

## ABSTRACT

Sant, Gaurav Niteen Ph.D., Purdue University, December, 2009. Fundamental Investigations Related to the Mitigation of Volume Changes in Cement-Based Materials at Early Ages. Major Professor: W. Jason Weiss.

The increased use of high-performance, low water-to-cement (w/c) ratio concretes has led to increased occurrences of early-age shrinkage cracking in civil engineering structures. To reduce the magnitude of early-age shrinkage and the potential for cracking, mitigation strategies using shrinkage reducing admixtures (SRAs), saturated lightweight aggregates, expansive cements and extended moist curing durations in construction have been recommended. However, to appropriately utilize these strategies, it is important to have a complete understanding of the driving forces of early-age volume change and how these methods work from a materials perspective to reduce shrinkage. This project uses a fundamental approach to understand the mechanism of shrinkage reducing admixtures (SRAs) to generate an expansion and mitigate shrinkage at early-ages, quantify the influence of a CaO-based expansive additive in reducing unrestrained shrinkage, residual stress development and the cracking potential at early-ages and quantify the influence of shrinkage reducing admixtures (SRAs) and cement hydration (pore structure refinement) on the reduction induced in the fluid transport properties of the material.

The effects of shrinkage reducing admixtures (SRAs) are described in terms of inducing autogenous expansions in cement pastes at early ages. An evaluation comprising measurements of autogenous deformation, x-ray diffraction (Rietveld analysis), pore solution and thermogravimetric analysis and electron microscopy

is performed to understand the chemical nature and physical effects of the expansion. Thermodynamic calculations performed on the measured liquid-phase compositions indicate the SRA produces elevated Portlandite supersaturations in the pore solution which results in crystallization stress driven expansions. The thermodynamic calculations are supported by deformation measurements performed on cement pastes mixed in solutions saturated with Portlandite or containing additional Sodium Hydroxide. Further, to quantify the influence of temperature on volume changes in SRA containing materials, deformation measurements are performed at different temperatures. The results indicate maturity transformations are incapable of simulating volume changes over any temperature regime due to the influence of temperature on salt solubility and pore solution composition, crystallization stresses and self-desiccation.

The performance of a CaO-based expansive additive is evaluated over a range of additive concentrations and curing conditions to quantify the reduction in restrained and unrestrained volume changes effected in low w/c cement pastes. The results suggest, under unrestrained sealed conditions the additive generates an expansion and reduces the magnitude of total shrinkage experienced by the material. However, the extent of drying shrinkage developed is noted to be similar in all systems and independent of the additive dosage. Under restrained sealed conditions, the additive induces a significant compressive stress which delays tensile stress development in the system. However, a critical additive concentration (around four percent) needs to be exceeded to appreciably reduce the risk of cracking at early-ages.

The influence of shrinkage reducing admixtures (SRAs) is quantified in terms of the effects of SRA addition on fluid transport in cement-based materials. The change in the cement paste's pore solution properties, i.e., the surface tension and fluid-viscosity, induced by the addition of a SRA is observed to depress the fluid-sorption and wetting moisture diffusion coefficients, with the depression being a function of the SRA concentration. The experimental results are

compared to analytical descriptions of water sorption and a good correlation is observed. These results allow for the change in pore-solution and fluid-transport properties to be incorporated from a fundamental perspective in models which aim to describe the service-life of structures.

Several experimental techniques such as chemical shrinkage, low temperature calorimetry and electrical impedance spectroscopy are evaluated in terms of their suitability to identify capillary porosity depercolation in cement pastes. The evidence provided by the experiments is: (1) that there exists a capillary porosity depercolation threshold around 20% capillary porosity in cement pastes and (2) low temperature calorimetry is not suitable to detect porosity depercolation in cement pastes containing SRAs. Finally, the influence of porosity depercolation is demonstrated in terms of the reduction effected in the transport properties (i.e., the fluid-sorption coefficient) of the material as quantified using x-ray attenuation measurements. The study relates the connectivity of the pore structure to the fluid transport response providing insights related to the development of curing technologies and the specification of wet curing regimes during construction.