

## Direct TEM observation of pozzolanic reaction of silica fume in $\text{Ca}(\text{OH})_2$ solution

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Glassy materials, such as fly-ash, silica fume and volcanic ashes are industrially used as resource materials of concrete aggregates, applied for cement-solidification technique. As a concept, advantage of utilization of these materials is based on their relatively higher solubility than crystalline materials. Until recently, there are numerous studies to optimize the solidification condition with cementitious materials involving alkalis and water. Currently, a number of concretion methods was proposed and still developed for construction. More recently, classical cement-based method is evolving to geopolymer technique, but the early reaction of concretion is essentially common because the dissolution is always prior to precipitation. In order to precise and optimize the concretion condition, we carried out direct observation of concretion using TEM equipped with newly developed cell (Protochips, Poseidon, e.g., Yamazaki et al., 2017) which is specialized for liquid-bearing samples. System comprised of silica fume,  $\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$  solution at room temperature was investigated in nanometer scale.

As the result, silica hydration can be detected semi-quantitatively from TEM images. Silica spheres in  $\text{H}_2\text{O}$  are expanded and reduce their integrated contrasts, suggesting simultaneous hydration and dissolution. The expansion was monitored for observation periods over 4000 s to be in the velocity of  $9.2\text{E-}3$  and  $3.7\text{E-}3$  nm/s at zero and  $1.0$  ul/min flow, respectively. Their dissolution rates were measured to be  $6.5\text{E-}5$  and  $2.0\text{E-}4$  mol/m<sup>2</sup>/s, respectively. When we switched the solution from  $\text{H}_2\text{O}$  to  $\text{Ca}(\text{OH})_2$  (equilibrated at  $25$  degC), the silica spheres start fast expansion again in the velocity of  $2.6\text{E-}2$  nm/s, but dissolution rates were extensively reduced over the measurement period of 2400 s. During these expansion processes in  $\text{Ca}(\text{OH})_2$  solution, silica spheres were not only expanded but also accompanied with precipitation of film to veil-shaped CSH (calcium silicate hydrate) phase which is surrounding the spheres. During propagation of this CSH phase in the velocity of  $5.3$  nm/s, the spheres were getting porous and losing its original density explained such by so-called “shrinking core” model. This should be interpreted as the true process of so-called “pozzolanic” reaction. Parallel to the in-situ observation, we reproduced the observation with ex-situ method on a batch reaction system held for 3000 min. It clearly exhibited that spheres after 60 min started 2-D nucleation of unknown phase, then filmy to veil-shaped phase successively developed and enclosed the original spheres together. Elemental analyses with FESEM-EDS represented that the Ca/Si ratios of these secondary phases increased from 0.1 to 0.2 with curing periods (20 to 72 h), probably due to the systematic dissolution/precipitation balance. This can be interpreted as the essential process of cement solidification. Thus, colloidal glassy material can be aggregated and evolved to be self-consolidation state in alkaline solution. Classical knowledge of pozzolanic reaction can provide us an important information about controlling and evolving the colloids to hard materials.

Keywords: direct TEM observation, pozzolanic reaction, silica fume