Origins of Saccharide-Dependent Hydration at Aluminate, Silicate, and Aluminosilicate Surfaces

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Sugar molecules adsorbed at hydrated inorganic oxide surfaces occur ubiquitously in Nature and in technologically important materials and processes, including marine biomineralization, abiotic biomolecule synthesis, bone resorption, heterogeneous catalysis, corrosion inhibition, and cement hydration. Among these examples, surprisingly diverse hydration behaviors are observed for oxides in the presence of saccharides with closely related compositions and structures. Importantly, the hydration kinetics of aluminosilicate-based cements are critical to a number of modern technologies, notably as synthetic structural materials for large-scale construction projects and oilwell cementing, where saccharide additives are used to slow hydration processes and alter rheological properties. Glucose, sucrose, and maltodextrin, for example, exhibit significant differences in their alkaline reaction properties, adsorption selectivities, binding strengths and coverages on hydrating aluminate, silicate, and aluminosilicate surfaces that are shown to be due to the molecular architectures of the saccharides.

Solution and solid-state nuclear magnetic resonance (NMR) spectroscopy measurements, including at very high magnetic fields (19 T), distinguish and quantify the different molecular species, their chemical transformations, and their adsorption behaviors on different aluminate and silicate moieties. Two-dimensional NMR results establish non-selective adsorption of glucose degradation products containing linear saccharinic and carboxylic acids on both hydrated silicates and aluminates. In contrast, sucrose, which is stable under alkaline conditions, adsorbs intact at hydrated silicate sites and selectively at anhydrous, but not hydrated, aluminate moieties. Quantitative surface forces measurements establish relatively weak binding of glucose degradation species on hydrated aluminosilicate surfaces; whereas, sucrose adsorbs strongly and forms multiple layers that result from sucrose−cation complexation. Maltodextrin exhibits intermediate alkaline reaction and sorption properties, due to its oligomeric architecture that yields linear carboxylic acids and stable ring-containing degradation products that are similar to those present for glucose and sucrose, respectively. The molecular structures and physicochemical properties of the saccharides and their degradation species correlate well with their adsorption behaviors and lead to different binding strengths and surface coverages in aluminosilicate-based cements. The results explain the dramatically different effects that small amounts of different types of sugar molecules have on the rates at which aluminate, silicate, and aluminosilicate species hydrate, with important implications for diverse materials and applications wherein organic species adsorb at heterogeneous oxide surfaces from aqueous solutions.