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HYDRATION AND CONVERSION REACTIONS OF CALCIUM ALUMINATE CEMENT WITH REACTIVE CALCITE AT VARIABLE TEMPERATURES

Goetz-Neunhoeffer*, Friedlinde & Goergens, Julian, FAU Erlangen-Nürnberg, GeoZentrum Nordbayern, Mineralogy, Erlangen, Germany

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ABSTRACT

The reaction and potential transformation behaviour during hydration of a calcium aluminate cement (CAC) mixed with reactive calcium carbonate (Cc) were investigated at different temperatures.

By introducing CO_3^{2-} into the pore solution of the hydrating CAC through calcite dissolution, a promising way was investigated to avoid or limit the metastable hydrate phases (CAH_{10}, C_2AH_x) that typically occur during the early hydration of pure CAC. Instead, the precipitation of mainly monocarbonate (Mc = $C_3A*Cc*11H$), is favoured. Analysis of the extensive data base (10-90°C) has shown the general conditions and temperature limits under which Mc is formed and stabilized. At 60°C, no thermodynamic stability or formation limit of Mc is found. In closed systems studies no conversion of Mc to C_3AH_6 (or dissolution-precipitation) was observed up to 80°C. This probably only occurs above a critical temperature, which is specified in databases as approximately 90°C.

We were able to show in a large number of measurements that C_2AH_X acts as a precursor for Mc formation in the early hydration of mixtures of CAC and Cc. Below 20°C no or only a small amount of C_2AH_x and thus also no or only minor Mc should initially form in CA-dominated CAC-Cc pastes. Here, CAH_{10} is prevailing. At elevated temperatures (40°C and 60°C), at which CAH_{10} does not initially precipitate, Mc is formed as a result of the rapid conversion of the precursor phase C_2AH_X.

INTRODUCTION | BACKGROUND

CACs are mainly used in refractory applications and - together with OPC and calcium sulphate and/or CSA cement - in ternary mixtures (e.g. self-levelling screeds and grouts), as the addition of CACs promotes early setting and reduces shrinkage. White CACs contain mostly CA along with CA_2, often with minor amounts of $C_{12}A_7$ or Al_2O_3. However, CA is mostly domi-

*friedlinde.goetz@fau.de

nant and greatly determines the hydration behaviour. The frequently mentioned problem of "conversion" is unfortunately still very often interpreted as a disadvantage for the use of CAC in binder formulations.

The prevention of subsequent, often harmful conversion was investigated for mixtures of CAC with silicate-containing materials such as blast furnace slag, micro silica or fly ashes[1-3] or limestone-containing additives[4,5] or both[6-8]. Studies on these mixtures have shown that much lower amounts of metastable hydrate phases were formed in the presence of Si- or CO_2-containing materials. The mechanical properties of many of these mixtures also showed significantly better results compared to reference mixtures without. Among the materials added, limestone proved to be the most suitable [6,8].

CAH_{10}, Monocarbonate (Mc) and C_3AH_6, the stable phases that can form in CAC-Cc pastes, play a particularly interesting and crucial role here. However, some ambiguity remained regarding their formation and stability. Several authors reported differing temperature or stability limits[9,10] of Mc, others the potential conversion of Mc to C_3AH_6 (the reverse is also possible).

Since the formation of Ca-Al-hydrate phases during CAC hydration were reported to be highly temperature-dependent, the investigations were carried out at four different temperatures (10, 23, 40, and 60 °C). Despite many individual studies, there is a lack of comprehensive research and deeper understanding of very early hydrate phase formation in combination with long-term stable hydrate phase contents for a single type and source of CAC. We therefore chose mixes of Fe-free CAC with reactive calcite in order to specifically improve the state of knowledge. Within the scope of the investigation, all experimental parameters, such as the w/c ratio, storage conditions, sample size, parameters for XRD analysis, etc., were kept unchanged and only modified for specific questions.

METHODS

We mainly performed time-resolved QXRD on the hydration of a commercial CAC mixed with reactive calcite (Cc) (w/CAC ratio = 1.1) stored for periods ranging from 1 d to 12 months and analyzed them in terms of their absolute phase fraction using the Rietveld method and G-factor quantification Thermodynamic calculations using GEMS modeling were used to indicate which hydrate phases are the predicted stable phases under the respective conditions.

KEY FINDINGS

The results of the extensive study are summarized for early hydration (0-16 h, Figure 1) and long-term hydration (up to 12 months, Figure 2).

Summary of early hydration (Fig. 1)

Dissolution of CA, CA_2, and calcite during early hydration is shown by in-situ XRD at different temperatures as upper part of the diagrams in Fig. 1. At 10°C and 23°C, main hydration begins shortly before 4 h, with CA rapidly dissolving to a residual level. At 40°C, the induction period is shorter, while at 60°C, CA is completely dissolved within the first 16 h. Hydration of CA_2 is

not detected at 10°C, but at 23°C and above CA_2 starts dissolving simultaneously with CA, albeit at a slower rate.

The formed hydrate phases are presented in the lower part of Fig. 1. At 10°C, "metastable" CAH_{10} is the first and only hydrate phase. At 23°C, both CAH_{10} and C_2AH_x precipitate. While CAH_{10} is not re-dissolving within the first 16 h, the initially formed C_2AH_X decreases and Mc is formed instead.

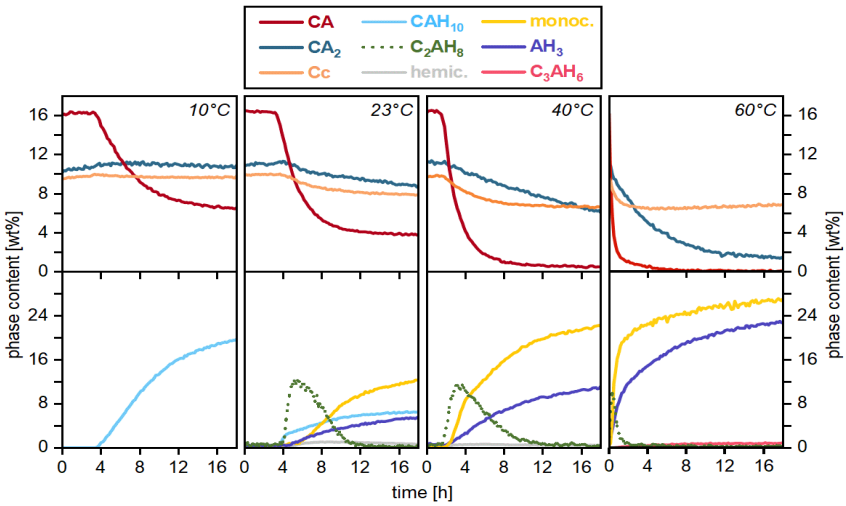

Figure 1: Mean values of the in-situ QXRD of the CAC-Calcite mixture with a w/CAC ratio of 1.1 of the first 16 h of the hydration are shown [12]. Rietveld scale factors of C_2AH_8 are plotted in dotted lines.

Overview of long-term hydration (Fig. 2)

Results of the CAC-Cc long-term tests demonstrated stable phase compositions and thus a high potential for applications in construction chemistry. At 5°C CAH_{10} remained the predominant hydrate phase until the end of the experiment after one year, with no signs of conversion. The coexistence of $AH_{3(am)}$ appears to condition CAH_{10}.

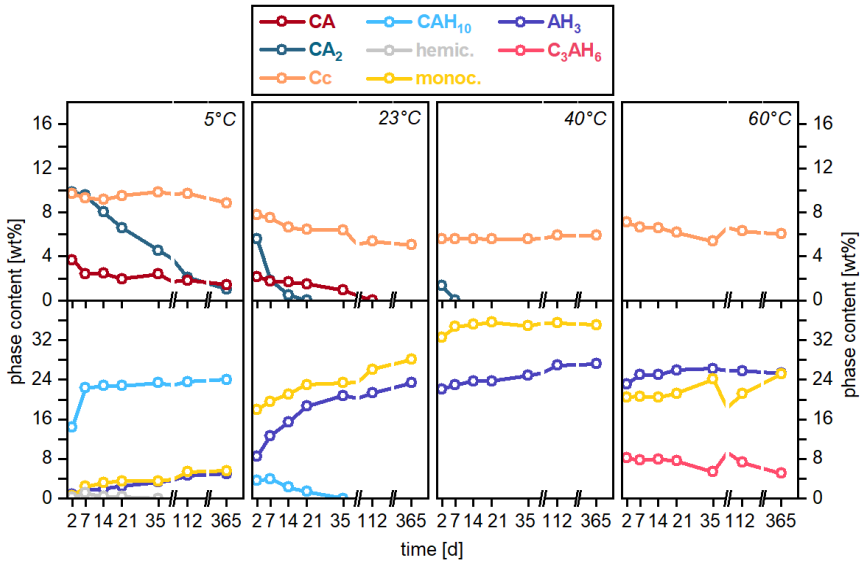

Figure 2: Mean values of the long-term sample QXRD (0-365 d) of the CAC-calcite mixture with a w/CAC ratio of 1.1 [13,14]

After the first day of hydration, C_2AH_x was no longer observed at any temperature in our investigations.
Mc was found to be stable[13,14] alongside AH_3 (Gibbsite) as the dominant phase across the entire temperature range from 5 to 60 °C. The conversion of Mc to C_3AH_6 could not be observed in a closed system at temperatures up to 80°C. However, evaporation of mixing H_2O in the early hydration stage stabilizes C_3AH_6 with a stoichiometric lower H_2O requirement than Mc.

CONCLUSIONS

- CA and CA_2 were completely dissolved within 365 days - at different rates - but only in the 5 °C samples were residues of <2 wt% detected.
- CAH_{10} is a “stable” hydrate phase at low temperatures for up to 365 d.
- The formation of Mc from CA in early hydration is preceded by precipitation of the precursor phase C_2AH_x.
- The AH_3 phase precipitates at all temperatures.
- No thermodynamic instability or formation limit of Mc was observed up to 60 °C.
- The evaporation of mixing H_2O at elevated temperatures shifts hydrate phase stability towards C_3AH_6 (lower w/Ca-ratio) instead of Mc.

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