

EFFECT OF SILICA FUME ADDITIONS ON THE HYDRATION BEHAVIOUR OF CALCIUM ALUMINATES

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ABSTRACT

In the recent refractory castables technology, the calcium aluminate cement is being replaced in increasing proportion by very fine matrix components, such as silica fume and colloidal alumina. More efficient particle packing and the resulting lower water requirements have been the proposed explanation for the improved green density and strength, without sacrificing the castable workability. However, the aluminates are still responsible for the hydraulic setting of the castable.

The hydration mechanisms of single calcium aluminates, and mixtures thereof, synthesised by combustion reaction of the appropriate nitrate-urea mixtures, were recently investigated. The present work describes the effect of silica fume additions on the hydration behaviour of pure single calcium aluminates, also produced by combustion reaction. Results on the hydration mechanisms, the microstructure development and the resulting physical and/or mechanical properties of the hydrated samples, as a function of the water/cement ratio and the silica content, are presented and discussed.

INTRODUCTION

Although calcium aluminate cements are present in an ever decreasing amount in the low- and ultra-low-cement castables for the new monolithic refractories technology [1], together with the key fine matrix components (micro-fillers), they are still responsible for the hydraulic setting of the castable.

Hydration studies of calcium aluminates and other related compounds normally require that the pure oxides be synthesised. Combustion synthesis has proven to be a straightforward preparation process to produce multicomponent oxide ceramic powders with characteristics comparable to those of powders produced by wet chemical and sol-gel methods [2-6]. Briefly, to produce a mixed oxide by combustion, a saturated aqueous solution containing the desired metal ions and a suitable organic fuel (typically, water soluble nitrates and urea are used) is brought to a boil, until the mixture ignites and a self-sustaining and rather fast combustion reaction takes off, resulting in a dry oxide powder. Redox reactions such as this are exothermic in nature and ignite at temperatures much lower than the oxide phase formation temperature. The heat released by the reaction causes the temperature to rise very fast and sustains it, even in the absence of an external heat source, at the high level ($> 1000^{\circ}\text{C}$) necessary for the synthesis to occur. The large amounts of evolved gases result in the formation of a foam whose structure is transmitted to the oxide produced. The fuel proportion is calculated based on the valencies that the intervening elements present in the reaction products (*i.e.* metal oxides, CO_2 , H_2O and N_2), the same way this is done in propellant chemistry calculations [7].

Given that the metal cations are mixed in a liquid phase, the boiling liquid sustains the homogeneity of the mixture and the reaction is very fast, the resulting powder is also homogeneous. The thinness of the liquid foam causes the oxide particles to be very fine and the high temperature reached is usually enough to promote their crystallisation.

Our recent work [6] showed that the combustion synthesis technique can be successfully used to produce pure and crystalline calcium aluminates, with good compositional control of the powders produced, made of soft agglomerates of submicron particles with a high crystallinity degree and the desired stoichiometry. In spite of the short reaction time, X-ray diffraction of the as-prepared powders showed well crystallised CA, CA₂ and C₁₂A₇ (full conversion) as the only phase present in each case. Lattice parameters were calculated and found to be in good agreement with published values (JCPDS), and crystallite size, investigated by TEM, was found to be ~45 nm for CA, ~113 nm for CA₂ and ~250x40 nm for C₁₂A₇.

The major phase present in commercial calcium aluminate cements is the monocalcium aluminate (CA*), which imparts high mechanical strength and refractoriness to the cement, whereas rapid setting is associated with C₁₂A₇, which dissolves rapidly.

Usually, only CA hydration studies are reported in the literature [8]. Implicitly, it is assumed that the hydration mechanisms of CA₂ and C₁₂A₇ follow a similar route, the proportions of the hydrates formed being accordingly changed. The proposed mechanism of CA hydration [9] starts with an induction period during which the hydration rate is extremely low, probably via a tarnishing-type reaction in which a layer of amorphous hydrates is formed over the entire surface of the particles. When the hydration layer grows to reach a critical thickness, the stress caused by intruded water molecules ruptures the layer and the induction period terminates (the reaction as a whole accelerates) with the formation of crystalline nuclei that grow by a dissolution-crystallisation mechanism, to produce the metastable hexagonal hydrate CAH₁₀. Depending on the initial crystallinity of the aluminate, CAH₁₀ can be detected after 6 to 24 hours [8]. The presence of C₂AH₈ can be detected after 24 hours. The phase transformations, called conversion, in which the metastable hydrates, CAH₁₀ and C₂AH₈, are transformed to the stable cubic hydrate C₃AH₆, results in a volume reduction (53% from CAH₁₀ to C₃AH₆, and 16% from C₂AH₈ to C₃AH₆) and increase in porosity.

Previous work [10] on the hydration of CA powders produced by combustion reaction, carried out at room temperature (~20 °C) with a water/cement weight ratio of 0.8, showed that a strong, exothermic reaction occurred almost immediately (within ~7 seconds). Although the characteristic X-ray peaks of CA could be seen to decrease, only after 14 hours CAH₁₀, and also C₂AH₈ and C₃AH_x, peaks could be detected. However, the weight loss upon heating, experienced by samples subjected to six hours hydration, suggested the presence of amorphous phases before the onset of crystallisation of the hydrates, supported by the observed rapid consumption of added water.

While the rate of formation of crystalline CAH₁₀ is highest around 18 hours, the amount deposited decreases after 20 hours. Simultaneously, the rate of formation of C₂AH₈ speeds up after 14 hours and seems to be faster than the rate of consumption of CA, suggesting that indeed some C₂AH₈ results from the decomposition of the CAH₁₀ already present, releasing AH₃ which can also be detected as gibbsite after 24 hours. The hydrating sample loses its paste consistency (hydraulic setting) after 14 hours, becoming a cohesive mass. C₃AH₆ can be detected after 20 hours, reaching 21% of the crystalline phase after 28 days. After 7 days, signs of carbonation can be observed and

* shorthand notation is used throughout the paper, viz. C=CaO, A=Al₂O₃, H=H₂O

65% of the original CA is converted to hydrates, reaching 84.5% after 28 days.

As suggested by other authors [9], the results obtained for the hydration of combustion synthesised CA, CA₂ and C₁₂A₇ support the hypothesis that the hydration reaction at room temperature starts with the build up of a layer of amorphous hydrates over the entire surface of the particles, which then dissolve [11].

After an induction period of varied length (~14 hours for pure CA and practically absent for C₁₂A₇), all metastable hydrates tend to crystallise almost simultaneously, followed by the conversion process of CAH₁₀, C₂AH₈ and C₃AH_x into C₃AH₆. The formation of vaterite (CaCO₃) as the result of the reaction with ambient CO₂ suggests that the formation of the crystalline hydrates also occurs by a dissolution / precipitation mechanism. At any time, the major phase resulting from CA hydration is C₂AH₈, whereas CA₂ produces mostly AH₃, and C₁₂A₇ mostly C₃AH_x. The presence of C₁₂A₇ changes the hydration course of both CA and CA₂, inhibiting the formation of CAH₁₀ (higher water requirements) and promoting the direct formation of C₃AH_x.

The kinetics of the hydration reactions were found to affect the degree of cohesiveness of the reaction products. With CA₂ and C₁₂A₇ the high hydration rate does not enable a homogeneous setting of the material and the hydration product remains crumbly, although with hard granules, even after 28 days.

In alumina and alumino-silicate based refractory castables, microsilica has become a common ingredient. Its widespread use is due to several reasons, the best known and appreciated of which is the flowability improvement of the castable, through selected particle size distributions and better particle packing. Also, microsilica has the potential to develop strong bonds, both at low and high temperature, by reacting with the castable other ingredients. However, the microsilica and cement contents have to be balanced to avoid detrimental effects at temperatures above ~1200 °C. The reaction between microsilica and the CaO from the cement leads to liquid phase formation, causing the castable to soften and loose strength. When the cement content is decreased and the microsilica content is increased, that liquid phase acquires a transient nature and mullite formation occurs, resulting in increased strength above 1300 °C. The effect of the introduction of microsilica into the compositions is generally studied in the presence of the refractory aggregate [12, 13] which can and does influence the mechanisms, kinetics and final phase equilibrium of the relevant reactions. Usually, the hydration process is reported to be retarded in the presence of microsilica, especially at hydration temperatures higher than room temperature.

The work that follows describes the hydration behaviour of mixtures of monocalcium aluminate, synthesised by combustion reaction, with silica fume investigated at different temperatures and with different water/cement weight ratios.

EXPERIMENTAL PROCEDURE

The synthesis of the monocalcium aluminate by combustion reaction, from Aldrich Ca(NO₃)₂·4H₂O and Al(NO₃)₃·9H₂O, using CO(NH₂)₂ as fuel is described in detail elsewhere [6].

The hydration behaviour of the as-prepared powders, pure and with 25, 50 and 75 wt% added silica fume (Elkem Microsilica 971 U) was investigated in pastes prepared with water/cement weight ratios of 0.8 and 2.0 (added water was pre-heated at the selected hydration temperature). Pastes were moulded into prismatic test pieces (1x1x7 cm) and cured in water vapour saturated atmosphere at 25 °C, inside a thermostatic water bath, for selected hydration periods, ranging from 1.5 hours to 3 days. After each period, hydration was terminated by acetone washing and drying at 50 °C, under ventilation. Apparent density and open porosity were determined by the Archimedes

method in paraffin. Cold crushing strength was determined with 1 cm cubes, sawed from the test bars, using a Shimadzu Universal Mechanical Testing machine, with a test speed of 0.5 mm/min and load cells of 1 and 20 kN, depending on the particular composition. The fracture surface microstructures were observed by Scanning Electron Microscopy (field emission HITACHI S-4100, at 25 kV, 10 μ A, after Au/Pd coating). The crystalline phases present in the hydrated test pieces were determined by X-ray diffraction (Cu α 1/Ni RIGAKU diffractometer with a scan speed of 2° 2 θ / min, in the 3-50° 2 θ range).

RESULTS AND DISCUSSION

Hydration behaviour at a water/cement weight ratio of 0.8

The hydration behaviour of the pure monocalcium aluminate, in the presence of a water/cement weight ratio of 0.8, was investigated first and Figure 1-A shows the relevant results. At 25 °C the induction period lasts for 14 to 16 hours, leading to the crystallisation of the C₃AH_x metastable hydrate in amounts that increase steadily during the three days hydration period. Between 20 and 24 hours, the presence of crystalline C₂AH₈ begins to be detectable, which, in turn, during the 1 to 3 days, converts to the C₃AH₆ stable hydrate, accompanied by AH₃. After 3 days, the conversion degree in terms of consumed CA content reaches ~67%. The dried set test pieces remain crumbly, which does not allow the determination of the corresponding cold compressive strength.

With the addition of 25 wt.% microsilica to the cement paste, the induction period is extended to 18 to 20 hours (Figure 1-B), ending with the simultaneous crystallisation of the C₂AH₈ and C₃AH_x metastable hydrates. After 24 hours, the deposited amount of C₂AH₈ seems to disappear while that of C₃AH_x continues to increase. This is probably due to conversion into the stable cubic hydrate C₃AH₆, which can be detected after 3 days. The conversion degree is lower than the observed with the pure cement.

The study of the changes in compressive strength as a function of hydration time (Figure 2-A) shows a steady increase up to 24 hours but some degradation can be observed between 24 hours and 3 days. Simultaneously, significant changes (Figure 2-B and C) occur in apparent density (increase) and open porosity (decrease).

When compared with the results obtained with the pure cement paste, and considering the presumably high specific surface area of the added microsilica, the results obtained with the pastes containing 25 wt.% microsilica suggest that the latter is sequestering some of the added water. In practical terms, the water available for the hydration process is less than expected, which might explain the extended induction period and supports the proposed hydration mechanism. The added microsilica would then be acting as a nucleation inhibitor.

With the addition of 50 wt.% microsilica to the cement paste, the tendencies observed with the 25 wt.% addition are inverted: the induction period is greatly reduced, even below that observed with the pure cement, although massive crystallisation of the hydrates (C₂AH₈ and C₃AH_x) only occurs after 24 hours (Figure 1-C). A possible explanation lies in the impurities present in the microsilica that might be favouring a fast nucleation of the hydrates. Between 1 and 3 days, the conversion of C₂AH₈ into C₃AH₆ can be observed, together with the crystallisation of AH₃. Once more, C₃AH_x does not seem to participate in this reaction and the conversion degree raises back to the level observed with the pure CA.

The slow conversion rate up to 24 hours is accompanied by the unchangeable apparent density, open porosity and cold compressive strength of the corresponding dried set test pieces (Figure 2-A, B and C). Nevertheless, mechanical strength is doubled relatively to that observed with samples

containing 25 wt.% microsilica. Better initial particle packing and an even lower apparent water/cement ratio, due to the higher silica content, might be the underlying explanation as this might counteract the disrupting effect of C_3AH_6 crystallisation.

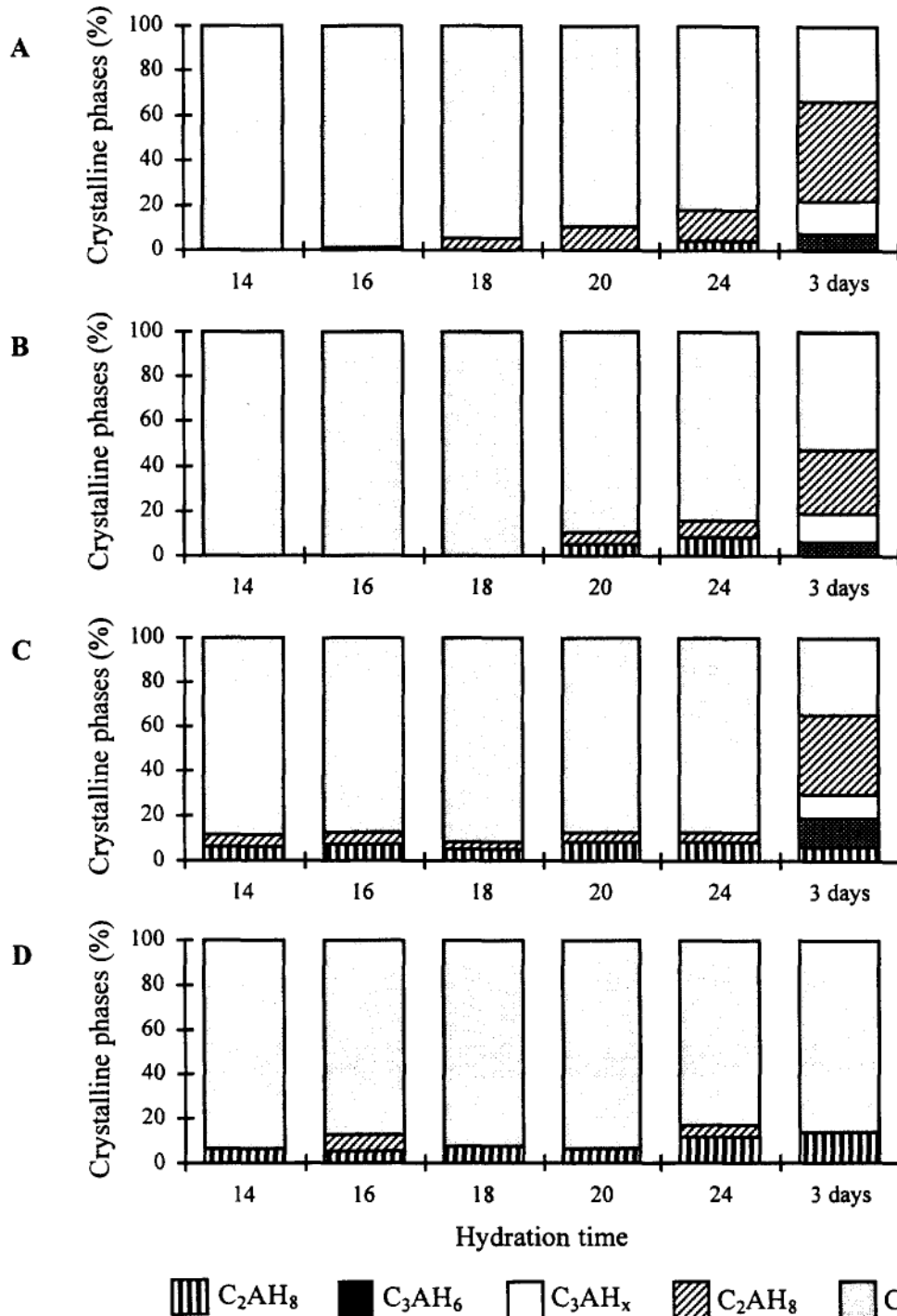


Figure 1. Hydrate development in the CA cement+microsilica mixtures with a 0.8 water/cement weight ratio, as determined from X-ray diffraction patterns, after selected hydration periods. (A) pure CA; (B) 25 wt.% microsilica; (C) 50 wt.% microsilica; and (D) 75 wt.% microsilica

The effect on the hydration process of the addition of 75 wt.% microsilica is qualitatively comparable to that of the 50 wt.% addition (Figure 1-D). Although crystalline hydrates can be detected before 14 hours, their massive crystallisation occurs only after 3 days, by which time the conversion degree is still rather low. Given the even lower apparent water/cement ratio, workability is drastically reduced with the consequent scatter in the experimental results (hydrate contents and defected macrostructures). Still, the compressive strength values are higher than those obtained with the 50 wt.% microsilica composition (Figure 2-A, B and C).

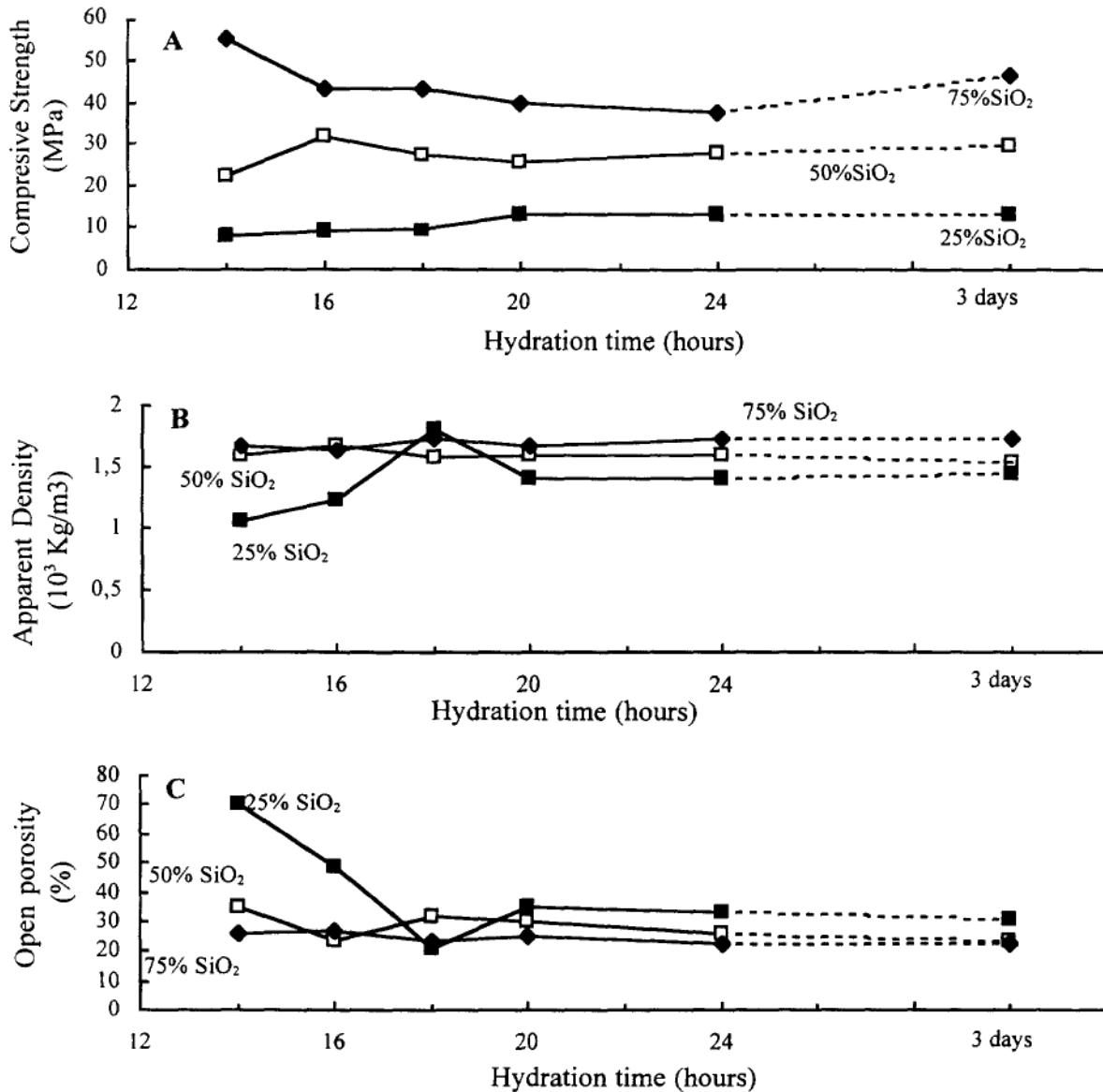


Figure 2. Physical properties determined with dried set test pieces after selected hydration periods

Hydration behaviour at a water/cement weight ratio of 2.0

At 25 °C, increasing the water/cement weight ratio to 2.0 entails some reduction of the induction period of the pure monocalcium aluminate to less than 10 hours. The induction period terminates with the crystallisation of the C₂AH₈ metastable hydrate followed, after only 12 hours, by

the crystallisation of C_3AH_x and CAH_{10} . At this time, the conversion degree already approaches 67 % and reaches 78 % after 18 hours. Figure 3-A shows the typical microstructure after 18 hours, with the C_2AH_8 hydrate large hexagonal thin plates. Figure 3-B shows the characteristic deltoic icositetrahedron $\{211\}$ morphology of the C_3AH_6 stable hydrate after 11 days.

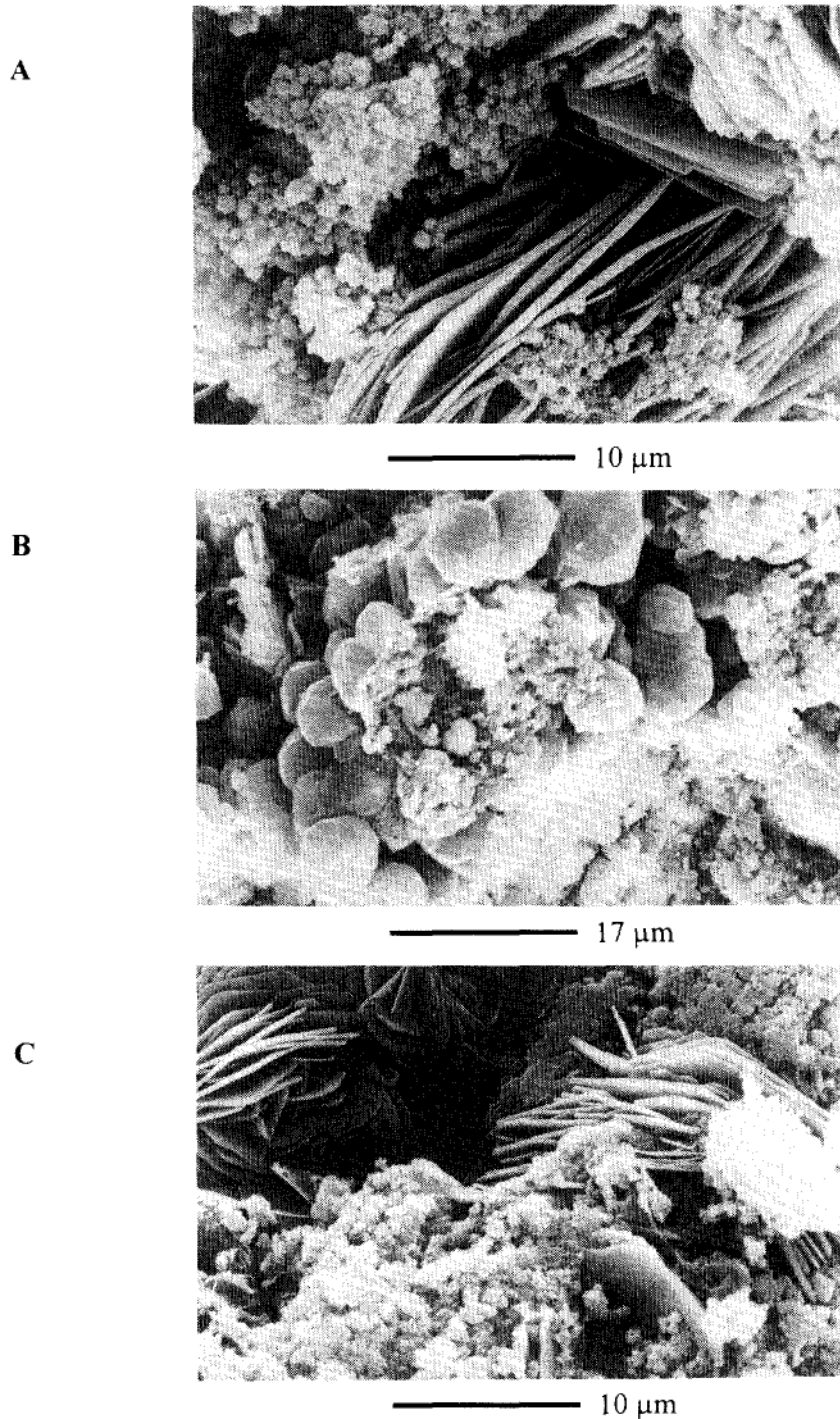


Figure 3. Typical morphology of the hydrates in the 2.0 water/cement ratio. (A) pure CA, after 18 hours; (B) pure CA, after 11 days; and (C) CA+50 wt.% microsilica, after 10 hours.

The effect of microsilica addition is also comparable to that observed with a water/cement ratio of 0.8, that is, the addition of 25 wt.% microsilica extends the induction period to between 12 and 14 hours, after which time crystalline C_2AH_8 and C_3AH_x can be detected. Conversion degree remains approximately constant up to 24 hours and then increases steadily to ~85 % after 3 days. The higher water/cement weight ratio induces segregation during casting with the consequent scatter in the values obtained for the physical properties.

With the addition of 50 wt.% microsilica the induction period is reduced to below 10 hours, by which time the conversion degree nears 70 %. The latter remains practically constant up to 24 hours and reaches 100 % before 3 days. The major hydrate phase is C_2AH_8 , accompanied by C_3AH_x and AH_3 . C_3AH_6 can be detected after 3 days, once again formed at the expenses of C_2AH_8 . The compressive strength of these mixtures follows the tendency observed in the conversion degree but the values reached are lower than those obtained for the equivalent composition with the 0.8 water/cement ratio. Also, there is a tendency for a decrease in compressive strength accompanying the formation of C_3AH_6 . Figure 3-C shows the tighter microstructure in the presence of microsilica, which limits the growth of the C_2AH_8 hexagonal plates.

The hydration behaviour of the mixture with 75 wt.% microsilica is very similar to that of the mixture with 50 wt.% microsilica: the induction period is shorter than 10 hours but the conversion degree is lower (~50%). After 24 hours, significant amounts of C_2AH_8 , C_3AH_x and AH_3 can be detected. The major singularity observed is the crystallisation at 25 °C, between 1 and 3 days, of gehlenite hydrate, C_2ASH_8 . Usually, this phase is observed only at higher hydration temperatures, after comparable CA hydration times with lower water/cement ratios [12] and CA_2 with the same water/cement ratio [14].

As before, increasing the amount of added microsilica causes a general increase in density and the corresponding decrease in open porosity.

CONCLUSIONS

The present work compares the hydration behaviour at 25 °C of monocalcium aluminate, synthesised by combustion reaction of the adequate nitrate-urea mixtures, with that of its mixtures with silica fume in varied proportions, and describes the effect of the water/cement weight ratio. The results obtained show that the addition of microsilica has a two-fold effect on the induction period: first, due to its high surface area, the microsilica acts as a water sequestrant reducing the amount of water available for the hydration process, which slows the crystal growth; however, presumably due to the impurities present in the microsilica, the hydrate nucleation process is favoured, which shortens the induction period.

The presence of microsilica favours the particle packing and leads to higher densities and lower porosities in the set samples, with the corresponding compressive strength increase.

Higher water/cement ratios slow the conversion of C_2AH_8 into C_3AH_6 and AH_3 , which occurs with the release of water (excess water favours the reverse reaction). The tendency for a decrease in compressive strength accompanying the formation of C_3AH_6 is clearly observed in these samples.

The presence of gehlenite hydrate, C_2ASH_8 , usually observed at higher hydration temperatures, was detected after 3 days in the mixtures containing higher proportion of added microsilica, prepared with the 2.0 water/cement ratio.

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