Microstructure of Ettringite Binder Exposed to Natural Carbonation

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Abstract. Ettringite binder which composes of Calcium Aluminate Cement (CAC), Ordinary Portland Cement (OPC), and Calcium Sulfate (Anhydrite - CaSO₄ or Hemihydrate - CaSO₄.0.5H₂O or Gypsum - CaSO₄.2H₂O) is one of the recent cementitious materials. The main advantage of this type of binder is the rapid hydration that leads to extremely rapid development of mechanical strength. This feature is obtained by the production of large amount of early ettringite during the hydration process. In this research work, the carbonation process of ettringite phases is analysed and discussed by means of infrared spectroscopy, X-ray diffraction. The goal of this work was to study the evolution of developed carbonated phases due to the action of CO₂ over the AFt phases developed in the CAC/PC/CaSO₄ system. After 1 year, the total carbonation depth of the samples stored outdoors is approximately 4 mm and there is no carbonation for the samples stored in endogenous condition. The carbonation process of ettringite gives gypsum, calcium carbonate and aluminum hydroxide. These phases are detected by both X-ray diffraction and Infrared spectroscopy method.

1. Introduction
Ettringite-based binders are used in applications that require a high compressive strength in a very short period of time to minimize construction times and disruption to the traveling public or user [1-5]. The binder system containing OPC, calcium aluminate cement (CAC) and calcium sulphate (anhydrite and/or other forms) is often used when fast setting and hardening and high early strength development are required [5-7]. The principle reaction causing the exceptionally fast strength development includes rapid and massive ettringite formation (C₃A.3CaSO₄.32H₂O) from CAC and anhydrite. Ettringite-based binders also carbonate at a faster rate than ordinary Portland cement (PC)-based systems as a result of the limited amount or absence of portlandite (CH). This ternary ettringite based binders are also known to carbonate more quickly than pure PC mixtures [8-9]. The carbonation of ettringite based binders is especially troubling as they are often used in repair applications where corrosion is already an issue. Most laboratory studies aimed at evaluating carbonation resistance employ accelerated methods to predict carbonation depths; however, as with most accelerated methods, there exists a large disconnect between the results of the accelerated methods and natural carbonation seen in the field [10]. With the increased use of ettringite based binders for repair applications it is of the utmost importance to fully, and accurately evaluate the carbonation resistance of these materials to ensure the quality and long term performance of repairs carbonation results in the conversion of ettringite into products that occupy less space, resulting in a loss of strength and increased porosity [11].

The carbonation process of the ettringite binder, depending on weather conditions, occurs more or less quickly depending on several factors. The concentration of CO₂ in the weather: the higher the CO₂ concentration, the faster the carbonation rate. The crystals CaCO₃, CSH₂ and AH₃ formed by the
decomposition of ettringite (found in the pores or on the surface of the mortar) make it possible to avoid or limit subsequent carbonation [12-13]. Weather conditions of heavy rain or snow and melting snow favor leaching. The phenomenon destroys the protective layer of mortar and increases the carbonation of ettringite. This study compared the microstructure of carbonated and noncarbonated ettringite binder by IR and DRX technique. A appearance of new phases of carbonated ettringite-based binders is also observed as a result of the conversion of ettringite. In this research work, the carbonation process of ettringite phases is analysed and discussed by means of infrared spectroscopy, x-ray diffraction. The goal of this work was to study the evolution of developed carbonated phases due to the action of CO₂ over the AFt phases developed in the CAC/PC/CaSO₄ system. In these samples, with high gypsum content, carbonation has been done in order to research the CO₂ incorporation to the ettringite or gypsum structures or ettringite decomposition is taking place when exposing to a natural carbonation environment.

2. Materials and methods

2.1. Materials
Sample was prepared by mixing calcium aluminate cement (57.7% CA, 37.5% CA₂), cement CEM II 42.5 (71.5% C₃S, 14.05% C₂S, 11.6% C₃A) and calcium sulphate anhydrite in the following proportions by weight, 70/22.5/7.5. The formulation used in this study is presented in the table 1:

| Materials          | Percentage composition of raw materials, %wt. |
|--------------------|-----------------------------------------------|
| Calcium aluminate cement CAC | 70                                             |
| Natural Anhydrite CaSO₄ | 22.5                                          |
| Cement CEM I – 42.5   | 7.5                                           |
| Ratio Water/Binder, by weight | 0.35                                         |

The working system was mixed with distilled-deionised water using 0.35 as the water/binder ratio (by wt). The pastes produced were cast in to the mold of 4x4x16 cm and placed in sealed plastic bag with moist air of 100 % R.H. at 20°C for 1 day. The hydrated pastes were divided into 2 groups: 1 group placed in sealed bag and 1 group submitted to a carbonation process in atmospheric air. After 360 days of hydration, the samples will be finely ground to a particle size of smaller than 0.09mm to evaluate the mineralogical composition.

2.2. Methods
The specimens were stored outside for one year. During that time, depth of carbonation measurements was taken at 6 months and 1 year. At each measurement interval, a slice with thickness of 50 mm of specimen was removed by using a saw. Then, a 5% phenolphthalein solution as a pH indicator was sprayed on the freshly broken surface. The use of a saw was necessary to provide a freshly broken surface capable of fully absorbing the phenolphthalein. The depth of carbonation for each specimen is the colourless region of the specimen, which is carbonated.

The mineralogical composition of the hydrated and carbonated materials was performed by an X-ray diffractometer (XRD) Bruker D8 Advance controlled by a computer coupled with DIFFRAC Plus EVA software (Bruker Software) which allows the exploitation of the results and an FTIR - Fourier transform infrared spectrophotometer Nicolet iS50 FT-IR with a frequency range of 400-4000 cm⁻¹ were used to obtain more detailed information of the morphology and elemental composition of phases.
3. Results and discussion

In this part, the Carbonation depth of ettringite binder was measured and the microstructure was analysed by XRD and IR was studied to evaluate the carbonation of the outdoor samples and compared to the samples in endogenous condition (no carbonation).

3.1. Carbonation depth

The carbonation depths at one year for the specimens exposed to natural carbonation are shown in Figure 1.

![Graph showing carbonation depths](image)

**Figure 1.** Depth of Carbonation for samples in endogenous condition and in natural environment (outdoor) at one year

The carbonation depth for this ettringite almost doubled between 6 months and 1 year. This system is a pure calcium aluminate binder, which relies solely on the formation of ettringite for strength gain. As stated earlier the decomposition of ettringite results in the formation of denser products such as calcite and gypsum, which results in an increase in porosity. This increased porosity then allows for faster diffusion of CO₂ and faster rate of carbonation at later ages. The phenolphthalein test indicates a total carbonation depth of approximately 4 mm for the samples stored outdoors and the binders in endogenous condition have no carbonation due to the absence of CO₂.

3.2. Microstructure analysis by XRD

The results of the X-ray diffraction are summarized in Figure 2. DRX data show that the average intensity of the main peak of ettringite of sample cured outdoors has decreased after 330 days. It means the ettringite decomposed and the aluminum hydroxide are formed in various forms as well as gypsum and aragonite. The results also shows the number of average intensity of the main peak of the gypsum (2θ = 11.65°), ettringite (2θ = 9.11°) and calcium carbonate CaCO₃ [calcite (C) at 2θ = 29.4°; Vaterite (V) at 24.9°; 27°; Aragonite (Ar) at 26.2°] depending on the method of curing (with or without carbonation).
XRD pattern of Ettringite peak at $2\theta = 9.11^\circ$

XRD pattern of Calcium Carbonate peak: Calcite (C) at $2\theta = 29.4^\circ$; Vaterite (V) at $24.9^\circ$, $27^\circ$; Aragonite (Ar) at $26.2^\circ$
According to previous research [11-13], ettringite which is the main product of hydration in our mortars, is very sensitive to the chemical reaction between atmospheric carbon dioxide (CO$_2$) and HCO$_3^-$ ions of the aqueous solution. The CO$_2$ in the air reacts quickly with cement hydrates. This carbonation of the system leads to the conversion of ettringite to calcite, gypsum, and aluminum gel [11]. It is generally accepted that ettringite breaks down into calcite, gypsum and alumina by carbonation, according to the equation:

\[
\text{C}_3\text{A}.3\text{CaSO}_4.32\text{H}_2\text{O}+3\text{CO}_2 \rightarrow 3\text{CaCO}_3+3\text{CaSO}_4.2\text{H}_2\text{O}+ \text{AH}_3 + 23\text{H}_2\text{O}
\]

No carbonate phase or gypsum was observed in samples stored in endogenous condition. That means ettringite binders in the endogenous sample are not influenced by carbonation. On the other hand, ettringite is no longer present in the matrix on the surface and has therefore been carbonated. The XRD analysis indicates that the matrix consists of CaCO$_3$ and gypsum and (the presence of AH$_3$ is not obvious because it is poorly crystallized). Weather conditions of heavy rain or snow and melting snow favor leaching. The phenomenon destroys the protective layer of mortar and increases the carbonation of ettringite.

3.3. Investigation of carbonatation by IRFT

From the equation for the decomposition of ettringite, the formation of AH$_3$, CaCO$_3$ [calcite, vaterite, aragonite] and gypsum was expected. The gypsum formation was detected and confirmed by X-ray diffraction in the sample. In theory, the amount of AH$_3$ on the skin of the sample should increase under the influence of carbonation, yet it is found that there is no big difference in the height of the peaks of AH$_3$. In order to verify this theory, we will analyse carbonate samples with IR. IR spectroscopy is other useful technique to investigate the carbonation of ettringite binder. The results of the IR analysis are presented in Figure 3.
FTIR investigations in the figure 3 revealed the interesting difference peaks of sample undergo carbonation and sample endogenous condition. Besides the water bands at about 1600 cm\(^{-1}\), outdoors samples exhibit large bands of carbonates at 1440 cm\(^{-1}\). In the sulphate region, a shift of the band at 1100 cm\(^{-1}\) in the endogenous system to 1120 cm\(^{-1}\) in the outdoors sample after weather exposure indicates the deformation of ettringite. The position of the absorption bands located near 1687, 1623, 1100, 710 cm\(^{-1}\) indicates the presence of a sulphate compound similar to gypsum. The intensity of the bands mentioned indicates that there is more sulphate in the outdoors sample. There is a decrease in the signal corresponding to ettringite on the skin in the compositions. This goes well with the DRX results. A modification of the CO\(_3^{2-}\) peak was observed at 850 cm\(^{-1}\), 875 cm\(^{-1}\) which reflects the carbonation on the skin of the samples \[14-16\], (The peaks around 744, 875 cm\(^{-1}\) show the appearance of vaterite \[14\], which is also a product of the decomposition of ettringite, the gypsum peak was not found at 1620 cm\(^{-1}\) and at 1680 cm\(^{-1}\) in the endogenous sample as was shown by the DRX results. In addition, the presence of an absorption band around 1020 cm\(^{-1}\) indicates the presence of poorly crystallized aluminium hydroxide compounds, which are difficult to detect by XRD. The higher peak of AH\(_3\) in the outdoors sample due to ettringite decomposition could indicate the development of this amorphous phase.

4. Conclusions
The aim of this study was to evaluate the carbonation of ettringite - rich binders through natural outdoor carbonation exposure. Based on the results of the study the following conclusions can be made:
- The decomposition products of carbonation are compatible with the theory. The carbonation process of ettringite gives gypsum, calcium carbonate and aluminium hydroxide.
- After 1 year, the total carbonation depth of the samples stored outdoors is approximately 4 mm and there is no carbonation for the samples stored in endogenous condition.
- The microstructure tests of samples by IR and XRD showed a good correlation. However, more work in the future is needed to evaluate the impact of carbonation of ettringite binder on the actual corrosion resistance such as: porosimetry analysis or mechanical performances.
5. References

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