# Molecular Calcium and Magnesium Species in Hydrating Cementitious Materials

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## Introduction

The characterization of the molecular compositions, structures, and changes that occur during cement hydration remain incomplete. Challenges significantly complicate the characterization of non-hydrated components that exhibit different polymorphs, crystal defects, or ion substitutions and commingled crystalline and disordered hydration products. Here, the local molecular compositions and structures of calcium species in individual cement components and more complex white Portland and grey oilwell cements are analyzed by natural-abundance solid-state single-pulse $^{43}$Ca magic-angle spinning (MAS) NMR and complementary natural-abundance spin-echo $^{25}$Mg MAS NMR under technologically relevant conditions.

## Experimental

Solid-state 1D $^{25}$Mg and $^{43}$Ca NMR experiments were performed at the NHMFL NMR Facility using the 19.6 T ultra-narrow bore NMR superconducting magnet equipped with a 3-channel Bruker DRX console. The high magnetic field mitigates the effects of second-order quadrupolar interactions and yields improved sensitivity and resolution of the $^{25}$Mg and $^{43}$Ca NMR signals. A single-resonance home-built low-γ MAS probe with a 7.0 mm Samoson MAS stator was used for all measurements. This large-volume MAS probe was built for low-*γ* nuclei where signal sensitivity issues can be compensated by a larger sample volume. All measurements were conducted at room temperature and under MAS conditions of 5 kHz.

## Results and Discussion

The solid-state 1D single-pulse $^{43}$Ca MAS spectra of non-hydrated and hydrated white Portland cements shown in **Figure 1** consist of broad $^{43}$Ca signals spanning a wide spectral range (-40 to 125 ppm) that is composed of unresolved $^{43}$Ca signals from different calcium-silicate/aluminate components. By combining the experimentally measured solid-state $^{43}$Ca NMR signals of the individual components in relative ratios that are consistent with X-ray diffraction measurements a good overall fit to the spectrum can be obtained. The $^{43}$Ca signals were fit to quadrupolar or Czjzek lineshapes to deconvolute signals associated with the non-hydrated components (purple) from those associated with hydration products such as $Ca(OH)_2$ (black), calcium-silicate-hydrates (C-S-H, green) and aluminate hydrates (green). The relative integrated intensities of the deconvoluted $^{43}$Ca signals are shown in parentheses in Figure 1 along with their associated peak positions.

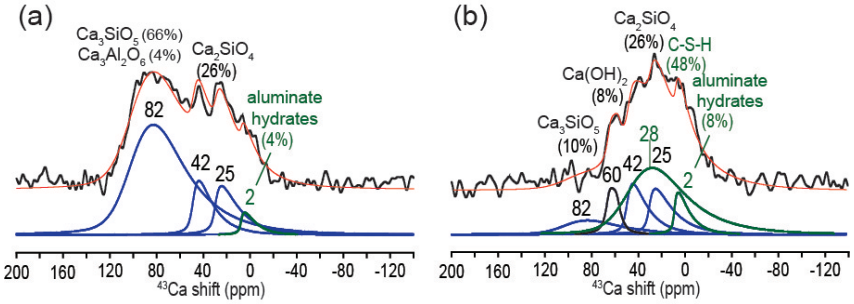


**Figure 1.** Solid-state 1D single-pulse $^{43}$Ca MAS NMR spectra acquired at 19.6 T and 25 °C (black) and simulated $^{43}$Ca lineshapes (color) for white Portland cement: **(a)** non-hydrated, and **(b)** hydrated for 28 days at 25 °C.

## Conclusions

The relative concentrations and molecular structures of different components in non-hydrated and hydrated white Portland and grey oilwell cements have been assessed by solid-state $^{43}$Ca and $^{25}$Mg NMR. These measurements provide new insights into the molecular characteristics of non-hydrated species in cements and the temperature-dependent products that form during hydration.

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