

Chemical structure-property relationships of alkali-activated aluminosilicate polymeric materials for the development of sustainable construction materials

Jennifer Mills

Advisor: Norman Wagner

Committee Members: Eric Furst, Christopher Kloxin, Paramita Mondal

Traditional cement production and usage has an incredibly large carbon footprint: up to 1 ton of CO₂ is emitted per ton of cement produced, and over 4 billion tons of cement are produced globally each year. A promising method to reduce the carbon footprint of traditional cement is by changing the chemistry from a calcium-based system, which produces CO₂ as a byproduct from the calcination of limestone, to an aluminosilicate-based inorganic polymer system, which cures by undergoing molecular rearrangement upon reaction with alkaline solution. Termed alkali-activated binders (AABs) or geopolymers, such materials can be activated from a variety of widely available starting materials including clays, fly ash, and slag, as well as in-situ resource utilization of regolith for lunar and Martian construction in support of human space exploration. However, key challenges preventing the widespread adoption of this solution are variability in the composition of alternate aluminosilicate-based source materials and lack of understanding how the chemical composition and reaction mechanism affect the microstructure formed during set and the resultant workability and strength of the material. As a result of the differences in chemical composition, design solutions developed to affect the set time, workability, or strength in calcium cements are not directly applicable to AABs. Therefore, it is the goal of the research in this thesis to experimentally connect chemistry, kinetics, structure, and material properties of alkali-activated materials (AAMs) as a necessary step toward the design of sustainable, low-CO₂ construction materials for a wide range of applications.

The reaction kinetics of AAB formation include both the dissolution of precursor aluminosilicate grains and a polycondensation reaction that forms an amorphous reaction network known as the N-A-S-H gel. Synthetic N-A-S-H gels are studied as a model AAM to probe the kinetics of polycondensation and the structure of the reaction product without the confounding effects of dissolution or unreacted precursor material in AABs. In this thesis, we use the aluminum concentration (limiting reactant) as a surrogate for extent of reaction in N-A-S-H gels to determine its role in structure formation and property development. We investigate the structure-property relationships as a function of aluminum concentration at fixed silicon and sodium concentrations for two types of N-A-S-H gels that differ in their aluminum source. The two aluminum sources studied also allow for an investigation into the role of pH in the aggregation kinetics and structure formation of the gels. New applications of polymer and colloidal theory allow interpreting the results of these measurements of N-A-S-H gel structure and rheological properties to develop an understanding of how bulk properties develop during the reaction.

We also investigate the kinetics of gel formation directly by following the development of the gels' rheological properties and demonstrate that the sodium aluminate N-A-S-H gels follow a single reaction mechanism at aluminum concentrations above the gel point. This leads to the discovery of a master curve for the rheological extent of reaction which can be successfully fit to both an autocatalytic reaction model with nucleation and growth steps as well as an Avrami model with Avrami exponent of 1.5. Further, it is demonstrated that these kinetic models provide a means to connect the kinetics and composition-property relationships of N-A-S-H gels to those of actual geopolymer binders, as is illustrated for alkali-activation of BP-1 lunar regolith simulant.

Another novel contribution of this thesis is the creation of a pseudo-ternary state diagram that connects the relative composition of N-A-S-H gels in terms of silicon, sodium, and aluminum concentration to their observed rheological properties. The proposed state boundaries also successfully demarcate trends in alkali-activated aluminosilicate gels from the literature. Further, we demonstrate that this state diagram also provides compositional context for comparing trends in composition between N-A-S-H gels and geopolymers. This state diagram can therefore also be used to inform future experiments on geopolymers by identifying key compositions of interest for studying property development, as is shown preliminarily for lunar geopolymers from BP-1 regolith simulant.

We further demonstrate how the approach of studying AAMs in this thesis can be used to design geopolymers for extra-terrestrial exploration using *in-situ* resource utilization (ISRU) of the regolith present on the lunar or Martian surface. Geopolymer binders are successfully formulated using three lunar and one Martian regolith simulants, and we identify key physical and chemical characteristics of the simulant that are hypothesized to affect its reactivity and ability to form a geopolymer binder. We also evaluate the strength of these binders after vacuum curing and exposure to high and low temperatures in comparison to strength after curing under ambient terrestrial conditions.

The results of the research in this thesis showing a mechanistic and quantitative understanding of the chemical kinetics and dynamics of microstructure formation and associated rheological development in model AAMs will facilitate broader application of sustainable construction materials from a variety of aluminosilicate materials.