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Accelerated microstructural evolution of a calcium-silicate-hydrate (C-S-H) phase in pozzolanic pastes using fine siliceous sources: Comparison with historic pozzolanic mortars

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Abstract

Traditional pozzolanic mortars such as those from Rhodes, Greece, or Hagia Sophia, Turkey, revealed the presence of a calcium-silicate-hydrate (C-S-H) binding phase. This phase, which is similar to that found in ordinary Portland cement (OPC), is produced under the pozzolanic reaction of slaked lime with fine reactive siliceous sources at temperatures < 100 °C. The traditional siliceous sources were replaced by fumed silica or tetraethyl orthosilicate (TEOS). A microstructural analysis revealed an enhanced reaction rate but similar morphologies of the resultant C-S-H phases, confirming that the reaction-limiting factor is the dissolution of the siliceous sources.

Keywords: Calcium-silicate-hydrate (C-S-H); Microstructure; Cement paste; Pozzolan; Mortar

1. Introduction

Pozzolanic mortars are cementitious materials first used by the Greeks around 1500 BC in Santorini Island as a wall covering [1]. These mortars were a mixture of slaked lime and naturally occurring reactive siliceous sources (volcanic ash). The Romans used this type of mortar too [2], utilizing thick deposits of reactive volcanic tuffs present near the town Pozuoli, from which the name of these hydraulic mortars is derived. The crushed brick mortars of the ancient Byzantine and Ottoman periods can be classified as pozzolanic mortars [3–5], in which the natural pozzolanas were replaced by artificial siliceous sources (fragments from tiles, crushed brick or pottery).

Hydraulic mortars are exceptionally durable to long-term static (structural) and dynamic (earthquake) stresses [6], as evidenced by the durability of various monuments utilizing these materials (e.g., Hagia Sophia in Istanbul, Turkey, and the medieval castle in Rhodes, Greece). Their durability was related to their hydraulicity and the nature of hydration products [4]. In addition, hydraulic mortars are more resistant to sulfate attack [4,7] compared to modern Portland cement, which has a limited life of approximately 70 years in marine and heavily polluted atmospheres [8]. The current practice in the field of preservation of monuments necessitates the use of compatible materials to avoid detrimental differential weathering effects. The chemical interactions between aggressive environments and traditional structural materials, such as hydraulic mortars, modify the microstructure of these materials. Knowing the nature of the interactions will allow the improvement of durability of modern Portland-cement-based materials.

The mixing of the reactive siliceous source with lime and water results in the formation of a series of hydrated calcium aluminates and calcium silicates, which are responsible for the hydraulic properties of the resulting mortar. Specifically, the mortar sets slowly, attains a much higher ultimate strength when cured in water than in air and hardens significantly. Portland cement clinker requires high-temperature reaction sintering (>1400 °C) to produce the hydraulic minerals like C_3S and C_2S that upon hydration produce the main binding phase known as calcium-silicate-hydrate (C-S-H). In contrast, pozzolanic mortars consist of hydrated

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phases formed at temperatures < 100 °C. The C-S-H phase formed by a pozzolanic reaction has a microscopic morphology similar to that developed by the hydration of the C_2S and C_3S found in Portland cement; the exact structural and chemical composition depends on the reactants [1,2]. The reactivity of Portland cement is higher than that of pozzolans with a corresponding effect on the setting time; Portland cement sets in < 1 day, whereas hydraulic mortars require weeks or even months.

The aim of the present work was to demonstrate an improvement in the rate of formation of the C-S-H phase formed by a pozzolanic reaction. It has been reported [1] that the pozzolanic reaction, in traditional pozzolanic mortars, is controlled by the dissolution of the siliceous phases in the aqueous solution. In this study, Cab-O-Sil fumed silica and tetraethyl orthosilicate (TEOS) solutions were used as fine siliceous sources to demonstrate the higher reaction rate possible compared to traditional volcanic siliceous powders.

2. Experimental procedure

2.1. Materials

The reactants were $Ca(OH)_2$ powder, USP grade (VWR Int., Bridgeport, NJ), Cab-O-Sil fumed silica, grade M-5 (Cabot, Tuscola, IL), with a mean particle size of 20–30 nm and a specific surface area of 200 m^2/g and $(CH_3CH_2O)_4Si$, TEOS aqueous solution (VWR Int.). The TEOS solution was used to study the hydration rate up to 1 h, whereas fumed silica was used for longer reaction times (from 1 h up to 3 weeks).

2.2. Sample preparation

Saturated solutions of $Ca(OH)_2$ were prepared by dissolving $Ca(OH)_2$ powder in CO_2-free distilled and deionized water. The solutions were then filtered through a Whatman No. 50 filter and centrifuged. The supernatant solution was used for subsequent experiments.

Various sample compositions were prepared in 25-ml plastic bottles. The initial Ca/Si ratio was 1:1 for the case of fumed silica (long reaction times), and 0.7:1, 1:1 and 2:1 for the case of TEOS (short reaction times). The reaction temperatures were 25 °C and 80 °C for the specimens containing fumed silica and 25 °C when TEOS was used as the siliceous source. All samples were allowed to react at their respective temperatures in a CO_2-free environment.

2.2.1. Pozzolanic samples with fumed silica

At the completion of the selected duration of reaction (1 h to 3 weeks), the samples prepared with fumed silica were repeatedly rinsed with deionized CO_2-free water and centrifuged to remove any quantity of nonreacted $Ca(OH)_2$. The rinsing–centrifuging steps were repeated until the pH value of the washing solution became 7. The gels were then air dried at 70 °C in a CO_2-free environment and the powders were stored in sealed glass containers. The rinsing of the gels obviously would leach out some of the Ca ions present in the C-S-H and possibly change the C-S-H phase morphology. However, the focus of this study was the evolution of the Ca/Si ratio versus time. It is true that the C-S-H left will have a morphology affected by the preparation and may not be representative of the initial C-S-H. However, a comparison between the C-S-H formed in the different systems is still valid as long as the same protocol of preparation is used. This comparison is not only limited directly to the microscopic morphology of the C-S-H but also indirectly (by comparing the time needed to obtain similar microscopic morphologies or extends of hydration) to the reaction kinetics and their dependence on the reactivity of the siliceous sources.

2.2.2. Pozzolanic samples with TEOS

Initial attempts that included a pH adjustment step (use of HCl) to terminate the pozzolanic reaction in those samples containing TEOS were abandoned due to the presence of a $C_xS\cdot CaCl_2\cdot yH_2O$ phase. Instead, the TEOS paste was quenched by pouring the reacting solutions into liquid nitrogen and subsequently removing water by freeze-drying.

2.2.3. Traditional mortars

The microstructure of traditional hydraulic mortars was studied in comparison with the pozzolanic pastes containing fumed silica or TEOS. These traditional mortars originated from the medieval castle of Rhodes, Greece (mortar sample No. 9cp), and the dome structure of Hagia Sophia in Istanbul, Turkey (mortar sample 26-Dome rib 7). These are typical pozzolanic mortars used before the advent of modern ordinary Portland cement (OPC).

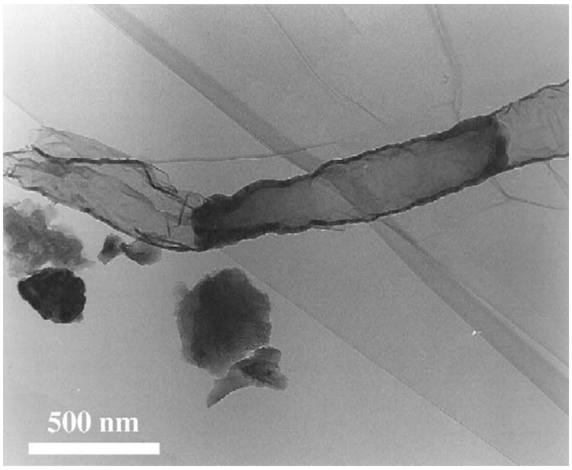

Fig. 1. TEM micrograph of a traditional pozzolanic mortar from Rhodes indicating the presence of C-S-H phase (filament-like entities).

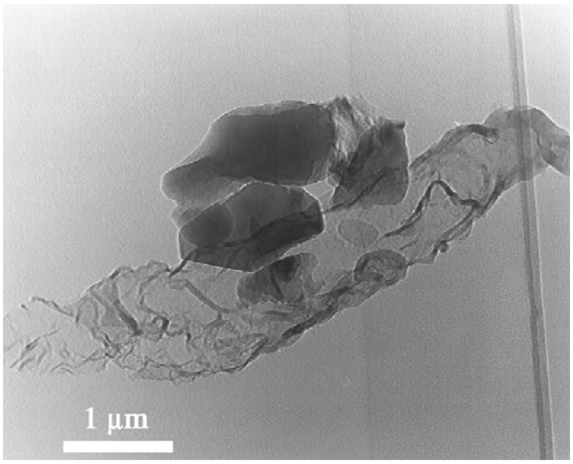

Fig. 2. TEM micrograph of a traditional pozzolanic mortar from Rhodes revealing the foil-like morphology of the C-S-H phase developed by pozzolanic reaction.

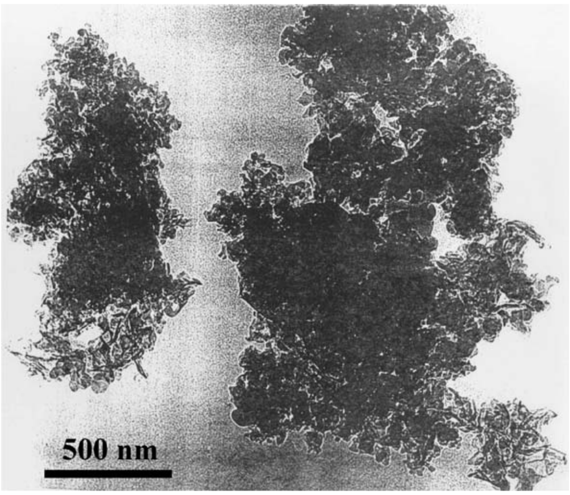

Fig. 4. TEM micrograph of the Cab-O-Sil paste. Formation of a C-S-H phase is indicated after 1 h. Reaction temperature was 80 °C.

2.3. Characterization techniques

The electron microscopes used were a Philips CM20/ST TEM (Mahwah, NJ) and a JEOL JEM-1200 EX STEM connected with a TRACOR Northern TN5500 microanalysis system to record point spectra. The EELS data of certain samples were recorded using a ZEISS EM902 at an acceleration voltage limited to 80 keV. The samples (both hardened pastes and ground traditional pozzolanas) were prepared using the dipping method from colloidal suspension of particles. The particles of the sample powder were suspended in methanol and ultrasonicated for 30 min. A carbon-Formvar-coated Cu grid was dipped into the suspension, air dried and stored for further use. XRD data were obtained for certain samples using a Philips XRD 3720. A CuK_a ($\lambda = 1.54049$ A) radiation was used from 5° to 60° with a scan rate of 2°/min.

3. Results and discussion

3.1. Microstructure of traditional pozzolanic mortars

Previous work on these materials [3] as well as traditional pozzolanic mortars of similar technology and composition [4–6] has revealed the composition of the amorphous (or more precisely, nanocrystalline) phase in these materials, and has indicated a wide range of Ca/Si ratios. Figs. 1–3 reveal the morphology of the C-S-H phase in the traditional mortars of Rhodes (Figs. 1 and 2) and Hagia Sophia (Fig. 3). The C-S-H phase has a foil-like morphology similar to that of the outer product of the hydration of

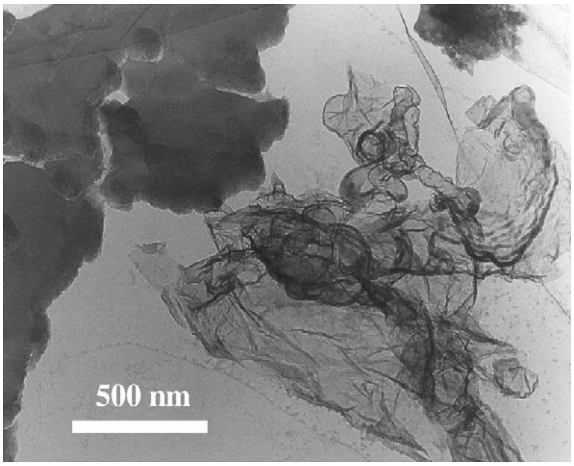

Fig. 3. TEM micrograph of the traditional mortar of Hagia Sophia revealing the morphology of the binding C-S-H phase developed by pozzolanic reaction.

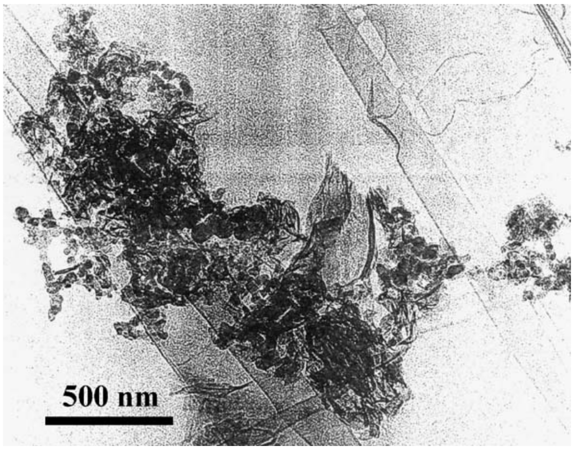

Fig. 5. TEM micrograph of a paste prepared with Cab-O-Sil. Formation of a C-S-H phase is indicated after 4 h. Reaction temperature was 80 °C.

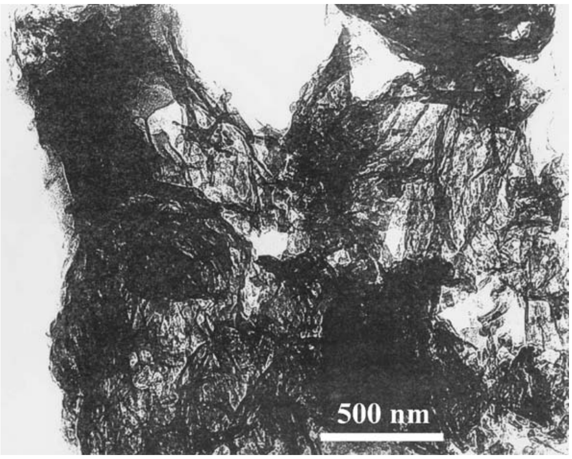

Fig. 6. TEM micrograph of a paste prepared with Cab-O-Sil. The C-S-H phase is prevailing after 24 h. Reaction temperature was 80 °C.

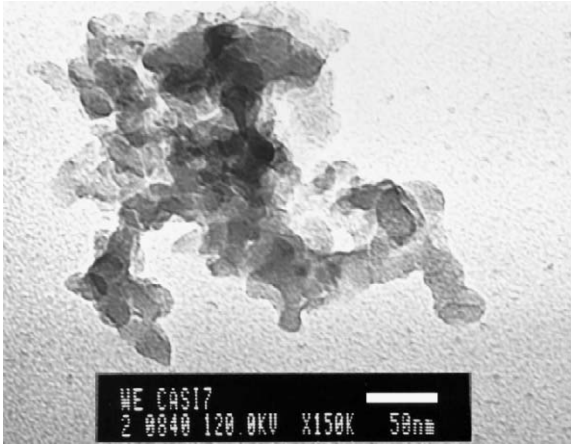

Fig. 8. STEM image of the cluster of particles from Fig. 7. The leaching of most of the Ca ions leads to a Si-rich microstructure.

tricalcium silicate (Op C-S-H) in the presence of silica fume [9]. The foil-like geometry could be expected, since at the high pH values determined during the preparation of these mortars (pH>12), aqueous silica exists as small oligomers, whereas C-S-H gel contains siloxane chains aligned on CaO_2 sheets. This implies that CaO_2 sheets in cements are formed first and impose order on the silicates [10].

3.2. Microstructure and composition of pastes containing fumed silica

Figs. 4–6 are typical TEM images of pastes prepared with fumed silica and reveal the morphology of the products of the pozzolanic reaction at its intermediate stages (1–24 h). Reaction temperature was 80 °C. A C-S-H phase is developing at the expense of the fine silica particles, binding them and eventually embedding them into a foil-like morphology.

The incorporation of silica particles (matrix effect) and the leaching out of the Ca ions during the washing step considerably decrease the Ca/Si ratio as shown in Fig. 7 (EELS spectrum of a cluster of particles bound by some C-S-H phase). The initial Ca/Si ratio was 0.7, and the samples were allowed to react at 80 °C for 4 h; at the end of the selected duration time and after the washing step, the resultant (apparent) Ca/Si was only 0.116, indicating the presence of silica particles and small amounts of C-S-H. This low Ca/Si ratio was typical for this temperature and duration of reaction, and suggests a small degree of reaction although the matrix effect from the presence of silica particles could not be ruled out completely. Fig. 8 is a STEM image of the cluster of particles measured in Fig. 7.

Ca/Si ratios of samples obtained at longer reaction times were always lower than the initial ones, and this was

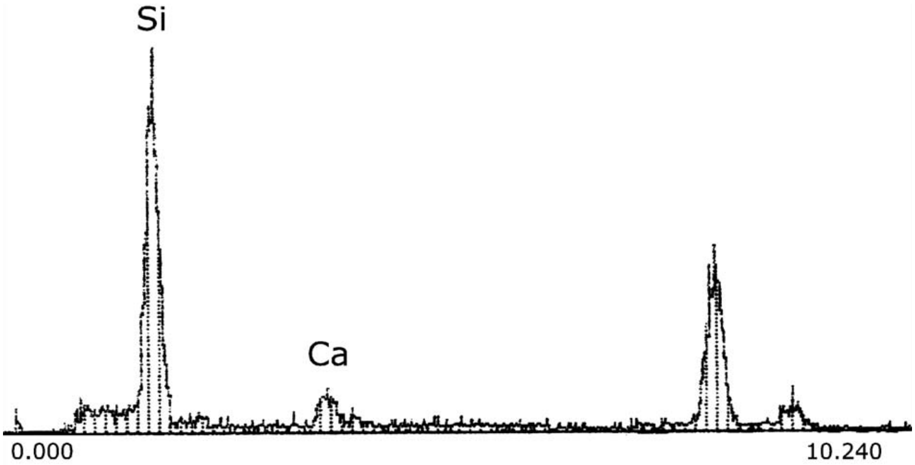

Fig. 7. EELS spectrum of a particle from a paste prepared with Cab-O-Sil and held at 80 °C for 6 days. The low Ca/Si ratio is probably the result of leaching of Ca ions during sample preparation.

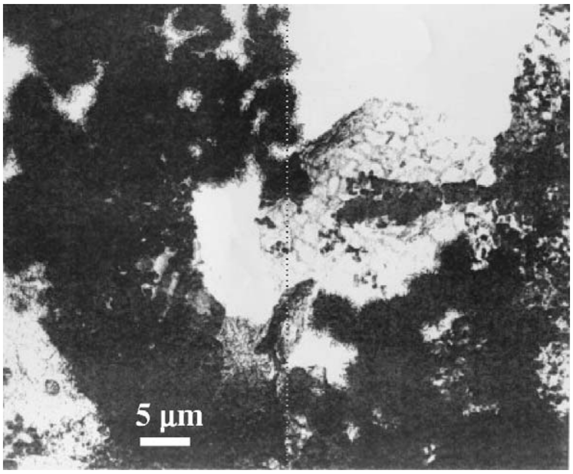

Fig. 9. TEM micrograph of the TEOS paste. The formation of a C-S-H phase is evident after 10 min of hydration. Initial Ca/Si = 0.7:1.

attributed to the leaching out of the Ca ions during the washing step in the sample preparation. However, when fumed silica (grains in the order of nanometers) was used as the siliceous source, a C-S-H phase (as in the case of Figs. 4–6) was observed at reaction times less than a day, clearly showing an accelerated reaction rate compared to experience with traditional pozzolanas (where it takes much longer to reach a similar extent of reaction).

3.3. Microstructure of pastes prepared with TEOS

The replacement of fumed silica with TEOS accelerates the pozzolanic reaction due to the elimination of the dissolution step of the silica particles (fumed silica). The increased reaction rate is evident in Figs. 9–11, where a C-S-H phase is observed as early as 10 min. The foil-like morphology of the C-S-H phase is similar to the morphology of the pastes with fumed silica (Figs. 4–6) or the traditional mortars (Figs. 1–3). Fig. 11 shows some particles with a “spherulitic” morphology, which appear to be consisting of bundles of dendrites diverging from a single crystalline nucleus [11]. Although such “spherulites” were present in all three Ca/Si ratios studied (with TEOS), the foil-like morphology was eventually prevailing with increasing reaction time.

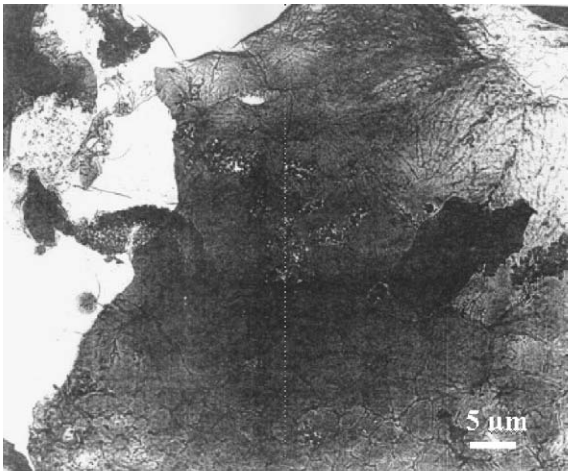

Fig. 10. TEM micrograph of the TEOS paste. The formation of a C-S-H phase is evident after 10 min of hydration. Initial Ca/Si ratio = 1:1.

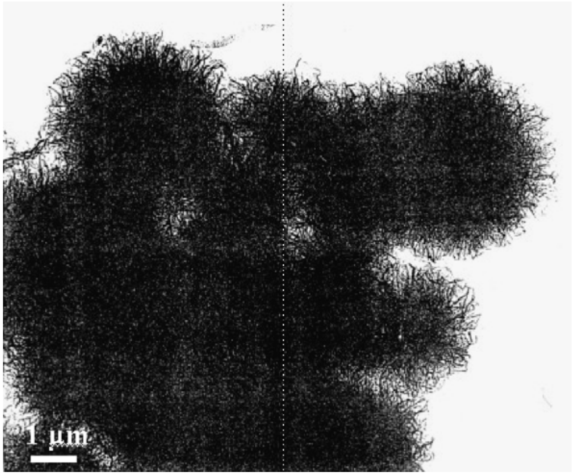

Fig. 11. TEM micrograph of spherulites from the TEOS paste. Reaction time was 10 min and initial Ca/Si ratio = 2:1.

4. Conclusions

The use of finer and more reactive siliceous sources demonstrates an accelerated evolution of a C-S-H phase during the pozzolanic reaction. This phase has a microscopic morphology similar to that of the binding phase in traditional pozzolanic mortars, indicating that the increased reactivity of the siliceous sources does not change significantly the eventual microstructure of the C-S-H phase. The elimination of the dissolution step of silica by the use of TEOS instead of fumed silica shows that the limiting factor in the reaction rate of the pozzolanic reaction is the dissolution of the siliceous source into the $Ca(OH)_2$ saturated solution.

The use of chemical activators has been reported to increase the reaction rate of the pozzolanic reaction [12,13]. Results in this study have demonstrated that the reaction rate of the pozzolanic reaction can be (further) increased by appropriate selection of the reactants, showing great potential for the use of pozzolanic mortars in modern-day applications.

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