Reactivity of titanium containing glasses during the hydration of hydraulic binders

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Résumé

Replacing Portland cement by supplementary cementitious materials is a promising way to decrease carbon emission of concrete. Ground-granulated blast-furnace slags are a common replacements of Portland cement in CEM II and III cements. However, this substitution induces various short and long-term effects on mechanical strength and durability of the resulting concrete. In addition to many other factors, the presence of minor elements in GGBS composition has proved to play a not negligible role on hydration rate. Among them, titanium, from 1 %wt, has been identified to have a negative impact on strength development of cement-based materials [1, 2]. The aim of our work was to better understand the titanium role on slag dissolution rate and the nature of hydrates as well as their kinetics of formation. Industrial slags have complex compositions, introducing chemical disorder or paramagnetic effects, therefore we used simplified lab-synthetized glasses with main element compositions close to industrial slag. We considered two different Ca/Si ratios and titanium contents (0 or 3 % wt TiO2). The cement hydration was mimicked using the R3 protocol [3], where glasses are mixed with Portlandite in a K2SO4/KOH solution. After various curing times (2, 7, 14 and 28 days), the hydration reaction was stopped and samples were characterized by XRD as well as 27Al and 29Si MAS NMR. Spectra were dominated by the broad signal of the glass, with overlapping narrower lines due to hydrates. Acquisition times were long and accurate signal processing had to be applied including accurate first order phase and baseline corrections, or considerations of satellite transition and spinning side bands. In addition, {1H}-27Al and {1H}-29Si CP-MAS spectra were acquired to edit specifically the signal of hydrated phases. A rigorous fit procedure of the complete set of spectra was conducted taken into account maximum constraints. Results showed a slower glass dissolution in the presence of titanium, at both Ca/Si ratios. More interesting we clearly evidence and quantify two disordered silicon sites in addition to those classically attributed hydration products of slag, probably related to the glass reactivity.

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