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Development of temperature-dependent phase composition during hydration of ternary OPC-CAC-C$ mixtures with two different CAC types

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ABSTRACT

Ternary mixtures composed of calcium aluminate cement (CAC), Portland cement (OPC) and calcium sulfates ($C\$H_X$) are commonly used as tile adhesives, self-levelling compounds, repair cements or technical mortars. Different setting and hardening times as well as expansion, shrinkage and early strength can be easily controlled by varying the proportions of the three components. Many studies have shown that formation of different hydrate phases in the mixtures is strongly influenced by both the OPC/CAC and the CAC/C$ ratio. In general, calcium aluminates (C_3A and/or CA) can react with the calcium sulfate, which is leading to formation of ettringite. However, the quality of the CACs, which is related to the reactive clinker composition, also influences the composition of the phase formed during and after hydration in the mixture. Depending on the CAC and C$ content or limestone addition (Cc), the conversion of ettringite to AFm (monosulfate or -carbonate) can also be accelerated or prevented.

The influence of two different CACs (iron-containing and iron-reduced) on the hydration of application-related ternary mixtures was therefore investigated. The reaction kinetics were determined using heat flow calorimetry and quantitative X-ray diffraction analysis (QXRD). Storage samples for up to 90 d at 10 °C and 23 °C were examined with G-factor method in order to clarify the influence of the CA and iron content of the respective clinker on the stable hydrate phase composition and on the amorphous phase content. It could be shown what differences in the phase composition occur during storage at 10 °C or 23 °C. In addition, strength measurements could provide further insights into the influence of the various CACs on the development of strength during hydration.

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INTRODUCTION | BACKGROUND

The hydration behaviour and resulting properties of cementitious materials can be finely tuned by combining calcium aluminate cement (CAC), ordinary Portland cement (OPC), and calcium sulfates ($C\$H_X$). A decisive factor controlling hydrate phase development in these systems is the balance between OPC and CAC, as well as the amount of calcium sulfate relative to the aluminate phases [1]. In the presence of sufficient sulfate, reactive calcium aluminates such as CA or C_3A preferentially form ettringite during early hydration. Thereby, the mineralogical quality and reactivity of the CAC clinker can play a crucial role in determining which hydrate phases form and remain stable over time. Furthermore, depending on the availability of silicon and the relative calcium aluminate content left during the late hydration reaction the formation of straetlingite may occur [2]. The hydrate phase development of such a ternary mixture was therefore investigated in relation to the added CAC source, examining the role played by the iron and silicon contained in the CAC during hydration.

METHODS

An Fe-rich CAC (CAC 40) and an Fe-reduced CAC (CAC 50) were each examined in combination with OPC and hemihydrate ($C\$H_{0.5}$) with a w/s ratio of 0.65 (Table 1 and Table 2). An additional 0.003 wt.% citric acid was added to both pastes to delay the reaction and thus ensure good workability of the paste.

Table 1. XRF analysis of the components used, sulfate content was determined by nephelometry.

[wt.%]	CAC 40	CAC 50	OPC	Hemihydrate
CaO	35.1	36.7	65.1	39.2
Al_2O_3	39.6	53.3	4.9	0.2
SiO_2	4.2	3.9	19.9	0.7
Fe_2O_3	17.1	1.3	3.3	---
MgO	---	0.1	1.0	---
TiO_2	1.9	2.5	0.2	---
K_2O	0.2	0.3	0.6	---
SO_3	---	---	3.2	54.9
LOI	1.3	1.8	1.9	5.0

Table 2. Compositions of the used mixtures with w/s=0.65.

	CAC40mix	CAC50mix
CAC 40 (Fe-rich CAC)	31.8	---
CAC 50 (Fe-reduced CAC)	---	31.8
OPC	15.2	15.2
Hemihydrate ($C\$H_{0.5}$)	13.6	13.6
Water (H_2O)	39.4	39.4

The phase composition of storage samples after 1, 7, 28 and 90 d at 23 °C and 10 °C was examined using quantitative X-ray diffraction analysis. The samples were stored at 100% r.H., then sawn in half and a fresh surface was prepared using sandpaper. At least two samples were stored for each test point and each mixture, so that four samples per test point could be measured after sawing. A Rietveld analysis was performed using the TOPAS 5.0 software and the absolute crystalline phase composition and amorphous fraction were determined using G-factor analysis [3].

KEY FINDINGS | CONCLUSIONS

The QXRD analysis of the storage samples at 23 °C for both systems is shown in Figure 1. The upper section shows the development of the clinker phases, with the triangles near the left axis indicating the starting contents. The lower section displays the hydrate phases and the amorphous fraction. Only minor differences between the two systems and thus between the two CACs can be seen. In both systems, CA and hemihydrate in particular reacted within one day, forming ettringite. In CAC40mix, CA has completely reacted after 7 d, while in CAC50mix CA takes 90 d. C_2S and C_3S were dissolving in both systems within 90 d. C_3A and C_4AF dissolved in CAC40mix within 90 d. It is remarkable that gehlenite (C_2AS) reacted completely in both systems within the measurement period.

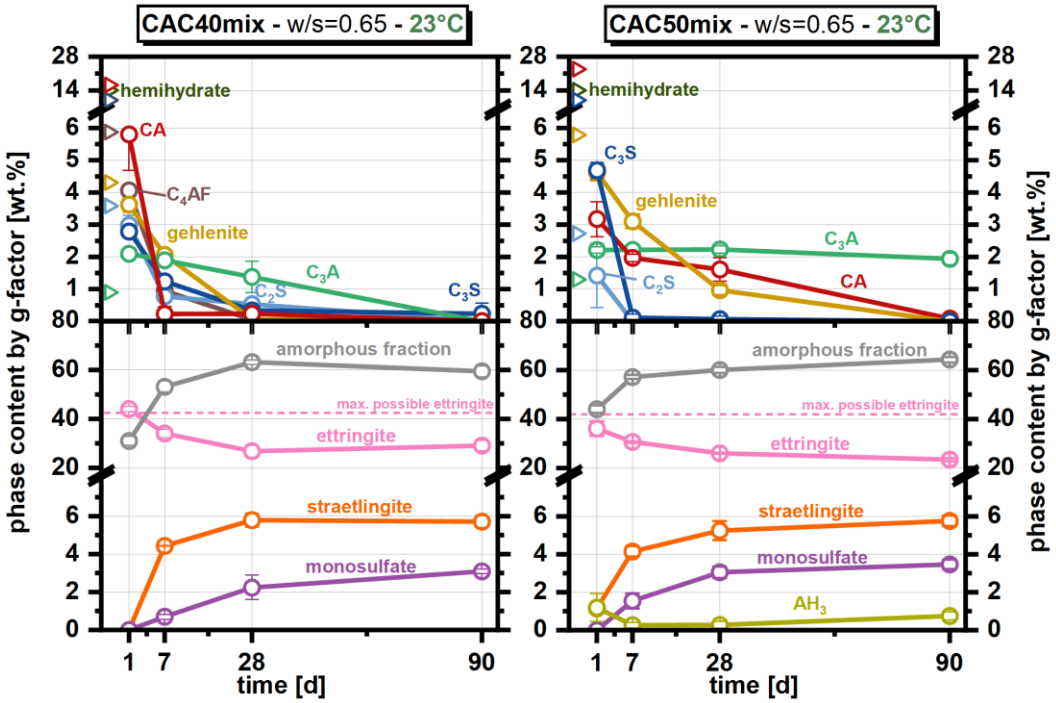

Figure 1. Main phase composition of stored samples determined with QXRD after 1, 7, 28 and 90 d at 23 °C; triangles on the left side of the upper sections indicate the starting values of the phases in the paste ($C\$H_{0.5}$ is not shown as it dissolves within 24 h).

After the maximum possible amount of ettringite (calculated based on sulfate content) has formed at the beginning of hydration, ettringite dissolved again during late hydration. Additionally, during the late hydration, monosulfate (partly from the dissolving ettringite) and straetlingite (from the

Si-containing clinker phases such as gehlenite) were precipitated. In the CAC50mix system, small amounts of crystalline AH_3 can also be detected. The results at 10 °C are shown in Figure 2, whereby the structure of the Figure is comparable to Figure 1. No significant difference in the (hydrate) phase development can be observed. Only a delay in the hydration reaction is visible, particularly with CAC40mix, as CA only dissolved significantly after 28 d, initially formed gypsum (from the hemihydrate) redissolved and only then the maximum possible amount of ettringite was detected.
In conclusion, it can be said that, despite different CACs, no significant differences occur during hydration at either 23 °C or 10 °C with regard to the phase development.

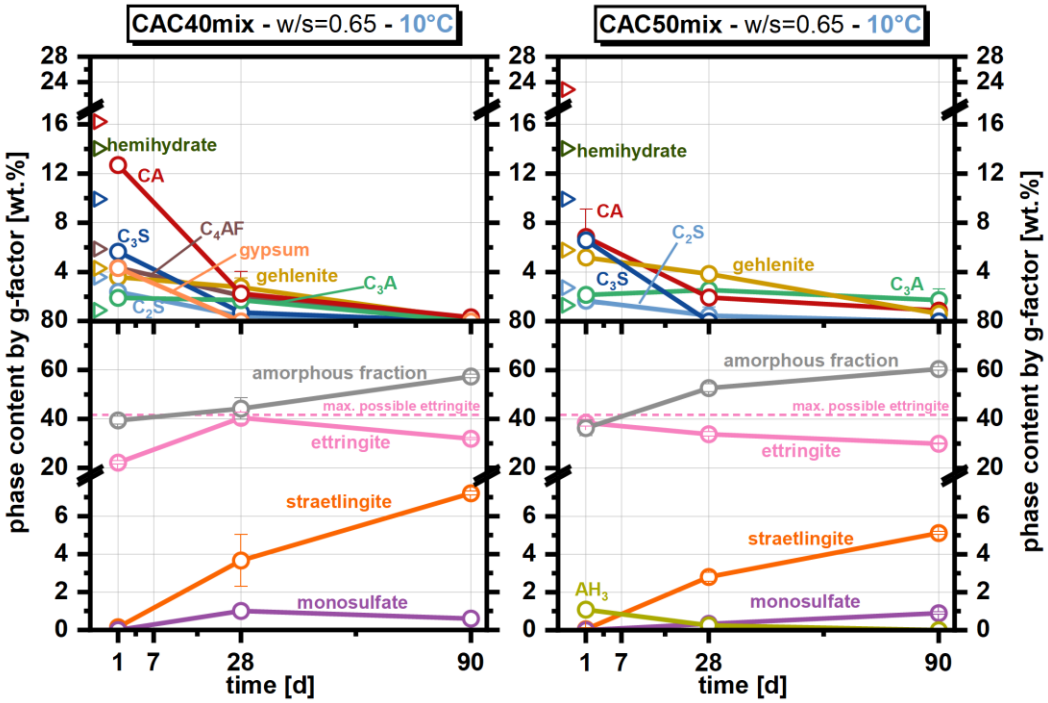

Figure 2. Main phase composition of stored samples determined with QXRD after 1, 28 and 90 d at 10 °C; triangles on the left side of the upper sections indicate the starting values of the phases in the paste ($C\$H_{0.5}$ is not shown as it dissolves within 24 h).

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