



## Changes in microstructure characteristics of cement paste on carbonation

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### ABSTRACT

This study investigates the influence of carbonation on the microstructure of cement paste cast with Ordinary Portland Cement (OPC), fly ash based Portland Pozzolana Cement (PPC) and Limestone Calcined Clay Cement (LC<sup>3</sup>) using X-ray diffraction (XRD), thermal analysis (TGA), scanning electron microscope (SEM) and mercury intrusion porosimeter (MIP). A comparison is made between samples exposed to 3% carbon dioxide concentration and those exposed to natural CO<sub>2</sub> concentrations. It is observed that the products formed on carbonation are similar in both the exposure conditions. Distinct rims corresponding to decalcified C-S-H are observed around clinker grains in the carbonated samples. Coarsening of pore structure is observed on carbonation in all the cements and an increase in the total porosity is observed in blended cements. Thermodynamic modeling indicates irrespective of the type of cement the total solid volume is reduced on complete carbonation. The volume change occurring on carbonation obtained from experimental results and thermodynamic modeling are compared.

### 1. Introduction

Corrosion of steel reinforcement in concrete is the leading cause of deterioration of concrete structures. Chloride ingress and carbonation are the two major processes that lead to the corrosion of reinforcement. Carbonation of concrete is a complex physicochemical process. Carbon dioxide diffuses from the atmosphere into the capillary pores of the concrete and dissolves in the pore solution forming carbonic acid. This, in turn, reacts with the ions from the dissolution of the solid phases. The overall alkalinity of the concrete is reduced as a result of this neutralization reaction. At reduced alkaline levels, the passive oxide layer protecting reinforcement in concrete becomes unstable resulting in its disintegration, thus making the reinforcement prone to corrosion [1–3].

The majority of cement available worldwide contains supplementary cementitious materials (SCMs) to improve their engineering, economic and environmental performance [4]. The pozzolanic reaction of the SCMs reduces the capacity of the concrete to bind CO<sub>2</sub> and slow down its inwards flow, making it more susceptible to carbonation.

All phases present in hydrated cement have a tendency to carbonate. Calcium from the hydrates will be precipitated as calcium carbonate. Calcium hydroxide (CH) and calcium silicate hydrates (C-S-H) make up 70–80% of the total solid volume of a completely hydrated Portland cement. While the proportion of CH is higher in OPC, a significant fraction of CH is converted to C-S-H in blended cements due to the pozzolanic reaction. Both calcium hydroxide and C-S-H produce

calcium carbonate upon carbonation. For C-S-H, this is accompanied by its decalcification and the formation of silica gel [5]. From a thermodynamic perspective all the CH should carbonate before the C-S-H, but in practice, it is found that they carbonate simultaneously [6–8]. AFt and AFm hydrates such as ettringite and monosulphate are the other major phases present in hydrated cement paste [1,4]. These phases are in equilibrium and stabilized by the high pH of the pore solution [3]. Carbonation of CH and the other alkalis in cement leads to a drop in the pH of the pore solution, resulting in the dissolution and subsequent carbonation of these phases. In presence of sufficient carbon dioxide, the calcium sulfoaluminate phases convert to calcium carbonate, alumina gel, gypsum and water [9]. The Polymorph of calcium carbonate (C̄) that precipitates on carbonation depends upon the kinetics and thermodynamics of the reaction. Calcite is the most stable polymorph under ambient conditions and is therefore usually the most predominant, however, the formation of vaterite and aragonite has also been reported [10–13]. The precipitation of type of polymorph of calcium carbonate on carbonation is reported to be dependent upon various factors like concentration of carbon dioxide, relative humidity, pH, Ca/Si, duration of exposure and phase of hydrated cement getting carbonated [6,7,12,14–17]. However, the exact conditions that favor the precipitation of these polymorphs are not well understood. Thermodynamics indicates that all the polymorphs will eventually transform into calcite [12]. González et al. [18] reported precipitation of amorphous calcium carbonate, which is kinetically favored and

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**Table 1**  
Chemical analysis of raw materials using XRF.

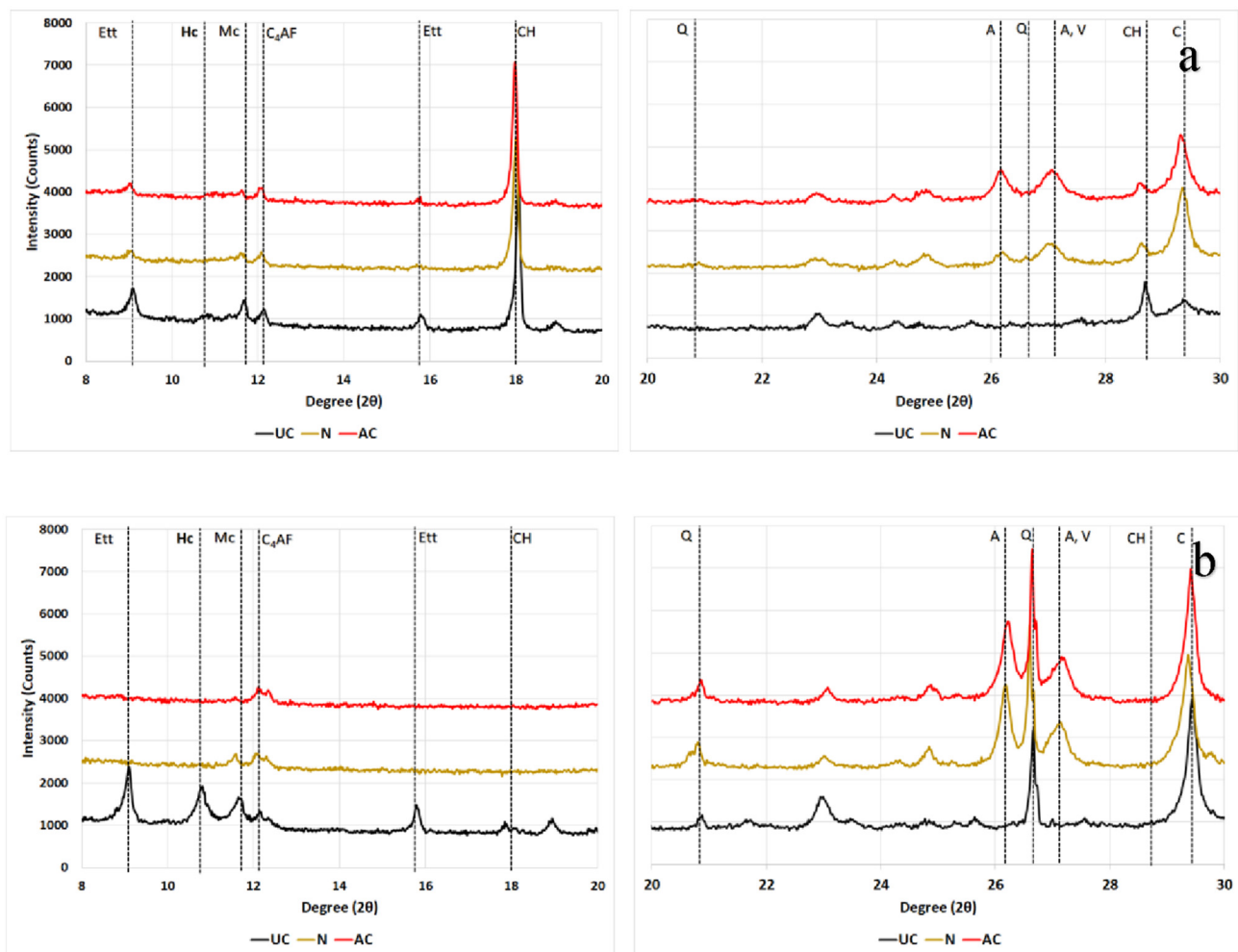
%	Clinker	Limestone	Gypsum	Calcined Clay	Fly-Ash
SiO <sub>2</sub>	21.07	11.02	2.77	52.70	58.82
Fe <sub>2</sub> O <sub>3</sub>	4.32	1.55	0.36	4.00	6.19
Al <sub>2</sub> O <sub>3</sub>	4.65	2.53	0.62	38.14	30.62
CaO	65.16	44.24	32.62	0.09	1.01
MgO	2.13	1.96	1.2	0.02	0.41
SO <sub>3</sub>	0.77	–	38.75	0.10	0.12
Na <sub>2</sub> O	0.38	0.50	0.06	0.18	0.19
K <sub>2</sub> O	0.2	0.28	0.037	0.17	1.3
LOI	0.96	36.96	23.02	4.24	1.11

converts to calcite with time. Black et al. [16] also reported the formation of amorphous calcium carbonate first on carbonation of fresh cement sample.

Carbonation leads to a change in the microstructure of the concrete due to the difference in the molar solid volume of the hydrates and the carbonated phases. Several studies have reported a reduction in the porosity of concrete on carbonation. The molar solid volume of C $\bar{C}$  formed is 11–14% higher than the CH reacted depending upon the type of polymorph precipitated [3,8]. However, the change in porosity on carbonation cannot be attributed only to CH [8,19]. The carbonation of C-S-H proceeds by the leaching of calcium ions from C-S-H, eventually leading to the formation of amorphous silica gel. This reaction is

accompanied by an overall reduction in the volume of solids and an increase in porosity and pore sizes, known as carbonation shrinkage [10,20–22]. The change in solid volume of C-S-H on carbonation is not exactly known as the reaction stoichiometry is not clearly established [8,23]. Coarsening of the pore volume and an increase in porosity upon carbonation has been reported in cements containing SCMs [12,24,25]. This can be attributed due to the higher amounts of C-S-H and absence of or low amount of CH. Nevertheless, some researchers have observed a reduction in pore volume and refinement of the pore structure for both OPC and cement containing SCMs [26–28], while an increase in critical pore diameter and reduced porosity on carbonation in Portland cement has been reported by others [18,29,30]. Lack of knowledge in evaluating the change in solid volume and discrepancy in results makes it difficult to accurately quantify the changes in porosity due to carbonation in cement, particularly cement containing SCMs.

In this study, the effect of carbonation on microstructural properties of cement paste is investigated. A comparison between samples exposed to accelerated and natural rate of carbonation is made. Two types of cements having different clinker replacement levels but similar mechanical properties are selected for the study. First cement is a binary system with 30% replacement of clinker by Fly Ash (Portland pozzolana cement, PPC) and the second cement is a ternary system with 50% clinker replacement by limestone and calcined clay (LC<sup>3</sup>). The results of blended cements are compared with that of Ordinary Portland cement (OPC). The compressive strength of the blended cements and OPC used in this study are similar [31,32]. X-ray diffraction (XRD) and



**Fig. 1.** XRD plots of uncarbonated (UC), natural (N) and accelerated carbonated (AC) samples (a): OPC, (b): LC<sup>3</sup> (Ett: Ettringite, Hc: Hemicarboaluminate, Mc: Monocarboaluminate, CH: Calcium hydroxide, A: Aragonite, V: Vaterite, C: Calcite, Q: Quartz).

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