A study of the effect of polymeric powder on calcium species in white cement via $^{43}\text{Ca}$ MAS NMR spectroscopy

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Concrete is one of the world’s most widely used construction materials and over the past few decades, polymeric fibres have been used as low level reinforcement, for instance in bridge decks, to improve crack control and crack resistance [1]. The chemical bond between polymeric fibres and the cementitious matrix is of utmost importance when the fibre is to contribute to the toughness of the fibre reinforced composite. In this work, a model system for fibre reinforced concrete was studied, namely fluoropolymeric and poly(ethylene-vinyl acetate) (EVA) powders in white cement paste (chosen for its low iron content). It is speculated that the polymer chemistry could affect the calcium species formed during cement hydration surrounding the polymeric inclusion.

The major component of hydrated cement paste is calcium silicate hydrate (CSH). Taylor et al. [2-4] postulated that the structure of CSH is like that of tobermorite or jennite. Bowers et al. [5], studied the calcium environments in crystalline tobermorite, jennite, and Ca(OH)$_2$ using $^{43}\text{Ca}$ NMR at the same magnetic field strength as our study. They found that tobermorite gave resonances between 0 and -40 ppm with maxima at -10 ppm and jennite between 5 and -60 ppm with maxima at 24 ppm in $^{43}\text{Ca}$ NMR spectra. They also investigated Ca(OH)$_2$ resonances between 30 and 70 ppm with a peak maximum at 60 ppm which partially overlaps with jennite resonances.

Our $^{43}\text{Ca}$ NMR spectra of fluoropolymer/white cement and EVA/white cement composites are essentially a summation of the spectral features of tobermorite, jennite, and Ca(OH)$_2$. In the EVA/white cement spectra (shown in Figure 1), consistent with Bowers et al. [5], we assign a broad jennite resonance between 0 ppm and 62 ppm with an apparent peak maximum at 31 ppm, the tobermorite resonance at -10 ppm, and the Ca(OH)$_2$ peak maximum at 53 ppm. Bryce et al. [6] shows CaCO$_3$ experimental resonances for calcite between 3 to 6 ppm and for vaterite between 0 and -30 ppm centered at 10 ppm. These resonances would overlap in the tobermorite region of the spectrum.

**Figure 1:** SPE $^{43}\text{Ca}$ NMR spectra of a) white cement (7 day hydration), b) EVA/white cement (1 day hydration), and c) EVA/white cement (28 days hydration).
Since there are not significant intensity changes in this region, we conclude that CaCO$_3$ is not significantly contributing to our $^{43}$Ca NMR spectra. Apparently, based on the $^{43}$Ca NMR spectra, the presence of the EVA admixture does not greatly affect the CSH structure or Ca(OH)$_2$ sites in the hydrated cement paste.

Similarly, in the fluoropolymer/white cement composite $^{43}$Ca NMR spectra (shown in Figure 2), we assign resonances as jennite (0 to 62 ppm with a peak maximum at 31 ppm), tobermorite (-10 ppm), and Ca(OH)$_2$ (53 ppm) consistent with the literature [5-10] and our recent $^{43}$Ca study of EVA/white cement composites [11].

From these spectra, it is difficult to determine if either the fluoropolymer or EVA additive caused structural changes in the cementitious $^{43}$Ca environments during hydration. It is speculated that the structural changes to CSH would occur locally at the polymer/cement interface (on the micron scale), which consequently could result in these structural changes being unobservable in the $^{43}$Ca NMR spectra as they are masked by the resonances of the more abundant bulk cementitious calcium sites. Although, structural changes in the CSH surrounding polymeric inclusions in white cement were unobservable in the presented $^{43}$Ca spectra, this work demonstrates the promise of $^{43}$Ca NMR spectroscopy as a tool for studying the complex calcium environments in cementitious materials.

References