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Effect of combined carbonation and chloride ion ingress by an accelerated test method on microscopic and mechanical properties of concrete

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HIGHLIGHTS

- Lower mechanical properties obtained in combined carbonation–chloride ion ingress.
- Combined carbonation–chloride ion ingress has no effect on nano structure.
- SEM shows less cubic, crystalline shape particles formed in the combined condition.
- Hexagonal portlandite ($Ca(OH)_2$) crystalline cubes observed in the nano graphs.
- XRD reveals that carbonation produces more $CaCO_3$ than the combined condition.

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ABSTRACT

In this study microscopic and mechanical properties of ordinary concrete exposed to CO_2 gas, saline water, and the combination of CO_2 gas and saline water were investigated by an accelerated test method. Specimens with different water to cement ratio of 0.35, 0.4, and 0.45 were retained in an apparatus which was developed to provide an environment to simulate tide cycles. The CO_2 gas pressure, NaCl solution concentration, temperature, and relative humidity were kept constant and controlled, and tide cycles were executed automatically each 6 h. Specimens were retained in CO_2 gas and in NaCl solution with environment characteristics tantamount to that of the apparatus. Microscopic structure and interfacial transition zones of the specimens maintained in all three conditions were studied by implementing scanning electron microscope (SEM). In order to identify crystalline phases and morphological and structural characteristics, nanographs were obtained by transmission electron microscopy (TEM), and phase change due to carbonation and chloride ion ingress were studied along with X-ray diffraction analysis (XRD). Moreover, in order to signify the mechanical properties of specimens, compressive strength, surface resistivity, and CO_2 consumption were measured. It was found that more C–S–H gel and CH crystals has been formed in the presence of sole CO_2 gas, and higher compressive strength is achieved compared to the combined CO_2 gas and chloride ion ingress, and separate saline water. Besides, due to the presence of moisture in the pore solution of specimens maintained in the combined condition, less CO_2 gas and chloride ion ingresses were observed.

1. Introduction

Deterioration of concrete structures, especially exposed structures, can happen because of several phenomena namely, carbonation, chloride ion attacks, sulfate attacks, freezing and thawing cycles, etc. Among such deleterious environmental conditions, carbonation and chloride ion attacks are more probable, especially in urban, and marine environment like large harbors, where the rate of carbonation and chloride penetration is high due to pollution and deicing salts used in winters, and sea water respectively. Using chloride-based deicing salts in urban regions has caused deleterious effects on infrastructures [1–3]. Its effect can be described in the reactions as follows [4]:

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2 \quad (1)$$

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$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3CaO + CaCl_2 + 15H_2O \quad (2)$$

Regarding the reaction (1), $CaCl_2$ and $Mg(OH)_2$ can cause a reduction in compressive strength. Many researches have been conducted on carbonation of concrete structures due to atmospheric CO_2 gas and pozzolans [5]. It is investigated that CO_2 gas affects the durability of reinforced concrete structures, and causes corrosion in the long run since the pH of pore solution may be reduced [6], and it may cause an increase in the concentration of chloride ions in the pore solution as well [7]. Moreover, due to the presence of CO_2 gas, concrete shrinkage happens when CO_2 penetrates into concrete structure: it polymerizes the silicate chains in C–S–H which can decrease the volume, and consequently causes cracks [8]; however, CO_2 gas can improve the compressive strength of specimen [9,10] because of developing homogeneous micro structure and reduction in porosity [11]. The following reactions happen in concrete structure in the proximity of CO_2 gas:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

$$C - S - H + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \quad (4)$$

According to the reactions above, CO_2 reacts with $Ca(OH)_2$, and by consuming $(OH)^-$ ion, the pH in the pore solution may increase which can increase the rate of corrosion [12], and reduce the porosity [11,13]. In fact, by the dissolution of CO_2 in water, reaction (7), according to the following reactions, $CaCO_3$, reaction (8) may be produced in concrete pore solution:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (5)$$

$$H_2CO_3 + H_2O \rightarrow HC_3^- + H_3O^+ \quad (6)$$

$$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+ \quad (7)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \quad (8)$$

Regarding the reaction (7), the main cause of reduction in pH after carbonation, is the liberation of H_3O^+ [14]. Many other researches have been performed on chloride ion ingress in the vicinity of sea shores and harbors [15–17]. It is well known that Kuzel's salt ($3CaO{\cdot}Al_2O_3{\cdot}0.5CaSO_4{\cdot}0.5CaCl_2{\cdot}10(11)H_2O$) and Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) may be formed when chloride ions presents while hydration of cement is continuing. Both of the salts are considered as AFm phases, i.e. hydrated calcium aluminate phases [18]. Depth of chloride penetration [19,20], and diffusion of chloride ions [21] have been studied as well. When chloride ions react with C_3H, Friedel's salt is formed. The chloride ion reaction with C_4AF leads to the formation of Kuzel's salt; Kobayashi et al. [22] found that Friedel's salt is formed because of mono sulfate (AFm) reaction with chloride ion. After the carbonation of Friedel's salt, some chloride ions fixed by Friedel's salt may dissolute into pore solution, and an increase in chloride ions may lead to more ingress of chloride ions. Such ions may reach the reinforcement bars according to the following reaction that can cause corrosion:

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \quad (9)$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \quad (10)$$

The effect of carbonation on chloride ion diffusion has been investigated [23–25], and it has been found that chloride binding reduces when exposed to CO_2 gas [26]. Since high amount of bound chlorides may release when pH goes below 12, such chlorides are considered as a potential risk for corrosion [27], however, carbonation may reduce the capacity of chloride binding [28] which may lead to an increase in the rate of chloride ion ingress [29].

In order to consider conditions that are more analogous to the reality, effect of combined carbonation and chloride ion ingress should be investigated so that a mixture design that has more durability in such conditions may be achieved; consequently, fewer budgets would be allocated to "bring the infrastructure to a good condition" [30]. However, few studies have been performed on the effect of combined carbonation and chloride ion attacks on concrete although both of those factors affect the durability of concrete structures [31], and even accelerate each other [32].

In this research, the effect of simultaneous carbonation and chloride ion ingress on mechanical properties and micro structure of concrete have been investigated. In order to perform an accelerated test method of simultaneous carbonation and chloride ion ingress, an apparatus was made to automatically maintain the temperature, humidity, concentration of CO_2 gas and execute wetting and drying cycles.

2. Materials and methods

2.1. Materials

All specimens were made with type I Portland cement, which meets ASTM C150 [33] specification, with different water/cement ratios. The physical and chemical characteristics of cement are presented in Table 1. Local natural river sand as fine aggregate, and crushed stone as coarse aggregate with maximum aggregate size of 4.75 mm, and 19 mm were used respectively. The water absorption, and specific gravity of fine and coarse aggregates are 2.5% and 1.6%, and 2490 and 2550 kg/m^3 respectively. The specimens were cast and cured with potable water. In order to maintain the workability, a liquid polycarboxylic-ether base with solid content of 45% and specific gravity of 1.2 was used as superplasticizer.

2.2. Mixture design and specimens preparation

The mixture proportion of all specimens is illustrated in Table 2. For all mixtures, by adding adequate amount of superplasticizer, slump was kept constant at about 80 mm. All materials were batched in a 60 l capacity vertical axis mixer with 3 different water/cement ratios: 0.35, 0.4, and 0.45 shown as S35, S40, and S45 respectively. In order to eliminate entrapped air, after casting fresh concrete, specimens were vibrated for 3–5 s and maintained at the temperature of 24 ± 1 °C. Having cured in moist room for 24 h, they were demolded and cured in water at 24 ± 2 °C before placing them in the apparatus for testing under carbonation and saline water. Since early carbonation can alter hydration procedure and calcium hydroxide content at the surface of concrete [32], specimens were cured for 7 days so that the test has less impact on the normal procedure of hydration. After this period, 50% of all specimens were placed in the apparatus for simultaneous carbonation and chloride ion ingress and only carbonation, 25% of them were cured in water for standard curing, and rest of them were maintained under saline water.

2.3. Apparatus

The apparatus for simultaneous carbonation and chloride ion ingress, and wetting and drying cycle simulation is illustrated in Fig. 1 schematically. In chamber 1 (Ch.1), by using a water pump and electric valve, saline water (0.3% NaOH and 3% NaCl [34]) was pumped and drained from chamber 2 (Ch.2) every 6 h to simulate the tide process and provide an environment in which we have tidal zone like marine structures; shorter or longer duration for cycles are achievable by commanding a programmable logic controller (PLC) which interpret all commands through a

Table 1
Characteristics of the cement.

Oxide elements (% by mass)		Cement (C)
SiO_2		21.10
CaO		62.08
Fe_2O_3		2.74
Al_2O_3		3.81
SO_3		2.6
MgO		3.22
K_2O		0.73
Na_2O		0.12
P_2O_5		0.22
TiO_2		0.24
Loss on ignition (%)		2.95
Physical properties	Specific gravity	3.17
	Blaine fineness (cm^2/g)	3519