

METAKAOLIN-LIME HYDRATION PRODUCTS AND PHASE STABILITY: A MICROSCOPY ANALYSIS

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Keywords: microscopy; XRD; TGA-DTA; lime; metakaolin

Introduction

The reaction of metakaolin (MK) with calcium hydroxide yields cementitious products, being the main phases formed at ambient temperature the calcium silicate hydrate (CSH¹), stratlingite (C₂ASH₈) and tetra calcium aluminium hydrate (C₄AH₁₃). Several discrepancies are presented in literature regarding these phases' stability, namely the transformation of stratlingite and C₄AH₁₃ into hydrogarnet at long term. The consequences of that instability are an increase in the porosity and a loss of compressive strength that can induce a complete material degradation [Bakolas, Aggelakopoulou, Moropoulou, (2006); Moisés Frias,(2006); Moisés Frias, Cabrera J. ,(2001); Aguilar-Sepulcre, A., Hernández-Olivares, F. (2010), De Silva, P.S., Glasser, F.G. (1992)].

With the objective of studying the compounds formed in lime/MK pastes and their stability during time, blended pastes were prepared with 50%, 33%, 25%, 17%, 9%, 5% and 0% of MK. These lime/MK pastes were stored at 95% RH and 23 ± 2 °C. After each predetermined curing time the hydration reaction was stopped subjecting the samples to acetone. TGA-DTA and XRD were used to follow the kinetics of the MK-lime reaction as well the reaction products formed. In this paper the results obtained by the application of microscopic methods, namely by SEM-EDX, are presented and compared with the thermal and mineralogical data.

Experimental

Pastes, with different molar ratios of lime/MK were prepared with a water/solid ratio of 1:1 (Table 3). The mix procedure was the same for all pastes, initially the amount of lime was mixed with the total amount of water, which was stirred for about 3 minutes using an external mixer, the MK was added afterwards slowly, maintaining the mixing for 20 minutes more. The pastes were then stored in open plastic containers and introduced in a sealed chamber at 95% RH and 23 ± 2 °C, to maintain ongoing hydration reactions. The hydration was stopped after each predetermined curing time, subjecting the samples to acetone for complete removal of the free water, which were then dried at 40°C, in order to be tested by XRD, TGA-DTA and SEM-EDX.

Results and discussion

The results of XRD, TGA-DTA and SEM-EDX for the MK1 and MK02 pastes were presented in this paper. The DTA results showed that the characteristic peak of stratlingite, at about 190° C as a sharp peak, appears in all pastes and ages, The peak regarding stratlingite seems to be broader after 90 days of curing, for all pastes. In the same range of temperature (~160-220° C) the dehydration of C₄A \bar{C} H₁₁ (3CaO·Al₂O₃·CaCO₃·11H₂O, monocarboaluminate) occurs. Other phases are also present in both pastes such as, CSH and C₄AH₁₃, calcite (C \bar{C}) and portlandite (mostly for MK02 paste). XRD results showed that for MK1 paste, stratlingite (C₂ASH₈) tends to increase with curing time, becoming the dominant crystalline phase whereas significant amounts of monocarboaluminate (C₄A \bar{C} H₁₁), quartz, calcite, CSH and calcium aluminate hydrates (C₄AH₁₃) are observed. On the contrary, with MK02 paste a lesser quantity of stratlingite is detected, which could be correlated with the less MK content in this blended paste. High amounts of portlandite (CH) are observed for all ages in this paste.

In this investigation, the presence of C₄AH₁₃, C₄A \bar{C} H₁₁ and C₂ASH₈ have been identified as the major crystalline phases.

The microstructure overview shows the evolution of the MK1 paste from highly crystalline to dense-like microstructure, where the predominant phase at higher ages is stratlingite and at lower ages (28 days) calcium aluminate hydrates (C₄AH₁₃).

In MK02 paste, the microstructure “evolution” does not vary like in MK1 from 28 days to 90 days, staying with a crystalline microstructure. A remarkable quantity of calcite is detected in MK02 paste, as consequence of the large quantity of lime present in this mix.

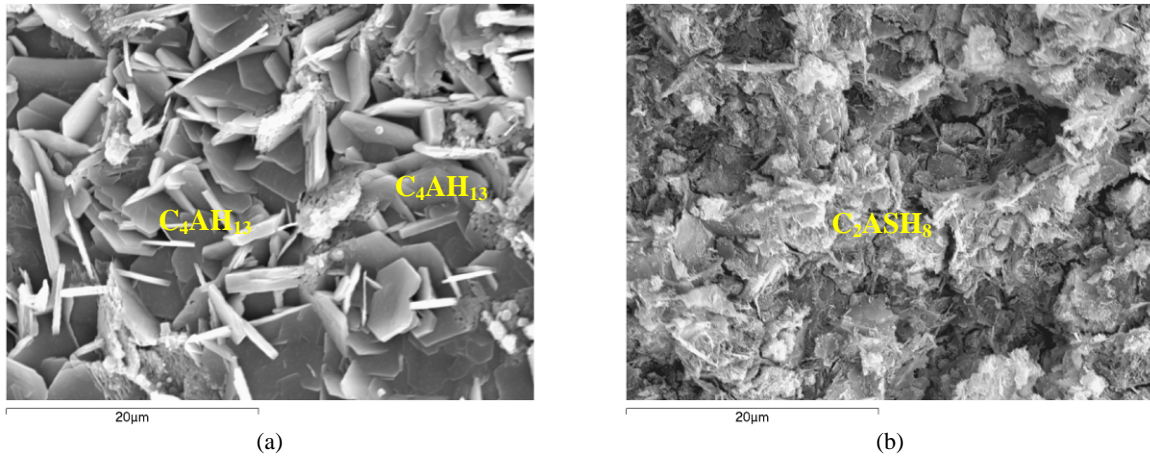


Fig. 1: SEM micrographs of MK1 at ages 28 and 90 days: a) SEM image of MK1 paste at 28 days (3000x), where is visible the presence of hexagonal C_4AH_{13} ; b) SEM image of MK1 (3000x) where is visible the predominance of C_2ASH_8 .

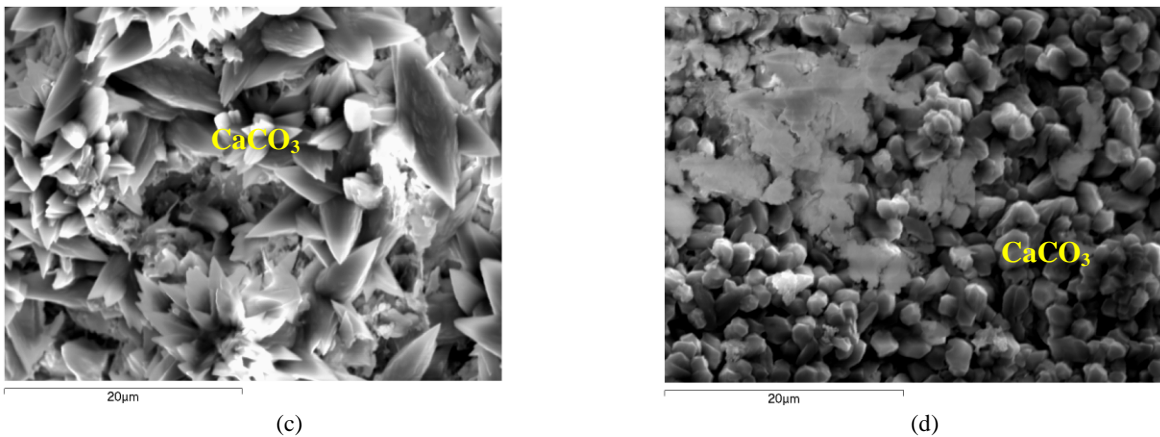


Fig. 2: SEM micrographs of MK02 at ages 28 and 90 days: c) SEM image (3000x) of the MK02 paste showing the presence of $CaCO_3$; d) SEM image of MK02 paste (3000x) where is visible an increase in the paste carbonation rate.

Conclusions

1. Stratlingite is the main crystalline phase in blended mixes rich in MK. Its formation is considered beneficial due to its high mechanical resistance in lime blended matrixes.
2. The formation, evolution, proportion and stability of the hydrated phases in MK-lime mixes is dependent according to several studies on various factors, such as the MK chemical composition, pozzolanic activity of MK, metakaolin-lime ratio, and curing temperature. In this paper, the influence of the MK-lime ratio was studied and according to the results obtained the products formed are the same for all blended mixes. The quantity of the products formed changes with the MK content, being the aluminum and calcium silicates more abundant in the higher MK content pastes.
3. The application of complementary mineralogical and microstructural techniques, such as TGA-DTA, XRD and SEM-EDS, are very effective in the study of the reaction mechanism and kinetics of MK-lime mixes.
4. Regarding the lime consumption, it is higher for the higher MK substitution.
5. In this investigation, the presence of C_4AH_{13} , $C_4A\bar{C}H_{11}$ and C_2ASH_8 have been identified as major hydration phases.

6. SEM results show that for MK1 and MK02 pastes at 28 days the microstructure consists essentially of C_2ASH_8 and C_4AH_{13} and $C_4A\bar{C}H_{11}$. However, at 90 days of curing there is a significant decrease of the presence of calcium aluminate hydrates, and a predominance of stratlingite. The presence of C_2ASH_8 , considered beneficial due to its high mechanical resistance in lime blended matrixes, is larger for the MK1 than for the MK02, which is related to the MK content in the blended MK mixes.

7. Up to 90 days of curing time, no hydrogarnet presence is detected. This compound is responsible for the steep decrease of mechanical resistance of pastes/mortars. However, a decrease in the amount of formed C_4AH_{13} and $C_4A\bar{C}H_{11}$ with curing time is verified. This situation that was not followed by a decrease in microstructural porosity, may influence in the case of mixtures with low MK content a decrease on the mechanical resistance of those mixtures.

8. These conclusions justify the need of further studies for more advanced curing times and the extension of the studies from pastes to mortars.

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