2008 兲 20:6 共 449 兲

[30] BS EN 12390-3:2009, Testing hardened concrete Part 3: Compressive strength of test specimens.

[31] D.O. McPolin, P.A.M. Basheer, A.E. Long, Carbonation and pH in mortars manufactured with supplementary cementitious materials, J. Mater. Civ. Eng. 21(5) (2009) 217-225.https://doi.org/10.1061/(ASCE)0899-1561(2009)21:5(217)

[32] B. Andrade, Analysis of water soluble chloride content in concrete, Mater. Struct. 35(253) (2002) 586-588

[33] Z. Ge, Z. Gao, R. Sun, L. Zheng, Mix design of concrete with recycled clay-brick-powder using the orthogonal design method, Constr. Build. Mater. 31 (2012) 289-293.https://doi.org/10.1016/j.conbuildmat.2012.01.002

[34] H. Yazıcı, M.Y. Yardımcı, S. Aydın, A.Ş. Karabulut, Mechanical properties of reactive powder concrete containing mineral admixtures under different curing regimes, Constr. Build. Mater. 23(3) (2009) 1223-1231.https://doi.org/10.1016/j.conbuildmat.2008.08.003

[35] T. Nochaiya, W. Wongkeo, A. Chaipanich, Utilization of fly ash with silica fume and properties of Portland cement–fly ash–silica fume concrete, Fuel 89(3) (2010) 768-774.https://doi.org/10.1016/j.fuel.2009.10.003

[36] M.H.N. Yio, J.C. Phelan, H.S. Wong, N.R. Buenfeld, Determining the slag fraction, water/binder ratio and degree of hydration in hardened cement pastes, Cem. Concr. Res. 56 (2014) 171-181.https://doi.org/10.1016/j.cemconres.2013.12.002

[37] T. Sumranwanich, S. Tangtermsirikul, A model for predicting time-dependent chloride binding capacity of cement fly ash cementitious system, Mater. Struct. 37(6) (2004) 387-396.https://doi.org/10.1007/BF02479635

[38] R. Luo, Y. Cai, C. Wang, X. Huang, study of chloride binding and diffusion in GGBS concrete, Cem. Concr. Res. 33 (2003) 1-7.https://doi.org/10.1016/S0008-8846(02)00712-3

[39] D.O. McPolin, P.A.M. Basheer, A.E. Long, K.T.V. Grattan, T. Sun, New Test Method to Obtain pH Profiles due to Carbonation of Concretes Containing Supplementary Cementitious Materials, J. Mater. Civ. Eng. 19(11) (2007) 936-946.https://doi.org/10.1061/(ASCE)0899-1561(2007)19:11(936)

[40] T. Cheewaket, C. Jaturapitakkul, W. Chalee, Long term performance of chloride binding capacity in fly ash concrete in a marine environment, Constr. Build. Mater. 24(8) (2010) 1352-1357.https://doi.org/10.1016/j.conbuildmat.2009.12.039

[41] R.K. Dhir, M.A.K. Elmohr, T.D. Dyer, Developing chloride resisting concrete using PFA, Cem. Concr. Res. 27(11) (1997) 1633-1639

[42] C. M, A. C, A. C, Chloride-binding isotherms in concrete submitted to non-steady-state migration experiments, Cem. Concr. Res. 29 (1999) 1799–1806.https://doi.org/10.1016/S0008-8846(99)00173-8

[43] K. Byfors, C.M. Hansson, J. Tritthart, Pore solution expression as a method to determine the influence of mineral additives on chloride binding, Cem. Concr. Res. 16(5) (1986) 760-770.https://doi.org/10.1016/0008-8846(86)90050-5

[44] K.O. Ampadu, K. Torii, M. Kawamura, Beneficial effect of fly ash on chloride diffusivity of hardened cement paste, Cem. Concr. Res. 29(4) (1999) 585-590.https://doi.org/10.1016/S0008-8846(99)00047-2

[45] P.S. Mangat, B.T. Molloy, Chloride binding in concrete containing PFA, gbs or silica fume under sea water exposure, Mag. Concrete Res. 47(171) (1995) 129-141.https://doi.org/10.1680/macr.1995.47.171.129

[46] C.L. Page, Ø. Vennesland, Pore solution composition and chloride binding capacity of silica-fume cement pastes, Mat. Constr. 16(1) (1983) 19-25.https://doi.org/10.1007/BF02474863

[47] J.K. Weng, B.W. Langan, M.A. Ward, Pozzolanic reaction in portland cement, silica fume, and fly ash mixtures, Can. J. Civil Eng. 24(5) (1997) 754-760.https://doi.org/10.1139/l97-025

[48] Y. Jun, S. Yoon, J.E. Oh, A Comparison Study for Chloride-Binding Capacity between Alkali-Activated Fly Ash and Slag in the Use of Seawater, Applied Sciences 7(10) (2017).https://doi.org/10.3390/app7100971

[49] H.F.W. Taylor, Ettringite in cement paste and concrete, in: J.-P.B.a.Y. Malier (Ed.) International RILEM Conference on Concrete: from Material to Structure, RILEM Publications SARL, 1996, pp. 66-76.

[50] J. Kwasny, P.A.M. Basheer, M.I. Russell, CO_2 Sequestration in Cement-Based Materials During Mixing Process Using Carbonated Water and Gaseous CO_2, 4th International Conference on the Durability of Concrete Structures, Purdue University, West Lafayette, IN, USA, 2014.

[51] V. G. Papadakis, C. G. Vayenas, M.N. Fardis, Fundamental Modeling and Experimental Investigation of concrete carbonation, ACI Mater. J. 88 (1992) 363-373.https://doi.org/10.14359/1863

[52] X. Zhu, G. Zi, Z. Cao, X. Cheng, Combined effect of carbonation and chloride ingress in concrete, Constr. Build. Mater. 110 (2016) 369-380.https://doi.org/10.1016/j.conbuildmat.2016.02.034

[53] H.U. Jensen, P.L. Pratt, The binding of chloride ions by pozzolanic product in fly ash cement blends, Adv. Cem. Res. 2(7) (1989) 121-129.https://doi.org/10.1680/adcr.1989.2.7.121

[54] R.D. Hooton, Permeability and Pore Structure of Cement Pastes Containing Fly Ash, Slag, and Silica Fume, ASTM Spec. Tech. Publ. (897) (1986) 128-143.https://doi.org/10.1520/STP36395S

[55] S.S. Sankaranarayannan, J.R. Jagadesan, Comparison of High Performance Fly Ash Concrete Using Nano Silica Fume on Different Mixes, Circuits and Systems 07(08) (2016) 1259-1267.https://doi.org/10.4236/cs.2016.78110

[56] S. Goñi, A. Guerrero, Accelerated carbonation of Friedel's salt in calcium aluminate cement paste, Cem. Concr. Res. 33(1) (2003) 21–26.https://doi.org/10.1016/S0008-8846(02)00910-9

[57] M.F. Bertos, S.J. Simons, C.D. Hills, P.J. Carey, A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2, J. Hazard. Mater. 112(3) (2004) 193-205.https://doi.org/10.1016/j.jhazmat.2004.04.019

[58] C.D. Hills, R.E.H. Sweeney, N.R. Buenfeld, Microstructural study of carbonated cement-solidified synthetic heavy metal waste, Waste Manage. (Oxford) 19(5) (1999) 325-331.https://doi.org/10.1016/S0956-053X(99)00146-4

[59] B.R. G.K. Glass, N.R. Buenfeld, The participation of bound chloride in passive film breakdown on steel in concrete, Corros. Sci. 42 (2000) 2013-2021.https://doi.org/10.1016/S0010-938X(00)00040-8