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CEMENT AND CONCRETE RESEARCH

Discussion

Reply to the discussion by Knut O. Kjellsen of the paper "Kinetics of the hydration reactions in the cement paste with mechanochemically modified cement: ^{29}Si magic-angle-spinning NMR study"☆

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EMC is a product with outstanding properties. It is not just 15–20% increase in strength as usually observed in cement blends treated by conventional milling techniques (from Refs. [1–3] in the discussion by Knut O. Kjellsen). It presents approximately 80% increase in compressive strength as has been reported previously [1]. A part of the improved cement hydration can be due to reduced porosity when reaction products fill up the pore space, as suggested by Kjellsen. However, we suggest that the vibration milling also leads to a modification of the cement/silica fume blend on a microscopic level. This can be seen in SEM images of the blend of 95 wt.% of rapid-hardening ordinary Portland cement with 5 wt.% of silica fume before and after the modification process. Fig. 1 shows the mixture before activation and Fig. 2 shows the mixture after 30 min of activation in a vibration mill. In Figs. 1 and 2, the images a and b show two different areas of the sample magnified 1000 × and in the images c and d the magnification is 5000 ×.

Silica fume exists as agglomerates and the microsilica particles are strongly bound to each other. The activation method does not only cause disintegration of agglomerates into individual microsilica particles but it also disperses and/or coats the cement grains by microsilica. The dispersion of microsilica around the cement grains and the filling of the spaces between the cement grains would enhance an even distribution of the pozzolanic reaction in the entire matrix, which would imply a more refined capillary pore system. The development of smaller pores within 7 days indicates that the coagulation and bonding of C-S-H are considerably progressed in the case of activated sample [2].

The other argument of Kjellsen concerns a possible increase of fineness of the cement blend after the vibration milling. The increased cement fineness may also lead to accelerated cement hydration. The particle size distribution of Portland cement and silica fume after mechanical treatment at different time periods is presented in Fig. 3 [2]. The results are summarized in Table 1 [2]. Obviously, there is no dramatic change of the BET surface area that can solely explain the improved properties. Therefore, it has to be an additional reason.

Silica fume particles are reported to have an average diameter of 0.1 μm with a specific surface area varying between 15 and 25 m^2 g^{-1}. The specific surface area of the current silica fume as measured by the BET method is 19.74 m^2 g^{-1}. The particle size distribution of silica fume obtained after 0.5 and 2.0 min of ultrasonic conditioning shows that the particles are strongly agglomerated in the original material: The d_{50} size of about 20 μm decreased to 1 μm with increased conditioning time. The measurements were made in aqueous media and in the presence of a good dispersing agent, which can prevent reagglomeration. The average diameter could possibly be in the order of 0.1 μm. The fact that silica fume is in the form of strongly bound agglomerates suggests the need of a method for separating the particles and distribute them evenly in the entire admixture in order to utilize its reported microfilling and pozzolanic properties [2].

The FT-IR spectra of the blend of cement and silica fume before and after activation in the vibration mill at different periods of time are presented in Fig. 4 [2]. The spectral features are found to be exactly the same before and after the modification process. However, the intensity of the band due to Si–O stretching vibration at 1126 cm^{-1} increases after the modification processes. With increasing vibration milling time, a band at 479 cm^{-1} characteristic of silica fume appears

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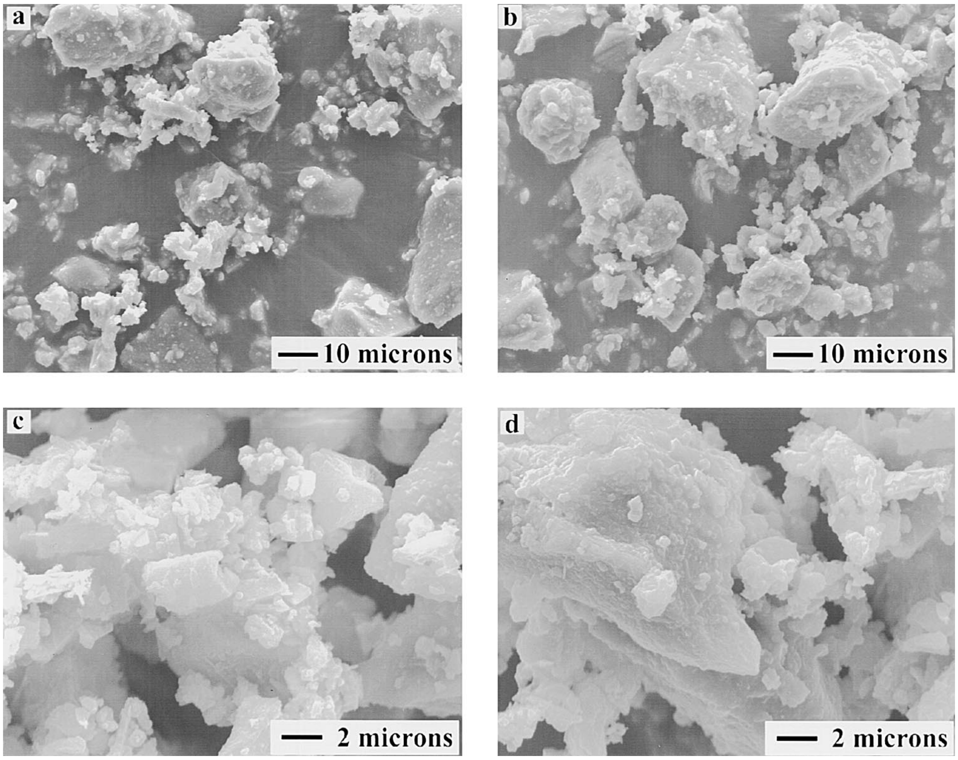


Fig. 1. Scanning micrographs (Philips XL 30 SEM with a LaB_6 emission source) of the homogenized mixture of 95 wt.% of rapid-hardening ordinary Portland cement (SH) and 5 wt.% of silica fume (SF). (a)–(d) Different regions of the same sample.

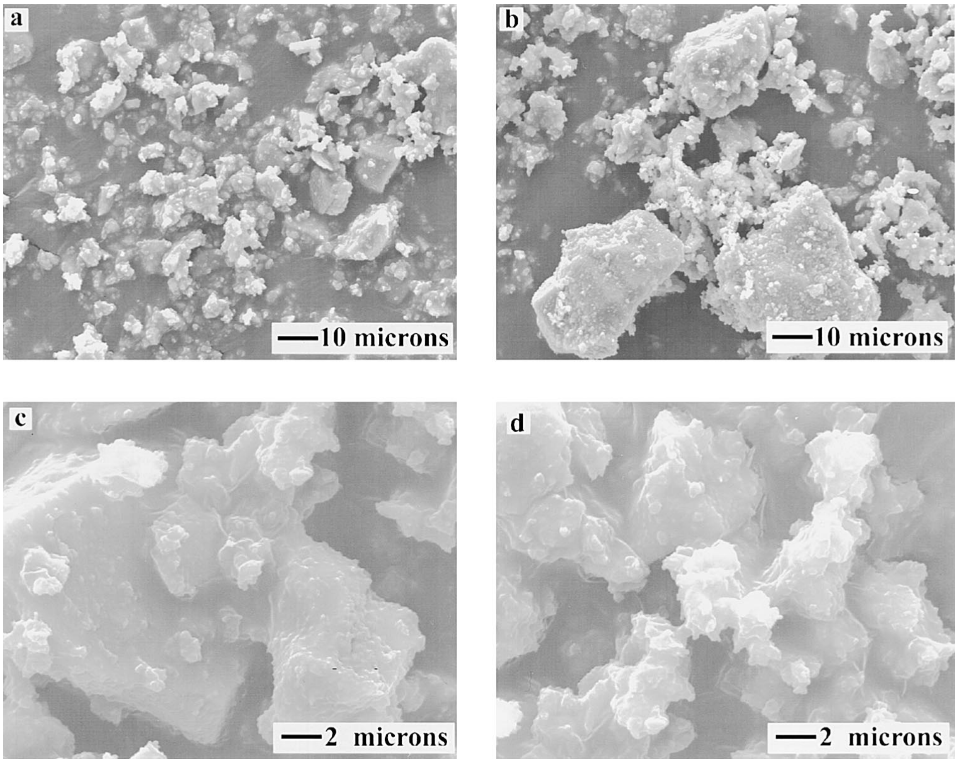


Fig. 2. Scanning micrographs of the same mixture as in Fig. 1 but after the blend was mechanically activated in a Humboldt Palla 20U vibration mill during 30 min. (a)–(d) Different regions of the same sample.

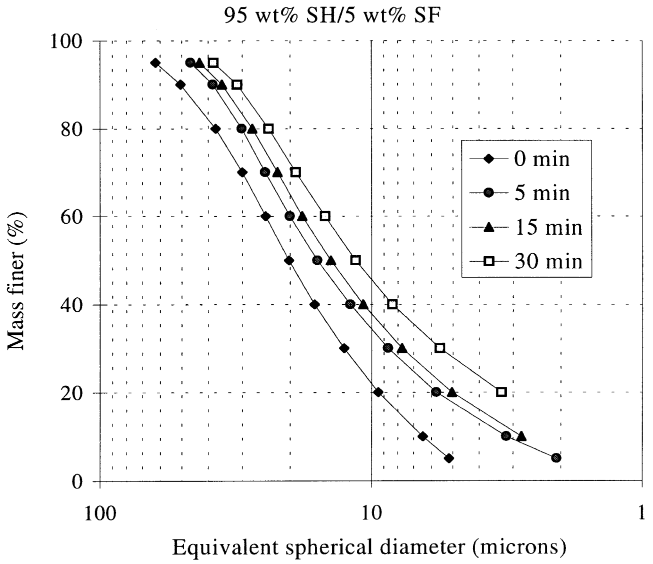


Fig. 3. The particle size distribution (Sedigraph Micromeritics, model 5100) of the same mixture as in Fig. 1 but after the mechanical activation in the vibration mill during 0, 5, 15 and 30 min.

in the spectrum. Thus, the modification process causes deagglomeration of microsilica and an improved distribution in the admixture leading to a possible coating on the cement particles. The beneficial effect of microsilica on the strength properties of concrete was previously reported by several authors to occur only when it is well dispersed in a concrete mixture. These spectra indicate that the microsilica particles have been well dispersed in cement by the applied vibration milling process [2].

Fig. 5 [2] shows the decrease in the porosity of the paste after 5, 15 and 30 min of vibration milling with reference to an untreated blend. It can be seen that the porosity distribution is the same after 15 min as it is after 30 min. These results indicate that the beneficial effects observed with vibration milling are the same after 15 min and with prolonged 30 min. This establishes the fact that the observed phenomena cannot be accounted to the increased fineness of the cement grains only [2].

At present, searching for reasons of outstanding properties of EMC, we cannot disregard a possible mechanochemical modification of surface layers of cement particles. A substantial chemical modification of various minerals such as synthetic and natural diopside, åkermanite and wollastonite in the course of long grinding (during 36 h) in a laboratory mechanical agate pestle-and-mortar mill (Retsch, type RMO) has been recently detected in our group by ^{29}Si solid state MAS NMR [3–5]. Initially, sharp resonance corresponding to Q^0 silicone sites became substantially broader and new resonance lines, corresponding to Q^1, Q^2, Q^3 and particularly Q^4 sites arose in the NMR spectra. For diopside and wollastonite, the formation of quartz in the process of long grinding has been detected [3–5].

In the case of cement/silica fume blends that are ground in the vibration mill during a short time of 30 min, only surface layers of cement particles might be chemically modified. The NMR signal from the surface layers may be screened by that from the bulk. However, the mechanochemical modification of surface layers of cement particles, i.e., the modification of Q^0 silicone sites to Q^1, Q^2, Q^3 and

Table 1
The particle size distribution of the blend of 95 wt.% of Portland cement with 5 wt.% of silica fume after mechanical treatment in a vibration mill at different time periods

Admixture	0 min	5 min	15 min	30 min
Particle size (μm)				
d_{80}	37.54	30.10	27.49	23.98
d_{50}	20.20	15.84	14.19	11.46
d_{20}	9.44	5.76	5.04	3.31
BET surface area (m^2 g^{-1})	2.68	2.73	2.86	2.95

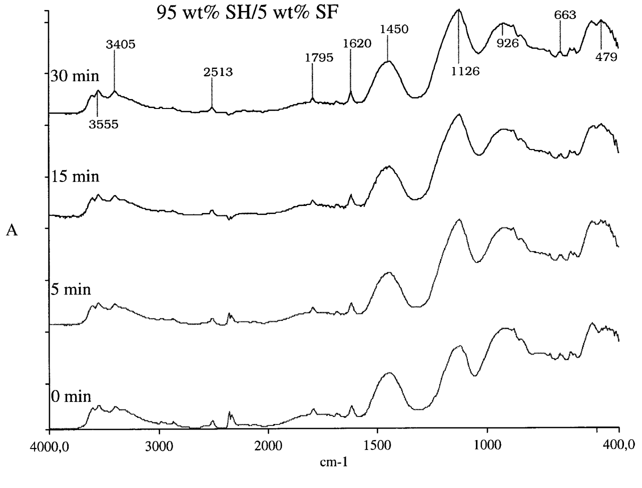
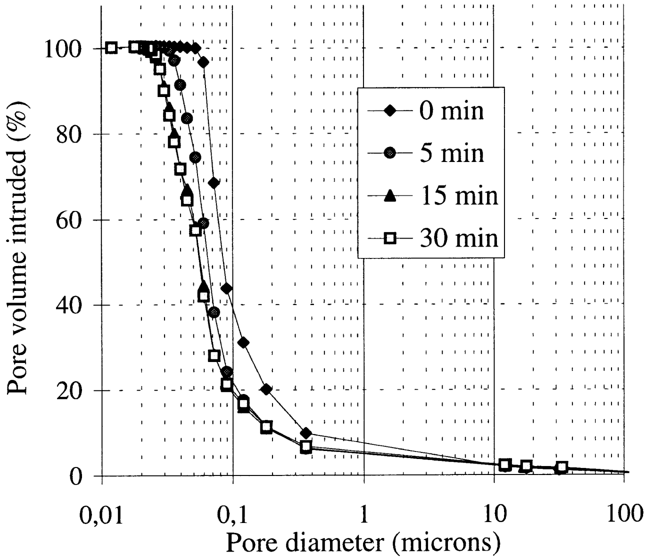


Fig. 4. Diffuse reflectance FT-IR (Perkin-Elmer 2000 FT-IR with a TGS detector) spectra of the same mixture as in Fig. 1 but after the mechanical activation in the vibration mill during 0, 5, 15 and 30 min.


95 wt% SH/5 wt% SF (curing time 7 days)

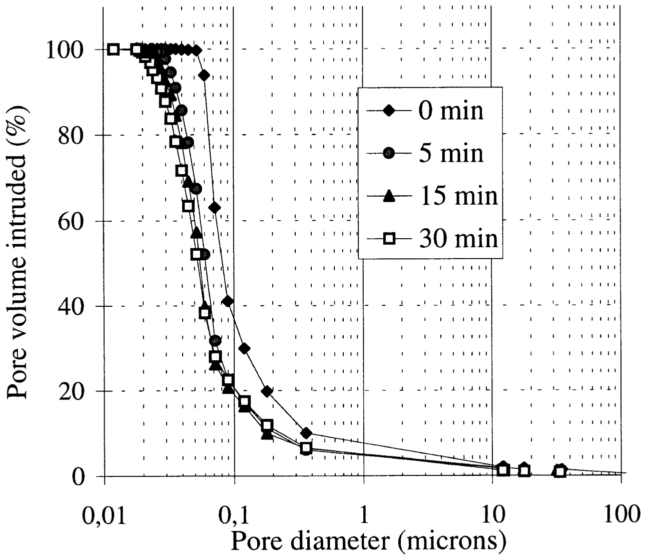

95 wt% SH/5 wt% SF (curing time 28 days)

Fig. 5. The porosity distribution of the hydrated cement paste with water–binder ratio of 0.25 after 7 and 28 days of curing time. The binder is the same as in Fig. 1 but after the mechanical activation in the vibration mill during 0, 5, 15 and 30 min.

Q^4 sites as was observed in calcium silicate minerals [3–5] would certainly affect the path of the hydration reactions in such modified systems.

The work along these lines is currently in progress.

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