

MICROSTRUCTURE DEVELOPMENT ON FILLER SURFACE IN BLENDED SYSTEMS AT THE EARLY HYDRATION PERIOD

E. Berodier^a, B. Mota Gasso^b, K. Scrivener^c

- a. *Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne, elise.berodier@epfl.ch*
b. *Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne, berta.mota@epfl.ch*
c. *Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne, karen.scrivener@epfl.ch*

Keywords: Cement hydration, Microstructure, C-S-H morphology, Quartz filler.

Introduction

New cementitious systems have allowed the reduction of the CO₂ emission associated with cement production. These systems combine ordinary Portland cement with other products from industry such as slag, fly ash or with natural materials such as limestone or clays. These materials are called supplementary cementitious materials (SCM) as they are able to display cementitious properties when they are blended with cement.

The replacement of ordinary Portland cement by another cementitious material leads to several changes notably in the kinetic of cement hydration. Many researchers have investigated the kinetics by isothermal calorimetry and found that the use of SCM increases the hydration rate of the clinker component (Collepari, Baldini et al., 1978; Gutteridge, 1990). This is commonly attributed to the extra surface area from SCM where more hydrates can nucleate and grow. Nevertheless few observations of the hydrates development and morphology on the SCM surface have been reported.

Isothermal calorimetry is a technique that measures the heat release over hydration time that is to say the overall rate of cement hydration rather the hydrates formation. While microscopy is a reliable way to observe the hydrate formation, the main difficulty is to distinguish the SCM surface from the cement surface.

Therefore, this work aims to study the microstructure development of hydrates on the surface of quartz particles. Quartz has been used in place of SCM because it is an inert material and its smooth surface makes the observation of small nuclei easier. Quartz was blended with alite, which is the major phase in ordinary Portland cement and dominates the early hydration period.

We combined the information from Back Scattered Electron and Secondary Electron images to analyse both materials during hydration. In BSE mode alite and quartz can easily be distinguished. This work generates new insights into the microstructure development in blended cementitious systems as well as the role of cement compared to alite.

Materials

Quartz powder with a mean diameter about 13 μm was used (from Bernasconi). The cement was an ordinary portland cement, CEM I 52.5 Type (Holcim). The phase composition was determined by XRD-Rietveld as: 75% C₃S, 5% C₂S-b, 9.9% C₄AF, 4.3% C₃A. Alite was synthesised in our lab by several heating and grinding cycles as detailed in (Quennoz and Scrivener, 2013). The chemical composition was CaO 77.5%, SiO₂ 19.5%, Mg 2.2%, Al₂O₃ 0.5%.

Methods

Prior to hydration, alite or cement and quartz powder were mixed together. Quartz replaced 40 % by mass of the solid content. Water was added to the anhydrous mix to reach a water/solids ratio of 0.4. The pastes were mixed in batches of 5g in a plastic vessel. In each case the paste was hand mixed for 2 minutes. Three grams of the paste was put in a glass vessel to record the heat release at 20° with a TAM-Air isothermal calorimeter. The rest of the paste was kept in the initial vessel, sealed and stored at 20°.

After 1, 3, 4 and 5 hours of hydration, the hydration was stopped by solvent exchange with isopropanol. At the required times 0.2g of the paste was take out and put in a filtrating funnel with two filter papers (retention 5 μm). The funnel was immediately filled of isopropanol and the sample stirred in the funnel for 2 minutes. Then the iso

propanol was removed with a vacuum pump. The procedure was repeated twice. Once the isopropanol was removed, the dried paste is collected from the filter paper. As the paste is quite young and not set, it collapsed to a powder made of quartz, cement or alite grains. All the powders were stored under vacuum in a dessicator for 1 day.

The SEM specimens were prepared from the dried powder. it was dispersed on an adhesive carbon tab and coated with a carbon layer of 15 nm.

The surface of the hydrated grains was observed with a FEI XLF-30 SFEG-SEM. First, we used the Back Scattered Electron mode that allows the identification of alite and quartz grains in a representative region of the sample (Fig 1). The identification of Quartz grains as the grey particles and alite the brighter ones, was verified by EDS microanalysis. The microscope parameters are shown on the micrographs. Then the secondary electron mode was used at the same location to observed with an ultra high resolution the development of the hydrates on the different surfaces. A minimum of 10 grains from each material were analyzed.

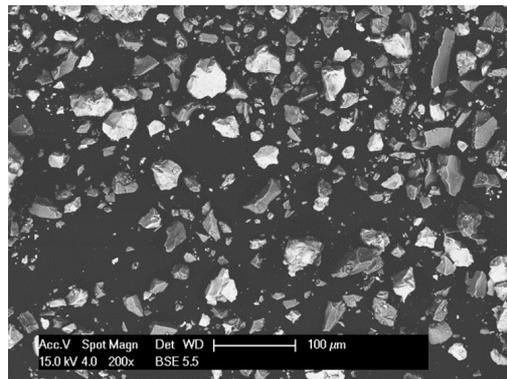


Figure 1: BSE image of the quartz -alite grains. Alite appears in white and quartz in grey.

Results

The kinetics of hydration of alite with 40% of quartz replacement has been monitored by isothermal calorimetry. The data were normalized to the mass of alite. The curve is displayed in Fig 2. The different times where hydration was stopped can be identified on the curve as following: 1 hour corresponds to the induction period (i.e. low and stable progress of heat), 3 hours is the end of the induction period then 4h and 5 hours cover the beginning of the acceleration period.

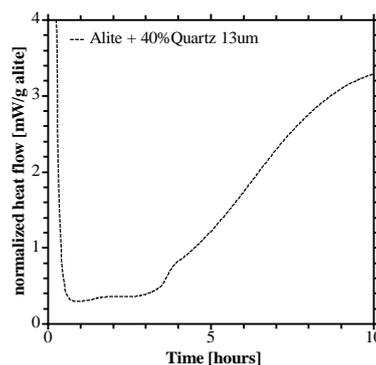


Figure 2: Calorimetry curve of alite blended system with 40% quartz replacement

Microstructure development in Alite - quartz systems

After hydration for 1 hour, the surface of the quartz seems unchanged from its unhydrated state. The surface is quite smooth and the presence of small quartz particles from the grinding stacked on the surface could be

confused with potential C-S-H nuclei. However, on alite surface some nuclei and growing C-S-H could be observed after 1 hour.

On further hydration at 3 hours, C-S-H nuclei and portlandite are clearly observed on the quartz surface. Some products may be formed in the water filled space, but because of the drying process, they fall back onto the surface of quartz and alite.

Based on the kinetics curves at 3 hours we are still observing the microstructure during the induction period. Thus C-S-H seems to already nucleate in the induction period on the quartz grains. In addition, the nucleation of C-S-H on quartz confirms the role of surface as nucleation sites and shows the supply of silica and calcium everywhere in the solution.

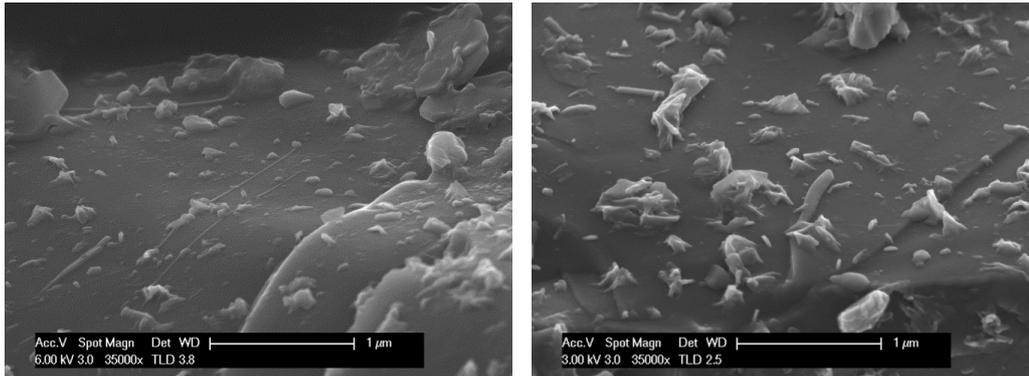


Figure 3: Surface of a. (left) quartz particle and b. (right) alite grain after 3 hours of hydration

Figure 4 depicts the surfaces of both quartz and alite after 5 hours of hydration. C-S-H phases have developed on both surfaces. The hydrates seem distributed in a regular fashion on a smooth surface. Figure 4.a shows well the morphology of the C-S-H: they are straight needles growing perpendicular to the surface. On the alite grains, C-S-H are more abundant and sometimes mixed with CH crystals (Figure 4.a). Unlike quartz, the alite surface is covered of many etch pits that becomes larger and more abundant with time. They form area of etch pits and we found C-S-H in these regions.

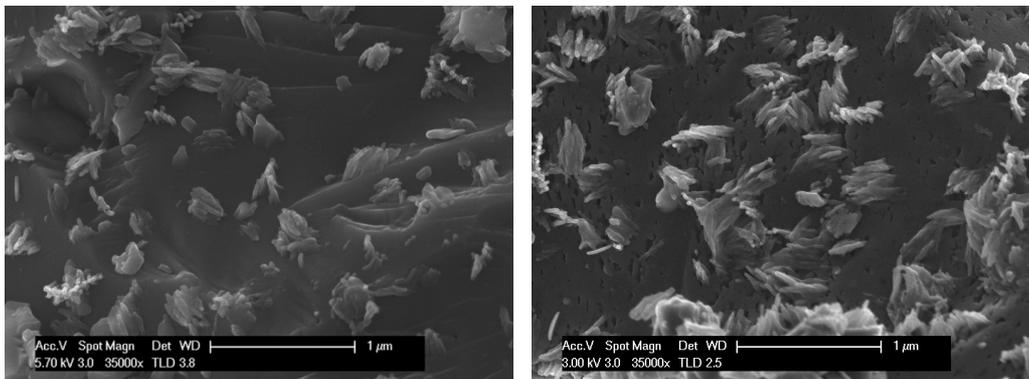


Figure 4: After 5 hours of hydration a) quartz surface b) alite surface

Microstructure development in cement-quartz paste

Quartz-alite systems are much easier to study from a microstructural point of view. First of all alite produces only two hydrate phases that makes the observation of C-S-H growth more evident. In cement paste from very early age we start to find many ettringite crystal as can be seen in Figure 5. In addition, ettringite is forming on the surface but also in the water filled space (Scrivener, 1984). So after drying, the surface is covered with products mainly ettringite crystals much larger than C-S-H nuclei (Figure 5). Thus, ettringite obscures the observation of C-S-H development and alite – quartz systems was a good solution to avoid this. However it was essential to verify that alite –quartz system exhibits a similar microstructure development to the cement system.

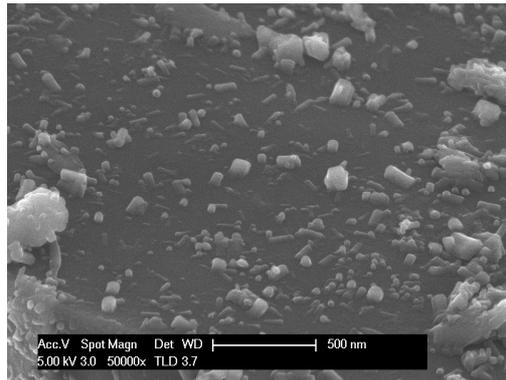


Figure 5: Surface of cement grain after 2 hours of hydration

After hydration for 5 hours, the surfaces of both cement and quartz start to be covered with many hydrates (Figure 6). Some areas still smooth but all grains are more covered by products than in alite-quartz systems. Ettringite is still present (both products forming in the water space and growing from surface). The C-S-H shape is well defined as needles and unlike in alite systems they do not form any agglomerates of parallel needles but the needles seem to diverge to give structures like sea anemones (see figure 6). Figure 7 a and b show well the different shape of C-S-H depending on the system.

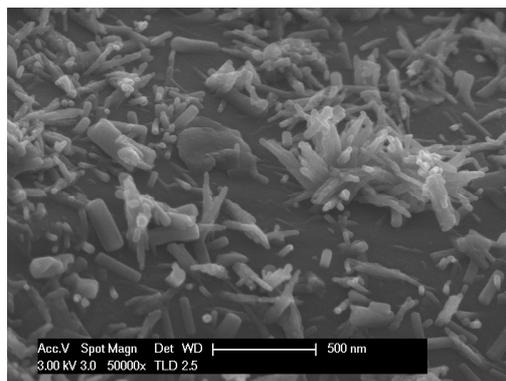


Figure 6: Surface of cement grain after 5 hours of hydration

Figure 7.a. corresponds to C-S-H growing on quartz in a cement-quartz paste. The C-S-H grows as several spikes. They seem forming from the same spot and growing as a sea-anemone structure. On the other hand, in alite system the C-S-H phase exhibits a different morphology. As we previously saw in Figure 4, the C-S-H growing on any surface is a cluster of spikes, sticking together side by side. They are in contact either at the top of the spikes or along the spike as seen in Figure 7.b. The difference in microstructure between alite and cement pastes have been reported but the studies were done on polished section and on specimens at later age (Kjellsen and Justnes, 2004; Gallucci and Scrivener, 2007). So it seems that the microstructure at later ages results of changes in the growth of C-S-H from the very beginning of the hydration.

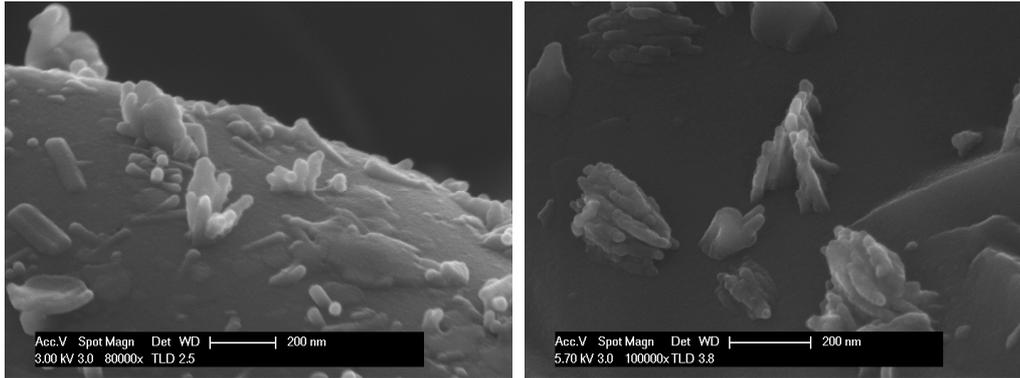


Figure 7: Morphology of C-S-H after 5 hours a. (left) in cement - quartz paste b. (right) in alite - quartz paste

Conclusions

The SFEG SEM provided micrographs of high resolution of the topography and so the microstructure in 3D of the hydrates. The combination of BSE and SE modes allows the distinction between quartz from alite and makes easier the observation of the microstructure development on both surfaces.

The microstructures on quartz and alite grains were similar. This indicates that both surfaces act as nucleation sites and that calcium and silicate ions are available everywhere. However, there is a slight delay in the start of growth on the quartz particles.

The cement - quartz paste microstructure was more complex to analyze owing to a larger variety of hydrates formed, notably ettringite. Nevertheless it has been observed that C-S-H morphology in quartz-cement significantly differs from that in quartz-alite. In the latter, C-S-H was made of a bundle of spikes side by side and perpendicular to the surface. On the other hand in quartz-cement paste, the C-S-H phase was made as well of several spikes but they formed a diverging structure.

References

- Collepari, M., G. Baldini, et al. (1978). "The effect of pozzolanas on the tricalcium aluminate hydration." *Cement and Concrete Research* Vol. 8 No.6: 741-751.
- Gallucci, E. and K. Scrivener (2007). "Crystallisation of calcium hydroxide in early age model and ordinary cementitious systems." *Cement and Concrete Research* Vol. 37 No.4: 492-501.
- Gutteridge (1990). "Filler cement: the effect of the secondary component on the hydration of portland cement." *Cement and Concrete Research* Vol. 20: 778-782.
- Kjellsen, K. O. and H. Justnes (2004). "Revisiting the microstructure of hydrated tricalcium silicate—a comparison to Portland cement." *Cement and Concrete Composites* Vol. 26 No.8: 947-956.
- Quennoz, A. and K. L. Scrivener (2013). "Interactions between alite and C3A-gypsum hydrations in model cements." *Cement and Concrete Research* Vol. 44 No.0: 46-54.
- Scrivener, K. (1984). "The development of microstructure during the hydration of Portland cement". London, *Imperial College of Science and technology*.