Molecular understanding of tricalcium silicate hydration in absence and in presence of aluminate ions

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The kinetics of hydration of tricalcium silicate is not yet fully understood. Different mechanisms have been proposed and NMR has proven to be very successful in elucidating the structure of hydrates when the reaction is stopped or completed. However, a precise picture of the dynamics of silicate hydrates formation in-situ is still lacking and impedes a definite choice between the proposed models. Here we show by a combination ^{29}Si NMR, ^{27}Al NMR and calorimetry that the synthesis of carefully designed ^{29}Si-enriched C_3S allows following quantitatively the hydration process under conditions close to in situ ones.[1]

In water, we obtain the transient local molecular composition of the hydrates at different stage of hydration. In particular, during the deceleration period the hydrate precipitation rate decreases faster than the amount of hydroxylated C_3S surface, suggesting that the C_3S surface is partially covered by C-S-H and that the surface area available for silicate dissolution decreases. Furthermore, by 2D-NMR a distribution of silica chain length can be proposed. In the proposed scheme, although the average chain length is five, pentamers do not constitute the predominant occurrence.

Then, the effect of aluminate ions on the hydration of C_3S is investigated. We show that a pH sensitive retardation of C_3S hydration by aluminate ions occurs at early age of reaction, but that the amount of the hydrates formed increases later. These experimental results can be interpreted assuming that aluminates hinder C_3S dissolution. This view is supported by molecular dynamics simulations establishing that aluminates can adsorb on hydroxylated C_3S through ionic interactions between aluminate and calcium ions, as well as through hydrogen bonding with silicate surface groups. This interaction is pH dependent and, consequently, the retardation effect of aluminates varies during the advancement of hydration.[2]

References

[1] E. Pustovgar, R.P. Sangodkar, A.S. Andreev, M. Palacios, B.F. Chmelka, R.J. Flatt, J.-B. d'Espinose de Lacaillerie, Understanding silicate hydration from quantitative analyses of hydrating tricalcium silicates, Nat. Commun. 7 (2016) 10952. doi:10.1038/ncomms10952.

[2] E. Pustovgar, R.K. Mishra, M. Palacios, J.-B. d'Espinose de Lacaillerie, T. Matschei, A.S. Andreev, H. Heinz, R. Verel, R.J. Flatt, Influence of aluminates on the hydration kinetics of tricalcium silicate, Cem. Concr. Res. 100 (2017) 245–262. doi:10.1016/j.cemconres.2017.06.006.