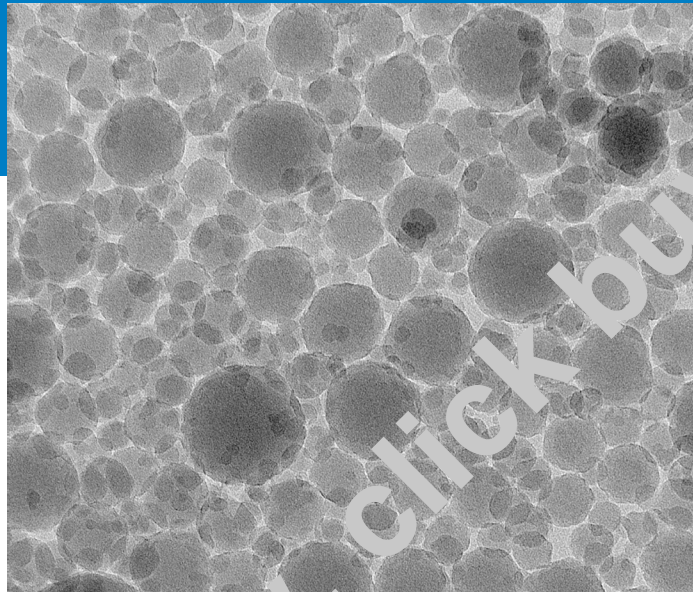


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SYMPOSIUM VOLUME



Nanotechnology for Improved Concrete Performance

Editors:

Mahmoud Reda Taha and Mohamed T. Bassuoni



American Concrete Institute  
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# Nanotechnology for Improved Concrete Performance

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Editors:  
Mahmoud Reda Taha and  
Mohamed T. Bassuoni



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## PREFACE

### Nanotechnology for Improved Concrete Performance

Preface: Many of the papers presented in this volume were included in the two-part session *Nanotechnology for Improved Concrete Performance*, sponsored by ACI Committee 241, Nanotechnology of Concrete at the ACI Convention in Philadelphia, PA, on October 26, 2016. In line with the practice and requirements of the American Concrete Institute, peer review, followed by appropriate response and revision by authors, has been implemented.

In the last decade, there have been considerable research efforts aimed at improving the mechanical and durability performance of concrete using nanotechnology. Exemplary work includes using nanoparticles to improve the hydration process of cement, incorporating nanomaterials to alter the mechanical and durability characteristics of concrete, and providing a new source for the self-sensing functionality of concrete. The scope of these papers encompasses experimental and applied research examining the use of nanomaterials to improve the performance of concrete at large. Readers are urged to critically evaluate the work presented herein, in light of the substantial body of knowledge and scientific literature on this topic.

We dedicate this volume of papers to the memory of Professor Robert (Bob) L. Day (1950-2014), of The University of Calgary, Canada and past chairman of Canadian Standards Association (CSA) Committee A23.1/A23.2 (Concrete Materials and Construction), for his invaluable contributions to the field of concrete science and his remarkable mentoring of numerous concrete professionals worldwide.

The editors sincerely thank all the presenters in the 2016 session and the authors of the articles included in this special publication, as well as the reviewers for their thorough and objective assessment of the papers. Their technical contributions provide a holistic perspective of *Nanotechnology for Improved Concrete Performance*.

Mahmoud Reda Taha, Editor  
Mohamed T. Bassuoni, Co-editor

## TABLE OF CONTENTS

### **SP-335-1:**

Multi-Scale Fiber Reinforcement for Cracking Resistance in Cement Mortars .....1-11  
Authors: Joshua Hogancamp, Cesario Tavares, and Zachary Grasley

### **SP-335-2:**

Tailoring The Piezoresistive Sensing of CNT Reinforced Mortar Sensors .....12-26  
Authors: Maria S. Konsta-Gdoutos, Panagiotis A. Danoglidis, and Surendra P. Shah

### **SP-335-3:**

Performance of Fiber-Reinforced Carbon Nanotubes-Nanofibers Composites ..... 27-36  
Authors: Joshua Hoheneder, Ismael Flores-Vivian and Konstantin Sobolev

### **SP-335-4:**

Investigation Methods for Characterizing Nanoparticles in Concrete ..... 37-48  
Authors: Douglas Hendrix, Nabil Bassim, and Kay Wille

### **SP-335-5:**

Prediction of Effective Properties of Fly Ash-Based Geopolymer Composites ..... 49-62  
Authors: Sumanta Das, Pu Yang, Sudhanshu S. Singh, James C. F. Mertens, Xianghui Xiao, Nikhilesh Chawla and Narayanan Neithalath

### **SP-336-6:**

Strength Recovery Through Nanosilica Coated Polypropylene Fiber Reinforcement..... 63-82  
Authors: Su-Jin Lee, Shiho Kawashima, and Jong-Pil Won

### **SP-335-7:**

Hydration and Strength of Cement Pastes Containing Different Nanoparticles..... 83-96  
Authors: Xin Wang and Kejin Wang

### **SP-335-8:**

Titania and Silica Nanoparticle-Modified Coatings for Cementitious Materials..... 97-111  
Authors: Qingxu Jin, Marcos Faraldos, Ana Bahamonde, Behnaz H. Zaribaf, and Kimberly E. Kurtis

### **SP-335-9:**

Nano-Modified Concrete Cast and Cured at Freezing Temperature .....112-127  
Authors: A. M. Yasien, A. Abayou, and M. T. Bassuoni

### **SP-335-10:**

Determination of Elastic Modulus and Creep of Nanoclay Modified Oil Well Cement ..... 128-144  
Authors: Vemuganti, S., Rahman, M.K., and Reda Taha, M. M.

## MULTI-SCALE FIBER REINFORCEMENT FOR CRACKING RESISTANCE IN CEMENT MORTARS

Joshua Hogancamp, Cesario Tavares, and Zachary Grasley

### SYNOPSIS:

The current state of the art in fiber-reinforced cement-based materials indicates that adding multiple fiber types or sizes primarily creates a superpositioned behavior state: the behavior from each fiber type separately is added to the composite behavior of the material. Carbon nanofibers (CNFs) and milled carbon microfibers (MCMFs) can increase cracking resistance in cement-based materials by bridging cracks, although CNFs bridge cracks that are significantly smaller than cracks bridged by MCMFs. This research suggests that multi-scale fiber reinforcement (CNFs with MCMFs) might add compounded benefits to cracking resistance. Tests evaluating cracking resistance were performed utilizing a restrained-ring drying shrinkage test with Portland cement mortar. The CNFs and/or MCMFs were pre-mixed with cement using a sonication/distillation technique and/or rotary tumbling. Concentrations of CNFs and MCMFs were tested up to 5% and 6% by mass of cement, respectively. Restrained ring tests on mortar with high concentrations of CNFs or MCMFs reveal delayed cracking time by factors up to 6.4 or 2.6, respectively. Combining CNFs with MCMFs delayed cracking by a factor of at least 52. The increase in cracking resistance is attributed to the combined effects of bridging cracks of multiple sizes.

Keywords: Carbon nanofiber; carbon microfiber; mortar; cracking resistance

**Tailoring the piezoresistive sensing of CNT reinforced mortar sensors**

**Maria S. Konsta-Gdoutos, Panagiotis A. Danoglidis, Surendra P. Shah**

Synopsis: The piezoresistive response and self-sensing ability of carbon nanotube reinforced mortar sensors have been investigated. The study aims on optimizing the development of a self-sensing nanoreinforced cement-based sensor for monitoring and evaluating the condition of concrete elements, in real time applications. It has been shown that the piezoresistive response of the nanomodified mortars was substantially enhanced just by adding a low amount of carbon nanotubes (CNTs), 0.1 wt%. Resistance measurements, using direct current (DC) and alternating current (AC), were conducted under the application of cyclic or monotonic compressive loading. The results show the sensor's great ability to detect crack propagation and damage accumulation at all stages of deformation up to failure.

**Keywords:** Carbon nanotubes, mortars, Self-sensing ability, piezoresistivity, multifunctionality, Young's modulus, fracture toughness

## Performance of fiber-reinforced carbon nanotubes-nanofibers composites

Joshua Hoheneder, Ismael Flores-Vivian and Konstantin Sobolev

**SYNOPSIS:** Fiber additions in portland cement composites is a regular practice for crack prevention and for increasing the flexural strength. In this research, fiber-reinforced composites (FRC) with polyvinyl alcohol (PVA) fibers and carbon nanofibers (CNF) or carbon nanotubes (CNT) were investigated. Specimens were tested to measure their flexural strength, water absorption and electrical conductivity in water or sodium chloride solution. It was found that the developed composites, depending on applied stress and exposure to chloride solutions, exhibit some electrical conductivity. These dependencies can be characterized by piezoresistive and chemo-resistive coefficients demonstrating that the material possesses self-sensing capabilities. The sensitivity to strain, crack formation, and chloride solutions can be enhanced by incorporating small amounts of CNF or CNT into a composite structure. Conducted research has demonstrated a strong dependency of electrical properties of the composite on crack formation in moist environments. The developed procedure is scalable for industrial application in concrete structures that require nondestructive stress monitoring, integrity under high service loads and stability in harsh environments.

**KEYWORDS:** Composites, carbon nanofibers, carbon nanotubes, electrical conductivity, flexural strength, polyvinyl alcohol fibers.

Investigation Methods for Characterizing Nanoparticles in Concrete

Douglas Hendrix<sup>1</sup>, Nabil Bassim<sup>2</sup>, Kay Wille<sup>3</sup>

**Synopsis** There is significant potential for the use of nanoparticles in cementitious materials, especially in ultra-high performance concrete. These nanoparticles can further increase packing density, accelerate the pozzolanic reaction or can be used to induce new properties to the material, such as air purification or self-cleaning. Little is known about the interaction mechanisms between nanoparticles in cementitious materials, including their dispersion quality. The characterization of these nanoparticles can be challenging, especially when these nanoparticles interact with cementitious materials and their reaction products during hydration. Thorough characterization of the nanoparticle system is essential to understand how to optimize mixing constituents, procedures, and parameters.

This study explores the feasibility and potential use of several characterization methods for investigating colloidal nanosilica in a concrete environment. These techniques include dynamic light scattering, zeta potential, atomic force microscopy, scanning electron microscopy, cryogenic SEM, and focused ion beam microscopy. These methods allow for characterization of nanoparticles, nanoparticles interacting with pore solution that represent a concrete environment, nanoparticles interacting with polymers used as superplasticizers, and nanoparticles interacting with a cementitious material. These tools allow for studies on the nano-length scale at short times to observe and measure parameters such as particle size distribution, polydispersity index, and zeta potential.

**Keywords:** characterization, nanoparticles, cementitious material, concrete, dispersion, size distribution, dynamic light scattering

Douglas Hendrix

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Doug Hendrix is a PhD candidate in the Materials Science and Engineering program at the University of Connecticut where he received his Bachelor's degree as well. His research is focused on material characterization and development of ultra-high performance concrete, advised by Dr. Kay Wille. In fall of 2018 he won the IMS Graduate Student Presentation Competition.

Kay Wille

<sup>3</sup>Associate Professor, Civil and Environmental Engineering, University of Connecticut

Dr. Wille graduated with a Ph.D. degree in Civil Engineering at the University of Leipzig, Germany in 2008. After postdoctoral research at the University of Michigan Dr. Wille accepted a faculty position at the University of Connecticut in 2010. Dr. Wille serves in several committees related to his research interest, such as ACI 239, ACI 241 and ACI 544. In 2015 he received the NSF CAREER award.

Nabil Bassim

<sup>2</sup>Associate Professor, Department of Materials Science and Engineering, McMaster University, ON, Canada,

Dr. Bassim graduated with a Ph.D. degree from the University of Florida in Materials Science and Engineering in 2002. He worked as a Materials Research Engineer at the U.S. Naval Research Laboratory in the high-resolution characterization of materials using ions and electrons. Bassim has since moved to McMaster University, where he continues to develop tomography techniques for mesoscale solids and currently acts as the Scientific Director of the Canadian Centre for Electron Microscopy.

## Prediction of Effective Properties of Fly Ash-based Geopolymers

Sumanta Das, Pu Yang, Sudhanshu S. Singh, James C.E. Mertens, Xianghui Xiao, Nikhilesh Chawla and Narayanan Neithalath

**Abstract:** A detailed microstructural and micromechanical study of a fly ash-based geopolymer paste including: (i) synchrotron x-ray tomography (XRT) to characterize the pores (size  $> 0.74 \mu\text{m}$ ) that are influential in fluid transport, (ii) mercury intrusion porosimetry (MIP) to capture the volume fraction of smaller pores, (iii) high resolution scanning electron microscopy (SEM) combined with a multi-label thresholding method to identify and characterize the solid phases in the microstructure, and (iv) nanoindentation to determine the component phase elastic properties using statistical deconvolution techniques, is reported in this paper. The 3D pore structure from XRT is used in a computational fluid transport model to predict the permeability of the material. The pore volume from XRT, solid phase volumes from SEM, and the phase elastic properties are used in a numerical homogenization framework to determine the homogenized macroscale elastic modulus of the composite. The homogenized elastic moduli are in good agreement with the flexural elastic modulus determined on macroscale paste beams. It is shown that the combined use of microstructural and micromechanical characterization tools at multiple scales provides valuable information towards the material design of fly ash-based geopolymers.

**Keywords:** Geopolymers, Nanoindentation, Synchrotron Tomography, Homogenization, Microstructure

ACI member Sumanta Das is an Assistant Professor of Civil and Environmental Engineering at University of Rhode Island, Kingston, RI. His research interests are in development of novel sustainable binders, advanced microstructural characterization of cementitious materials, durability of cementitious

**STRENGTH RECOVERY THROUGH NANOSILICA COATED POLYPROPYLENE FIBER REINFORCEMENT**

Su-Jin Lee, Shiho Kawashima, and Jong-Pil Won

**Synopsis:** In this study, nanosilica was applied to the surface of polypropylene (PP) fibers to introduce self-healing abilities when incorporated into cement-composites. When the fiber is at the site of a crack, the nanosilica can form additional hydration products through pozzolanic reaction to effectively seal the crack. Nanosilica was synthesized onto the fibers through a sol-gel process. Then the fibers were dried at room temperature or 50°C (122°F) to remove the excess solution and adhere the nanosilica particles onto the fiber surface. The existence of nanosilica was confirmed by observing the mass change before and after the sol-gel process, water absorption, soluble matter loss and microscopy. The self-healing performance of cement-composites reinforced with treated and untreated macro and micro PP fibers at dosages of 1.8kg/m<sup>3</sup> (3.0lb/yd<sup>3</sup>) and 0.9kg/m<sup>3</sup> (1.5lb/yd<sup>3</sup>), respectively, were evaluated through flexural strength testing according to ASTM C348. To evaluate strength recovery, samples were loaded to 60% of the peak load to induce cracking. The cracked specimens were cured for 28 days under laboratory conditions to undergo self-healing. A significant recovery in flexural strength (112.8%) was observed by using nanosilica treated micro PP fibers dried at room temperature.

**Keywords:** fiber reinforced; nano silica; polypropylene fiber; self-healing; sol-gel; strength recovery.

## Hydration and Strength of Cement Pastes Containing Different Nanoparticles

Xin Wang and Kejin Wang

**Synopsis:** In this work, effects of nanosilica (NS), nanolimestone (NL), and nanoclay (NC) additions on hydration and strength of cement pastes were studied. The pastes were made with Type I ordinary Portland cement (OPC), 0 and 30% Class F fly ash (FA), and 0 or 1% nanomaterials. All pastes had a water-to-binder ratio of 0.5. Chemical shrinkage was monitored as an indication of cement hydration process. X-ray diffraction (XRD) was conducted to identify crystalline hydration products. Thermogravimetric analysis (TGA) was used to quantify calcium hydroxide (CH) and chemically bound water. The results indicate that the rate of chemical shrinkage curve can be divided into five stages, similar to that observed from the rate of cement hydration curve measured from a calorimetry test. All nanomaterials increased the rate of chemical shrinkage associated with  $C_3S$  and  $C_2S$  reactions; but different types of nanomaterials had different effects on the rate of chemical shrinkage associated with secondary  $C_3A$  reaction. All nanomaterials improved strength of OPC paste at ages up to 28 days; but the improvement was not clear for OPCFA pastes. Through reaction with OPC and FA, NL stabilized voluminous ettringite and produced hemicarbonate (Hc) instead of less voluminous monosulfate (Ms).

**Keywords:** Nanomaterials, fly ash, cement, hydration, chemical shrinkage, compressive strength

**Titania and Silica Nanoparticle-Modified Coatings for Cementitious Materials**

**Qingxu Jin, Marisol Faraldos, Ana Bahamonde, Behnaz H. Zaribaf, Kimberly E. Kurtis**

**Synopsis:** Due to the ubiquity of concrete in the urban environment and the upscaling of nanomaterial production, the incorporation of nanoparticles into cementitious materials has gained increased attention. This study compares the performance of various titania ( $\text{TiO}_2$ ) and silica ( $\text{SiO}_2$ ) nanoparticles-modified coatings, including their photocatalytic performance and the quality of their adhesion to the cementitious substrates. The photocatalytic performance with respect to air purification and self-cleaning are evaluated by nitrogen oxide ( $\text{NO}_x$ ) and methylene blue (MB) dye photodegradation, respectively. The results show that the Portland cement (OPC)-based cementitious materials exhibit greater photocatalytic efficiency than calcium aluminate cement (CAC)-based ones. It is proposed that the superior performance is due to a greater proportion of finer porosity and the presence of high surface area calcium silicate hydrates (C-S-H) in OPC-based cementitious materials. Interactions between coatings and cementitious substrates are examined through wettability and adhesion. The results show that the inclusion of silica layer can affect the interaction of coated cementitious surface with water, as well as the bond strength between coating and cementitious substrate.

**Keywords:** Self-cleaning; Air purification;  $\text{TiO}_2$ ;  $\text{SiO}_2$ ;  $\text{NO}_x$ ; Coating; Photocatalytic cementitious materials

## **NANO-MODIFIED CONCRETE CAST AND CURED AT FREEZING TEMPERATURE**

A. M. Yasien, A. Abayou, and M. T. Bassuoni

### **ABSTRACT**

In cold regions, freezing temperatures limit the construction season to few months, usually between May and September. The use of nanoparticles, which have high specific surface and vigorous reactivity, may potentially enhance the performance of concrete placed at low temperatures. Therefore, this study focused on developing concrete mixtures incorporating nano-silica which were mixed, placed and cured at  $-5^{\circ}\text{C}$  ( $23^{\circ}\text{F}$ ) without any insulation or protection targeting field applications in late fall and early spring periods. Eight mixtures incorporating general use (GU) cement, fly ash (up to 25%), and nano-silica (up to 4%) were tested for this purpose, with water-to-binder ratios of 0.32 and 0.4. All mixtures contained a combination of calcium nitrate and calcium nitrite as an antifreeze admixture. Testing involved concrete setting time (placement), 7 and 28 days compressive strengths (hardened properties) and resistance to freezing-thawing cycles (durability). Moreover, mercury intrusion porosimetry, thermal analysis and scanning electron microscopy were performed to corroborate the trends from the macro-scale tests. It was found that nano-silica significantly improved the overall performance of concrete placed and cured at  $-5^{\circ}\text{C}$  ( $23^{\circ}\text{F}$ ), which implicates its promising use for construction applications under low temperatures.

**Keywords:** Nano-silica, fly ash, concrete, cold weather, antifreeze admixtures.

## **EVOLUTION OF ELASTIC MODULUS AND CREEP OF NANOCLAY MODIFIED OIL WELL CEMENT**

Vemuganti, S., Rahman, M.K., Reda Taha, M. M.

**Synopsis:** Nanomaterials like nanosilica, nanoalumina and nanoclay have shown improvement in workability and increased compressive strength when used with cement. However, the potential of using nanoclay to alter the elastic modulus and limit creep of oil-well cement (OWC), specifically when cured under high temperature and pressure, has not been explored. In this investigation, Type-G cement mixed with 1.0 wt.%, 3.0 wt.% and 5.0 wt.% nanoclay and with water/cement ratio of 0.45 was prepared and cured for 7 days under high temperature and pressure of 80 °C (176 °F) and 10 MPa (1500 psi) respectively. Dynamic mechanical analysis was conducted under high temperature to reveal the evolution of the elastic modulus and creep compliance of the different cement-nanoclay mixture with curing time. Thermogravimetric analysis, Scanning Electron Microscope and X-ray Diffraction measurements were performed to support observations of elastic modulus and creep compliance evolution of OWC incorporating nanoclay explaining the microstructural changes that take place in OWC mixture incorporating nanoclay when hydrated under high temperature and pressure.

**Keywords:** Creep, elastic modulus, high pressure, high temperature, nanoclay