Analysis of carbonate and sulphate attack on concrete structures

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ABSTRACT

The current study was designed to explain the progress and causes of damage to structural concrete exposed to atmospheric CO_2 and rainwater (23-year old slab) and interactions of atmospheric CO_2, rainwater and gypsum (50-year old columns). The testing programme included SEM with EDXA and XRD analysis, and tests determining compressive strength and water absorption. During the carbonation process the basic product identified in the concrete microstructure was calcite or "secondary" calcite, which appeared at the surface of concrete, in the cracks or in the form of dripstone. The formation of ettringite and calcite was observed in the concrete columns exposed to interactions of gypsum, carbon dioxide and rainwater for 50 years. Ultimately, the only product present on the exterior of the concrete was calcite. This is attributed to the conversion of ettringite to calcite due to a direct reaction with CO_2. The test results were compared to the theoretical hypotheses.

1. Introduction

Carbonate attack on concrete is related to the ingress of carbon dioxide into the hardened cement paste (hcp), exclusively in the presence of water from the air and in the pores of the hcp. Gaseous carbon dioxide dissolves to form weak carbonic acid (with a low dissociation constant $K_{a1} = 4.2 \cdot 10^{-7}$ and extremely small secondary constant $K_{a2} = 4.8 \cdot 10^{-11}$), which dissociates mainly into hydrogen and carbonate ions [1]. Collett et al. [2] describe the equilibrium between free carbon dioxide and dissociated carbonic acid with the use of the equation below, indicating that the reactions may only take place under humid air conditions or in the solution, and are possible in both directions:

$$CO_2 + H_2O \xleftarrow{H_2O} H_2CO_3 + H_2O \rightleftarrows H^+ + HCO_3^- + H_2O \tag{1}$$

Although all hcp phases are sensitive to carbonate attack, portlandite is considered to be the most CO_2 reactive phase (from chemical perspective). In some cases carbonation of other phases, e.g. C-S-H, may be faster due to a greater specific surface area [3]. Carbonation of C-S-H phase will also be accelerated when the portlandite content in the hcp is as low as that in fly ash cement composites [4].

Drever [6] explains that in the natural atmospheric conditions (humid air containing CO_2), the pH value of the solution in which the reaction takes place is the decisive factor contributing to the occurrence of one of the two carbonates – $CaCO_3$ or $Ca(HCO_3)_2$. When the pH value exceeds 12, calcium carbonate, usually in the form of calcite, is a predominant product of carbonate attack. Therefore, when the hcp contains portlandite in the quantity sufficient for protecting the saturated pore solution, calcium carbonate may be expected to form.

$$CaOH^+ + OH^- + H^+ + HCO_3^- + H_2O \rightleftarrows CaCO_3\downarrow + 3H_2O \tag{2}$$

Sodium and potassium (alkalis) present in the cement maintain high pH (even over pH = 13.5) of the pore solution and affect the kinetics of CO_2-hcp reaction. However, they are very soluble and any contact with water makes them leave the hcp quickly.

A thorough review of the carbonate attack literature draws attention to the permanent and progressive depletion of portlandite and the formation of $CaCO_3$ penetrating inward across the layers even beyond the concrete cover [7]. The progress of carbonate attack may be explained using the theory developed by Cowie and Glasser [8], who prove that in a concentrated solution of calcium hydroxide (i.e. when pH > 12, as in the pore solution of the cement paste), $CaCO_3$ precipitates from calcium bicarbonate and crystallizes in the form of calcite:

$$CaOH^+ + OH^- + Ca^{2+} + 2HCO_3^- + H_2O \rightarrow 2CaCO_3 \downarrow + 3H_2O \tag{3}$$

This is only possible when $Ca(HCO_3)_2$ is formed in the most outward layers of concrete. When a portion of alkali (Na, K) has left the paste and during the carbonation process, the pH of the pore solution is lower and the flux of calcium ions from the outer surface is increased due to higher permeability of the carbonated paste.

The formation of the calcium bicarbonate seems obvious, but it is important to note that this reaction is reversible (Eq. (4)) when the ambient conditions change.

$$CaCO_3 + HCO_3^- + H^+ + H_2O \xleftarrow{CO_2}\rightarrow Ca^{2+} + 2HCO_3^- + H_2O \tag{4}$$
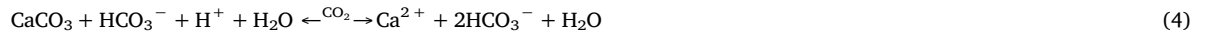
Thus, the process of $CaCO_3$ formation will be progressing in deep layers of concrete without direct access of carbonic acid. It must be remembered, though, that the long-term carbonate attack on deeper layers of concrete (continuation of reaction (3)) is affected by the attack of aggressive CO_2 and water, leading to the formation of calcium bicarbonate in the external layer of concrete, carbonated at the onset of the attack.

Collett et al. [2] and Lea [9] describe in detail two types of carbon dioxide – aggressive CO_2^A ($ĉ^A$) and CO_2^S ($ĉ^S$) stabilizing calcium bicarbonate. The aggressive part of carbon dioxide is the one which exceeds the amount required to stabilize $Ca(HCO_3)_2$. Considering the two forms, aggressive and stabilizing, of CO_2, the formation of calcium bicarbonate takes place according to the following equation.

$$Cĉ + H + (ĉ^A) + ĉ^S \xleftarrow{CO_2} Cĉ_2H + (ĉ^S) \tag{4a}$$
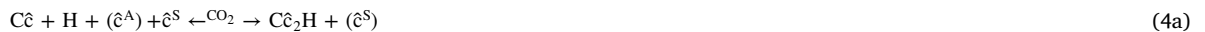
Before the reactions (4), and (4a) can occur, total disappearance of $Ca(OH)_2$ is necessary for the reduction of pH value in the pore solution [10]. Hydrogen carbonate ions considerably dominate carbonate ions in terms of their activity and solubility only when pH < 10 [5,8]. The pH value of concentrated $CaCO_3$ solution, which according to Lea [9] is 10.2, validates this thesis.

Calcium bicarbonate (calcium hydrogen carbonate) occurs exclusively in water solutions at the maximum concentration of 166 g/dm^3 (20 °C). In concrete, $Ca(HCO_3)_2$ formed from $CaCO_3$ occurs in the pore solution of the hcp only in a dissociated form. The harmlessness of this reaction (4 and 4a) for concrete is obvious. This reversible reaction has been successfully used in the controlled mode in laboratory experiments [11], with the cracks healed by calcite precipitation. This paper describes the results of the tests on a real concrete structure – a field steel reinforced slab – in which the cracks were filled with calcite precipitation.

Conventional sulphate attack in the hcp consists in the formation and expansion of gypsum and ettringite, $C_3A \cdot 3CaSO_4 \cdot H_{32}$. The reactants are portlandite, calcium monosulphoaluminate and aluminate hydrates and sulphate ions. Gypsum is formed in the reaction between portlandite and sulphate salts solutions. The reactions between sulphate salts and calcium aluminate hydrates (AFm phases) result in the formation of ettringite.

According to the latest research [12,13], crystallization pressure is the most probable cause of expansion (increase in solid volume) of cement composites immersed in a sulphate solution. Expansion is related to the transformation of monosulphate crystals embedded in the C-S-H to ettringite; although in large pores ettringite forms without expansion [12]. The co-existence of ettringite and gypsum is said to result in higher expansion. Expansive forces within C–S–H occur when monosulphate and gypsum are both present locally and the pore solution can be highly supersaturated in ettringite [13].

The expansion of the ordinary Portland cement composites immersed in the sulphate solution is reduced when bicarbonate ions are present at high concentrations [14]. At high concentrations of bicarbonate, ettringite and gypsum become unstable. Consequently, the pressure of ettringite crystallization does not generate expansive forces [14]. This issue was investigated in real conditions and presented in this paper.

The aim of the study was to determine and analyze carbonate and sulphate attack on concrete samples. They were derived from old reinforced concrete structures significantly deteriorated due to environmental impact. Like the scientists who investigated the causes of Swiss tunnels damage [15], the author of this paper considered both concrete microstructure and the cracks, where a different process, often accelerated, takes place.

2. Materials and methods

The test samples were taken from two sources. One source was the 23-year-old reinforced concrete slab (25 cm thick) from a three-storey car park with dimensions of 39 × 44 m in horizontal projection. The 25 cm thick slab was the main load-carrying element of the roofless upper car park floor. To identify the properties of the concrete, the samples were tested for compressive strength and absorption. The slab being the topmost level of the three-storey car park was in contact with atmospheric air and rainwater, which infiltrated very slowly through its cracks. The cracks were filled with white substance. The microstructure of the concrete in the vicinity of the crack and the substance filling the crack were analyzed. Dripstone stalactite microstructure was also