Supporting Information

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SI Text

Solid-State NMR Experimental Details. Solid-state ^{1}H, ^{13}C, and ^{27}Al NMR experiments were conducted on a Bruker AVANCE III spectrometer (18.8 T) operating at frequencies of 800.43 MHz for ^{1}H, 201.26 MHz for ^{13}C, and 208.56 MHz for ^{27}Al and under conditions of magic angle spinning (MAS) at 298 K. Solid-state ^{1}H, ^{13}C, and ^{29}Si NMR experiments were conducted at 298 K on a Bruker AVANCE-II spectrometer (11.7 T) operating at frequencies of 500.24 MHz for ^{1}H, 125.78 MHz for ^{13}C, and 99.38 MHz for ^{29}Si. Two-dimensional ^{27}Al{^{1}H}, ^{29}Si{^{1}H}, and ^{13}C{^{1}H} heteronuclear correlation (HETCOR) experiments were conducted at 298 K under MAS conditions with cross-polarization contact times of 0.5, 1.0, and 1.5 ms, respectively, at 11.7 or 18.8 T for tricalcium silicate and tricalcium aluminate, respectively. The ^{1}H, ^{13}C, and ^{29}Si chemical shifts were referenced to tetramethylsilane using tetrakis(trimethylsilyl)silane $[(CH_3)_3Si]_4Si$ as a secondary standard, and the ^{27}Al chemical shifts were referenced to an aqueous solution of 0.5 M aluminum nitrate $[Al(NO_3)_3]$.

Solid-state 1D single-pulse ^{1}H, ^{13}C, and ^{29}Si MAS measurements were performed at 11.7 T, 298 K, and under 10-kHz MAS conditions using a Bruker 4-mm H-X double-resonance probehead and zirconia rotors with Kel-F® caps. One-dimensional single-pulse ^{13}C experiments were conducted using a 90° pulse length of 4.0 μs (3.0 dB), under conditions of proton decoupling (3.4 μs 90° ^{1}H pulses, 4.0 dB), and using a recycle delay of 60 s. One-dimensional single-pulse ^{29}Si experiments were conducted using a 90° pulse length of 3.7 μs (3.0 dB), under conditions of proton decoupling (3.4 μs 90° ^{1}H pulses, 4.0 dB), and using a recycle delay of 100 s. One-dimensional single-pulse ^{1}H experiments were performed using a 90° pulse length of 3.4 μs (4.0 dB) and a recycle delay of 2 s.

Solid-state 1D single-pulse ^{1}H, ^{13}C, and ^{27}Al measurements were performed at 18.8 T, 298 K, and under 20-kHz MAS conditions using a Bruker 3.2-mm H-X-Y triple-resonance probehead with zirconia rotors and Kel-F® caps. One-dimensional single-pulse ^{13}C experiments were conducted using a 90° pulse length of 4.0 μs (−0.19 dB), under conditions of proton decoupling (3.4 μs 90° ^{1}H pulses, −0.19 dB), and using a recycle delay of 60 s. One-dimensional single-pulse ^{27}Al experiments were conducted using a high-power 1.0-μs pulse length (−0.19 dB) for ^{27}Al, corresponding to a 30° tip angle, and a recycle delay of 10 s. The high magnetic field mitigates the effects of second-order quadrupolar interactions and improves signal sensitivity and resolution of the ^{27}Al signals. The single-pulse ^{27}Al NMR measurements were calibrated using a dense 4.7-mg piece of AlN as an external reference for spin counting and establish that >95% of the ^{27}Al species are NMR visible. One-dimensional single-pulse ^{1}H experiments were performed using a 90° pulse length of 3.4 μs (−0.19 dB) and a recycle delay of 2 s.

All solid-state HETCOR NMR spectra were acquired using frequency-switched Lee–Goldberg (FSLG) homonuclear decoupling during the ^{1}H evolution period and a radio-frequency field of 70 kHz to enhance resolution in the ^{1}H dimension. All 2D ^{13}C{^{1}H} HETCOR spectra were acquired with a 1.5-ms contact time and FSLG homonuclear decoupling. The 2D ^{27}Al{^{1}H} HETCOR spectra were acquired with a 500-μs contact time and a ^{1}H spin-diffusion time of 10 μs to probe immediate molecular proximities. The 2D ^{29}Si{^{1}H} HETCOR spectra were acquired with a 1-ms ^{1}H contact pulse to enable efficient ^{1}H-^{29}Si cross-polarization. The 2D ^{13}C{^{1}H}, ^{27}Al{^{1}H}, ^{29}Si{^{1}H} experiments were acquired with 64 t_1 increments of 24 μs, 3024 transients, and using a recycle delay of 1 s that resulted in an experimental time of 27 h for each 2D experiment.

NMR lineshape analyses were conducted using the software "dmfit #20090330," with lineshapes fit according to signal amplitude, position, and width (1). One-dimensional single-pulse ^{27}Al and ^{29}Si MAS spectra were deconvoluted by collectively fitting peak positions with Gaussian lineshapes that were subsequently kept the same across spectra obtained for similar samples, but with different saccharide species present.

Surface Forces Apparatus Experimental Details. Surface forces measurements were performed using a surface forces apparatus (SFA) 2000 to determine the normal force-distance profiles during approach of the mica surfaces (2). A 1–5-μm-thick mica sheet was glued onto a cylindrical silica disk of radius $R = 1.5$ cm, and then two curved and Ag-backed mica surfaces were mounted in the SFA chamber in a crossed-cylinder geometry. Aqueous solutions were prepared by titrating distilled water with NaOH to pH 12.7 and dissolving glucose or sucrose to form 0.2 wt% solutions. The solutions were comparable to those associated with hydrating aluminate and silicate powders, except for the presence of the Na^+ cations, instead of Ca^{2+}, which avoided precipitation of $Ca(OH)_2$ that would have interfered with the SFA measurements. After 1 h, approximately 200 μL of the alkaline aqueous solution, with or without saccharide, was injected between the mica surfaces when separated at a relatively large distance (approximately 1 μm) and allowed to equilibrate for 30 min before the initial approach ($\nu_{\mathrm{approach}} \sim 10$ nm/s). All experiments were performed at 25 °C.

Scanning Electron Microscopy Experimental Details. Scanning electron micrographs were conducted using a FEI XL40 Sirion FEG digital electron scanning microscope at a magnification of 5000× and an electron beam voltage of 10 kV.

1. Massiot D, et al. (2002) Modelling one- and two-dimensional solid-state NMR spectra. *Magn Reson Chem* 40:70–76.

2. Israelachvili J, et al. (2010) Recent advances in the surface forces apparatus (SFA) technique. *Rep Prog Phys* 73:12850–12853.

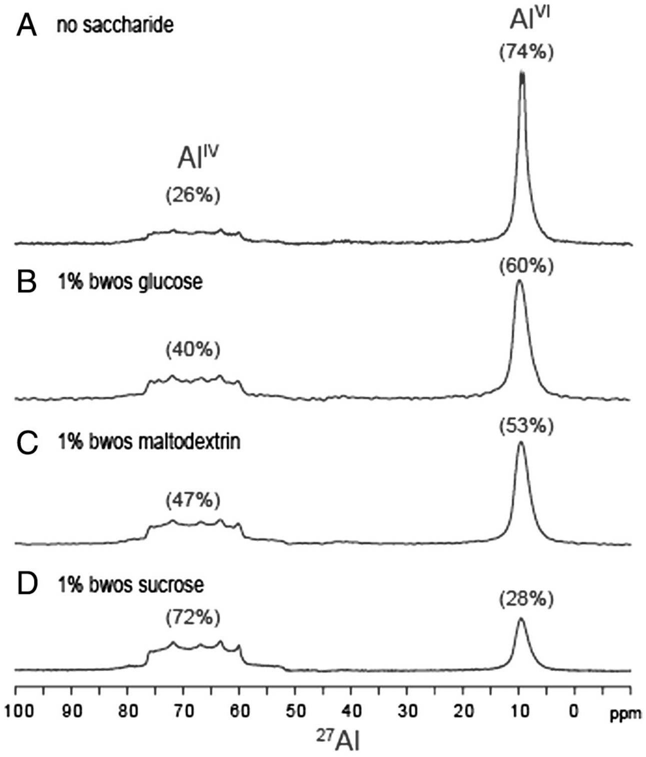

Fig. S1. Solid-state 1D ^{27}Al MAS NMR spectra acquired at 18.8 T, 298 K and 20 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) in the presence of $CaSO_4 \cdot 2H_2O$ (50% by weight of tricalcium aluminate) and containing: (*A*) no saccharide, (*B*) 1% glucose, (*C*) 1% maltodextrin, or (*D*) 1% sucrose by weight of tricalcium aluminate. The conversion of NMR-visible ^{27}Al species is determined by integrating and comparing the relative $^{27}Al^{IV}$ and $^{27}Al^{VI}$ peak areas, as shown above and tabulated in Table 1.

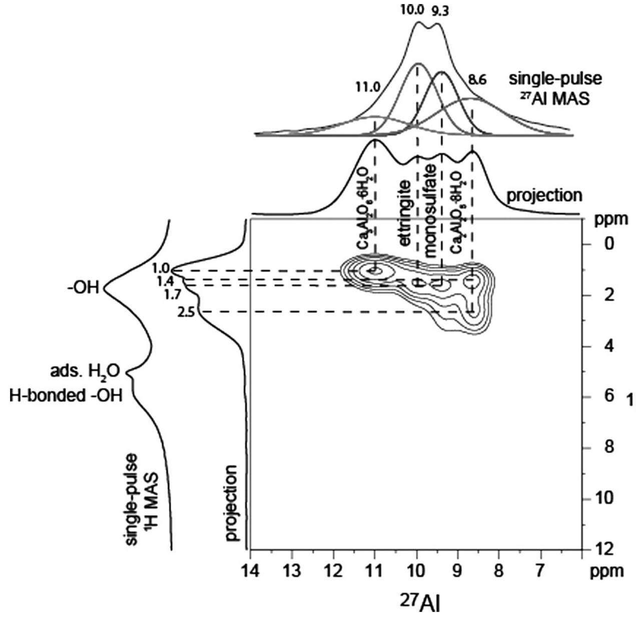

Fig. S2. Solid-state 2D $^{27}Al\{^1H\}$ HETCOR NMR spectrum acquired at 18.8 T, 298 K, and 10 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) without saccharides in the presence of $CaSO_4 \cdot 2H_2O$ (50% by weight of tricalcium aluminate). A short spin diffusion time of $t_{sd} = 10$ μs was used to probe the immediate molecular proximities (<1 nm) of different resolved ^{27}Al and ^1H species. One-dimensional single-pulse ^{27}Al and ^1H spectra are shown along the horizontal and vertical axes, respectively, for comparison with the 1D projections of the 2D spectrum. The much higher resolution of the 2D spectrum allows the ^{27}Al signals to be assigned (1, 2) to tricalcium aluminate hexahydrate ($Ca_3Al_2O_6 \cdot 6H_2O$, 11.0 ppm), ettringite (10.0 ppm), calcium aluminate monosulfate (9.3 ppm), and dicalcium aluminate octahydrate ($Ca_2Al_2O_5 \cdot 8H_2O$, 8.6 ppm). Strong correlated 2D signal intensity observed between the ^{27}Al signals at 11.0, 10.0, 9.3, and 8.6 ppm and the ^1H signals at 1.0, 1.4, 1.7 and 2.5 ppm, respectively, correspond to hydroxyl groups bound to ^{27}Al species in the different aluminate hydration products. Gaussian fits to these $^{27}Al^{VI}$ signals, which are otherwise only partially resolved in the 1D single-pulse ^{27}Al MAS spectrum, allow their relative populations to be estimated.

1 Rawal A, et al. (2010) Molecular silicate and aluminate species in anhydrous and hydrated cements. *J Am Chem Soc* 132:321–7337.
2 Skibsted J, Henderson E, Jakobsen HJ (1993) Characterization of calcium aluminate phases in cements by ^{27}Al MAS NMR spectroscopy. *Inorg Chem* 32:1013–1027.

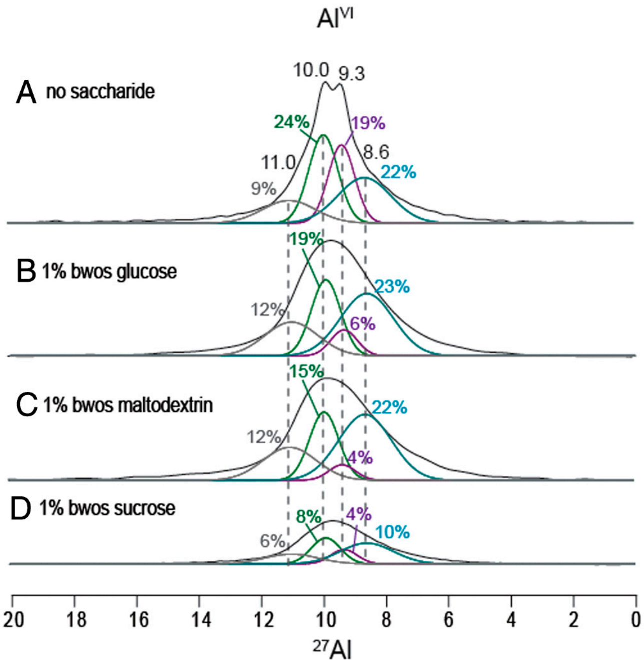

Fig. S3. Solid-state 1D ^{27}Al MAS NMR spectra acquired at 18.8 T, 298 K, and 20 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) in the presence of $CaSO_4 \cdot 2H_2O$ (50% by weight of tricalcium aluminate) and containing: (*A*) no saccharide, (*B*) 1% glucose, (*C*) 1% maltodextrin, or (*D*) 1% sucrose by weight of tricalcium aluminate. The ^{27}Al peaks were fit to Gaussian lineshapes at the same peak locations as resolved in the 2D ^{27}Al{^{1}H} HETCOR spectrum in Fig. S2, allowing the spectra to be deconvoluted and relative ^{27}Al^{VI} populations estimated, as shown above and tabulated in Table 1.

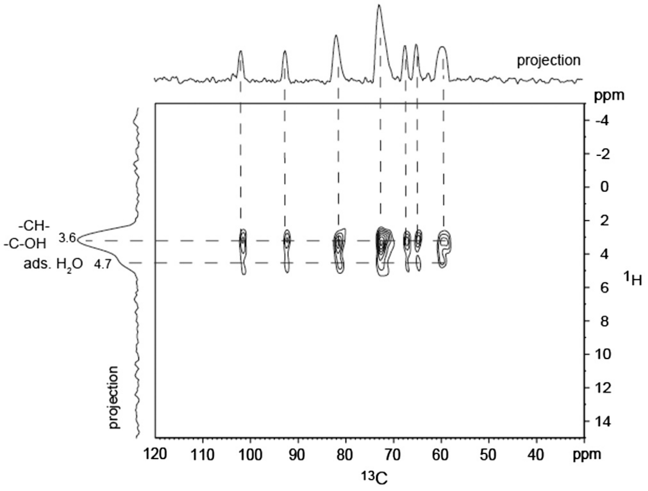

Fig. S4. Solid-state 2D ^{13}C{^{1}H} HETCOR NMR spectrum acquired at 11.7 T, 298 K and 10 kHz MAS for crystalline sucrose. Intensity correlations are observed between ^{13}C signals and ^{1}H signals centered at 3.6 ppm due to intramolecular -CH- and -COH interactions. Intensity correlations between ^{13}C signals and ^{1}H signals at 4.7 ppm establish the presence of adsorbed water.

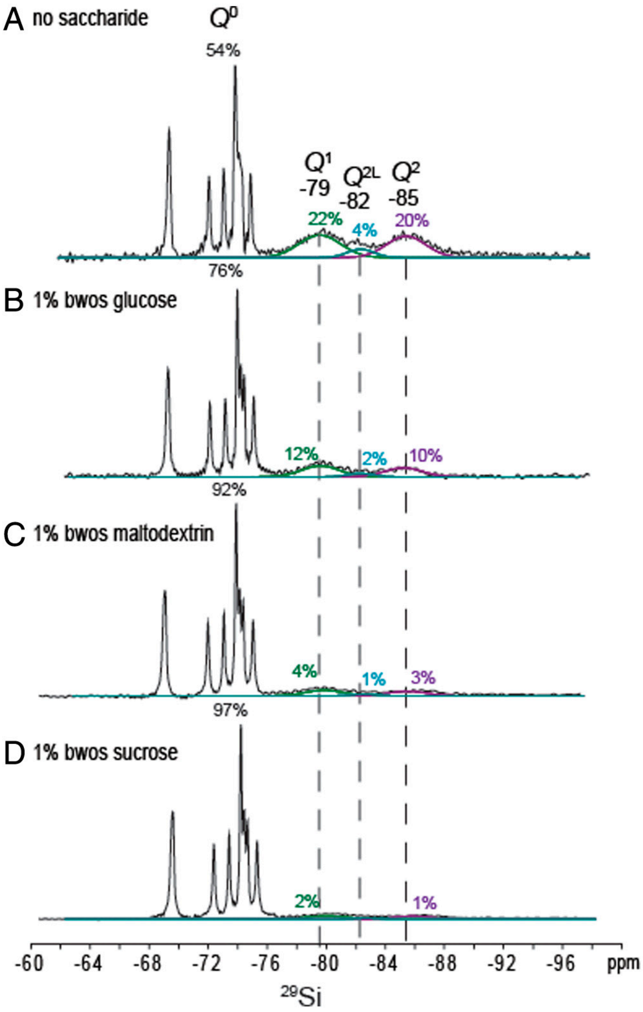

Fig. S5. Solid-state 1D single-pulse ^{29}Si MAS NMR spectra acquired at 11.7 T, 298 K and 10 kHz MAS for hydrated tricalcium silicate (4 h, 95 °C) containing: (*A*) no saccharide, (*B*) 1% glucose, (*C*) 1% maltodextrin, or (*D*) 1% sucrose by weight of tricalcium silicate. The conversion of NMR-visible ^{29}Si species is quantified by integrating and comparing the relative Q^0 to Q^1, Q^{2L}, and Q^2 ^{29}Si species peak areas, as shown above and tabulated in Table 2.

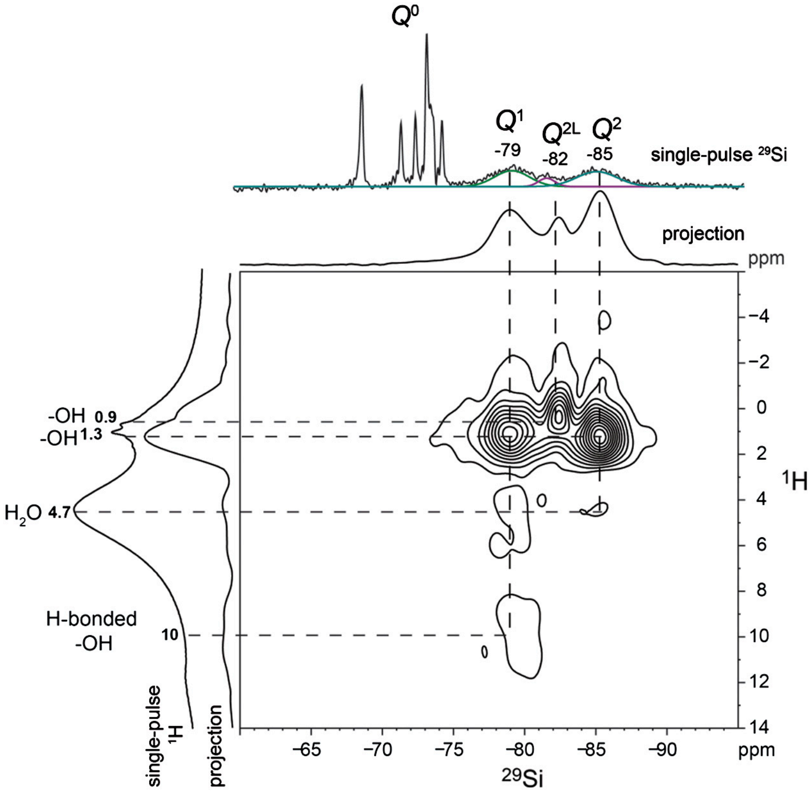

Fig. S6. Solid-state 2D ^{29}Si{^{1}H} HETCOR NMR spectrum acquired at 11.7 T, 298 K, and 6.5 kHz MAS, for hydrated tricalcium silicate (4 h, 95 °C) without saccharides. A 1-ms contact time was used to probe the immediate molecular proximities (<1 nm) of different resolved ^{29}Si and ^{1}H species. One-dimensional single-pulse ^{29}Si and ^{1}H MAS spectra are shown along the horizontal and vertical axes, respectively, for comparison with the 1D projections of the 2D spectrum. Gaussian fits to the ^{29}Si MAS signals for the Q^1, Q^{2L}, and Q^2 ^{29}Si species are shown along the top horizontal axis. Strong correlated 2D signal intensity observed between the ^{29}Si signals at −79, −82, and −85 ppm and the ^{1}H signals at 1.3, 0.9, and 1.3 ppm, respectively, correspond to Q^1, Q^{2L}, and Q^2 hydroxyl species in calcium-silicate-hydrate. Additional intensity correlations observed between the ^{29}Si signals at −79 and −85 ppm and the ^{1}H signal at 4.7 ppm indicate that some adsorbed water is in molecular proximity to the Q^1 and Q^2 silicate species.