Solid state NMR study of the impact of set modifiers on the hydration of a ternary hydraulic binder

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Résumé

The fast-setting tile adhesive formulations generally include a mix of multiple mineral binders with additives such as set retarders, accelerators, rheology modifiers, water reducers, etc. These additives are commonly used to modify and tailor cement properties like mechanical strength development over short and long time periods. However, their effects on the structure and microstructure of the phases resulting from the hydration remain rather unclear. Indeed, cement hydration is already a complex process involving precipitation of multiple stable and metastable phases and the addition of set modifiers can make its hydration process even harder to tackle. In this study, high resolution solid-state NMR was used to investigate the hydration kinetic and the structural modifications within a ternary binder composed of white Portland cement, calcium aluminate cement and calcium sulfate, with or without addition of two set modifiers separately (the lithium carbonate Li2CO3 and the tri-sodium citrate Na3C6H5O7). 27Al MQ-MAS and {1H}-27Al Cross-Polarization MAS NMR experiments were combined to distinguish all the aluminum species present in the system before and during the hydration process. Similarly, {1H} -29Si CP-MAS NMR and 29Si MAS NMR were employed to characterize the different silicate phases on the mixture during the cement setting. The NMR experiments were performed ex-situ on samples hydrated between two hours and 28 days. Simultaneous fits of complete set of spectra with stoichiometric constraints were performed to quantify the aluminum and silicon present in each phase. The precipitation kinetic and proportions of hydrate phases and their microstructural organization were correlated to the early age mechanical strength. The plain ternary binder was considered as a reference to observe the acceleration and delay as well as the structural impact of the set accelerator and the set retarder. Keywords: Lithium carbonate, tri-sodium citrate, NMR, cement, hydration, hydrated phases, microstructure.

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