Hydration of cubic C_3A in the presence of polycarboxylate-based superplasticizers

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Resumo

O presente trabalho avalia a influência de dois aditivos diferentes à base de éter de policarboxilato (PCEs) (variando o comprimento das cadeias laterais) na hidratação do C_3A cúbico com uma razão gipsita/C_3A de 0,637. Foram realizadas análises de difração de raios X in situ utilizando fonte de energia síncrotron e calorimetria isotérmica para monitorar a hidratação dos sistemas C_3A-gipsita/aditivo. Observou-se que os PCEs retardaram a hidratação inicial (primeiras 5 horas) do C_3A cúbico, mas aceleraram a reação posterior do C_3A e a formação de fases do tipo monossulfoaluminato (AFm), que ocorreram antes do esgotamento da gipsita. O uso do PCE com cadeias laterais menores levou a uma formação mais precoce de AFm nas pastas de C_3A cúbico em comparação com as pastas contendo o outro PCE.

Palavras-chave: C_3A cúbico, superplastificante policarboxilato, gipsita, hidratação, DRX in situ.

ABSTRACT

The present work assesses the influence of two different admixtures of polycarboxylates ether (PCEs) (varying the side chains length) on the cubic C_3A hydration with gypsum/C_3A ratio of 0.637. In situ X-ray diffraction using synchrotron source of energy and isothermal calorimetry were performed to follow the hydration of the C_3A -gypsum/admixture systems. It was observed that PCE delayed the very early hydration (first 5 hours) of cubic C_3A but accelerated the renewed C_3A reaction and the monosulfoaluminate-type phases (AFm) formation, which happened before gypsum depletion. The use of the PCE with lower side chains led to an earlier AFm formation in the cubic C_3A pastes compared to the pastes with the other PCE.

Keywords: Cubic C_3A, Polycarboxylate superplasticizer, Gypsum, Hydration, In-situ XRD.

1 INTRODUCTION

In the 1980s, a new family of superplasticizers was developed, known as polycarboxylates ether (PCE). Studies describe that PCE admixtures can produce concrete with high fluidity or a very high reduction in the water demand (up to 40%) (Plank; Sachsenhauser, 2008). The use of PCE contributes to the water reduction, and the improvement in the workability, mechanical properties and durability are increased, and better-quality material is produced. On the other hand, Alonso et al. (2012) suggested that superplasticizers, of any nature, modify the cement hydration process, which can substantially change the dissolution rates or nucleation of new species, impacting the hydrated products' growth.

The C_3S is the main phase of Portland cement. However, the adsorption of superplasticizers occurs preferentially in the aluminate type phases (C_3A and C_4AF) (Pourchet et al., 2009). The mechanism associated with controlling the dissolution and hydration of C_3A by the calcium sulfates is not yet fully understood. Recent

studies suggest that the key inhibiting mechanism is the adsorption of S and/or Ca-S ions pair onto the Al-rich leached layer formed at the partially hydrated C_3A surface (Liu et al., 2020).

The high reactivity of C_3A requires rapid data acquisition to obtain quantifiable diffractograms before significant hydration occurs. While conventional in situ X-ray diffraction (XRD) using modern laboratory diffractometers—equipped with accessories such as humidity-controlled chambers—allows for monitoring hydration kinetics, it typically requires 20-30 minutes per scan. In contrast, synchrotron-based in situ XRD enables data collection within approximately 1 minute, significantly enhancing time resolution and capturing transient phase evolution with greater accuracy. This advantage is particularly relevant for highly reactive phases like C_3A, where early-stage transformations can occur within minutes. Several studies in the literature (e.g., De la Torre et al., 2008; Matos et al., 2025) have demonstrated the superior time resolution and sensitivity of synchrotron XRD in tracking rapid phase changes, enabling a more precise understanding of hydration mechanisms compared to conventional laboratory-based methods. Additionally, laboratory equipment may introduce additional contributions into the XRD pattern, such as “tube tails” and satellite components in the emission profile. In contrast, Synchrotron XRD measurements significantly minimize instrumental contributions, offering extremely low axial divergence, high energy (which reduces absorption effects), and a highly clear radiation emission (Matos et al., 2025).

The effect of PCE-based chemical admixtures on C_3A hydration needs better understanding, especially regarding a high SO_4^{2-}/C_3A molar ratio. Thus, this paper aims to evaluate the effect of two PCE superplasticizers (varying their molecular structures) on the hydration of cubic C_3A paste with SO_4^{2-}/C_3A molar ratio of 1.792, using isothermal calorimetry and Synchrotron XRD.

2 METHODOLOGY

2.1 MATERIALS

The tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) was produced by Mineral Research Processing Cie (MRP). X-ray diffraction and Rietveld analysis showed that the C_3A contains approximately 99% of cubic C_3A (ICSD# 1481) and 1% of C_3AH_6 (ICSD# 202316). According to physical characterization, cubic C_3A had a mean particle size of 16.26 µm, and a B.E.T. specific surface area of 5.25 m²/g. Gypsum ($CaSO_4{\cdot}2H_2O$) was used as the sulfate source with a mean particle size of 11.28 µm, and a B.E.T. specific surface area of 13.16 m²/g. Two polycarboxylate ester-based superplasticizers with different dispersing capacities were used. The first one is PCE OP to provide high initial workability to concrete for a limited time. The second one is PCE MN to maintain the workability/plasticity of the concrete for more extended periods but with a lower degree of initial fluidity.

2.2 SAMPLE PREPARATION

In table 1, the mix design of all combinations is shown. The gypsum/C_3A ratio was based on the stoichiometric calculation of the formation of a complete C_3A hydration product. A gypsum/C_3A ratio of 0.637 (*i.e.* a SO_4^{2-}/C_3A molar ratio of 1.792) was used to obtain the complete conversion of ettringite into monosulfate. The water/dry material ratio of 1.2 was established.

Table 1: Mix design of samples

C_3A	GYPSUM/C_3A RATIO	SO_4^{2-}/C_3A MOLAR RATIO	TYPE OF ADMIXTURE	CONTENTS (wt. %)
Cubic	0.637	1.792	PCE MN	0, 0.5, 1.5, 3
			PCE OP	

2.3 TESTS CONDUCTED

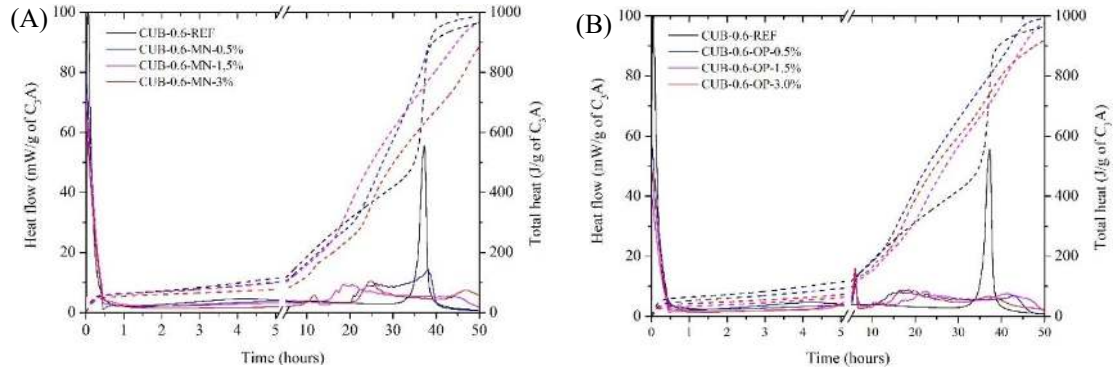
The hydration was monitored by isothermal calorimetry using a TAM Air microcalorimeter (TA Instruments) with a sensitivity of ±20 mW. TAM Air Assistant software was used to collect the data. In situ X-ray diffraction analysis was performed at the National Synchrotron Light Laboratory (LNLS) in Campinas/Brazil in the XRD1 beamline. The power used was 12 keV, equivalent to the wavelength 1.0332 Å. Diffractograms were taken from 0° to 120 degrees° for one minute at an ambient temperature of 25 °C. The samples were loaded into quartz capillaries of 1.0 mm in diameter. From the obtained X-ray diffractograms, the quantification of the phases was performed using the Rietveld method.

3 RESULTS AND DISCUSSIONS

3.1 ISOTHERMAL CALORIMETRY

Figure 1 shows the calorimetry curves for the cubic C_3A/gypsum ratio of 0.637, in the absence and presence of the PCE admixtures (MN or OP). The initial sharp and great exothermic peak that occurs in the first minutes of reaction in all systems corresponds to the wetting and dissolution of C_3A, as well as the initial precipitation of ettringite (Kirchheim *et al.,* 2011). A second exothermic peak of heat flow is observed around 15 and 38 hours of hydration for the CUB-C_3A systems. In the cubic C_3A pastes, the total heat released after 50 hours of hydration was very similar, indicating that the PCE admixture only influences the C_3A hydration in the first days.

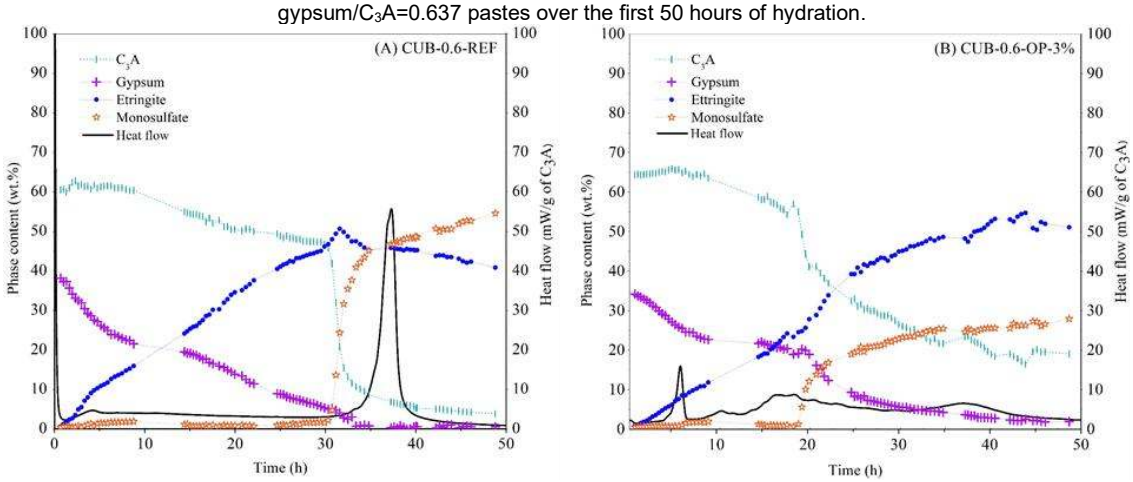
Figure 1: -Heat flow (continuous lines) and total heat (discontinuous lines) of pastes: (A, B) cubic samples with gypsum/C_3A ratio=0.637.



3.2 IN-SITU X-RAY DIFFRACTION

Figure 2 presents the quantitative analysis obtained by in situ-XRD/Rietveld analysis (coloured points) and the heat flow obtained by calorimetry (black continuous line) for the C_3A pastes.

Figure 2: Phase content (determined by in-situ XRD) and heat flow (black continuous line determined by calorimetry) of the gypsum/C_3A=0.637 pastes over the first 50 hours of hydration.



In the reference paste (Fig. 2A), one can note a continuous dissolution of C_3A and gypsum and formation of ettringite (Equation 1), up to the point of gypsum depletion and then rapid C_3A dissolution together with ettringite dissolution leading to the formation of monosulfate (Equation 2) (Bullard et al., 2011).

$$C_3A + 3CaSO_4 \cdot 2H_2O + 32H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \text{ (ettringite)} \quad (1)$$

$$2C_3A + C_3A \cdot 3CaSO_4 \cdot 32H_2O + 4H_2O \rightarrow 3(C_3A \cdot CaSO_4 \cdot 12H_2O) \text{ (monosulfate)} \quad (2)$$

The addition of PCE-OP resulted in an earlier formation of AFm phases, shifting from approximately 30 hours to around 19 hours, in agreement with the calorimetry data. However, it is noteworthy that neither the ettringite precipitation rate nor the gypsum dissolution rate was significantly affected by PCE-OP up to the onset of

AFm precipitation, which occurs in the PCE-OP samples without complete gypsum depletion. This suggests that the earlier AFm formation may be attributed to a “false depletion” mechanism, where PCE adsorption on the gypsum surface hinders its dissolution, leading to a local sulfate ion deficiency in the solution.

4 CONCLUSIONS

The hydration of cubic C_3A in the presence of gypsum is well defined. For a C_3A/gypsum ratio of 0.637, it is observed the formation of ettringite, and after sulfate depletion, the formation of monosulfate. In the pastes with a C_3A/gypsum of 0.637, both PCE admixtures slightly delayed the cubic C_3A hydration in the first 5 hours of hydration. However, the presence of the chemical admixture led to a much earlier AFm formation, which occurred when gypsum was still presented in the mixture. This probably happens to the decrease of gypsum solubility in the presence of PCE admixtures, resulting in a “false sulfate depletion” (*i.e.*, there is still solid gypsum, but the sulfate in the solution is depleted).

These findings highlight the distinctive hydration behavior of cubic C_3A in the presence of PCE. In commercial clinkers, C_3A can occur in cubic and/or orthorhombic forms, depending on the raw material composition and the fuel used during clinker production. The orthorhombic C_3A phase exhibits different reaction kinetics and interactions with chemical admixtures, which can significantly influence the formation and stability of hydration products. While this study focused on the cubic phase, further research is needed to elucidate how the molecular structure of PCE influences the hydration mechanisms of the orthorhombic C_3A phase.

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