

## GEOPOLYMERS: STRUCTURAL INORGANIC POLYMERS AND A POTENTIAL PARTIAL SOLUTION TO GLOBAL WARMING

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“Geopolymers” are polysialates which are charge-balanced, aluminosilicate, ceramic-like materials made from an aluminosilicate source such as metakaolin, i.e., calcined clay and alkali metasilicate “waterglass” solution. A stoichiometric chemical composition is  $M_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 11H_2O$  where M may be Group I element such as Na, K, or Cs and the water content depends on particle size, specific surface area and aluminosilicate source. The inorganic polymer is made by high shear mixing with the liquid suspension undergoing dissolution, polycondensation or precipitation under ambient conditions. The resulting inorganic polymer has a microstructure which is impervious, nanoporous (diameter  $\sim 6.8$  nm), of  $\sim 40$  vol % nanoporosity, and is nanoparticulate (10-40 nm).

The ceramic-like, cross-linked product shares the brittle nature of ceramics, but can be reinforced with particulates, platelets, chopped fibers, uniaxial fibers, or fiber weaves yielding a strong and tough composite, which is fire and acid corrosion resistant. Geopolymer composites reinforced with various with biological fibers (hemp, curua, sisal, malva, jute, etc) have been made. In the Amazon the clays under the jungles consist of fine high quality kaolinite clay containing 25 wt % particulate quartz reinforcements. Such geopolymer composites have comparable flexure strengths to high strength concrete, when reinforced with chopped reinforcements of Guadua Angustifolia bamboo. Their mechanical properties, durability and shrinkage behavior were measured to assess their suitability as building construction materials.

Geopolymers also have refractory and adhesive properties up to  $1,000^\circ\text{C}$  whereupon they crystallize into ceramics of tailorable, crystallographic thermal expansion. The CTE's of crystallized geopolymers range from  $\sim 0.45 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $\sim 50 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  depending on the compositions and ratios of Cs, K, or Na charge balancing cations. The charge balancing cations lie in pore channels in the [111] unit cell directions. Comparing across temperatures, phases with cubic symmetry exhibit a monotonic decrease in volumetric thermal expansion at all temperatures with increasing cesium content. Comparing across K-Cs compositions, the linearity of each curve increases with increasing cesium content. Only crystalline  $K[AlSi_2O_6]$  and  $K_{0.8}Cs_{0.2}[AlSi_2O_6]$  existed in tetragonal symmetry above RT. In contrast to cubic phases, the tetragonal phases exhibited increasing thermal expansion with temperature. Thermal expansion tensors can give insight into the asymmetry of expansion in this system. From these, it is apparent that the volumetric expansion is due to expansion along the [100] and [010] axes. The cell contracts along the [001] axis contracts and does so more rapidly with increasing temp.

Under inert nitrogen or argon gases at  $1400^\circ\text{C}$  to  $1600^\circ\text{C}$ , nanoparticulate geopolymers with only nano length diffusion distances undergo carbothermal reduction or carbothermal nitridation forming soft agglomerates of SiC,  $Si_3N_4$  or SiAlON nanoparticles. Geopolymers are a potential partial solution to global warming. This is  $\sim 900^\circ\text{C}$  below the formation of SiC via the Acheson process, and requires only minor grinding of the resulting nano SiC agglomerates.

While the term “geopolymers” is used widely in the alkali activated community which uses waste streams of Class F fly ash and slag with sodium hydroxide, our recent studies show that this actually results primarily in the formation of C-N-A-S-H (calcium sodium aluminum silicate hydrate) gel binder phase rather than the stoichiometric geopolymer described above. NASH steadily loses its tensile strength and Young's modulus by  $\sim 700^\circ\text{C}$ .